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THE REACTIVITY OF POLYNUCLEAR AROMATIC HYDROCARBONS TOWARD STYRYL RADICALS

A THESIS SUBMITTED TO THE GRADUATE SCHOOL OF THE UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

JANUARY 1963

By

Satya Pal Sood

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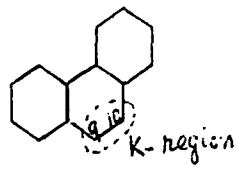
INTRODUCTION

The condensed-ring aromatic hydrocarbons, which were investigated in these studies, constitute an important group of organic molecules. A large majority of the important carcinogens belong to this group and to very closely related molecules such as condensed-ring aromatic amines and aromatic heterocyclic compounds. These compounds have been the subject of very extensive study over the past few decades, both from the experimental and theoretical points of view. The purpose of previous investigations was to determine which substances produced cancer,[1,2] and to account for the differences in the reactivity of these hydrocarbons especially from the point of view of carcinogenesis.

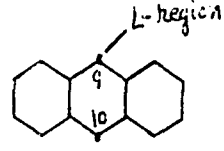
The riddle of carcinogenesis was approached both from the theoretical and experimental points of view, but no satisfactory explanation has ever been provided. The experimental approaches included investigations of absorption spectra, fluorescence, phosphorescence, magnetic susceptibility, oxidation-reduction potentials, etc.[3]

A characteristic feature of these carcinogens is that they possess mobile pi-electrons. Consequently absorption spectra, magnetic anisotropy, chemical reactivity, and many other physical and chemical properties which are characteristic of pi-electron systems are ascribed to these more loosely bound electrons. The various theoretical treatments deal with the evaluation of the distribution and density of

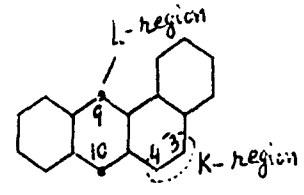
pi-electrons in these compounds. The differences in these approaches lie in the quantum-mechanical method employed and the simplifying assumptions used. Schmidt[4] first attempted to relate the carcinogenicity of aromatic hydrocarbons with the distribution of pi-electrons in these compounds. Later, Svartholm[5] suggested that these very mobile pi-electrons give rise to the properties of the so-called "K-region" in these molecules and that certain special electrical properties are associated with this region which can be calculated theoretically. Thus, the "K-region" is the center of reactivity in these molecules, its very shape makes it exceedingly accessible to any approaching radical; it is less easily screened than most of the rest of the molecule. It may be regarded as an "exposed bond" and resembles a double bond in its reactivity. The "K-region" may be clearly visualized by considering simple molecules like anthracene, phenanthrene and 1,2-benzanthracene.



Phenanthrene



Anthracene



1,2-benzanthracene

Position 9,10 in phenanthrene, which displays greater reactivity towards the addition of hydrogen, bromine, osmium tetraoxide etc. compared to the rest of the molecule, constitutes the "K-region". In anthracene the meso-positions (carbon atoms 9,10) are reactive and constitute "L-region". This molecule has no "K-region". Hydrocarbons which can be regarded as derivatives of phenanthrene would possess one or more "K-regions". They may also have a pair or more of meso-atoms. We might expect the latter to be able to influence the reactivity of the former and vice versa. Thus, in 1,2-benzanthracene position, 3,4 constitutes the "K-region" and carbon-atoms 9,10 the "L-region" or "meso-atoms". The "K-region" would be expected to be reactive for addition and the meso-atoms for substitution reactions. All the known carcinogens in this class of compounds have the "K-region". Since Svartholm's postulation of the "K-region" hypothesis many attempts have been made[6-15] to explain the phenomenon of carcinogenesis on this basis.

The above mentioned theoretical treatments employ quantum-mechanical methods for the pi-electron systems, the valence bond (V.B.) or the molecular orbital (M.O.) method. The exact valence bond method, even for very simple molecules, involves very laborious and tedious calculations, and is virtually impossible for molecules as large and complex as these carcinogens. The several approximation methods developed during the past have been unsatisfactory, and the results

obtained are of rather doubtful application to molecules of this type.[12] On the other hand, the M.O. method is more readily applicable to large aromatic molecules, such as these carcinogenic compounds. Consequently, most of the chemical and physical methods of dealing with pi-electron systems are based on this method. Earlier theoretical treatments have dealt entirely with pi-electrons in such compounds, but during the past decade various workers have questioned the validity of these theories and feel that pi-electrons may not be treated entirely separately from the ordinary localized sigma-bond electrons. March[16] has shown that, when accurate electron density patterns are drawn, the pi-electron cloud merges quite indistinguishably into the sigma-electron cloud. Some other workers[17] have shown, that alternative descriptions of conjugated molecules are often possible, in which no specific division into sigma and pi-electrons takes place; in fact this separation is not a rigorous quantum-mechanical one. Altman[18] has demonstrated that even when using sigma and pi-classification, one must allow electron exchange to take place between members in different classes. This means essentially that pi-electrons cannot be treated as entirely independent entities. It should also be recognized that these theoretical methods contain certain simplifying assumptions of a semi-empirical nature. These approximations are necessary for calculations of the properties of such complex and large molecules as these polynuclear aromatic

hydrocarbons. This means that we shall probably never be able to get bond orders and related quantities with as great a precision as we should like. For example, we shall never be able to incorporate all the possible structures in a valency bond calculation or even determine the individual weights of those which are already incorporated in the wave function. Similarly, in the molecular orbital calculations, we shall never know the coulombic terms and resonance integrals with complete reliability. Thus, considering the complexities of the problem, it is not surprising that no simple correlation exists between these studies and the problem of carcinogenic activity. As for the chemical reactivity of these hydrocarbons, during the past decade several theoretical indices have been proposed to account for this. These indices are: pi-electron density,[19] self-polarizability,[20] free valency,[21] localization energy,[19] approximate localization energy,[11] frontier electron density,[22] super delocalizability[22] and others.[23-26]

The chemical reactivity of the pi-electron system has been approached in two different ways in the molecular-orbital theory: the "localization method"[19] and the "static method."[20] In the localization method, it is assumed that the rate of reaction at a certain position in a molecule is determined by the "localization energy" which is required in localizing a requisite number of electrons at that position. In the "static method" the chemical reactivity at a position in a

molecule is correlated with the density of all the pi-electrons at that position in an isolated molecule. The fundamental assumption in the localization method is that a parallelism exists between localization energy and chemical reactivity. On the other hand, in the static method the interaction between the molecule and the reagent is regarded as being very small. In both these methods the type of reaction is not directly considered ie., the mechanism of formation and dissociation of sigma-bonds is not taken into consideration. However, in one of the more recent treatments, the "frontier electron" method,[22] the electronic interaction between the molecule and the reagent has been divided into sigma and pi-parts. In this method, the chemical reactivity of these molecules is attributed to the distribution and density of frontier electrons.

The frontier electrons are defined as the <u>two</u> electrons occupying the highest pi-orbital in the ground state, distinct from other pi-electrons. These electrons are regarded as valence-electron-like in nature. In a covalent sigma-bond formation between the pi-electron system and the reagent, the position which has the higher density of the two electrons occupying the highest molecular orbital in the ground state is most susceptible to an attack by an electrophilic reagent. However, in the case of reaction with a nucleophilic reagent, it is the lowest vacant orbital in the ground state which is most susceptible to an attack.

In the case of the reaction with a radical, the position which has higher density of the two electrons, one occupying the highest orbital and the other occupying the lowest orbital of the ground state is most susceptible to an attack. Thus, the position which is most susceptible to an attack by an approaching reagent is that of the highest value of these indices. This is the case in substitution, addition and molecular complex formation.

The above mentioned theoretical treatments of Pullman,[6,7,13,15] Fukui,[12] and others afford a possibility of a correlation of calculated bond orders and other molecular parameters with empirical investigations of free radical reactivity towards these hydrocarbons. It may, however, be pointed out that the proponents of the "K-region theory" are critical of some of the assumptions of the "frontier electron" method.[27-29]

Verification of these theories has been sought by using diverse experimental approaches. Badger[30] investigated the rate of addition of osmium tetraoxide to these hydrocarbons. This reagent adds across the "K-region". Szwarc[31] and Kooyman[32] have investigated the relative reactivities of these hydrocarbons towards methyl and trichloromethyl free radicals respectively and have sought a correlation between radical reactivity and free valence number in these hydrocarbons. Waters[33] investigated the reactivity of these hydrocarbons towards radicals produced by oxidation of benzal-

dehyde, but the uncertainties of the mode of chain initiation, nature of competive side reactions and a large variety of chain termination steps added to the complexity of the system, and the interpretation of the results was not clear.

Some very qualitative work on the effect of these hydrocarbons on the thermal polymerization of styrene has been reported in brief by Magat[34] and by Belonovskaya.[35] In view of the fact that only a few of these hydrocarbons were investigated by these workers and the studies were only of a qualitative nature, no correlations between these studies and the theoretical work can be drawn. As these investigations are somewhat similar to the ones reported in this thesis, a closer examination of their results is warranted. Magat[34] reported the efficiency of some of these hydrocarbons in slowing down the reaction in the order: 3,4-benzpyrene > phenanthrene > 1,2,5,6-dibenzanthracene. Chrysene and pyrene had no effect. Considering, that all these compounds possess a K-region, these investigations were probably carried out to furnish further experimental evidence on the "K-region" hypothesis. As only a few of these were found to be reactive towards styryl radicals, there appears to be no correlation between free radical reactivity and the existance of the "K-region".

It may, however, be noted that the reactivity of phenanthrene as reported by Magat[34] is very doubtful. This hydrocarbon was found to be unreactive by Belonovskaya[35]

and by us. Kooyman[36] attributed this observed reactivity of phenanthrene as being probably due to some impurities in the hydrocarbon sample used by Magat, the probable impurities being anthracene, naphthacene etc. This leaves only 3,4-benzpyrene and 1,2,5,6-dibenzanthracene as being reactive towards styryl radicals. It is interesting to note that both these hydrocarbons have a high pi-electron density in the K-region compared to the other hydrocarbons investigated by Magat; both these hydrocarbons are carcinogenic while phenanthrene, chrysene and pyrene non-carcinogenic. This would lead one to believe that some type of correlation might exist between carcinogenicity and the reactivity of these hydrocarbons towards free radicals. It was this observation and the fact that the kinetics of inhibition and retardation of vinyl polymerization by these compounds had not been investigated thus far, which aroused our curiosity to pursue these studies on a quantitative basis.

Recently, Belonovskaya[35] reported that anthracene and dibenzopyrene retarded the thermal polymerization of styrene, whereas naphthalene, phenanthrene, pyrene and chrysene had no effect. Among these hydrocarbons, only dibenzopyrene is carcinogenic and possesses fairly high pi-electron density at its K-region. This would appear to bear out the expectation of seeking a correlation between carcinogenicity and free radical reactivity. However, the observed reactivity of anthracene destroys the possibility of seeking such a corre-

lation as this hydrocarbon is non-carcinogenic and possesses no K-region. As will be seen later from our studies, several other non-carcinogenic hydrocarbons also retarded the polymerization of styrene. It can be implied that this chemical reactivity does not constitute a basis for differentiation between carcinogens and non-carcinogens. Thus, no correlation between carcinogenicity and their reactivity towards free radicals may be expected. Similar conclusions may also be drawn from the studies of Szwarc[31] and Kooyman.[32]

However, a common feature among these compounds is that those hydrocarbons which possess a high pi-electron density in localized regions (K or L-regions), were also found to be reactive towards free radicals, and as will be seen later a correlation does exist between the pi-electron density of these regions and their chemical reactivity.

Since the kinetics of inhibition and retardation of vinyl polymerization by condensed ring hydrocarbons has not yet been studied systematically, the research described in this thesis was undertaken to elucidate the mechanism of inhibition and retardation by these compounds. It was further hoped that the data obtained would provide experimental support for one or more of the existing theories relating pi-electron density and free radical reactivity.

EXPERIMENTAL

(1) Preparation and Purification of Materials.

Styrene: Ram Chemicals Inc. Styrene was purified following the procedure of Szwarc.[37] Monomer was fractionated under reduced pressure in an inert (N_2) atmosphere. The distillate was washed several times with 2% sodium hydroxide, distilled water, 1% sulfuric acid and finally with distilled water until the washings were neutral. Monomer was then dried overnight over calcium hydride and fractionated under reduced pressure and nitrogen atmosphere using a 90cm vacuum-jacketed column packed with glass helices (all-glass apparatus was used). Only the constant-boiling middle fraction was collected. The exact boiling point for each distillation depended on the reduced pressure. The purified monomer was stored in specially constructed containers under nitrogen and kept frozen in dry ice-acetone mixture until used.

2,2'-azo-bis-isobutyronitrile: Eastman Organic Chemicals. Was purified by recrystallization several times from methyl alcohol. Only the first crop of crystals was collected in each crystallization. The initiator was stored under refrigeration and recrystallized again from time to time.

Naphthalene: Baker Chemicals (resublimed). Recrystallized from ethyl alcohol thrice, adsorbed on alumina twice and eluted with pentane; m.p. 80-80.5°C. (80°);[38] (79.6-81.2°)[39]

Anthracene: Eastman Organic Chemicals (blue-violet fluorescence grade). Recrystallized from benzene thrice, adsorbed on alumina twice and eluted with hexane; m.p. 217-218°C. (218°)[38]

Phenanthrene: Eastman Organic Chemicals (white label). Recrystallized from ethyl alcohol thrice, adsorbed on alumina and eluted with hexane, readsorbed on alumina and eluted with pentane; m.p. 98-99°C. (100°);[38] (97.8-99.5°)[39]

Chrysene: Eastman Organic Chemicals (violet-fluorescence grade). Recrystallized from benzene thrice, adsorbed on alumina twice and eluted with hexane, adsorbed on silica and eluted with pentane; m.p. 255-256.5°C. (255-256°);[38] (254.8-256.9°)[39]

Pyrene: Chemical Procurement Co. Adsorbed on silica twice and eluted with pentane, recrystallized from ethyl acetate twice, adsorbed on silica and eluted with pentane; m.p. 153.5-155°C. (153.2-155.2°);[39] (156°)[38]

Triphenylene: K & K Laboratories Inc. Adsorbed on silica-alumina thrice and eluted with pentane; m.p. 199-200.5°C. (196.5° uncorr.);[38] (199-202.4°)[39]

Perylene: K & K Laboratories Inc. Adsorbed on alumina and eluted with pentane (first fraction was discarded), adsorbed on alumina twice and eluted with benzene; m.p. 268.5-269.5°C. (268.5°);[39] (273-274°)[38]

1,2,5,6-dibenzanthracene: L. Light & Co. Ltd. Was treated with lead tetra-acetate twice, recrystallized from

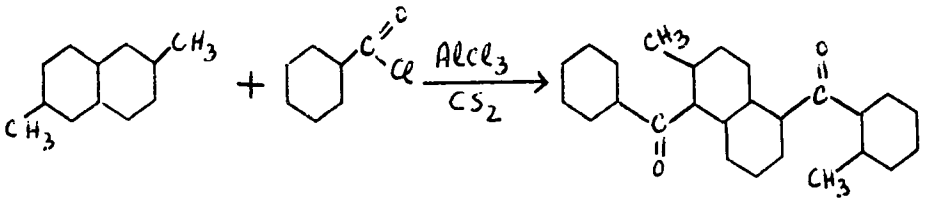
benzene twice, adsorbed on alumina-silica thrice and eluted with benzene; m.p. 261.5-262°C. (262°)[38] Lead tetra-acetate was synthesized following standard procedure.

1,2-benzanthracene: Eastman Organic Chemicals. Recrystallized from benzene twice, adsorbed on alumina four times and eluted with benzene; m.p. 158-159°C. (158-159°)[38]

3,4-benzpyrene: (Synonym: 1,2-benzpyrene or benzo [a] pyrene). L. Light & Co. Ltd. Picrate prepared in benzene and recrystallized to constant melting point, formed long purplish black needles; m.p. 197-198°C. The hydrocarbon was regenerated from pure picrate with sodium carbonate, adsorbed on alumina thrice, eluted with benzene, and finally recrystallized from benzene thrice; m.p. 176.5-177.5°C. (176.5-177.5°)[38]

1,2-benzpyrene: (Synonym: 4,5-benzopyrene or benzo [e] pyrene). Chemical Procurement Co. Picrate prepared in benzene, recrystallized to constant melting point 229-230°C, ruby red needles. The hydrocarbon was regenerated from picrate with sodium carbonate, adsorbed on alumina-silica twice and eluted with benzene, adsorbed on alumina thrice and eluted with benzene, adsorbed again on alumina and eluted with petroleum ether and finally recrystallized from benzene-methyl alcohol twice; m.p. 178-179°C. (178-179°)[38]

1',1-anthra-1,2-anthracene: 1,5-dibenzoyl-2,6-dimethylnaphthalene was synthesized according to procedure,[40]

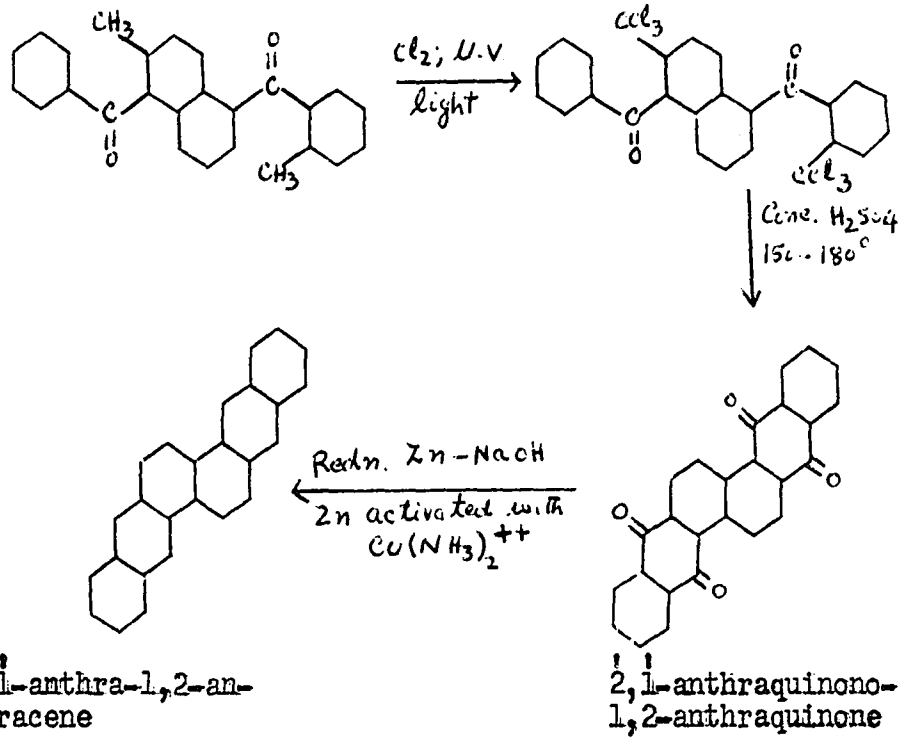


2,6-dimethyl-naphthalene

1,5-dibenzoyl-2,6-dimethyl-naphthalene

but the pyrolysis of this ketone employing a variety of conditions of heating and distillation under reduced pressure failed to yield the desired hydrocarbon. Ring closure of 1,5-dibenzoyl-2,6-dimethyl-naphthalene was also attempted by heating with sulfur to obtain a tetraquinone, and by heating with polyphosphoric acid under different reaction conditions and subsequently distilling under reduced pressure, but the desired products were not obtained. Attempts were also made to oxidize the two methyl groups to the carboxylic groups using conventional oxidizing agents, but without any success. This may be due to the deactivating influence of the carbonyl groups in ortho position to the methyl groups. Oxidation of the methyl groups has been claimed[41] by using SeO_2 as an oxidizing agent.

The hydrocarbon was, however, synthesized following the procedure below:[42]



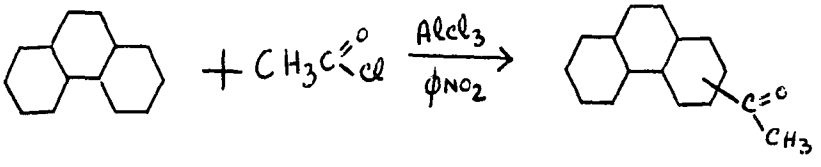
2',1'-anthra-1,2-anthracene

2',1'-anthraquinono-1,2-anthraquinone

The hydrocarbon was recrystallized several times from xylene and purified further by adsorption on alumina, eluted with xylene, and finally sublimed under vacuum in a current of carbon dioxide; m.p. ca. 400°C. (ca. 400°)[38]

<u>1,2,7,8-dibenztetracene and 1,2,9,10-dibenztetracene</u>:

2,3-acetylphenanthrenes were synthesized by the following procedure:[43]

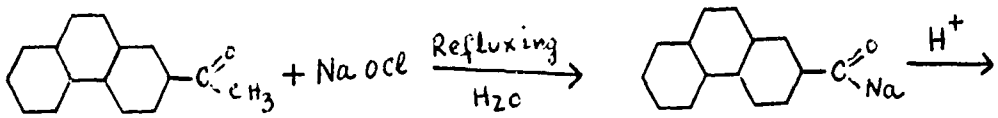


Phenanthrene

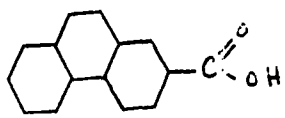
2,3-acetyl-phenanthrenes

Difficulty was encountered in crystallizing the acetylphenanthrenes from the crude, oily dark brown mass. A small portion of this viscous mass upon distillation yielded a product which soon crystallized, and this was used to seed the crude material which induced rapid crystallization. The 2-and 3-substituted isomers were separated.

Phenanthrene 3-carboxylic acid: Oxidation of the 3-acetylphenanthrene was carried out with sodium hypochlorite. Yield: 80-85%.



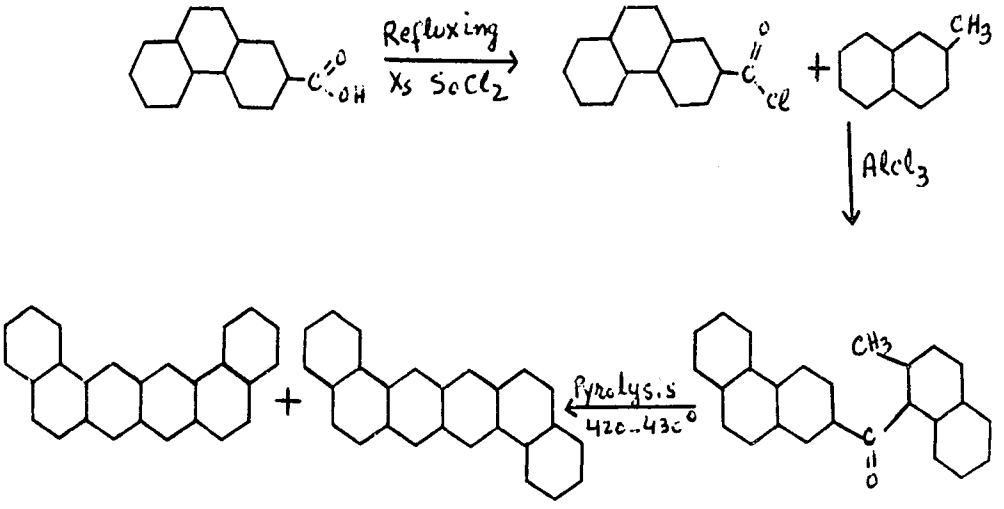
3-acetylphenanthrene



3-phenanthroic acid

3-(2'-methyl-1'-naphthyl) phenanthrene: Was synthesized following procedure,[44] which on pyrolysis gave a mixture of hydrocarbons.

The isomeric mixture of the hydrocarbons was then separated on the basis of their solubilities differences. The lower melting isomer (1,2,9,10-dibenztetracene) was extracted with acetone while 1,2,7,8-dibenztetracene is soluble in xylene, benzene and other high boiling solvents.



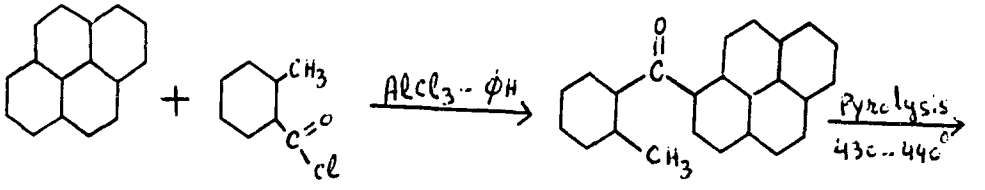
1,2,9,10-dibenz-tetracene | 1,2,7,8-dibenz-tetracene | 3-(2-methyl-1-naphthyl)-phenanthrene

1,2,9,10-dibenztetracene: The acetone extract was decolorized with charcoal in benzene solution, adsorbed on alumina thrice and eluted with benzene, and recrystallized from benzene-ethyl alcohol five times; m.p. 253-254°C. (253-254°)[38]

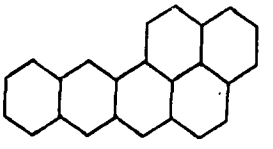
1,2,7,8-dibenztetracene: The residue from the acetone extraction was decolorized with charcoal in xylene solution, recrystallized from xylene several times, adsorbed on alumina twice, and eluted with xylene. It was recrystallized from xylene twice and only first crops of crystals were used; m.p. 344-345°C. (345°)[38]

2,3-naphtho-3,4-pyrene: In view of the fact that this hydrocarbon acted as a very strong retarder, it was synthesized via two different routes.[45,46]

Procedure I:[45]



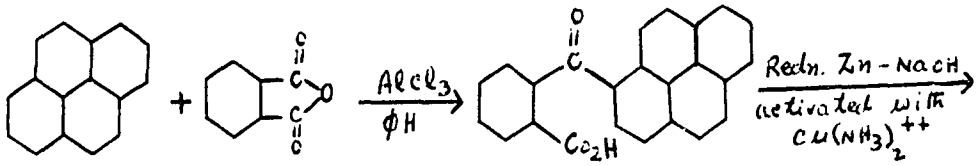
Pyrene 3-o-toluyl-pyrene



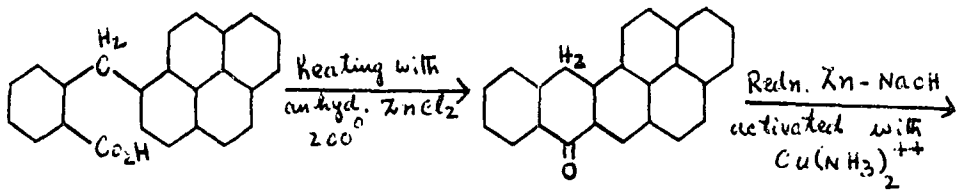
1',2'-naphtho-3,4-pyrene

The crude hydrocarbon, obtained after distillation under reduced pressure of the pyrolysis product, was sublimed under reduced pressure in a current of carbon dioxide. The sublimate was then adsorbed on alumina several times, eluted with benzene, and recrystallized from benzene thrice; m.p. 265-266°C. (265-266°)[45] o-Toluic acid was synthesized according to procedure,[47] the acid cloride formed by refluxing in benzene with excess thionyl cloride, and purified by distillation. (b.p. 207-209°C.)

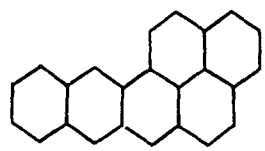
Procedure II:[46]



Pyrene | phthalic-anhydride | 1-pyrenoyl-o-benzoic acid



1-o-carboxybenzyl-pyrene



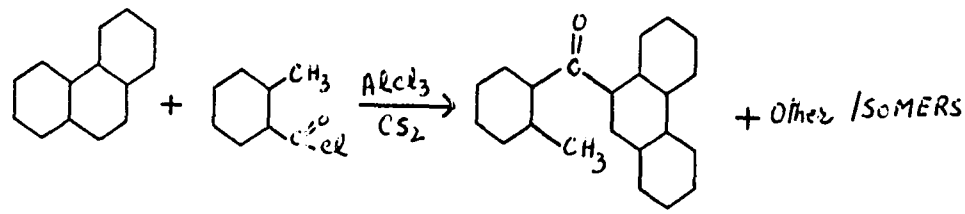
1',2'-naphtho-3,4-pyrene

(Commercial phthalic-anhydride was dehydrated immediately before use.)

The crude hydrocarbon was sublimed, recrystallized from benzene thrice, adsorbed on alumina thrice, eluted with benzene, and finally recrystallized from benzene four times; m.p. 273°C. (273°)[38]

1,2,3,4-dibenzanthracene and 2,3,7,8-dibenzphenanthrene.

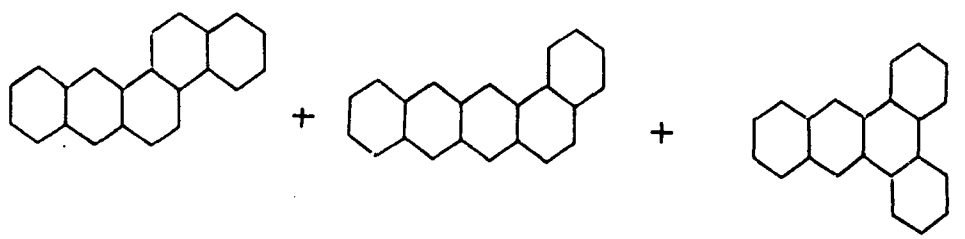
These hydrocarbons were synthesized as follows:[48]



Phenanthrene

9-(o-tolyl)-phenanthryl ketone

Pyrolysis 400-420° with Zn dust[49]



2,3,7,8-dibenz-phenanthrene

1,2,6,7-dibenz-anthracene

1,2,3,4-dibenz-anthracene

These isomers were separated by complexing with maleic anhydride.[50]

1,2,3,4-dibenzanthracene: The crude hydrocarbon, obtained after concentration of the xylene mother liquor from the maleic anhydride separation, was treated with picric acid in benzene and the picrate decomposed with sodium carbonate. The hydrocarbon was then adsorbed on alumina thrice, eluted with benzene, and recrystallized from acetic acid twice. Colorless silky needles were obtained; m.p. 205°C. (205°)[38]

2,3,7,8-dibenzphenanthrene: The crude hydrocarbon was re-

crystallized from xylene six times. Pale yellow-green leaflets were obtained; m.p. 293-294°C. (294°)[38]

1,2,6,7-dibenzanthracene: Yield of this hydrocarbon was poor. An insufficient quantity of pure hydrocarbon was obtained for kinetic investigation.

1,2,3,4-dibenzpyrene: Ruetgerswerke-Aktiengesellschaft (Germany). Was adsorbed on alumina thrice, eluted with benzene, and recrystallized from benzene thrice; m.p. 226-227°C, (226-227°)[38]

In Figures 1-6 are reported the infrared spectra of only those hydrocarbons that were either synthesized or were found to have an effect on the rate of polymerization. These spectra were taken to confirm the purity of these hydrocarbons. The most probable impurities in the hydrocarbons that were synthesized would be methyl ketones and quinones. The absence of carbonyl and $C-CH_3$ absorption peaks in these spectra was considered a criterion for the absence of these impurities. Similar impurities could also be expected in the commercially-procured hydrocarbons. Thus, these spectra and the melting points of these hydrocarbons were regarded as a criterion of the purity of these compounds.

Attempted syntheses of 1,2-anthra-1,2-anthracene, 1,2,3,4,5,6-tribenzanthracene and 3,4,8,9-dibenzpyrene.

Many attempts were made following several procedures[51-53] to synthesize these hydrocarbons but without any success.

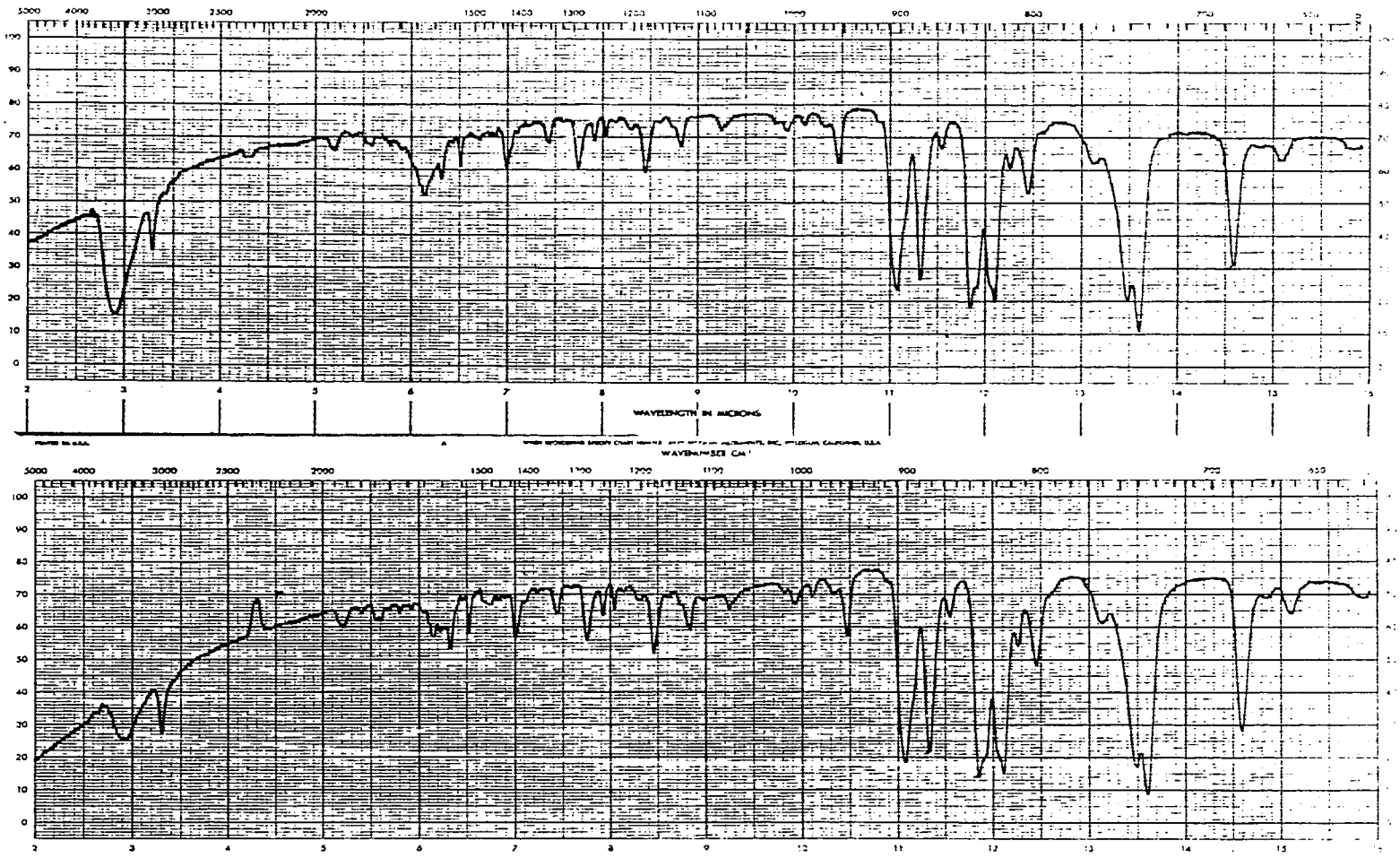


FIGURE 1. INFRA RED SPECTRA OF 2',3'-NAPHTHO-3,4-PYRENE IN POTASSIUM BROMIDE. UPPER HYDROCARBON SYNTHESIZED VIA KETONE; LOWER VIA QUINONE.

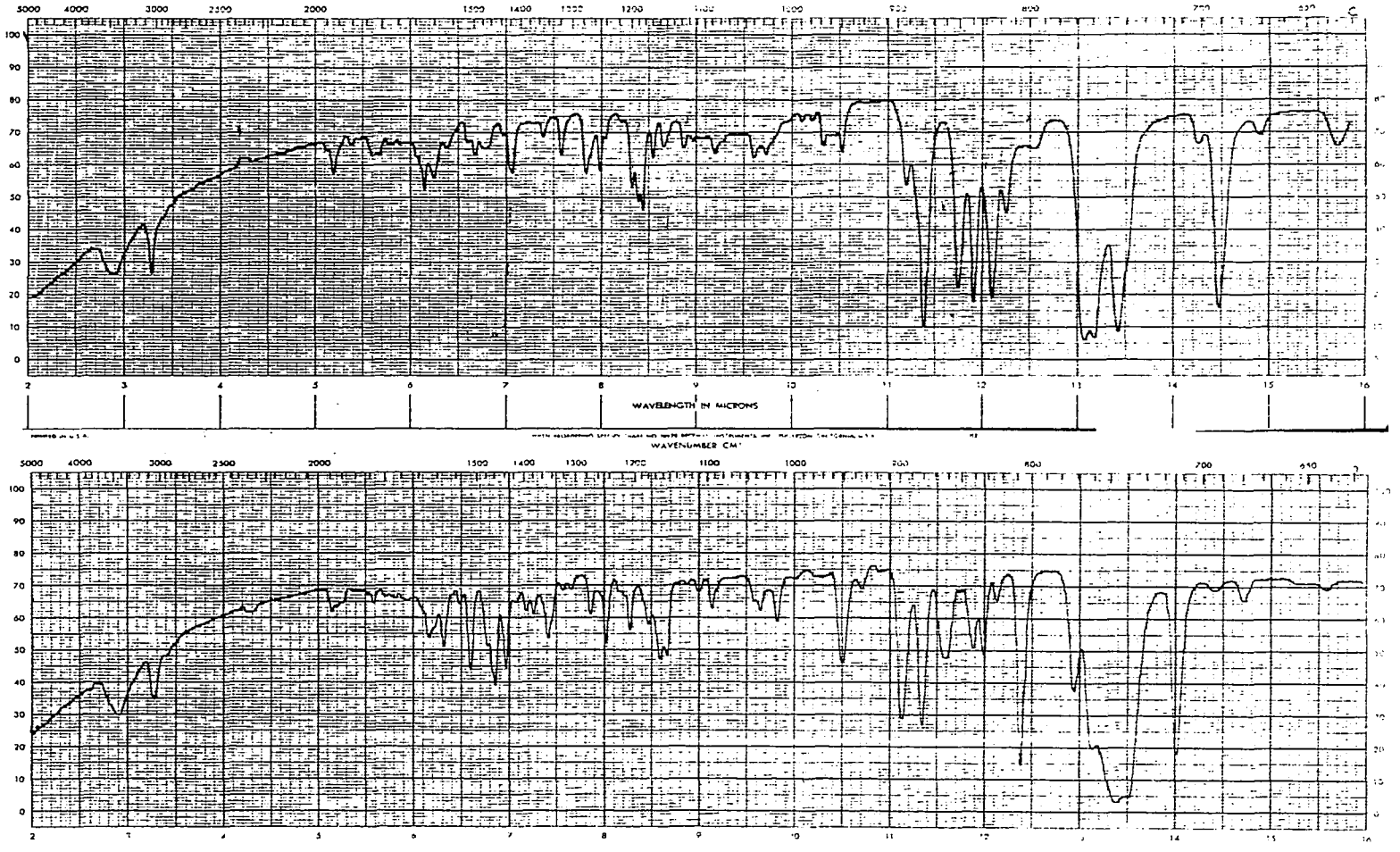


FIGURE 2. INFRA RED SPECTRA OF 3,4-BENZPYRENE (UPPER) AND 1,2,3,4-DIBENZ-PYRENE (LOWER) IN POTASSIUM BROMIDE.

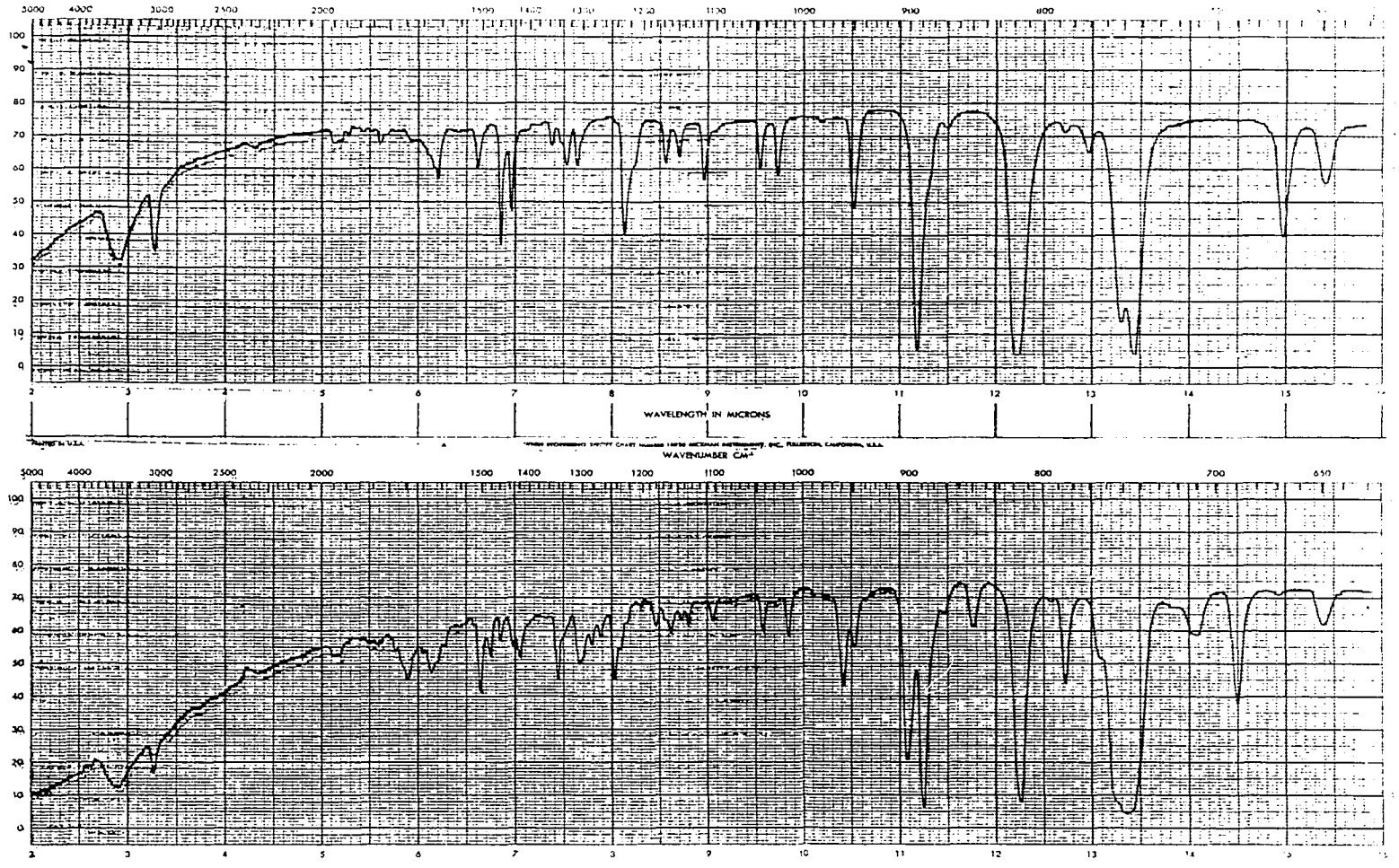


FIGURE 3. INFRA RED SPECTRA OF 1,2,5,6-DIBENZANTHRACENE (UPPER) AND 1,2-BENZANTHRACENE (LOWER) IN POTASSIUM BROMIDE.

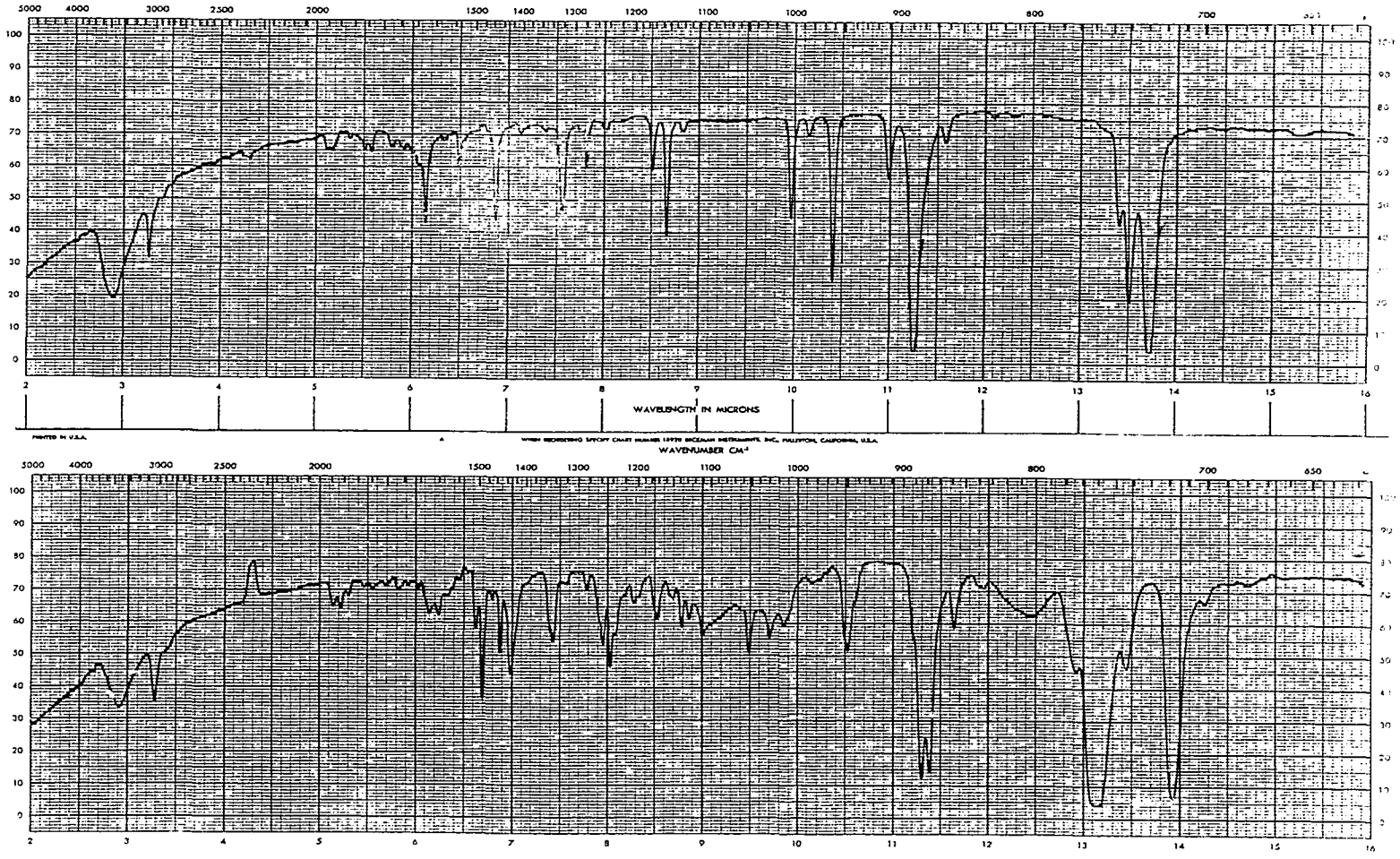


FIGURE 4. INFRA RED SPECTRA OF ANTHRACENE (UPPER) AND 1,2,3,4-DIBENZ-ANTHRACENE (LOWER) IN POTASSIUM BROMIDE.

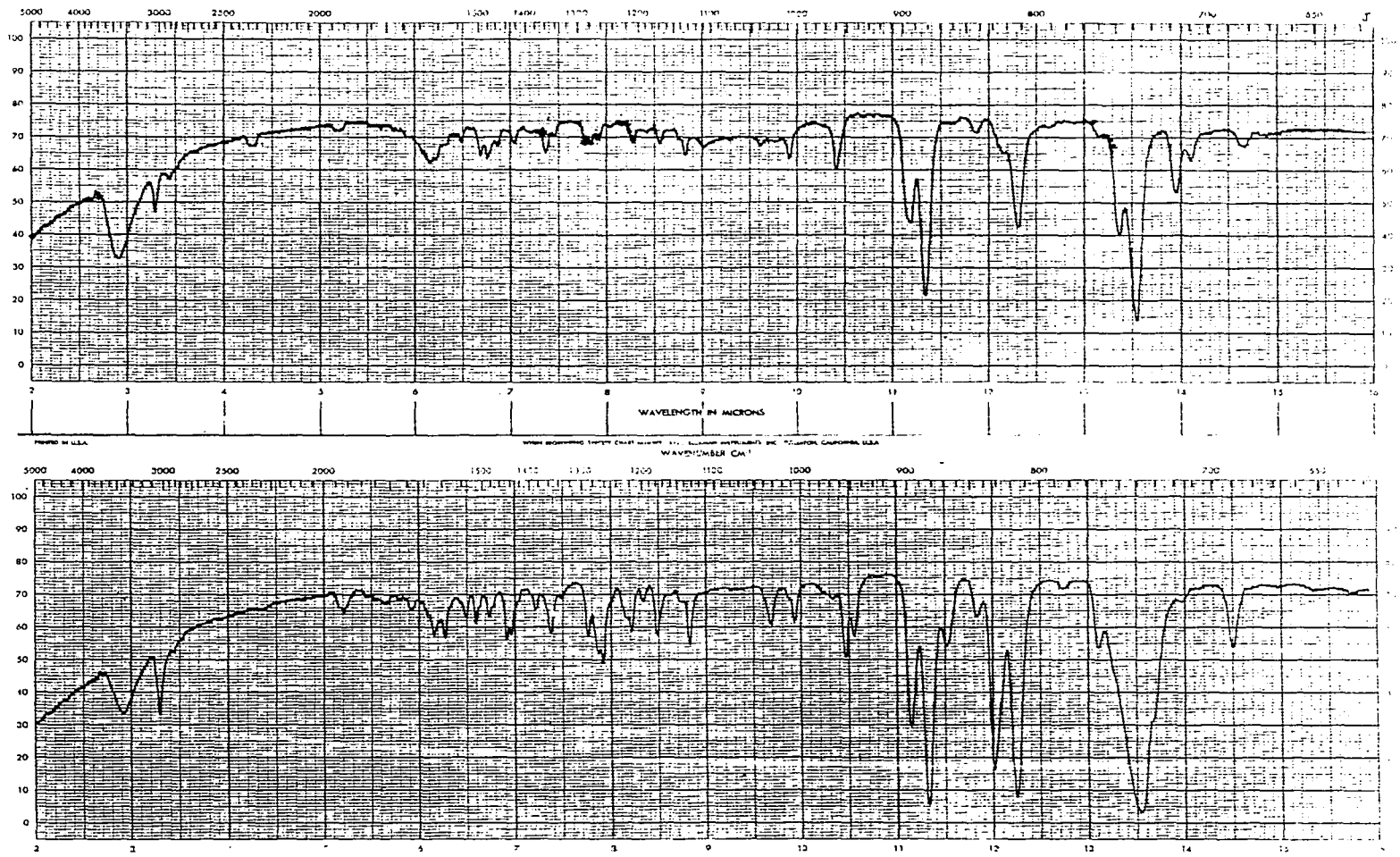


FIGURE 5. INFRA RED SPECTRA OF 2,1-ANTHRA-1,2-ANTHRACENE (UPPER) AND 2,3,7,8-DIBENZPHENANTHRENE (LOWER) IN POTASSIUM BROMIDE.

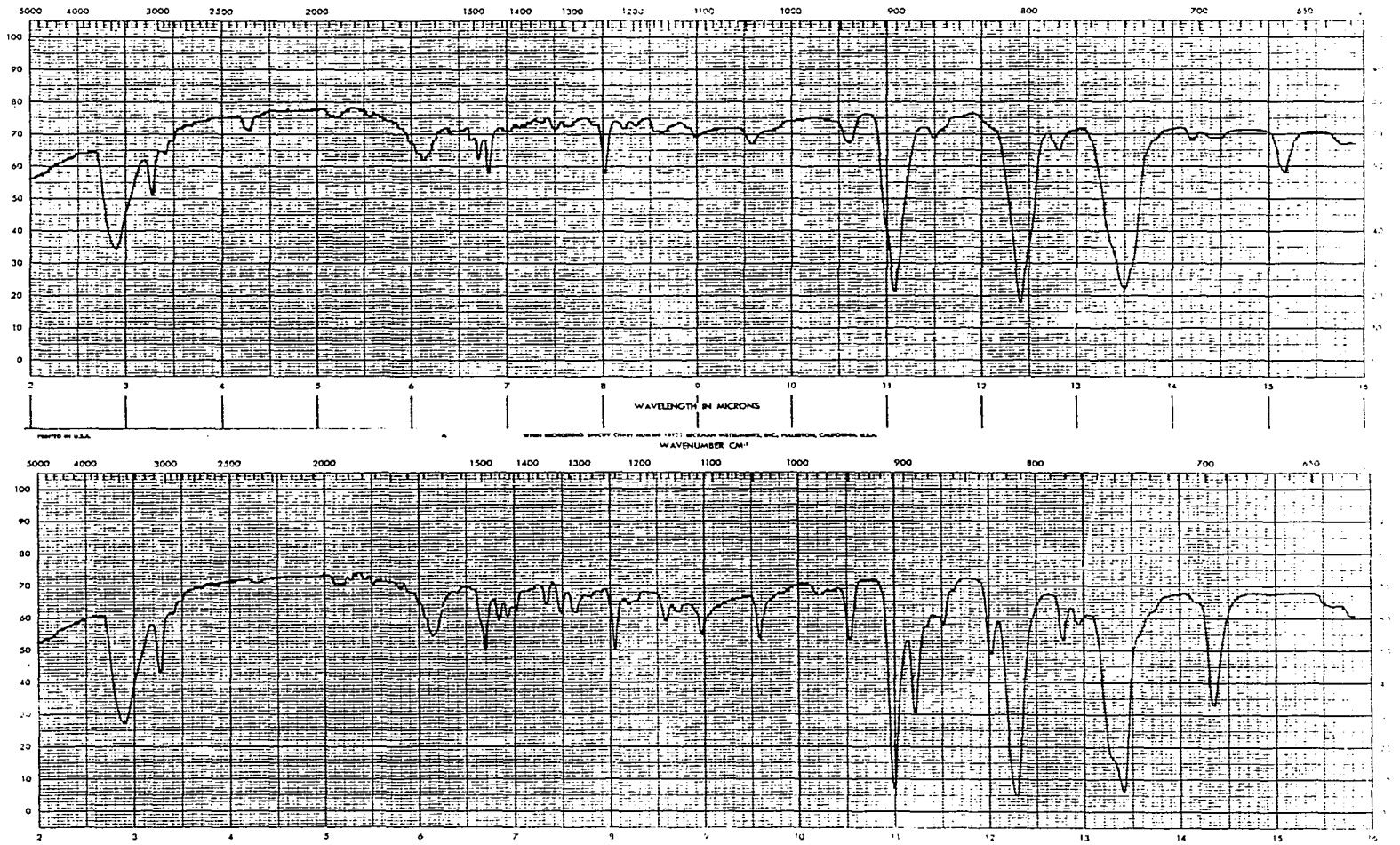


FIGURE 6. INFRA RED SPECTRA OF 1,2,9,10-DIBENZTETRACENE (UPPER) AND 1,2,7,8-DIBENZTETRACENE (LOWER) IN POTASSIUM BROMIDE.

(2) Vacuum Dilatometry.

The best understood free radical chain reactions in the liquid phase are homopolymerizations of the vinyl type. The fact that a large volume change accompanies vinyl polymerization and a linear relationship holds between the rate of polymerization and the change in volume, especially during the initial stages of the polymerization reaction, renders dilatometry a very sensitive and delicate tool for the investigation of polymerization kinetics. The influence of added low concentrations of inhibitors and retarders to the polymerizing system can thereby be studied. The effects of the various compounds on the rate of polymerization are evidenced by their varying degree of influence on the rate curve and allow conclusions to be drawn regarding their efficiencies as inhibitors or retarders.[54]

The apparatus and experimental procedures used for these studies were similar to those of Bartlett and Kwart.[55] The polymerization initiator chosen was 2,2'-azo-bis-isobutyronitrile (AIBN). This initiator was chosen because of its apparently clear cut mechanism of polymerization initiation. Unlike peroxides it does not appear to be subject to induced decomposition or to present other undesirable side effects.[56]

A schematic representation of the vacuum dilatometer used in the present work is given in Figure 7. The dilatometer was constructed of Pyrex glass with precision-bore capillary tubing. The procedure for its use was as follows:

After a weighed amount of the hydrocarbon was placed in reservoir B, the dilatometer opening A was sealed off. The desired amount of AIBN was weighed into a low-actinic glass flask with ground glass joint and the necessary volume of styrene was pipetted into this flask. The styrene-AIBN solution was prepared, and a 50ml aliquot transferred quickly into reservoir C of the dilatometer. The monomer was allowed to warm to the room temperature before adding to AIBN. The temperature of monomer and monomer-AIBN solution was recorded for the purpose of calculating the molarities of AIBN and the hydrocarbon at the polymerization temperature. Density data for styrene[57] was used to obtain its volume at the polymerization temperature. All weighings in the present work were performed on a semi-micro balance using calibrated weights. Immediately after pipetting 50ml aliquots of styrene-AIBN solutions into the dilatometers, the dilatometers were connected to a high vacuum system by means of the ground glass joint D, and the monomer-AIBN solution in the reservoir C was frozen in dry ice-acetone mixture. Since oxygen interfers with this reaction, the monomer was degassed as follows:

Monomer in reservoir C was frozen in dry ice-acetone mixture and the hydrocarbon, if present, was cooled by immersion of reservoir B in this freezing mixture in order to prevent possible sublimation. The dilatometer was evacuated to a pressure of about 10^{-5}mm of mercury. The part of the vacuum system including the dilatometer was then cut off from

the vacuum pump by closing a stop-cock adjacent to the ground glass joint at D. The monomer was allowed to thaw, permitting the dissolved gases to escape into the evacuated dilatometer. The monomer and the hydrocarbon were then refrozen and the dilatometer again evacuated. This process was repeated four times, freezing time in each case was approximately one hour and pumping time 10,15,30 and 60 minutes respectively. The monomer was then considered to be essentially free of dissolved oxygen.

After sealing off from the vacuum system at E, the monomer-AIBN solution in reservoir C was kept frozen in dry ice-acetone mixture until the rate studies were made. The constant temperature bath, in which the reactions were carried out was maintained at $44.4^{\circ} \pm 0.005^{\circ}C$ and was heated by an infrared lamp covered by a red-glass filter. The thermostat was located in a dark-room and the dilatometer illuminated by a red safe-light during the course of reaction. All these precautions were necessary to avoid photo-initiation due to U.V. light.

Before starting a run, the sample was treated by the following procedure which took between 10-20 minutes depending on the solubility of a particular hydrocarbon. It was found necessary that this period of treatment prior to zero time for each run on a certain hydrocarbon be kept the same, especially for those runs where definite inhibition periods were observed. The frozen monomer-initiator solution in reservoir C of the

dilatometer was thawed by immersion in the constant temperature bath and allowed to warm to about the reaction temperature. The hydrocarbon was then dissolved in the monomer-initiator solution by inverting the dilatometer, shaking it and intermittently heating reservoir C in the bath for some time. After the reactants had dissolved, the reservoir F was partially filled and emptied two or three times to ensure a homogeneous solution. Then reservoir F and the capillaries were filled with the reaction mixture (excess remaining in reservoirs C and B) and the dilatometer inserted into the constant temperature bath. It was made sure that there were no discontinuties in the liquid column in between the reservoir F and the capillaries or in the capillaries themselves. The time of insertion of the dilatometer in the bath was regarded as time zero for each experiment. (The exact zero time is immaterial in cases where no inhibition periods were observed, since the experimental quantity of interest is the initial rate of polymerization which remains constant for a period exceeding the time range during which measurements were made.)

After the monomer solution had come up to about the reaction temperature, the dilatometer was removed from the bath momentarily, the liquid level in the capillaries adjusted to a convenient position, and the dilatometer was reinserted into the bath. This usually was done after about six minutes after initial immersion of the dilatometer into the bath. Readings of the liquid levels in the capillaries during the

course of reaction were taken with a cathetometer through the glass sides of the thermostat. The first reading was made after about 10-12 minutes had elapsed from the time of immersion of the dilatometer. The liquid levels in the capillaries were read to the nearest 0.01cm and the time recorded. The rate of fall of the liquid level in the capillaries is linearly related to the rate of polymerization.

Immediately after the run the polymer-monomer mixture was precipitated in methyl alcohol and stabilized with hydroquinone. The precipitated polymer was filtered, dried and saved. The dilatometers were cleaned by filling with hot toluene and allowed to stand. The toluene was then poured out, dilatometers rinsed with acetone and then with water. After resealing the ground glass joint D and side arm A on to the dilatometer, the latter was filled with a hot nitric-sulfuric acid mixture; this was allowed to stand until the acid mixture had cooled to room temperature. The acid was removed and the dilatometer rinsed six times with distilled water and five times with reagent grade acetone. The dilatometer was then pumped out under vacuum, checked for any pinhole leaks and put away for the next run.

(3) Calibration of the Dilatometers.

The calibration of dilatometers was carried out following an "indirect method" of Caldwell.[58] The dilatometer bulb was filled with purified mercury so that the mercury projected several centimeters up into the capillaries. The dilatometer

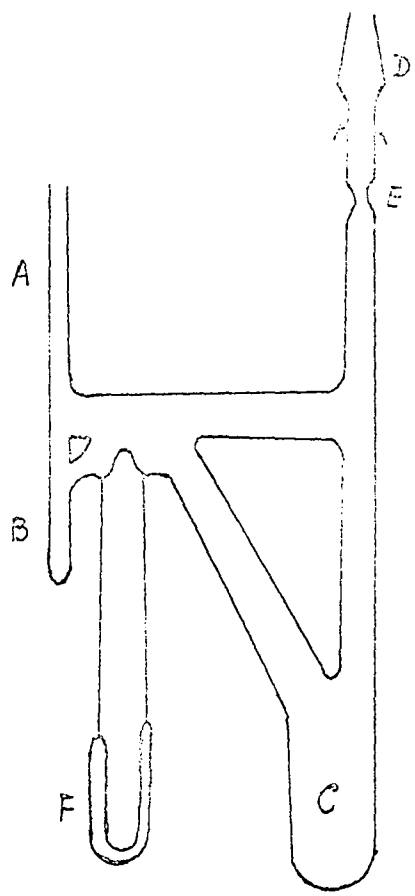


FIGURE 7. SCHEMATIC DIAGRAM OF A VACUUM DILATOMETER

was placed in a constant temperature bath at room temperature, the level of mercury in the capillaries read with a cathetometer, and the temperature of the bath recorded. The temperature was then raised to $44.4^{\circ} \pm 0.005^{\circ}C$ (the reaction temperature) and the new mercury levels in the capillaries read with the cathetometer. This provided all the necessary data for the calibration of the dilatometers.

The dilatometer constants were calculated using the average change in mercury levels in the two capillaries, the change in temperature as found experimentally, and the empirical relationships from the literature for the expansion of mercury:[59]

$V_t\ ^{Hg} = V_o\ ^{Hg} (1 + 1.816904 \times 10^{-4}t + 2.951266 \times 10^{-9}t^2 + 1.14562 \times 10^{-10}t^3)$ and of Pyrex glass:

$$V_t\ ^{Py} = V_o\ ^{Py} (1 + 9.679 \times 10^{-6}t + 3.107 \times 10^{-9}t^2),$$

the apparent temperature coefficient of expansion of mercury in pyrex was found to be $V_t = V_o (1 + F_t)$ where V_t is the volume at a temperature of $t^{\circ}C$, V_o is the volume at $0^{\circ}C$ and $F_t = \alpha t + \beta t^2 + \gamma t^3$ (α, β and γ are the constants in the relationship for mercury expansion). From the above relationships, the equation $V_2 - V_1 = V_o (F_2 - F_1)$ can be obtained. The subscripts denote the different temperatures and the symbols have the same significance. A relation of the same form holds for the equivalent lengths, giving $E_o = (E_2 - E_1)/(F_2 - F_1)$ $(E_2 - E_1)$ is the difference between the levels of mercury measured at two temperatures. From these relationships

the capillary length equivalent (E), that would hold the complete dilatometer reservoir volume, was calculated. Using the empirical relationship of Fox and Loshaek:[60]

$$(V)_p = 0.767 + 5.5 \times 10^{-4} T + 643 \times 10^{-4} T/M$$

where $(V)_p$ is the specific volume of the polymer; M, the molecular weight of polymer formed, and T is the temperature in degrees Kelvin, it was calculated that 100% polymerization of styrene at 44.4°C would result in a volume contraction of 18.85%. This would also correspond to the same per cent change in the capillary length equivalent to (E). As the molecular weight of the polymer formed is greater than 10^5 under these conditions, the last term, $643 \times 10^{-4} T/M$, is negligible and may be ignored in the calculation of specific volume of the polymer. It was found that a fall of one centimeter in the level of styrene in the capillary corresponded to 100/(0.1885 E)% polymerization. Representative values for the different dilatometer constants were 0.2954, 0.2891, 0.2837, 0.2882% polymerization/cm fall of styrene level in the capillaries.

(4) Experimental Results.

Sample plots of data from two typical kinetic runs are shown in Figures 8 and 9. From the slopes of lines it is a simple matter to find the corresponding rates of polymerization by use of the appropriate dilatometer constants.

For the unretarded runs the following relation for the rates was found: $r_o = 6.12\ (AIBN)^{\frac{1}{2}}$, where r_o is the rate of

unretarded polymerization in per cent per hour, and (AIBN) is the molar concentration of the initiator.

With the unretarded rate available for a given initiator concentration, it is convenient to define the degree of retardation, $\phi = r/r_o$, where r is the observed rate of polymerization and r_o is the rate of unretarded polymerization calculated for the same initiator concentration used in the retarded run. Thus, $r/r_o \backsim 1$ would mean that the added hydrocarbon has no effect on the rate of polymerization. A ratio of $r/r_o < 1$ means that the rate of reaction has been retarded.

A summary of the experimental results is given in Table 1 together with the corresponding values of ϕ.

For some of the hydrocarbons inhibition periods were observed. The length of inhibition period, T, is given in the Table, and the rate of polymerization (r) is the rate after inhibition period.

In this Table an additional column "Calculated rate per cent per hour at $(AIBN)^{\frac{1}{2}} \times 10^2 = 4.75$ M" is also included only for those hydrocarbons with which retardation effects were observed. These calculated rate values have been used in our kinetic treatment. This was done in order to obtain comparable rate constants for various reactions under similar initiator concentrations.

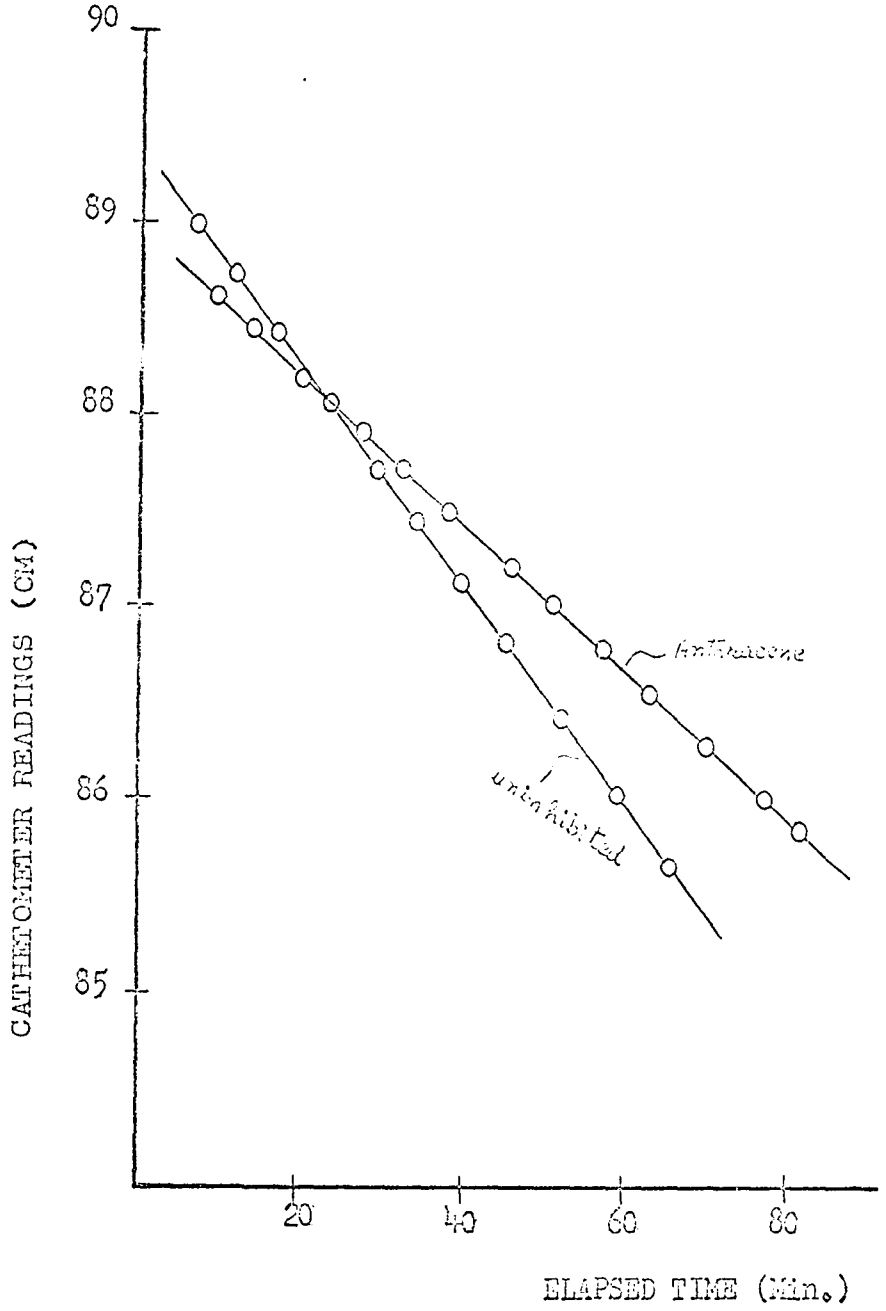


FIGURE 8. SAMPLE PLOTS OF PRIMITIVE KINETIC DATA FOR VACUUM DILATOMETRIC EXPERIMENTS; UNINHIBITED AND WITH ANTHRACENE

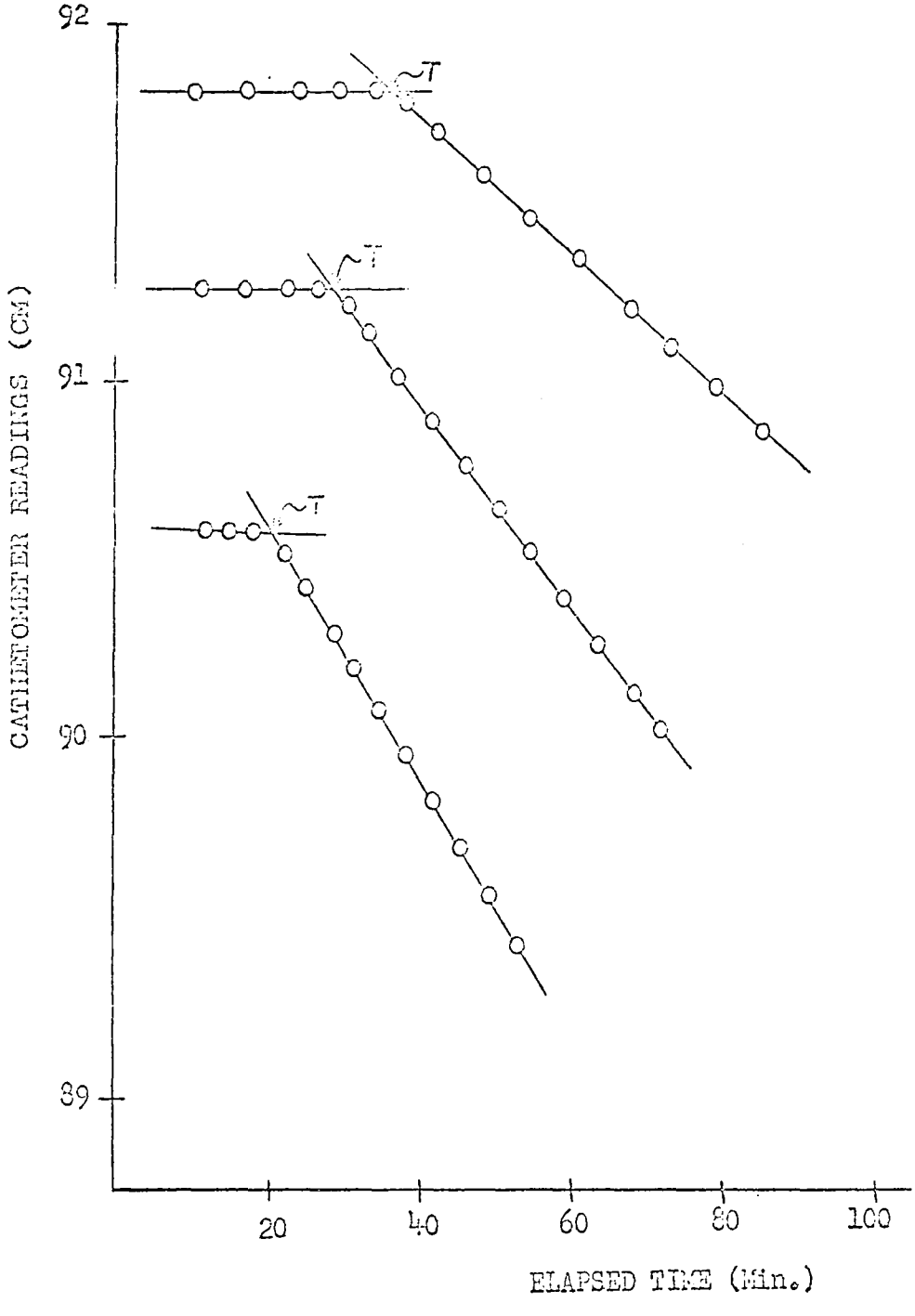


FIGURE 9. SAMPLE PLOTS OF PRIMITIVE KINETIC DATA FOR INHIBITION EXPERIMENTS WITH 3,4-BENZPYRENE

TABLE I

SUMMARY OF EXPERIMENTAL RESULTS FROM DILATOMETRIC MEASUREMENTS.

Hydrocarbon	Hydrocarbon Conc'n	$(AIBN)^{\frac{1}{2}}$ x 10^2M	T min.	r %/hr	ø	Calc. rate %/hr at $(AIBN)^{\frac{1}{2}} \times 10^2 = 4.75$M
Naphthalene	3.90×10^{-2}M	6.16	-	0.357	0.954	-
	12.1 "	7.49	-	0.455	0.993	-
Phenanthrene	2.77 "	5.77	-	0.357	1.01	-
	2.11 "	6.83	-	0.415	0.993	-
Chrysene	1.27 "	4.64	-	0.267	0.942	-
	1.46 "	6.73	-	0.400	0.971	-
Pyrene	2.97 "	5.49	-	0.347	1.03	-
	5.28 "	6.35	-	0.395	1.02	-
Triphenylene	2.37 "	5.47	-	0.361	1.08	-
	4.54 "	6.30	-	0.382	0.991	-
Perylene	1.04 "	6.67	-	0.405	0.992	-
	1.58 "	6.67	-	0.405	0.992	-
Anthracene	0.370 "	4.75	-	0.252	0.866	-
	0.665 "	4.75	-	0.226	0.777	-
	0.892 "	4.75	-	0.208	0.715	-
	1.04 "	4.75	-	0.199	0.684	-
	1.26 "	4.75	-	0.184	0.631	-
	1.58 "	4.75	-	0.163	0.560	-
	1.80 "	4.75	-	0.151	0.520	-
	1.925 "	4.75	-	0.147	0.509	-
	3.31 "	4.75	-	0.126	0.433	-
	3.49 "	4.75	-	0.121	0.416	-

TABLE I (Continued – Page 2)

Hydrocarbon	Hydrocarbon Conc'n	$(AIBN)^{\frac{1}{2}}$ x 10^2M	T min.	r %/hr	ϕ	Calc. rate %/hr at $(AIBN)^{\frac{1}{2}} \times 10^2 = 4.75M$
1,2-benzpyrene	0.756 x 10^{-2}M	4.64	–	0.285	1.00	–
	1.37 "	4.64	–	0.287	1.01	–
1,2,3,4-dibenz-anthracene	5.43 x 10^{-3}M	4.87	–	0.301	1.01	–
	1.46 "	4.87	–	0.298	1.00	–
1,2-benz-anthracene	4.21 "	4.65	16	0.292	1.01	–
	4.82 "	4.65	17	0.289	1.02	–
	5.49 "	4.65	18½	0.267	0.94	–
	6.22 "	4.65	20½	0.257	0.91	–
	8.11 "	4.65	24½	0.286	1.00	–
	9.20 "	4.65	27	0.290	1.02	–
3,4-benzpyrene	1.95 "	4.66	19	0.188	0.660	–
	2.19 "	4.66	20	0.180	0.632	–
	2.78 "	4.66	22½	0.165	0.579	–
	3.47 "	4.66	25½	0.148	0.520	–
	4.12 "	4.66	28	0.136	0.478	–
	5.61 "	4.66	34½	0.136	0.478	–
1,2,9,10-dibenz-tetracene	0.175 "	4.75	–	0.277	0.953	–
	0.619 "	4.75	–	0.245	0.843	–
	1.31 "	4.75	–	0.203	0.698	–
	1.73 "	4.75	–	0.182	0.625	–
	2.445 "	4.75	–	0.152	0.523	–
	3.54 "	4.75	–	0.125	0.430	–
	4.34 "	4.75	–	0.113	0.388	–
	5.09 "	4.75	–	0.100	0.344	–

TABLE I (Continued - Page 3)

Hydrocarbon	Hydrocarbon Conc'n	$(AIBN)^{\frac{1}{2}}$ x 10^2M	T min.	r %/hr	Ø	Calc. rate %/hr at $(AIBN)^{\frac{1}{2}}x10^2 = 4.75$M
1,2,3,4-dibenzpyrene	0.980 x 10^{-3}M	4.75	-	0.258	0.887	-
	1.42 "	4.75	-	0.245	0.842	-
	1.904 "	4.75	-	0.230	0.790	-
	3.20 "	4.75	-	0.198	0.680	-
	3.65 "	4.75	-	0.188	0.646	-
	4.26 "	4.75	-	0.175	0.601	-
1,2,7,8-dibenztetracene	0.425 "	4.75	-	0.254	0.873	-
	0.597 "	4.75	-	0.240	0.825	-
	0.700 "	4.75	-	0.233	0.801	-
	0.812 "	4.75	-	0.224	0.770	-
	0.938 "	4.75	-	0.216	0.742	-
2,3,7,8-dibenzphenanthrene	0.712 "	5.42	-	0.271	0.816	0.242
	0.935 "	5.42	-	0.254	0.765	0.223
	1.17 "	5.42	-	0.236	0.711	0.207
	1.45 "	5.42	-	0.219	0.660	0.191
	1.63 "	5.42	-	0.208	0.629	0.183
1',2',3-naphtho-3,4-pyrene	0.21 "	6.43	-	0.176	0.451	0.131
	0.494 "	6.43	-	0.103	0.262	0.076
	0.807 "	6.43	-	0.072	0.183	0.053
	1.84 "	6.43	-	0.042	0.107	0.031
	2.25 "	6.43	-	0.034	0.0864	0.025

TABLE I (Continued - Page 4)

Hydrocarbon	Hydrocarbon Conc'n	$(AIBN)^{\frac{1}{2}}$ x 10^2M	T min.	r %/hr	Ø	Calc. rate %/hr at $(AIBN)^{\frac{1}{2}} \times 10^2 = 4.75$M
1,2,5,6-dibenz-anthracene	0.832 x 10^{-3}M	4.65	14½	0.289	1.01	-
	1.01 "	4.65	15½	0.320	1.12	-
	1.47 "	4.65	17½	0.249	0.875	-
	1.90 "	4.65	19	0.233	0.82	-
	2.15 "	4.65	20	0.305	1.07	-
	3.50 "	4.65	25½	0.294	1.03	-

The following hydrocarbons had very poor solubility in the monomer and in other non-polar aromatic and alphatic solvents. Thus, no rate studies could be made:

(1) 2,3-benzanthracene

(2) Pentacene

(3) Picene

(4) 1',1'-anthra-1,2-anthracene

KINETIC ANALYSIS OF POLYMERIZATION RETARDATION BY POLYNUCLEAR AROMATIC HYDROCARBONS.

(1) Basic Kinetic Equations.

Since the kinetics of polymerization retardation are sufficiently well known,[61] only a brief sketch of the particular equations used in this treatment is given below. It is generally accepted that any substance which retards the polymerization of a vinyl monomer does so by reaction with either initiator or polymer free radicals, $R^{\bullet}$, yielding a new free radical $Z^{\bullet}$. This new radical $Z^{\bullet}$ being relatively unreactive towards monomer, is consumed chiefly by reacting with other free radicals, resulting in chain termination. There also exists another possibility that a fraction of the $Z^{\bullet}$ produced is removed by reaction with monomer as in true copolymerization or as in chain transfer. This means that the mode of disappearance of a $Z^{\bullet}$ radical results in the formation of another chain carrying radical. The following scheme of Kice[62] was used in this work:

	Reaction		Rate	
Initiation	$I \rightarrow 2\,R^{\bullet}$		$2\,k_d f\,(I)$	...(1)
Propagation	$R^{\bullet}+M \rightarrow$	$R^{\bullet}$	$k_p\,(R^{\bullet})(M)$	...(2)
Transfer (or addition)	$R^{\bullet}+X \rightarrow$	$Z^{\bullet}$	$k_x\,(R^{\bullet})(X)$	...(3)
Copolymerization	$Z^{\bullet}+M \rightarrow$	$R^{\bullet}$	$k_o\,(Z^{\bullet})(M)$	...(4)
Termination	$Z^{\bullet}+R^{\bullet} \rightarrow$	Inact.Prod.	$k_c\,(R^{\bullet})(Z^{\bullet})$	...(5)
	$Z^{\bullet}+Z^{\bullet} \rightarrow$	" "	$2k_z(Z^{\bullet})^2$	...(6)
	$R^{\bullet}+R^{\bullet} \rightarrow$	" "	$2k_t(R^{\bullet})^2$	...(7)

In this scheme, I represents an initiator molecule, $R^\bullet$ a chain carrying radical, f the initiator efficiency, M a monomer molecule, X the added retarder and $Z^\bullet$ the radical formed by reaction of $R^\bullet$ with retarder. $Z^\bullet$ may be formed either by addition of $R^\bullet$ to X or by transfer of an atom to $R^\bullet$ from X. Whichever happens, cannot be distinguished from rate measurements alone. Whenever these symbols appear in a mathematical expression, they represent molar concentrations of the corresponding species.

Only kinetically significant terms are given above. Polymer molecules will be generated in reaction (3), but since they do not appear in any of the derived rate equations, they are not included explicitly.

After the usual steady state assumptions, the following equation which gives functional relationships between the variables involved is obtained.[62]

$$\frac{\phi^2(X)}{1-\phi^2}\left[1+\sqrt{1+\frac{C(1-\phi^2)}{\phi^2}}\right]=\frac{2k_tR}{k_pk_x}\sqrt{1+\frac{C(1-\phi^2)}{\phi^2}}+\frac{k_o}{k_c}\,\frac{2k_t(M)}{k_x} \quad ..(8)$$

In this equation ϕ is the degree of retardation as defined before, X the retarder concentration, $C = 4k_tk_z/k_c^2$, the values of C are assumed to be one or $\ll 1$, (the upper limit of one for C was chosen because previous work in the field of copolymerization[63,64] had shown that cross termination is usually a favoured mode of termination for dissimilar radicals, i.e. $k_c^2/k_tk_z \gg 1$), R is the fractional conversion per second of the monomer to polymer:

$$R = - d \ln(M)/dt \qquad \ldots(9)$$

other constants k_t, k_p, k_x, etc. are as defined before.

In the equation (8) the experimentally determined parameters are plotted as follows:

$$\frac{\phi^2(X)}{1-\phi^2}\left[1+\sqrt{1+\frac{C(1-\phi^2)}{\phi^2}}\right] \text{ vs. } R\sqrt{1+\frac{C(1-\phi^2)}{\phi^2}}$$

where the slope = $2k_t/k_pk_x$ and the intercept = $k_o 2k_t(M)/k_ck_x$ The values of k_x and k_o/k_c are thus determined from the plot. The limitation of this kinetic expression is, that the concentration of X must remain effectively constant at its initial value for a long enough period of time to allow an accurate measure of the initial rate, and the initial rate must be large enough to be accurately measured.

This means that the polymerization should be retarded and not inhibited and, for runs with very low ϕ values where ($R^\bullet$) is much smaller, deviation from linearity of the plot of experimental data may be found. Since k_t and k_p are known from the work of Matheson et al.[65] the value of k_x can easily be ascertained, while with somewhat less accuracy, k_o/k_c can be found.

In our work an assumed value of $C = 1.0 \times 10^{-4}$ gave straight line plots of our experimental data, and the equation (8) further simplified to:

$$\phi^2X/(1-\phi^2) = k_t R/k_p k_x + k_o k_t M/k_x k_c \qquad \ldots(10)$$

Kice has noted that the form of equation (8) is not altered

if the following reactions are also included in the kinetic scheme.[66]

$$Z^{\bullet} \rightarrow R^{\bullet}+X \qquad \text{rate} = k_y(Z^{\bullet}) \qquad \ldots(11)$$

$$Z^{\bullet}+M \rightarrow ZH+R^{\bullet} \qquad \text{rate} = k_s(Z^{\bullet})(M) \qquad \ldots(12)$$

These additional reactions may be included in the kinetic scheme by making the replacement:

$$k_o' = k_o + k_s + k_y/M \qquad \ldots(13)$$

which is still constant under our conditions. Reaction (11) takes account of the fact that the retarder radical might be an addition complex and its first order breakdown kinetically significant. Reaction (12) allows for hydrogen atom abstraction from the monomer by the retarder radical.

Caldwell[67] incorporated into the kinetic scheme the possible transfer reactions <u>via</u> an aromatic compound in which intermediate radical was again some kind of complex. Such a reaction was postulated by Mayo[68] to account for the reactions similar to the action of halobenzenes in transfer reactions. This possibility was included by addition of one further elementary reaction

$$Z^{\bullet} + M \rightarrow X + P + R^{\bullet}; \text{ rate} = k_m(Z^{\bullet})(M) \qquad \ldots(14)$$

where P represents a polymer molecule which is not kinetically significant and hence omitted, $R^{\bullet}$, represents a monomeric chain carrying radical. This reaction after inclusion in the kinetic scheme leads to the following form of the equation (13)

$$k_o' = k_o + k_s + k_y/M + k_m \qquad \ldots(15)$$

where k_o' represents a combination of several constants. k_o in the kinetic equations (8,10) should be considered to mean k_o'.

Kice,[62] Caldwell[67] and other workers have found reaction (6) to be unimportant. In the present work, with $C = 1 \times 10^{-4}$, this was also the case.

For the special case in which most $Z^\bullet$ radicals disappear from solution by reinitiating chains, a simplification of equation (8) is permitted. Using the approximate relation $k_x (R^\bullet)(X) \cong k_o (Z^\bullet)(M)$ of previous workers,[69,70] Caldwell obtained the following relation neglecting equation (6) again:

$$(1-\phi^2)/\phi^2 = (k_x k_c/k_o k_t)(X)/(M) \qquad \ldots(16)$$

This equation is equivalent to the long-chain expression of other workers.[69,70] The long-chain mechanism implies that almost all the retarder radicals disappear from solution by reinitiating kinetic chains. Comparing equations (8) and (16) one finds that the condition for the long-chain expression to hold is given by

$$k_o/k_c \gg R/k_p (M) \qquad \ldots(17)$$

Kice has noted that the ratio k_o/k_c can be taken as a measure of the stability of the intermediate radicals ($Z^\bullet$).[71] Thus, for any given rate of polymerization, the stability of the intermediate retarder radicals determines whether or not the long-chain expression is valid.

Kice[62] has shown that from the values of k_o/k_c the fraction of $Z^\bullet$, which disappears by reaction (4) can be ex-

pressed as:

$$\gamma = 1/1 + (R/k_p(M))\ (k_c/k_o) \qquad \ldots(18)$$

where γ is the fraction of terminator molecules consumed which fail to stop chains.

(2) Application of the Kinetic Equation to Experimental Results.

All the runs were carried out in vacuo on carefully degassed solutions as described in the experimental section. In order to calculate the values of ϕ (where ϕ = observed rate/uninhibited rate), the uninhibited rate of polymerization for application of equation (10) was determined and found to be

$$-(d\ \ln(M)/dt)_{\text{uninhibited}} = R_o = 6.12(AIBN)^{\frac{1}{2}} \text{ \% per hour}$$

$$= 14.4 \times 10^{-5}(AIBN)^{\frac{1}{2}} \text{ mole}^{-1} \text{ lit.}^{-1} \text{ sec.}^{-1}$$

This value of R_o calculated for a typical initiator concentration $(AIBN)^{\frac{1}{2}} = 4.75 \times 10^{-2}$, is 6.85×10^{-6} from our experimental results, and agrees well with the R_o value calculated from the relation given by Mayo et al.[65] From this relationship the calculated values for R_o are 6.97×10^{-6} for initiator efficiency = 0.78 and 5.11×10^{-6} for initiator efficiency = 0.58. In the literature the values of initiator efficiency reported range from approximately 0.6 - 0.8 (100% efficiency being = 1). An initiator efficiency of 100% means that the free radicals formed from the decomposition of the initiator are all consumed in a reaction with monomer molecules to give growing chain radicals and are not destroyed

by any other side reactions.

The data from our experimental section is plotted according to simplified equation (10), and the typical plots are shown in Figures 10-15. In all cases it was found that a value of $C = 1 \times 10^{-4}$ (where $C = 4k_t k_z / k_c^2$) gave the least deviation of the experimental points from a straight line. This means that reaction (6) in the kinetic scheme was unimportant and the $Z^\bullet$ radicals formed by the attack of a growing radical on the retarder molecule are not terminated by combination with another similar radical. This is not unusual as the relative concentration of these radicals compared to other species in the reaction mixture is very low and such a reaction should not be very probable. We conclude that the intermediate $Z^\bullet$ radicals disappear from the reaction mixture by some other reaction as postulated in the kinetic scheme. Termination by dissimilar radicals is the favoured mode of reaction of radicals.

Moreover, with the hydrocarbons used in this work dimerization of these radicals $Z^\bullet$would be very improbable for steric reasons except in the case of a simple linear hydrocarbon like anthracene. Although a dimer of anthracene is known to exist, such a possibility may be discounted solely on the basis of the very small relative concentration of $Z^\bullet$ radicals of this species.

From the slopes and the intercepts of these plots, the rate constants k_x and k_o/k_c were obtained using the values of

$2k_t$ and k_p calculated for this temperature from the relationships given by Mayo et al.[65] ($2k_t = 6.13 \times 10^7$, $k_p = 98.4$). The results are listed in Table II.

TABLE II

RATE CONSTANTS FOR TERMINATORS IN STYRENE POLYMERIZATION.

Compound	k_x mole lit.$^{-1}$ sec.$^{-1}$	k_x/k_p	$k_o/k_c \times 10^{10}$
Class A:			
2,3-naphtho-3,4-pyrene	22,000	240	8.5
1,2,7,8-dibenz-tetracene	1,460	15	4.5
1,2,9,10-dibenz-tetracene	1,260	13	3.4
Anthracene	170	2	2.0
Class B:			
3,4-benzpyrene	1,360	14	24.0
2,3,7,8-dibenz-phenanthrene	1,260	13	0.5
1,2,3,4-dibenz-pyrene	550	6	10.6

(3) Discussion of Results.

The compounds, which affected the rate of polymerization, have been classified into Groups A and B in the table above. This classification is not based upon their structural similarities, but, as will be evident from the section following, the criterion for this differentiation is the pi-electron density in the K-and the L-regions of these molecules. In

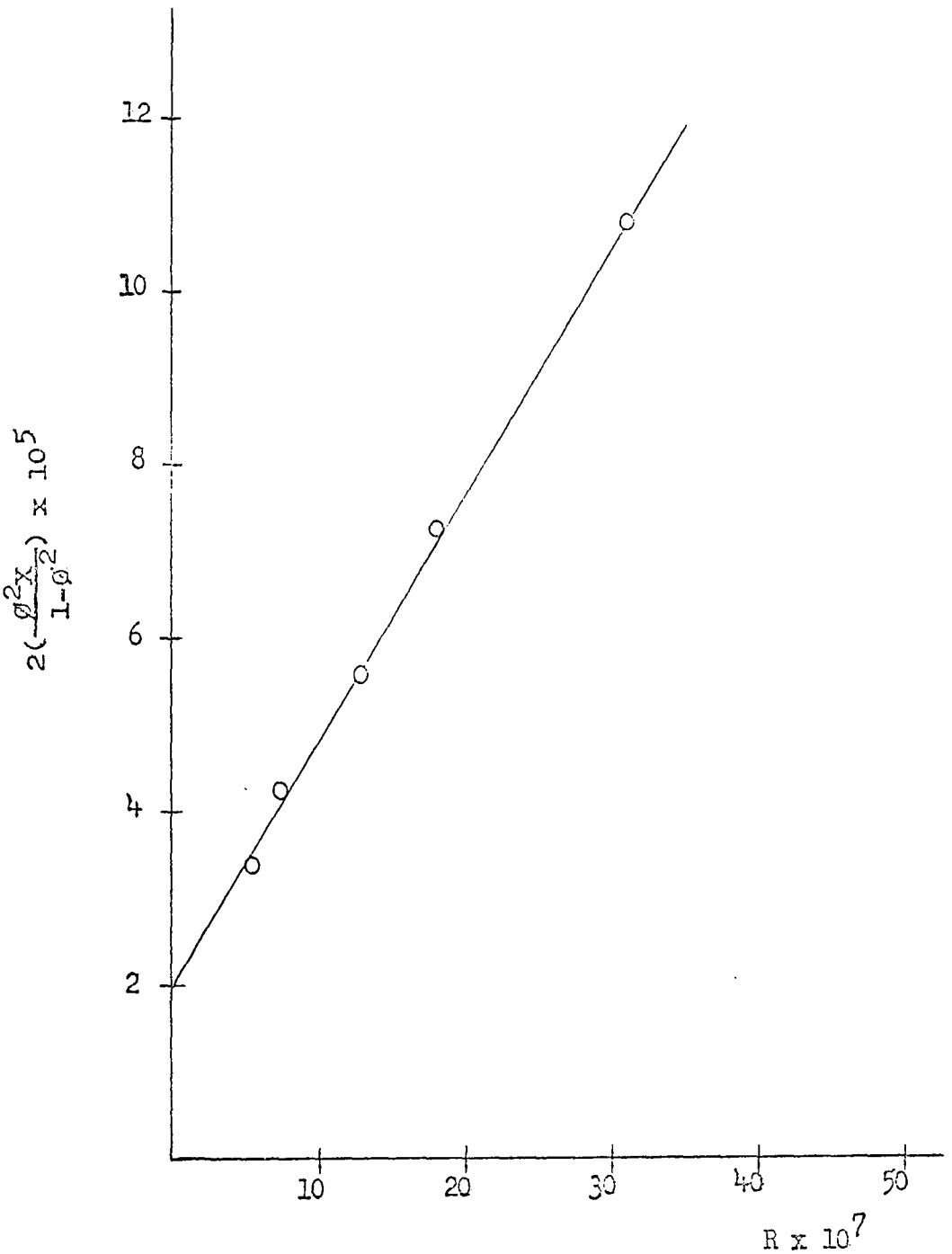


FIGURE 10. RESULTS FOR 2,3-NAPHTHO-3,4-PYRENE PLOTTED ACCORDING TO EQUATION 10

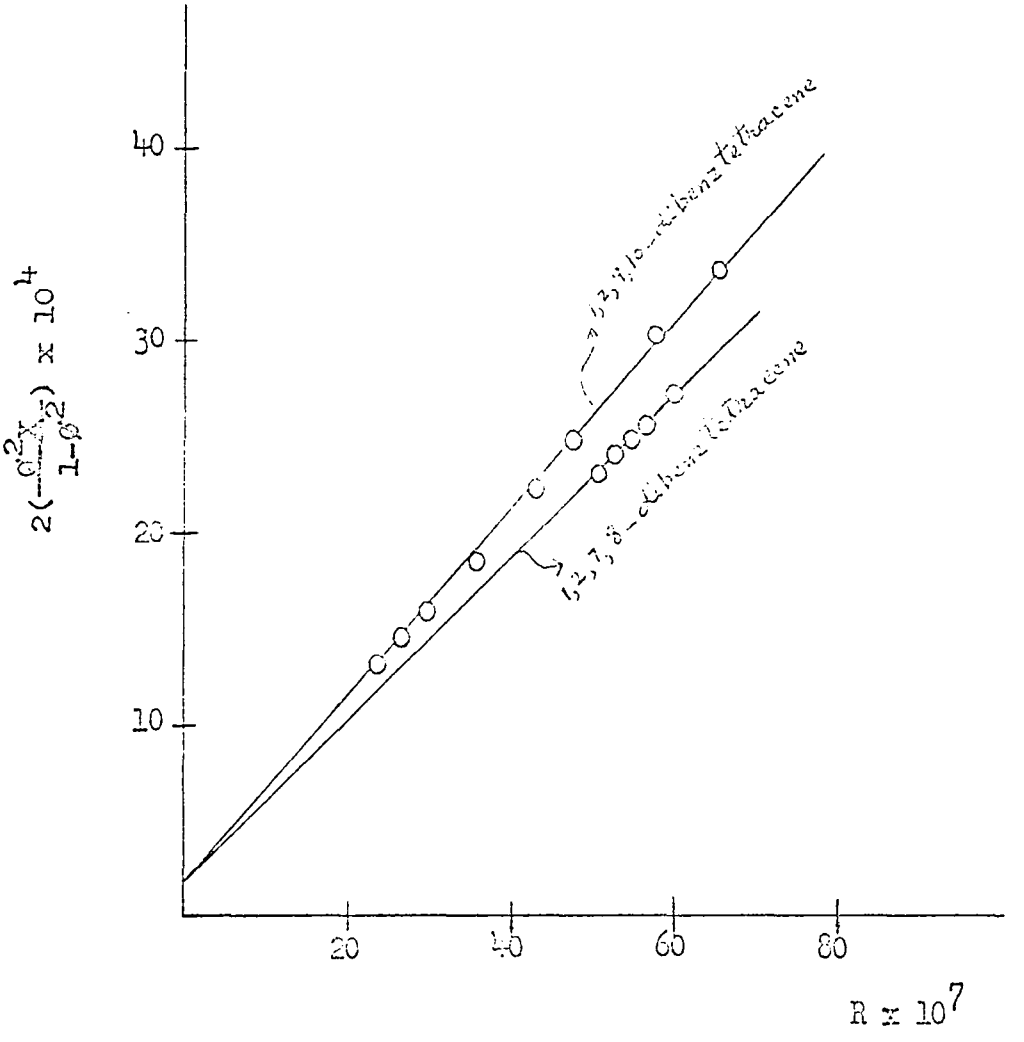


FIGURE 11. RESULTS FOR 1,2,7,8-DIBENZTETRACENE AND 1,2,9,10-DIBENZTETRACENE PLOTTED ACCORDING TO EQUATION 10

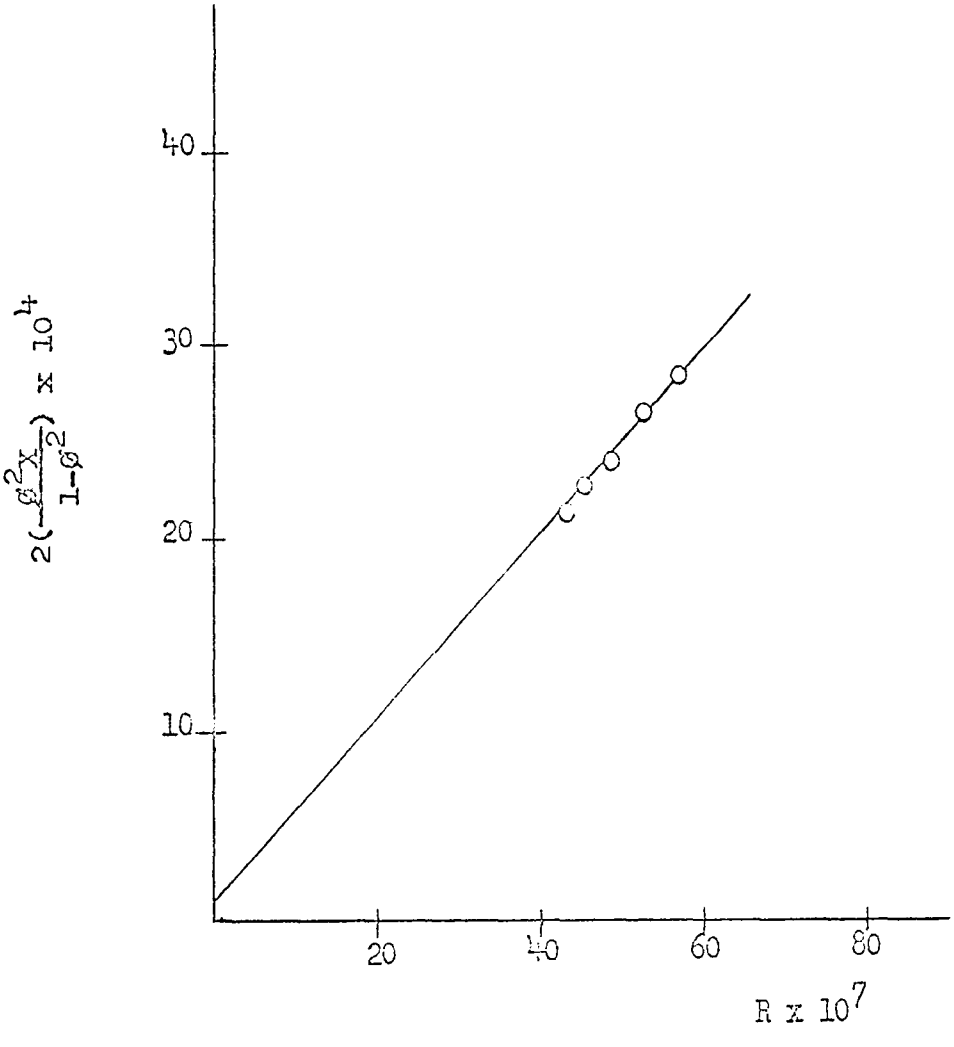


FIGURE 12. RESULTS FOR 2,3,7,8-DIBENZ-PHENANTHRENE PLOTTED ACCORDING TO EQUATION 10

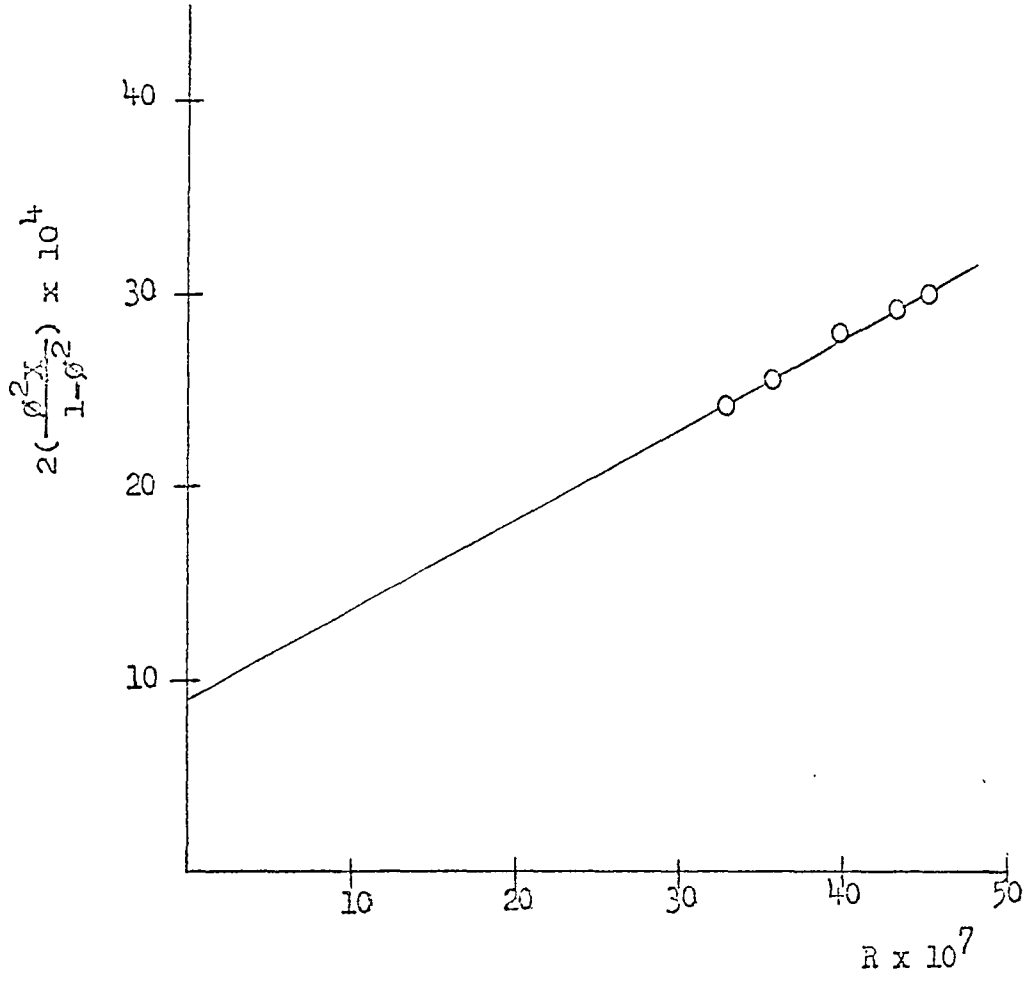


FIGURE 13. RESULTS FOR 3,4-BENZPYRENE PLOTTED ACCORDING TO EQUATION 10

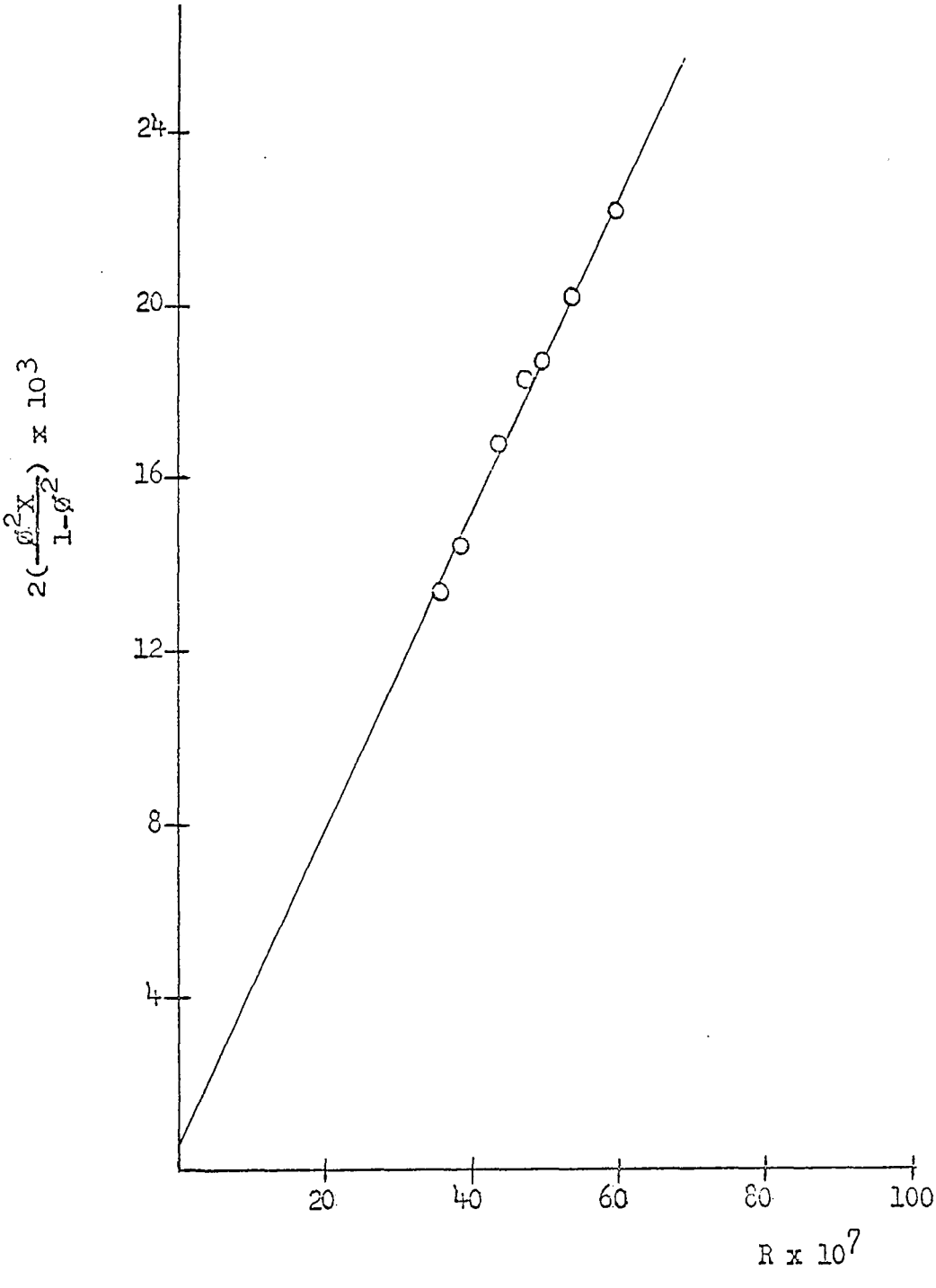


FIGURE 14. RESULTS FOR ANTHRACENE PLOTTED ACCORDING TO EQUATION 10

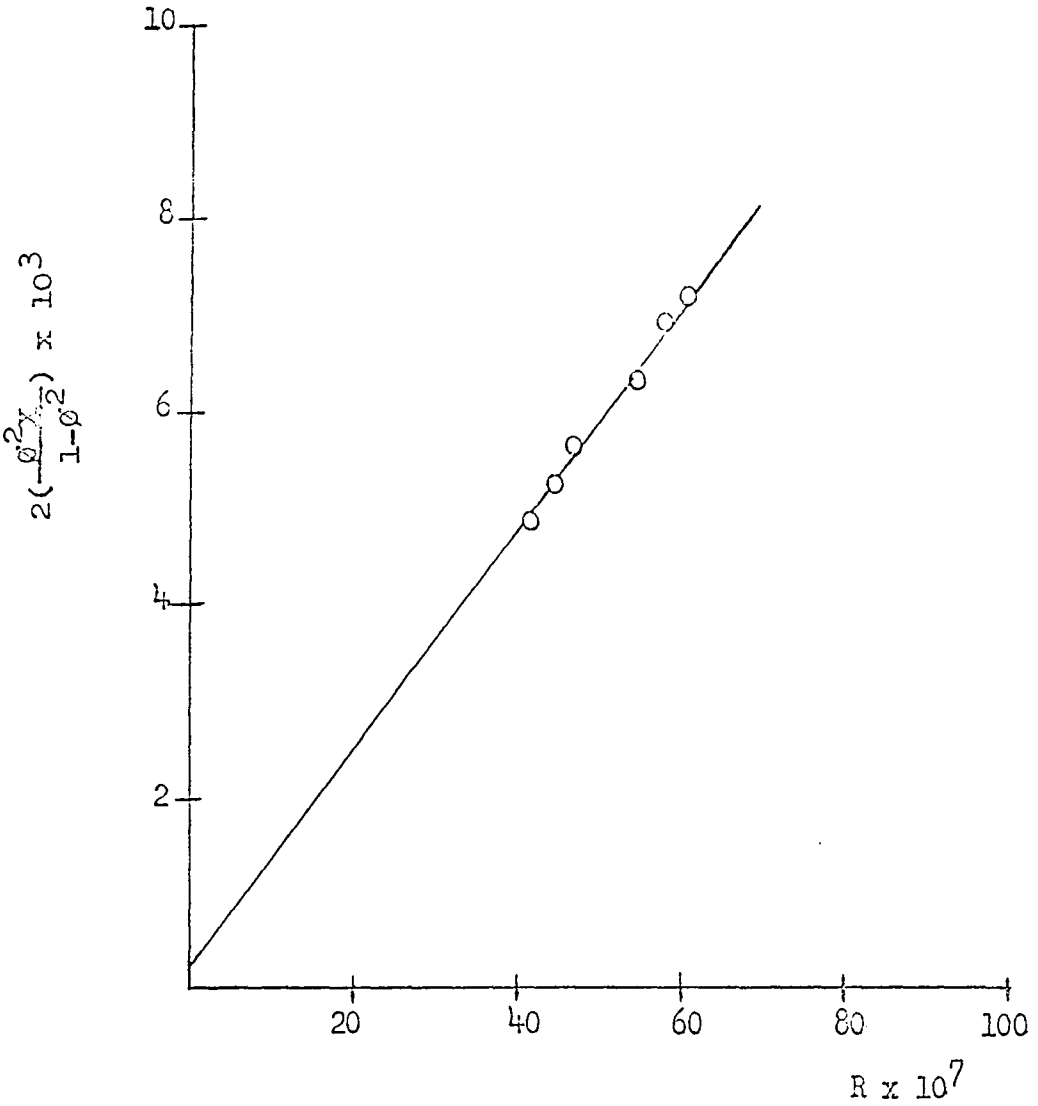


FIGURE 15. RESULTS FOR 1,2,3,4-DIBENZPYRENE PLOTTED ACCORDING TO EQUATION 10

the terminology of the "frontier electron" method[12] the K-region is referred to as the (S_p) region and the L-region, or meso-positions, as the (S_s) region. In order to maintain clarity of the discussions, the K-and the L-regions will be referred to as (S_p) and (S_s) regions respectively. Also the inferences drawn from the k_x/k_p values (the relative reactivities) of these hydrocarbons towards growing chain radicals is discussed in this section.

Discussion of k_o/k_c Values:

These two rate constants (k_o and k_c) deal with the reactivities of the free radical intermediates, $Z^\bullet$, formed from the initial reaction of growing chain radicals with hydrocarbon molecules ($R^\bullet + X \rightarrow Z^\bullet$ where rate = $k_x(R^\bullet)(X)$. The rate constant k_c is for the reaction $Z^\bullet + R^\bullet \rightarrow$ inactive products, while k_o represents a combined rate constant (see equation 15) and pertains to reactions (4), (11), (12) and (14) of the kinetic scheme. From the calculated value of $k_p \backsim 10^2$ and the ratio of k_o/k_c the relative order of magnitude of k_o and k_c can be estimated. As both k_o and k_p pertain to the reactivity of the free radicals towards monomer, the k_o may be estimated to be $\backsim 10^2$ or less. Thus, from the ratio $k_o/k_c \backsim 10^{-10}$ and $k_o \backsim 10^2$, k_c should be of the order of 10^{11} to 10^{12}. This means essentially that the most favored mode of disappearance of $Z^\bullet$ radicals is reaction (5) $Z^\bullet + R^\bullet \rightarrow$ inactive products. This is the usual cross termination reaction for radical destruction in the liquid phase.

Thus, the relative magnitude of the k_o/k_c values can be regarded as a measure of the stability of the Z• radicals. However, in view of the uncertainties involved in the extrapolations to obtain the intercepts from the plots of equation (10), this must be regarded only as a qualitative measure.

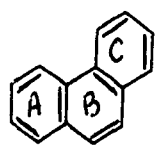
From the relative values of k_o/k_c (Table II), for the various Z• radicals, it would appear that their order of magnitude of reactivity (or stability) is about the same. Some differences in the numerical values for these ratios can be accounted for by the varying degree of copolymerization reaction occurring in these cases.

The experimentally found reactivities of the various Z• radicals would appear unreasonable according to the concept of resonance stabilization. A Z• radical, which is derived from a three-ring aromatic hydrocarbon, would not be expected to have the same degree of conjugation as a radical derived from six-ring hydrocarbon. Although many equivalent resonance contributors can be written for these large molecules, for the corresponding intermediate Z• radicals there are far fewer resonance contributors.

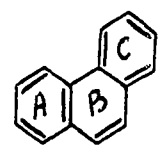
There is sufficient experimental evidence[29,72,73] to the effect that only certain positions in these hydrocarbons are reactive for an attack of an approaching reagent molecule. Thus, after an initial free radical attack to give Z• radicals,

it can be demonstrated that only a few equivalent canonical structures can be written for these Z° radicals. Thus, resonance stabilization of these species should not be expected to play a significant role. Approximately the same order of magnitude of the constant k_c for the reactivity of various Z° radicals supports this point of view.

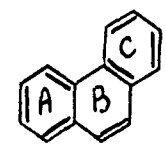
In the following paragraphs the resonance structures of phenanthrene and anthracene are discussed in order to draw some generalizations, which can be applied to more complex molecules. The same arguments should be generally applicable. In all of these hydrocarbons the presence of (S_p) and (S_s) regions is due to the fact that these molecules may be regarded as derivatives of these two simple hydrocarbons. The polycyclic aromatic hydrocarbons possess partially non-aromatic character. Thus, in the case of phenanthrene, the following canonical resonance structures can be drawn:



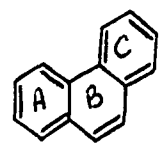
I



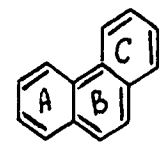
II



III



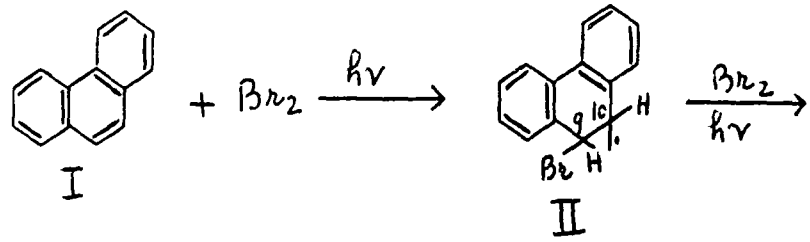
IV



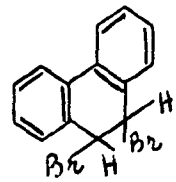
V

This molecule is a resonance hybrid of five structures I-V. Structure I contains three benzenoid rings, structures II, III, IV contain two benzenoid rings and structure V contains only one benzenoid ring. The major contributing structure would be I, which is completely aromatic.

Positions 9,10 in this molecule are more reactive than the others and if a free radical mechanism for bromine (photo-chemical reaction) addition is considered for this molecule

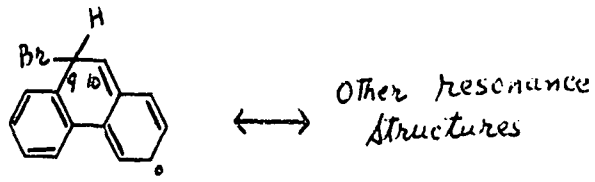


I II



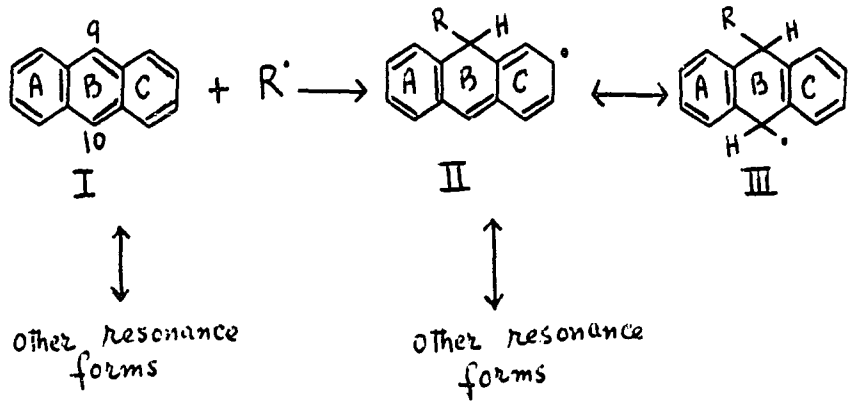
III

an intermediate free radical II is first formed. Although several resonance structures can be drawn for the radical under consideration, any such structures would possess quinoid or partially quinoid character and hence would contribute less to the total structure of the molecule. Such structures would lead to only one benzenoid ring (A) or (C), as shown,

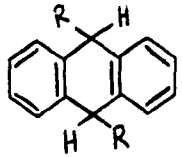


while structure II has two benzenoid rings. This structure II will contribute the most to the structure of this radical. Thus, attack of another free radical will take place in position 10. This is in accord with the experimental evidence as product III, stable at room temperature, is formed. Thus, in those molecules where an attack of a free radical at the (S_p) region is postulated, it is the second carbon atom of this region which is the center of further reaction.

If a similar addition of a free radical is considered in the case of anthracene, where the (S_s) region is reactive, the following reaction would proceed:

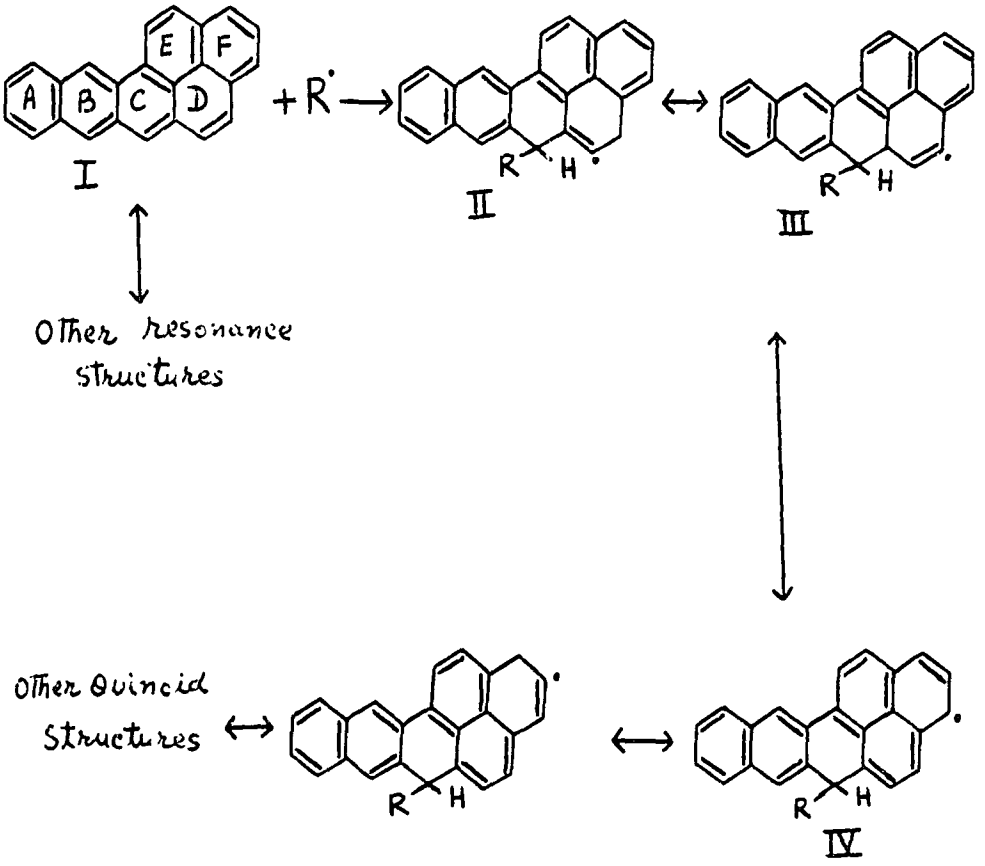


For the intermediate radical Z• formed from anthracene only <u>one</u> resonance contributor III can be written which possesses two benzenoid rings. The other resonance structures, like II, would possess only one benzenoid ring and would not contribute appreciably to the resonance stabilization energy. Hence, the quinoid structure contribution is relatively unimportant. Thus, the site of further reactivity of the Z• radical will be position 10, as shown in structure III. This is in accord with the experimental evidence. Attack of another free radical at position 10 of structure III will lead to structure IV,



IV

which would be stable at room temperature or under our experimental conditions. If a similar addition reaction is considered for 2,3-naphtho-3,4-pyrene, where the second carbon atom of its (S_s) region is blocked, the following situation would arise:



(a) In structure I rings A, B, E and F are benzenoid, while C and D are quinoid.

(b) Only two of these resonance structures II and III for the radical Z• have four benzenoid rings and two quinoid, while in structure IV and V there are only three benzenoid rings. Structures such as IV and V cannot be regarded as equivalent resonance contributors, hence are relatively unimportant.

This means, that after an initial free radical attack at the (S_s) region, the subsequent reaction in this intermediate radical Z• should take place at its (S_p) region.

Only a very few resonance contributors for this radical Z• can be written.

An alternate route, by which the Z• radicals may be formed from these hydrocarbons, is the chain transfer or substitution reaction ($R^{\bullet} + X \rightarrow RH + Z^{\bullet}$). A consideration of the resonance structures for such radicals would lead to the fact that only <u>one</u> structure exists and no other equivalent resonance contributors can be written for a particular resonance structure. It is recognized that radical-ion structures may be written, but their contribution in the free radical reaction under consideration should be small. This would lead to even lesser resonance contributors than the case where free radical addition to a hydrocarbon takes place. This is a situation where the position of the free electron is essentially fixed. Consider a Z• radical formed by hydrogen-atom abstraction from anthracene. This Z• radical will react with another growing chain radical and disappear from the reaction mixture.

In free radical reactions as in other types, bond energies, steric effects and resonance stabilization determine the course and the rate of reaction.

(4) <u>Conclusions</u>.

The following conclusions can be drawn:

(1) From considerations of resonance structures, it can be seen that relatively fewer equivalent resonance contributors can be written for the Z• radicals compared to their

parent hydrocarbons. However, there would be appreciable differences in the number of resonance structures that can be written for different Z° radicals. For a simple molecule like anthracene relatively fewer resonance contributors can be written for its radical compared to that of naphtho-pyrene, etc. Differences in the reactivities of the various radicals might be expected. Yet from the k_c values for different Z° radicals it can be concluded that their reactivity is about the same and resonance stabilization differences do not play a significant role.

(2) It has been shown on the basis of resonance considerations, that in these Z° radicals the position of further free radical attack is the second carbon atom of the (S_p) or K-region, or the second (S_s) or L-region position. In those cases, eg. 2,3-naphtho-3,4-pyrene, where the second (S_s) position is blocked, the position of further attack is the (S_p) position.

(3) The favored mode of disappearance of Z° radicals is reaction (5) of the kinetic scheme and reaction (6) is unimportant.

KINETIC ANALYSIS OF POLYMERIZATION INHIBITION BY POLYNUCLEAR HYDROCARBONS.

There were relatively few compounds in this series of hydrocarbons that gave definite inhibition periods. These hydrocarbons were:

(1) 3,4-benzpyrene

(2) 1,2,5,6-dibenzanthracene

(3) 1,2-benzanthracene

From the plots in Figure 9 it is evident that no polymerization was observed during the inhibition periods and at the end of these periods an abrupt change in the course of the reaction takes place. With hydrocarbon (1) the rate of reaction after the inhibition period was also retarded while with (2) and (3) the reaction takes place at a normal rate ie. as in the case of uninhibited polymerization. The inhibition periods with hydrocarbons (1) and (2) were identical for the same inhibitor concentration while with (3) shorter inhibition periods were observed. However, in all three cases the duration of the inhibition periods observed was very much shorter than would be expected in an "ideal" inhibition, assuming that two radicals react with one inhibitor molecule. Such shortening of inhibition periods and the appearance of retardation effects after these periods has been reported in the literature[74-78] and is, therefore, not unusual. No induced decomposition of the initiator due to these hydrocarbons would be expected.

The empirical relationship ($t_i = UZ_o/K_1 m_o^2$) for thermal polymerization of styrene,[77] can be modified to give an empirical relationship for the case of initiated polymerization, simply by substituting $2 k_d f (I)$ for $K_1 m_o^2$, which are the rates of initiation for initiated and thermal polymerizations respectively. Thus, the following equation is obtained:

$$t_i = UZ_o/2k_d f (I)$$

where t_i is the length of inhibition period, Z_o the initial concentration of inhibitor, $2k_d f (I)$ the rate of initiation (reaction 1 of the kinetic scheme) and U is the number of inhibitor molecules reacting with a chain radical.

This is the same relationship derived by Bartlett et al.[79] and others. With its help the functionality, or chain-stopping equivalence of these inhibitors can be determined. However, to evaluate this, it is assumed that the inhibitor is essentially consumed during the inhibition period. Such data is compiled in Table III.

(1) Discussion of Results.

From the calculated values of the number of kinetic chains terminated per inhibitor molecule by the end of inhibition period or the number of inhibitor molecules consumed per radical, it can be seen that $\sim 10^3$ inhibitor molecules are consumed per radical. Such a situation would arise only under two conditions:

Either $\sim 10^3$ inhibitor molecules are incorporated into

a growing chain as would be the case in a true copolymerization, or for each chain radical reacting with an inhibitor molecule to form a $Z^{\bullet}$ radical, this intermediate $Z^{\bullet}$ radical must disappear from the reaction mixture not by reacting with another radical but by regenerating a new radical. This statement implies that instead of two radicals reacting with an inhibitor molecule, only one initial radical reacts and the disappearance of $Z^{\bullet}$ radicals results in the formation of a new radical.

As no observable polymerization takes place during the inhibition periods, there is little probability of extensive copolymerization occurring. This means, that the most probable course of reaction during the inhibition periods is the second choice referred to above. However, this leads to an interesting question that in those hydrocarbons, where retardation effects were observed, the most favored mode of disappearance of $Z^{\bullet}$ radicals was by cross termination, $R^{\bullet} + Z^{\bullet} \rightarrow$ inactive products, reaction (5) of the kinetic scheme, with a rate constant $k_c \sim 10^{11} - 10^{12}$, but during inhibition periods this reaction appears to be unimportant. This is discussed later and it is shown that due to steric effects involved on the adjacent carbon atom, cross termination is not favored.

Inhibition effects were observed only in those hydrocarbons where the pi-electron density in the (S_p) or K-regions of these molecules is the highest as compared to other molecules.

TABLE III

CHAIN-STOPPING EQUIVALENCE OF THE VARIOUS INHIBITORS.

Hydrocarbon	Z_o moles/ lit. x 10^3	(AIBN)moles/ lit. x 10^3	Observed inhibition period	Number of chains term'ed/Z	Number of inhibitor molecules per $R^\bullet$
3,4-benzpyrene	1.95	2.172	480 sec.	0.93 x 10^{-3}	
	2.19	2.172	540 "	0.93 "	
	2.78	2.172	690 "	0.93 "	
	3.47	2.172	870 "	0.94 "	$\sim 1 \times 10^3$
	4.12	2.172	1020 "	0.93 "	
	5.61	2.172	1410 "	0.92 "	
1,2,5,6-dibenz-anthracene	0.832	2.162	210 "	0.94 "	
	1.01	2.162	255 "	0.94 "	
	1.47	2.162	375 "	0.95 "	$\sim 1 \times 10^3$
	1.90	2.162	480 "	0.94 "	
	2.15	2.162	540 "	0.94 "	
	3.50	2.162	870 "	0.93 "	
1,2-benz-anthracene	4.21	2.162	570 "	0.5 "	
	4.82	2.162	630 "	0.5 "	
	5.49	2.162	720 "	0.5 "	$\sim 2 \times 10^3$
	6.22	2.162	840 "	0.5 "	
	8.11	2.162	1080 "	0.5 "	
	9.20	2.162	1230 "	0.5 "	

The inhibition periods given in this table are after subtracting T_o, where T_o is the time zero and was determined from the plot of inhibition period vs. conc. and extrapolating the straight line to t = 0.

(2) Conclusions.

From the earlier considerations, the following conclusions can be drawn:

(1) The centers of reactivity in these inhibitors are the (S_p) regions.

(2) In retarders, where growing chain radicals react with the hydrocarbon molecules, the k_x values range from 170 - 22,00 (see Table II). During retardation, observable polymerization reaction also takes place, whereas in inhibitors no polymerization is observed during the inhibition periods. When inhibitors or retarders are present in a polymerizing system, two competive reactions need to be considered: the reaction of a growing chain radical with monomer or with the added inhibitor or retarder. The relative reactivity of the chain radical towards either the monomer molecule or the added species, will determine the ultimate effect on the rate of polymerization. In the case of retarders k_x is greater than k_p, and both these reactions are taking place, whereas during the inhibition period k_p is $\sim$ zero. Thus, k_x, which has not been evaluated in the inhibitors, must be much greater than the k_x values for retarders. It can be said, that the initial radicals of very low molecular weight must react with the inhibitor molecules to give $Z^\bullet$ radicals.

(3) In the kinetic scheme, the modes of disappearance of $Z^\bullet$ radicals is postulated by reactions (4), (11), (12) and (14). In reactions (11) and (14), these radicals disappear

by reforming inhibitor molecules, X_1, and if these two reactions were of any importance the duration of inhibition periods should have been much greater than the observed periods. Thus, both these reactions can be disregarded. In order to account for the shortening of inhibition periods regeneration of another free radical for each radical used in reactions with the inhibitor molecules, is postulated. Reactions (4) and (12) do satisfy this requirement, but both these reactions are also considered unimportant. In reaction (4) $Z^{\bullet} + M \rightarrow RM^{\bullet}$, the addition of a monomer molecule to the $Z^{\bullet}$ radicals would involve steric hinderance, while in reaction (12) $Z^{\bullet} + M \rightarrow ZH + M^{\bullet}$, abstraction of a hydrogen atom by the $Z^{\bullet}$ radical would not be favored energetically. Chain transfer to styrene monomer is known to be low.[80]

Thus, in order to satisfy the objections arising from the consideration of reactions (4) and (12), the following reaction is proposed:

$$Z^{\bullet} + M \rightarrow \overset{\bullet}{X} + MH^{\bullet}$$

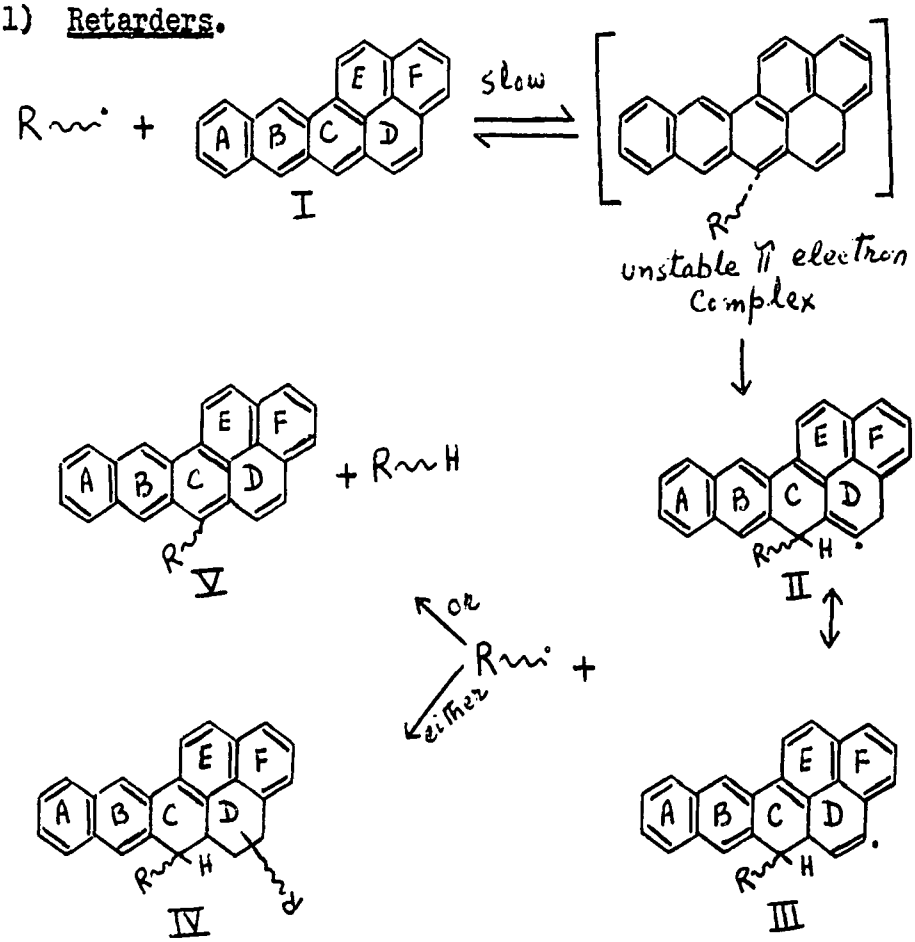
In this reaction $\overset{\bullet}{X}$ - is a substituted hydrocarbon and $MH^{\bullet}$ another radical, $Z^{\bullet}$ and M have the same significance as before.

This proposed reaction does not invoke any steric effects at the center of reactivity, the (S_p) region, and aromatization results.

PROPOSED MECHANISMS.

There is sufficient evidence, both experimental[29,72,73] and theoretical[12,13] that the centers of reactivity in these hydrocarbons are the (S_p) or K-region and (S_s) or L-region. In order to illustrate the proposed mechanisms a typical retarder or inhibitor molecule has been chosen. The same mechanism would apply to other compounds.

(1) Retarders.



Only those hydrocarbons that possess fairly high pi-electron density in the (S_s) region were found to show retardation effects. Thus, the position of free radical attack in this class of hydrocarbons will be the (S_s) region.

In those cases where both the (S_s) positions are accessible for an attack of a reagent, both these positions will react eg. positions 9,10 in anthracene, while in those cases where one of these positions is blocked as in 2,3-naphtho-3,4-pyrene, the subsequent center of reactivity of these Z• radicals will be the (S_p) region. This has been shown earlier on the basis of resonance considerations. The disappearance of Z• radicals by the attack of another chain radical is proposed. In the kinetic analysis reaction (5),

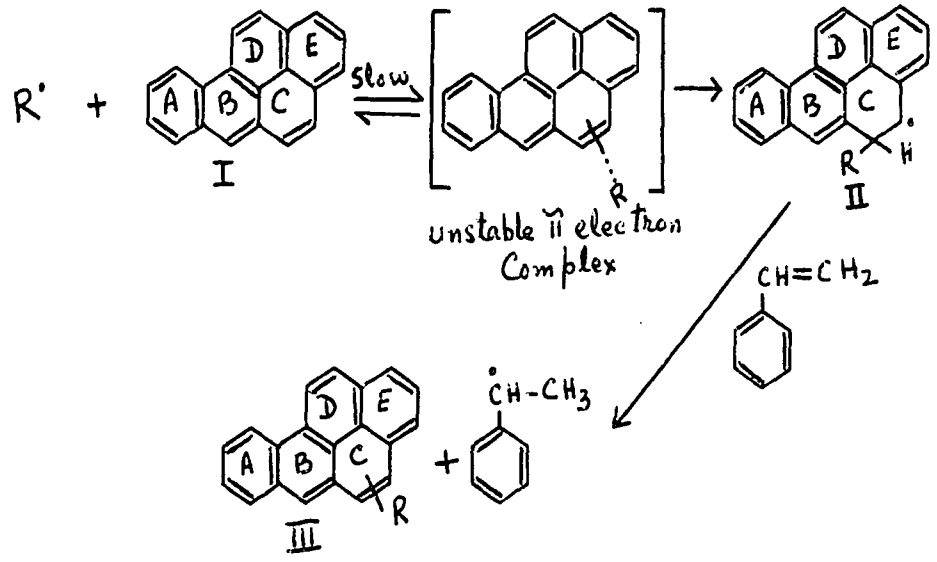
$$Z^{\bullet} + R^{\bullet} \rightarrow \text{inactive product}$$

was found to be the most favored.

The product IV would be expected to be stable under our experimental conditions.

(2) Inhibitors.

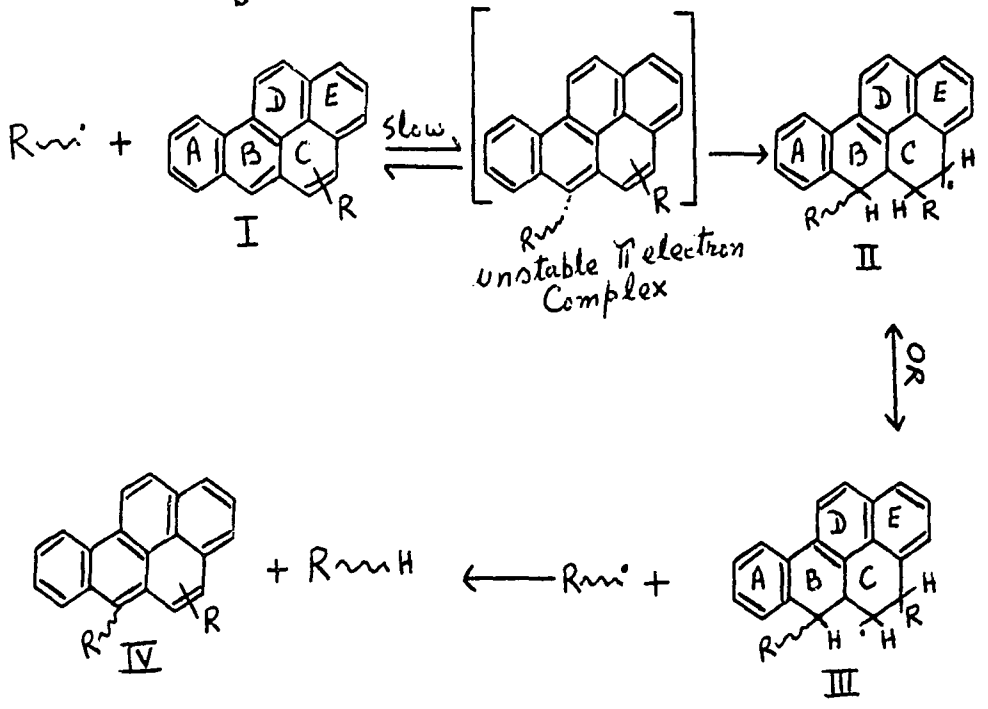
As mentioned earlier, the (S_p) regions are the centers of reactivity in these compounds, and the initial radicals react with these compounds to form Z• radicals.



In structures I, II and III, rings A, B, D and E are benzenoid. As shown earlier reactions (4), (11), (12) and (14) of the kinetic scheme have been considered to be unimportant; the proposed reaction $R^{\bullet} + M \rightarrow \overset{\bullet}{X} + MH^{\bullet}$ would be most favored energetically and involves no steric hinderance effects. Moreover, aromatization will be a strong influence to yield the products shown.

(3) Retardation after Inhibition Periods.

According to the statement above, at the end of inhibition periods, all the inhibitor molecules would exist as substituted hydrocarbons. This substituent at the (S_p) region of these hydrocarbons would be expected to exert a strong influence on the further reactivity of the adjoining carbon atom of the (S_s) regions of these molecules.



In these unsubstituted hydrocarbons reactivity arises due to higher pi-electron density in localized regions compared to the rest of the molecule. Thus, hydrocarbons with approximately the same order of magnitude of pi-electron density would be expected to show about the same order of reactivity. From Table I of the Appendix I and Table II it is evident that 1,2,7,8-dibenztetracene, 1,2,9,10-dibenztetracene and 2,3,7,8-dibenzphenanthrene have approximately the same pi-electron density in the (S_p) and (S_s) regions, and their relative efficiencies (k_x/k_p) as retarders were found to be about the same. Thus, on these considerations of pi-electron densities, the relative reactivities of 3,4-benzpyrene and 2',3'-naphtho-3,4-pyrene would be expected to be the same, but this was not the case as found experimentally. 2',3'-naphtho-3,4-pyrene was found to be much more reactive than 3,4-benzpyrene. This means, that with 3,4-benzpyrene during the inhibition period a substituted hydrocarbon must have resulted, and this substituent affects the reactivity of the adjoining (S_s) region carbon for further attack. The influence of this substituent could be either due to steric effects or change in the electronic configuration of the (S_s) region of this intermediate substituted species or both these factors contribute towards this affect. Thus, a decrease in the relative efficiency as a retarder is observed in this hydrocarbon.

The kinetic analysis of retardation has shown that the

$Z^{\bullet}$ radical formed by the reaction of a growing chain radical with a retarder molecule "X", disappear by reacting with another growing chain radical. In the case where retardation effects were also observed after inhibition periods, a substituted hydrocarbon "$\overset{1}{X}$" is postulated to have been formed during inhibition period. Like typical retarders, this substituted species undergoes similar reactions to form "$\overset{1}{Z}^{\bullet}$" radicals which disappear by reacting with an other growing chain radical. This cross termination reaction

$R^{\bullet} + Z^{\circ} \rightarrow$ inactive products can occur via two routes:

(1) $R^{\bullet} + \overset{1}{Z}^{\bullet} \rightarrow R\text{-}\overset{1}{Z}$ (addition)

(2) $R^{\bullet} + \overset{1}{Z}^{\bullet} \rightarrow RH + \overset{1}{Z}$ (transfer)

The center of reactivity of this $\overset{1}{Z}^{\circ}$ radical would be the unsubstituted carbon atom at the (S_p) region or the K-region. But in view of the steric considerations, attack of another growing chain radical at the (S_p) region to give addition products by reaction (1) mentioned above would not be the favored mode of disappearance of $\overset{1}{Z}^{\bullet}$ radicals.

Thus, the alternate reaction (2) would be the most probable mode of disappearance of these $\overset{1}{Z}^{\bullet}$ radicals, as no steric effects will be involved and moreover aromatization occurs. The hydrogen atom may be abstracted from the (S_p) or (S_s) region of this $\overset{1}{Z}^{\bullet}$ radical. If hydrogen atom abstraction from its (S_p) region takes place, then by transfer of a hydrogen atom from the (S_s) region carbon atom to its (S_p) region will result in aromatization, whereas a hydrogen atom

abstraction from its (S_s) region would not involve any subsequent transfer of a hydrogen atom. The (S_s) region or the "peri-hydrogen" is easier to abstract and this position may be the site of this reaction. In either case the same product III will result. However, this situation cannot be resolved on the basis of these rate measurements.

A CORRELATION BETWEEN PI-ELECTRON DENSITY IN LOCALIZED REGIONS OF THE HYDROCARBONS AND THEIR REACTIVITY TOWARD STYRYL FREE RADICALS.

The hydrocarbons investigated in these studies may be classified into the following categories on the basis of their effects on the rate of polymerization of styrene.

(a) Inhibitors.

3,4-benzpyrene, 1,2,5,6-dibenzanthracene and 1,2-benzanthracene gave definite induction periods, the duration of which varied linearly with the hydrocarbon concentration. The observed induction periods were identical in the case of 3,4-benzpyrene and 1,2,5,6-dibenzanthracene, but were approximately one half in the case of 1,2-benzanthracene for the same concentrations. In the case of 1,2,5,6-dibenzanthracene and 1,2-benzanthracene, the rates of reaction after the induction periods were approximately the same as for the unretarded reaction, but with 3,4-benzpyrene varying degrees of retardation effects were also observed after the induction periods.

(b) Retarders.

2',3'-naphtho-3,4-pyrene, 2,3,7,8-dibenzphenanthrene, 1,2,9,10-dibenztetracene, 1,2,7,8-dibenztetracene, 1,2,3,4-dibenzpyrene and anthracene gave no induction periods but merely slowed down the rate of reaction. The order of their efficiency as retarders was found to be 2',3'-naphtho-3,4-pyrene > 2,3,7,8-dibenzphenanthrene $\cong$ 1,2,7,8-dibenz-

tetracene $\cong$ 1,2,9,10-dibenztetracene > 1,2,3,4-dibenzpyrene > anthracene.

(c) No Effect:

Naphthalene, phenanthrene, chrysene, perylene, triphenylene, pyrene, 1,2-benzpyrene and 1,2,3,4-dibenzanthracene had no effect on the rate of polymerization, and the observed rates were approximately the same as for unretarded reaction.

All these hydrocarbons possess important pi-electron systems, and the chemical reactivity in these is ascribed to the density and distribution of pi-electrons. Thus, the observed reactivity of these hydrocarbons towards free radicals should correspond to the pi-electron distribution and density in localized regions of these compounds. For the purpose of seeking a correlation between our work and that of others, the results of various experimental and theoretical treatments dealing with pi-electron density in these hydrocarbons are listed in the Appendix I. Comparing our results with the various theoretically calculated molecular parameters, it is evident that no clear-cut correlation exists between these studies and of others, except that of Fukui and co-workers.[12]

Thus, the ensuing discussions will deal entirely with seeking a correlation between the observed chemical reactivity and the pi-electron densities calculated by Fukui. It will be seen from the discussions that the experimentally determined reactivities correspond to the pi-electron density in localized regions of these molecules, i.e. greater re-

activity parallels higher pi-electron density.

The theoretical values of superdelocalizabilities calculated by the "frontier electron" method are listed in Table IV only for those molecules that were investigated in these studies for the purpose of discussing our experimental results in conjunction with these theoretical indices.

In order to make clear the significance of these results, some of the terminology employed must be defined. The term "threshold values" of pi-electron density at the (S_p) and (S_s) regions for the manifestation of inhibition or retardation effects refers to a minimum value of pi-electron density in these localized regions. This value has been empirically established on the basis of the inhibition and retardation behaviour of these hydrocarbons found in this study. Moreover, the (S_p) region is the K-region and (S_s) region the L-region or meso-positions. In future these regions will be referred to exclusively as (S_p) or (S_s) regions.

From Table IV, it is evident that the hydrocarbons investigated in these studies covered a wide range of pi-electron density values at the (S_p) and (S_s) regions, and these empirical "threshold values" should enable a prediction of the behaviour of hydrocarbons which have not been investigated. As will be seen later, two predictions about the behaviour of these hydrocarbons, based on these "threshold values" have been experimentally substantiated. These "threshold values" of pi-electron density for (S_p) and (S_s) region are listed

below:

	(S_p) region	(S_s) region
Inhibitors	0.7594	0.5725
Retarders	0.5332	0.7899 or a value $\geq$ 0.9348 for (S_s) region alone.

The k_x/k_p values refer to the efficiency of these hydrocarbons as retarders and are the ratios of the rate constants of the reactions (3) and (2) of the kinetic scheme. These reactions again are:

$$R^\bullet + X \rightarrow Z^\bullet \qquad \text{rate} = k_x (R^\bullet)(X) \qquad \ldots(3)$$

$$R^\bullet + M \rightarrow R^\bullet \qquad \text{rate} = k_p (R^\bullet)(M) \qquad \ldots(2)$$

A value of $k_x/k_p > 1$ means that reaction (3) is favored over reaction (2). $k_x/k_p >> 1$ would imply that the polymerization reaction is completely inhibited.

A study of the numerical values of the superdelocalizabilities for these hydrocarbons (Table IV and Appendix I) reveals the following features:

(1) For those hydrocarbons in which inhibition effects were observed, the (S_p) region values are higher than for the rest of the molecules except for 1,2,3,4-dibenzpyrene and 2,3,7,8-dibenzphenanthrene. All these compounds also possess an (S_s) region of fairly high pi-electron density. The lowest value of pi-electron density for the (S_p) region is 0.7594 and for the (S_s) region is 0.5725.

(2) In the case of 1,2,3,4-dibenzpyrene and 2,3,7,8-dibenzphenanthrene the (S_p) region values are greater

TABLE IV

FRONTIER ELECTRON DENSITIES AND THE RELATIVE REACTIVITIES OF THE VARIOUS HYDROCARBONS.

Hydrocarbon	Super-delocalizability index at principal carcinogenophore (S_p)	Super-delocalizability index at subsidary carcinogenophore (S_s)	k_x/k_p
(a) Inhibitors:			
3,4-benzpyrene	0.8151	1.0148	14
1,2,5,6-dibenzanthracene	0.7844	0.5725	-
1,2-benzanthracene	0.7594	0.8757	-
(b) Retarders:			
1,2,3,4-dibenzpyrene	0.7818	0.9696	6
2,3,7,8-dibenzphenanthrene	0.7722	0.8189	13
2',3'-naphtho-3,4-pyrene	0.7209	1.0542	240
1,2,7,8-dibenznaphthacene	0.5703	0.7899	15
1,2,9,10-dibenznaphthacene	0.5332	0.8649	13
Anthracene	-	0.9348	2

TABLE IV (Continued - Page 2)

Hydrocarbon	Super-delocalizability index at principal carcinogenophore (S_p)	Super-delocalizability index at subsidary carcinogenophore (S_s)	k_x/k_p
(c) No Effect:			
1,2-benzpyrene	0.8491	-	-
Pyrene	0.7865	-	-
Chrysene	0.7811	-	-
Phenanthrene	0.7306	-	-
1,2,3,4-dibenzanthracene	-	0.7159	-
Perylene	-	-	-
Triphenylene	-	-	-
Naphthalene	-	-	-

than the threshold value for inhibitors, yet no inhibition periods were observed in these compounds.

(3) In 1,2-benzpyrene the (S_p) value of 0.8491 is greater than the (S_p) values of all other molecules, and in pyrene and chrysene values for the (S_p) region are greater than threshold values for inhibitors, yet no inhibition periods or any other effect on the rate of polymerization was observed. However, none of these molecules possess an (S_s) region.

(4) The pi-electron density in the (S_p) and the (S_s) regions of 3,4-benzpyrene and 2,3-naphtho-3,4-pyrene are approximately the same, yet k_x/k_p values of these two compounds are widely different. The (S_p) region value in naphthopyrene is below the threshold value for inhibitors.

(5) In the case of 3,4-benzpyrene, where retardation effects were also observed after an inhibition period, the (S_s) region value is greater than those of anthracene, 1,2,5,6-dibenzanthracene, and 1,2-benzanthracene.

(6) Anthracene has only the (S_s) region and acted as a retarder.

(7) 1,2,7,8-dibenznaphthacene, 1,2,9,10-dibenznaphthacene and 2,3,7,8-dibenzphenanthrene whose (S_s) region values are less than those of anthracene were found to be more efficient retarders than anthracene.

(8) The threshold value of pi-electron density in these retarders is 0.5332 for (S_p) region and 0.7899 for (S_s) region or a value at least equal to 0.9348 for (S_s) region

if no (S_p) region is present.

(9) Those compounds which possess the (S_p) or (S_s) region only, or fairly low pi-electron density values in both these regions were found to be unreactive towards styryl radicals.

For these unsubstituted hydrocarbons, the differences in their reactivity would be expected to arise from the differences in the pi-electron densities in the (S_p) and (S_s) regions and this was experimentally found to be so. Widely different reactivities of these hydrocarbons have been observed and this diversity corresponds to the differences in the pi-electron density of the (S_p) and (S_s) regions. As shown in the previous section, in the inhibitors the center of reactivity is the (S_p) region while in the case of retarders it is the (S_s) region where reaction initially takes place. If the center of reactivity in both inhibitors and retarders were the same, then the differences in the reactivity of 3,4-benzpyrene compared to 2',3'-naphtho-3,4-pyrene cannot be explained, for the pi-electron density in the (S_s) region of both these molecules is approximately equal. The reactivity differences of these two hydrocarbons can be rationalized on the basis of the mechanism proposed. In the case of 3,4-benzpyrene, during the inhibition period, a substituted hydrocarbon is formed, and this reacts further with a growing-chain radical at its (S_s) region to give rise to the retardation effects. Thus, changes in the electronic configuration of its (S_s) region or the steric effects due

to the bulky substituent at carbon atom adjoining this region or both these factors would cause a decrease in the reactivity of this substituted hydrocarbon intermediate. On the other hand, on account of low (S_p) region pi-electron density, no such intermediate is postulated for 2,3-naphtho-3,4-pyrene. This supports the hypothesis that the pi-electron density at the (S_p) or (S_s) regions determines whether inhibition or retardation or both these effects arise. Some other features of the Table IV are of interest:

(a) With regard to points 1 and 3 mentioned above, it seems that for the manifestation of inhibition effects, apart from the presence of fairly high pi-electron density in the (S_p) region, the presence of an (S_s) region is also essential. Thus, it seems that the (S_s) region plays an important role for the manifestation of this reactivity. This is substantiated by the fact that 1,2-benzpyrene, pyrene and chrysene, whose pi-electron density in the (S_p) region is greater than the threshold value for inhibition, were found to be unreactive. In all these molecules the (S_s) region is missing. Thus, it can be predicted that 1,2,5,6-dibenzphenanthrene, whose (S_p) region value of 0.8172 is greater than the threshold value for inhibition would be expected to be unreactive. This compound does not have any (S_s) region.

The "threshold values" for inhibition effects are found to be:

(S_p) region	(S_s) region
0.7594	0.5725

From the above considerations, 1,2,3,4-dibenzpyrene and 2,3,7,8-dibenzphenanthrene should have inhibited the reaction as well as retarded it. In both these hydrocarbons their (S_p) and (S_s) region values are greater than the threshold values for inhibition and retardation effects. No inhibition was observed in either of these cases. However, considering the (k_x/k_p) values for these hydrocarbons and their pi-electron densities, the order of expected reactivities is different than the experimentally found. These hydrocarbons will be discussed at a greater length later.

(b) Anthracene which possesses no (S_p) region and acted as a retarder, indicates that for the manifestation of retardation effects only the (S_s) region is essential if its electron density is high enough. The position of attack of a free radical in these retarders is the (S_s) region. 1,2,3,4-dibenzanthracene which has only the (S_s) region, like anthracene, was found to be unreactive but its (S_s) region value is less than that of anthracene. This means that a certain "threshold value" in the (S_s) region is essential for retardation. The "threshold value" for retardation is found to be:

(S_p) region	(S_s) region
0.5332	0.7899 or a value of at least 0.9348 for (S_s) region only.

However, considering the relative reactivities of

anthracene, 1,2,7,8-dibenznaphthacene, and 1,2,9,10-dibenznaphthacene where the pi-electron density in the (S_s) regions of the dibenznaphthacenes is less than that of anthracene, both these hydrocarbons were more reactive than anthracene. This points to the fact that (S_p) region plays an important role in affecting the reactivity of the (S_s) region.

(c) In the case of 3,4-benzpyrene and 1,2-benzanthracene, the (S_s) region values are greater than the "threshold values" for retarders, yet no retardation was observed in the case of 1,2-benzanthracene, while 3,4-benzpyrene acted both as an inhibitor and a retarder. This will be discussed later.

(d) For those hydrocarbons which had no effect on the rate of polymerization, either the (S_s) or (S_p) region or both were absent, or else there were low pi-electron densities in these localized regions.

Thus, from Table IV, the following generalized statements about the reactivity of these hydrocarbons can be made:

(1) On the basis of the experimentally established empirical threshold values for inhibitors and retarders, it should be possible to predict the reactivity of hydrocarbons not investigated.

(2) In order to seek a correlation between pi-electron density and the observed reactivity, inhibitors and retarders should be considered separately, because these effects arise from the reactivity of two different regions: (S_p) or (S_s) regions. This means, that while seeking some order between

the experimental k_x/k_p values and the pi-electron densities, such cases like 3,4-benzpyrene, whose k_x/k_p values refer to retardation effects after an inhibition period, should not be considered along with other hydrocarbons with which only retardation effects were observed. As mentioned before, during the inhibition period, a substituted 3,4-benzpyrene is postulated and due to this substituent the electronic configuration of the (S_s) region would be expected to change. Also the bulky substituent would give rise to steric effects. Thus, such a comparison between the reactivity of a substituted and a non-substituted species would be invalid.

(3) The (S_p) and (S_s) regions appear to influence the reactivities of each other. This is essentially a stipulation of (S_p) and (S_s) region interaction.

(4) From the earlier considerations, it is evident that 1,2,3,4-dibenzpyrene and 2,3,7,8-dibenzphenanthrene would be expected to give both inhibition and retardation effects, but no inhibition periods were experimentally found with these compounds. Moreover, 1,2-benzanthracene was expected to give retardation effects after inhibition periods but this was not experimentally found to be so. Thus, these <u>three</u> hydrocarbons would be expected to present an anomolous behaviour in attempting to seek a correlation between pi-electron density and the chemical reactivity. The following attempts to explain this anomoly.

(1) Inhibitors.

In order to seek a correlation between pi-electron density in the (S_p) regions of these hydrocarbons and the observed reactivity, several tables have been constructed for the sake of clarity and elucidation of the various factors under consideration.

TABLE V

FRONTIER ELECTRON DENSITIES AND THE RELATIVE REACTIVITIES OF THE INHIBITORS AND RETARDERS ARRANGED ACCORDING TO DECREASING (S_p) REGION VALUES.

Hydrocarbon	(S_p) region	(S_s) region	k_x/k_p
3,4-benzpyrene	0.8151	1.0148	14
1,2,3,4-dibenzpyrene	0.7818	0.9696	6
2,3,7,8-dibenzphenanthrene	0.7722	0.8189	13
2',3'-naphtho-3,4-pyrene	0.7209	1.0542	240
1,2,7,8-dibenznaphthacene	0.5703	0.7899	15
1,2,9,10-dibenznaphthacene	0.5332	0.8649	13
Anthracene	-	0.9348	2

In Table V, based upon decreasing (S_p) region values, there appears to be no correlation between pi-electron density at the (S_p) region and k_x/k_p. This, however, would be expected, because it is the (S_s) region which appears to be the center of reactivity, and retardation effects are thus attributed to the pi-electron density of this region.

If the retardation effects arise due to the reactivity of the (S_s) region we should expect to find some correlation

between the pi-electron density of this region and the k_x/k_p values.

TABLE VI

FRONTIER ELECTRON DENSITIES AND THE RELATIVE REACTIVITIES OF THE INHIBITORS AND RETARDERS ARRANGED ACCORDING TO (S_s)REGION VALUES.

Hydrocarbon	(S_p) region	(S_s) region	k_x/k_p
2',3'-naphtho-3,4-pyrene	0.7209	1.0542	240
3,4-benzpyrene	0.8151	1.0148	14
1,2,3,4-dibenzpyrene	0.7818	0.9696	6
1,2,9,10-dibenznaphthacene	0.5332	0.8649	13
2,3,7,8-dibenzphenanthrene	0.7722	0.8189	13
1,2,7,8-dibenznaphthacene	0.5703	0.7899	15
Anthracene	-	0.9348	2

From the Table VI it is evident, that the k_x/k_p values appear to correspond to the electron density of the (S_s) region of these hydrocarbons except in the case of 1,2,3,4-dibenzpyrene. The k_x/k_p values of 13 - 15 are about the same order of magnitude, but considering the pi-electron densities at the (S_s) regions of 3,4-benzpyrene and 1,2,3,4-dibenzpyrene the expected k_x/k_p values would be much greater than the observed ones. The reactivity of 3,4-benzpyrene should have been approximately the same as 2',3'-naphtho-3,4-pyrene. Moreover, 1,2,3,4-dibenzpyrene should have been more reactive than the other compounds listed in the table.

It has been pointed out earlier, that in the case of

3,4-benzpyrene a substituted hydrocarbon intermediate is formed during the inhibition period and the observed retardation effects with this compound are due to this intermediate species. Thus, on the basis of the steric effects and changed electronic configuration of the (S_s) region of the intermediate species of this hydrocarbon, decrease in its chemical reactivity has been rationalized. In order to explain the anomolous behaviour of 1,2,3,4-dibenzpyrene, it is postulated that in this hydrocarbon an initial free radical attack at its (S_p) region leads to a substituted hydrocarbon as in 3,4-benzpyrene and the observed retardation effects arise due to this postulated substituted species.

Table VII is constructed by listing inhibitors and retarders separately. Among the inhibitors 1,2,3,4-dibenzpyrene has been included in view of the remarks above.

From Table VII it appears that there is a good correlation between pi-electron density and the observed reactivity.

TABLE VII

FRONTIER ELECTRON DENSITIES AND THE RELATIVE REACTIVITIES OF THE INHIBITORS AND RETARDERS.

Hydrocarbon	(S_p) region	(S_s) region	k_x/k_p
(a) Retarders:			
2',3'-naphtho-3,4-pyrene	0.7209	1.0542	240
1,2,9,10-dibenznaphthacene	0.5332	0.8649	13
2,3,7,8-dibenzphenanthrene	0.7722	0.8189	13
1,2,7,8-dibenznaphthacene	0.5703	0.7899	15
Anthracene	-	0.9348	2
(b) Inhibitors:			
3,4-benzpyrene	0.8151	1.0148	14
1,2,5,6-dibenzanthracene	0.7844	0.5725	-
1,2,3,4-dibenzpyrene	0.7818	0.9696	6
1,2-benzanthracene	0.7594	0.8757	-

However, as pointed out earlier, 2,3,7,8-dibenzphenanthrene should also have shown weak inhibition effects along with retardation. This hydrocarbon should therefore be considered among the class of inhibitors rather than retarders. It is included in Table VIII.

TABLE VIII

FRONTIER ELECTRON DENSITIES AND THE RELATIVE REACTIVITIES OF THE INHIBITORS.

Hydrocarbon	(S_p) region	(S_s) region	k_x/k_p
3,4-benzpyrene	0.8151	1.0148	14
1,2,5,6-dibenzanthracene	0.7844	0.5725	-
1,2,3,4-dibenzpyrene	0.7818	0.9696	6
2,3,7,8-dibenzphenanthrene	0.7722	0.8189	13
1,2-benzanthracene	0.7594	0.8757	-

From the Table VIII it would appear that the relationship between the (S_p) and (S_s) region and the k_x/k_p values, which appeared to be good (Table VII), has been destroyed by including 2,3,7,8-dibenzphenanthrene among inhibitors. It should be noted that the (S_s) region values for the hydrocarbons are considered in seeking a correlation between k_x/k_p values and pi-electron densities. An inclusion of this hydrocarbon among the class of inhibitors implies that a substituted hydrocarbon intermediate is formed by an initial attack of a free radical at its (S_p) region. Such a situation would be expected to lead to a decreased reactivity of its (S_s) region as was found to be the case in 3,4-benzpyrene and

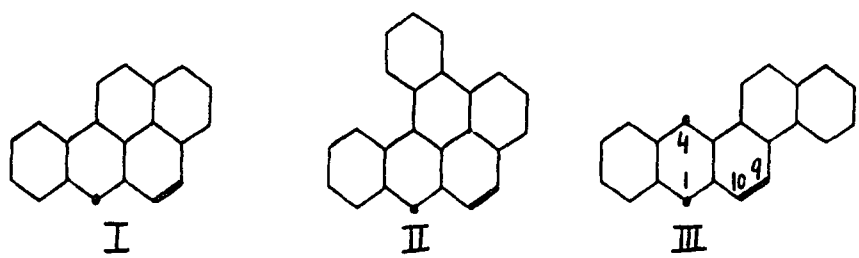
1,2,3,4-dibenzpyrene. As the substituent for all these postulated intermediate species is the same, similar steric effects are involved. The predicted order of reactivity of these hydrocarbons would be:

3,4-benzpyrene > 1,2,3,4-dibenzpyrene > 2,3,7,8-dibenzphenanthrene, but the experimentally found order is:

3,4-benzpyrene > 2,3,7,8-dibenzphenanthrene > 1,2,3,4-dibenzpyrene.

The observed reactivity of 2,3,7,8-dibenzphenanthrene does not follow the pattern of these predictions. Thus, in order to explain this anomolous behaviour, some factors other than the pi-electron density of the (S_s) region carbon atom adjoining (S_p) region must play an important role.

An explanation for this anomoly is presented below on the basis of the considerations of the structures of these hydrocarbons.



I II III

3,4-benzpyrene | 1,2,3,4-dibenzpyrene | 2,3,7,8-dibenzphenanthrene

(In these structures the solid line indicates the (S_p) region and the black spot the (S_s) region.)

From these structures it can be seen that:

(a) The interatomic distances in all these hydrocarbons are the same between the (S_p) region carbon atoms and the (S_s) region adjacent to the (S_p) region. Thus, the influences of steric effects due to a substituent at the (S_p) region should be identical.

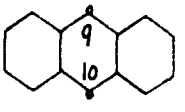
(b) Also the influences due to changes in electronic configuration after substitution would be expected to be approximately identical on the (S_s) region carbon atom adjacent to (S_p) region.

Thus, both these considerations would lead to the same order of reactivities as might be predicted on the basis of (S_s) region pi-electron densities. The order of reactivity would be: 3,4-benzpyrene > 1,2,3,4-dibenzpyrene > 2,3,7,8-dibenzphenanthrene. However, the most important difference between these hydrocarbons is that compounds I and II have <u>only one</u> (S_s) region carbon atom available for attack by a reagent, while the second position is blocked. This is not so in compound III and its both the (S_s) region carbon atoms are accessible for further reactions.

As shown earlier on the basis of resonance structures, it is the (S_p) and (S_s) regions <u>only</u> which are the centers of reactivity in these compounds, thus the accessibility of the second (S_s) region carbon in 2,3,7,8-dibenzphenanthrene and the fact that position (4) in this compound would not be sterically hindered due to a substituent at its (S_p) region, would

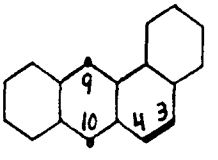
lead to a higher reactivity as found experimentally.

Thus far a plausible explanation based on steric considerations and the accessibility of the second (S_s) region carbon atom for subsequent attack by a growing chain radical has helped elucidate the observed reactivity of 3,4-benzpyrene and 2,3,7,8-dibenzphenanthrene. These factors, however, do not provide an explanation for the anomolous behaviour of 1,2-benzanthracene. The (S_s) region pi-electron density (0.8757) of this hydrocarbon is greater than the threshold value (0.7899) for retardation, yet no retardation effects after the inhibition periods were observed with this compound. This hydrocarbon is structurally anologous to 2,3,7,8-dibenzphenanthrene and considering the (S_s) region pi-electron densities of both these compounds approximately the same order of magnitude of relative retardation reactivities (k_x/k_p) would be expected.



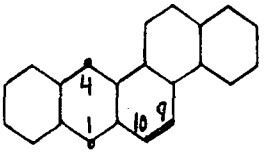
I

Anthracene



II

1,2-benz-anthracene



III

2,3,7,8-dibenz-phenanthrene

The (S_p) and (S_s) region reactivities of these unsubstituted hydrocarbons towards many reagents have been investigated by many workers[3,29,72] and others, both these regions in 1,2-benzanthracene were found to be relatively unreactive. This was also the case in the present investigations. According to the present scheme of threshold values of pi-electron densities and the inhibition or retardation effects, 1,2-benzanthracene is a borderline case and also the very weak inhibition effects may be accepted only with reservations. However, in view of similar experimental evidence of other workers, for example Waters[33,72] reported the reactivity of some of these hydrocarbons towards benzoyl radicals in the order:

3,4-benzpyrene >> anthracene; 1,2-benzanthracene > 1,2,5,6-dibenzanthracene > phenanthrene and chrysene, and towards benzaldehyde in the order:

3,4-benzpyrene > anthracene > 1,2-benzanthracene > etc. Thus, very weak inhibition effects found with 1,2-benzanthracene in these studies may be regarded as real and not an experimental error.

Consequently, this leads to the problem of absence of retardation reactivity (reactivity of its (S_s) regions). As pointed out earlier, this hydrocarbon is very anologous to 2,3,7,8-dibenzphenanthrene and a plausible explanation may be sought by considering the following features of these two compounds:

(a) With 1,2-benzanthracene, inhibition effects were observed ie. an initial free radical attack takes place at its (S_p) region. As discussed earlier, it is postulated that (S_p) region of 2,3,7,8-dibenzphenanthrene is also the center of initial reactivity. This means, that in both these hydrocarbons position 10 and 1 of compounds II and III respectively will be equally sterically hindered. Since a similar substituent (R) is attached to the (S_p) region of these compounds, an identical pi-electron shift from position 9 of compound II and position 4 of compound III may be expected, but it is probable that <u>one</u> additional fused benzene ring in the case of 2,3,7,8-dibenzphenanthrene plays an important role in contributing towards pi-electron shift to the (S_p) region of this compound and thereby leaving its position 4 relatively less effected as compared to position 9 in 1,2-benzanthracene. It is recognized that the question of deactivation of these positions to a varying degree in these molecules can be further elucidated by carrying out molecular orbital calculations of pi-electron densities of these meso-positions. However, this may be expected to yield only qualitative indication.

(b) There is some additional experimental evidence based on Bergman's[81] polarographic studies on the stepwise reduction of the various hydrocarbons. For the present discussion the half wave potentials for these two hydrocarbons are:

	$E_{\frac{1}{2}}$ potential in volts	
	a	b
1,2-benzanthracene	1.53	1.985
2,3,7,8-dibenzphenanthrene	1.435	1.88

From the numerical values of the second half wave potentials it can be seen that 1,2-benzanthracene would be relatively less reactive than 2,3,7,8-dibenzphenanthrene, which was the case in these investigations. It may be remarked here that all the hydrocarbons which were found to be reactive towards styryl radicals in these investigations had much lower values of these reduction potentials as compared to the unreactive compounds. However, there were a few exceptions.

(2) Retarders.

In order to discuss the retardation effects and to bring out the salient features of relation between pi-electron density in these molecules and this reactivity, the (S_p) and (S_s) region values for all these hydrocarbons where retardation effects were observed, are tabulated in Table IX.

In this table, the hydrocarbons listed as Group A may be regarded as the compounds in which both (S_p) and (S_s) regions react with the styryl radicals ie. they are considered as inhibitors and retarders, while in Group B compounds (S_s) region is the center of reactivity ie. retarders only. It may be noted, that only 3,4-benzpyrene showed both, inhibition and retardation effects, while on the basis of earlier discussions, it is assumed that the (S_p) region of 1,2,3,4-dibenzpyrene and 2,3,7,8-dibenzphenanthrene is also reactive.

TABLE IX

FRONTIER ELECTRON DENSITIES AND THE RELATIVE REACTIVITIES OF RETARDERS.

Hydrocarbon	(S_p) region	(S_s) region	k_x/k_p
Group A			
3,4-benzpyrene	0.8151	1.0148	14
1,2,3,4-dibenzpyrene	0.7818	0.9696	6
2,3,7,8-dibenzphenanthrene	0.7722	0.8189	13
Group B			
2,3-naphtho-3,4-pyrene	0.7209	1.0542	240
1,2,7,8-dibenznaphthacene	0.5703	0.7899	15
1,2,9,10-dibenznaphthacene	0.5332	0.8649	13
Anthracene	-	0.9348	2

From the earlier discussions, the following points may be recapitulated:

(1) In view of the observed reactivity of anthracene, which has only an (S_s) region, retardation effects are attributed to the reactivity of the (S_s) region of these compounds.

(2) Considering the relative reactivities of 1,2,7,8-dibenznaphthacene, 1,2,9,10-dibenznaphthacene and anthracene, it is evident that (S_p) region, although is not essential for the manifestation of retardation effects, yet plays an important role in augmentation of this reactivity.

(3) The empirical threshold pi-electron density values for retardation are:

(S_p) region	(S_s) region
0.5332	0.7899, or a value $\geq$ 0.9348 for (S_s) region only.

Thus, on the basis of these considerations, some other hydrocarbons which have not been investigated, but whose pi-electron densities for the (S_p) regions fall above the empirical threshold values, would be expected to act as retarders. They are listed in Table X.

TABLE X

SOME HYDROCARBONS WHICH ARE PREDICTED AS RETARDERS.

Hydrocarbon	(S_p) region	(S_s) region
3,4,8,9-dibenzpyrene	0.7440	1.0704
1,2,7,8-dibenzanthracene	0.6719	0.8930
2-1-anthra-1,2-anthracene	0.6295	0.5970
2,3,5,6-dibenzphenanthrene	0.6034	0.8089
Anthanthrene	0.5945	0.9725
1,2-benznaphthacene	0.5530	0.9741
Pentacene	-	1.2818

From the above table it is seen that only pentacene has no (S_p) region and that its pi-electron density in (S_s) region is greater than that of anthracene. If the centers of reactivity for the retardation effects are the (S_s) regions in these compounds, this hydrocarbon should be more reactive than anthracene. The (S_s) region value in this hydrocarbon is greater than all others. An experimental k_x/k_p value for this compound would have furnished some very interesting evidence. If the observed efficiency had been

found to be greater than anthracene and less than 2',3'-naphtho-3,4-pyrene, it would have further substantiated the postulation of (S_s) and (S_p) region interaction. If, on the other hand, its efficiency were about the same as 2',3'-naphtho-3,4-pyrene it would have shown that there is no (S_s) and (S_p) region interaction. Unfortunately, this hydrocarbon could not be investigated on account of its very poor solubility. Polar solvents cannot be used as they would cause complexities in the reaction kinetics due to chain transfer to solvent, etc.

The case of 2',1'-anthra-1,2-anthracene needs special mention. The (S_p) region value of this hydrocarbon is above the threshold value for retardation effects, but (S_s) region value is lower. This hydrocarbon should be a borderline case. It also was not investigated because of its very low solubility.

On the basis of the postulations, that the (S_s) region alone is essential for the manifestation of retardation effects and that (S_p) and (S_s) interaction for unsubstituted hydrocarbons leads to enhanced reactivity, it may be remarked that the hydrocarbons which have been predicted to act as retarders, could be expected to show the following order of reactivity:

3,4,8,9-dibenzpyrene $>$ anthanthrene $\geq$ 1,2-benznaphthacene $>$ 1,2,7,8-dibenzanthracene $\geq$ 2,3,5,6-dibenzphenanthrene $\geq$ pentacene $>$ anthracene.

No inhibition effects would be expected and a wide range of reactivity could be anticipated. However, solubilities

of these hydrocarbons in this monomer would likely be very poor.

It may be pointed out that from our earlier experimental evidence it was predicted that 1,2,3,4-dibenzpyrene would be reactive towards styryl radicals. After the major portion of the kinetic investigation was completed, we were able to procure a sample of this hydrocarbon to test the validity of the prediction, which was confirmed.

A further evidence for the validity of the scheme was provided by Belonovskaya et al.,[35] who recently reported the effect of a few of these hydrocarbons on the thermal polymerization of styrene. They report that "both, anthracene and dibenzopyrene, merely decrease the rate of polymerization of styrene more or less, they do not cause any inhibition period to appear". The reactivity of dibenzopyrene was found to be greater than that of anthracene. These workers do not report which dibenzopyrene isomer was investigated. Considering their mention of the very poor solubility of this hydrocarbon and the solubilities of other known isomers, it was assumed that they investigated 3,4,8,9-dibenzopyrene.

The observed reactivities of 3,4,8,9-dibenzpyrene and 1,2,3,4-dibenzpyrene support our assumption and the validity of our predictions regarding their reactivities based on certain "threshold" values of "frontier electron" density in the (S_p) and (S_s) regions.

In the foregoing we have assumed that inhibition effects

arise from the attack of a free radical at the (S_p) or the K-region of the molecule, while retardation effects arise due to the reactivity of the (S_s) region or the L-region (meso-positions). There appears to be some other experimental evidence in support of these assumptions. Waters[72] investigated the reactivity of some of these hydrocarbons towards benzoyl radicals formed by the homolytic decomposition of benzoyl peroxide and found that the meso-positions in anthracene, 1,2-benzanthracene and 3,4-benzpyrene were substituted by benzoate groups. No significant reactions was found to occur with clorobenzene, naphthalene, phenanthrene pyrene. This substantiates the point of view that, where sufficiently high pi-electron density exists in meso-positions, only those hydrocarbons were found to be active for this radical attack. However, a final proof of the assumptions must await the isolation and identification of reaction products of a free radical attack on these hydrocarbons.

SUMMARY OF CONCLUSIONS.

(a) There exists a reasonably good correlation between the observed reactivities and the "frontier electron" densities calculated by Fukui et al.[12]

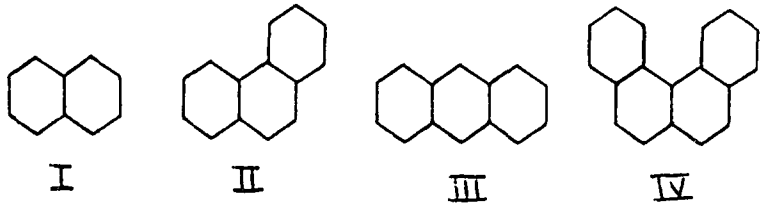
(b) There appears to be no direct correlation between chemical reactivity of these hydrocarbons towards free radicals and carcinogenicity. A similar conclusion was also drawn by Pullman[3] and by Coulson[82] on the basis of the scanty experimental evidence of Magat et al.[34]

(c) It is postulated that the inhibition effects due to these hydrocarbons arise by an attack of a free radical at the (S_p) or K-region. However, the manifestation of retardation effects has been attributed to the reactivity of the (S_s) region or the meso-positions in these compounds.

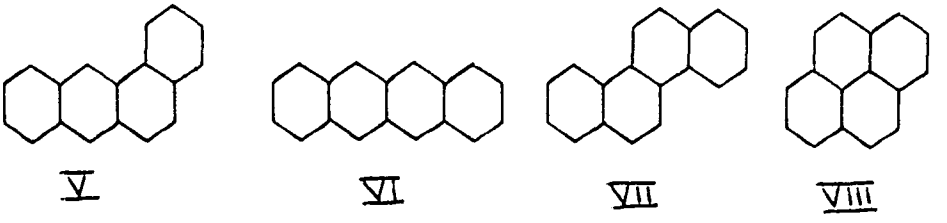
(d) On the basis of the relative reactivities of these hydrocarbons, electronic interaction between the (S_p) and (S_s) or the K and L-regions has been postulated. The relative pi-electron densities in these two regions influence the reactivity of each other.

APPENDIX I

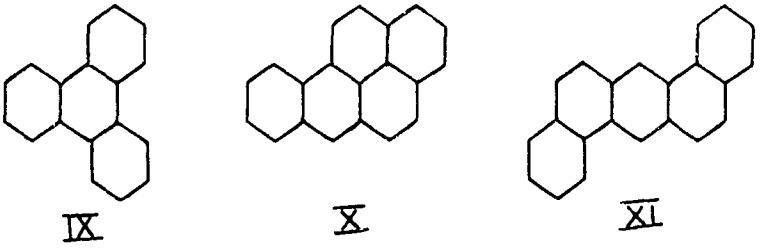
STRUCTURES OF HYDROCARBONS.



I II III IV



V VI VII VIII



IX X XI

I. Naphthalene

II. Phenanthrene

III. Anthracene

IV. 3,4-benzphenanthrene

V. 1,2-benzanthracene

VI. Naphthacene

VII. Chrysene

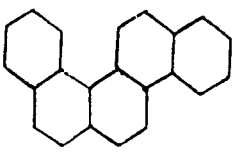
VIII. Pyrene

IX. Triphenylene

X. 3,4-benzpyrene

XI. 1,2,5,6-dibenzanthracene

STRUCTURES OF HYDROCARBONS.



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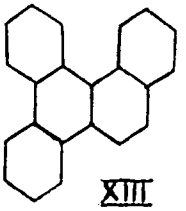

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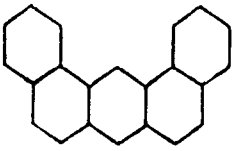

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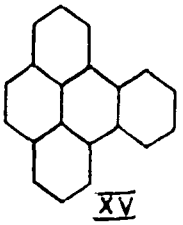

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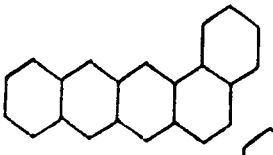
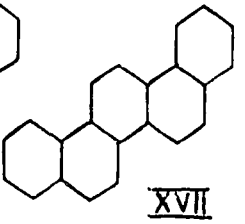


XVI



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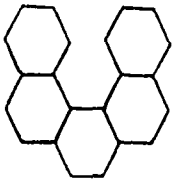

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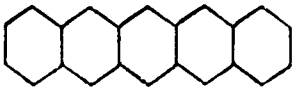

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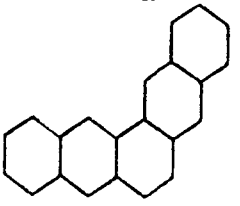


XX

XII. 1,2,5,6-dibenz-phenanthrene

XIII. 1,2,3,4-dibenz-phenanthrene

XIV. 1,2,7,8-dibenz-anthracene

XV. 1,2-benzpyrene

XVI. 1,2-benznaphthacene

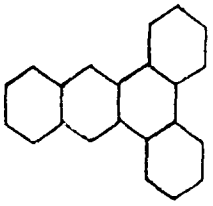
XVII. Picene

XVIII. 3,4,5,6-dibenz-phenanthrene

XIX. Pentacene

XX. Pentaphene

STRUCTURES OF HYDROCARBONS.



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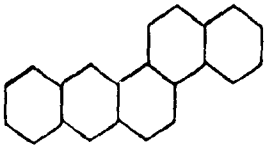

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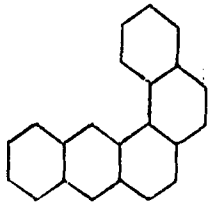

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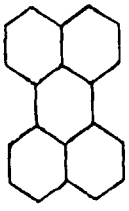

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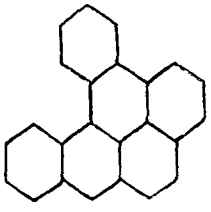

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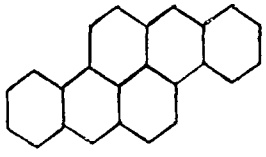

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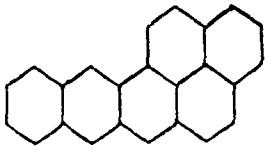

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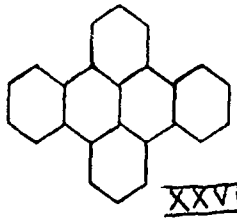
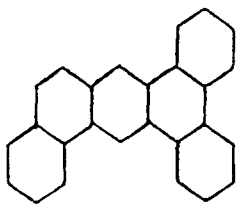


XXVIII

XXI.	1,2,3,4-dibenz-anthracene	XXV.	1,2,3,4-dibenz-pyrene
XXII.	2,3,7,8-dibenz-phenanthrene	XXVI.	3,4,8,9-dibenz-pyrene
XXIII.	2,3,5,6-dibenz-phenanthrene	XXVII.	1',2',3-naphtho-3,4-pyrene
XXIV.	Perylene	XXVIII.	1,2,6,7-dibenz-pyrene

STRUCTURES OF HYDROCARBONS.



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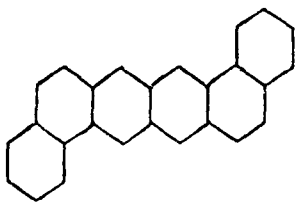

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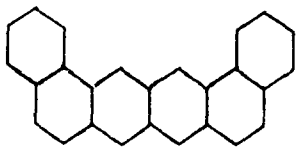

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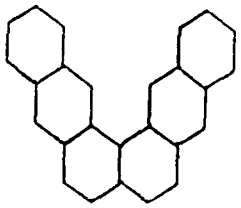

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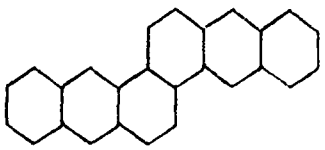

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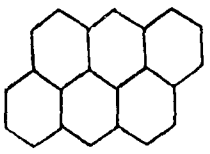


XXXIV

XXIX. 1,2,3,4,5,6-tribenz-anthracene

XXX. 1,2,7,8-dibenz-naphthacene

XXXI. 1,2,9,10-dibenz-naphthacene

XXXII. 1',2'-anthra-1,2-anthracene

XXXIII. 2',1'-anthra-1,2-anthracene

XXXIV. Anthanthrene

TABLE I

COMPARISON OF THE VALUES OF SUPER-DELOCALIZABILITIES AT CARCINOGENOPHORES WITH CARCINOGENIC ACTIVITIES. FUKUI ET AL.[12]

Compounds	Super-delocalizability at principal carcinogenophore (S_p)	Super-delocalizability at subsidiary carcinogenophore (S_s)	Carcinogenic activity
Class A:			
3,4-benzpyrene	0.8151	1.0148	+ + + +
1,2,5,6-dibenzanthracene	0.7844	0.5725	+ + +
1,2,3,4-dibenzpyrene	0.7818	0.9696	+
2,3,7,8-dibenzphenanthrene	0.7722	0.8189	-
1,2-benzanthracene	0.7594	0.8757	+
3,4,8,9-dibenzpyrene	0.7440	1.0704	+
2',3'-naphtho-3,4-pyrene	0.7209	1.0542	-
1,2,7,8-dibenzanthracene	0.6719	0.8930	+
1,2-benzpyrene	0.8491	-	-
1,2,5,6-dibenzphenanthrene	0.8172	-	+
Pyrene	0.7865	-	-
Chrysene	0.7811	-	‡

TABLE I (Continued - Page 2)

Compounds	Super-delocalizability at principal carcinogenophore (S_p)	Super-delocalizability at subsidiary carcinogenophore (S_s)	Carcinogenic activity
Class B:			
Picene	0.7371	-	-
Phenanthrene	0.7306	-	±
3,4,5,6-dibenzphenanthrene	0.7020	-	-
3,4-benzphenanthrene	0.6144	-	+
1,2,3,4-dibenzphenanthrene	0.5753	-	+
2,1-anthra-1,2-anthracene	0.6295	0.5970	-
2,3,5,6-dibenzphenanthrene	0.6034	0.8089	-
Anthanthrene	0.5945	0.9725	-
1,2,7,8-dibenznaphthacene	0.5703	0.7899	-
1,2,3,4,5,6-tribenzanthracene	0.5676	0.3989	-
1,2-benznaphthacene	0.5530	0.9741	-
1,2,9,10-dibenznaphthacene	0.5332	0.8649	-

TABLE I (Continued - Page 3)

Compounds	Super-delocalizability at principal carcinogenophore (S_p)	Super-delocalizability at subsidiary carcinogenophore (S_s)	Carcinogenic activity
Class C:			
Pentaphene	0.4841	0.4237	-
1,2-anthra-1,2-anthracene	0.3632	0.5253	-
Pentacene	-	1.2818	-
Anthracene	-	0.9348	-
1,2,3,4-dibenzanthracene	-	0.7159	-
Naphthacene	-	0.4876	-
Triphenylene	-	-	-
Perylene	-	-	-
1,2,6,7-dibenzpyrene	-	-	-

TABLE II

POLYCYCLIC HYDROCARBONS - ENERGY INDICES OF THE K AND L-REGIONS.

PULLMAN ET AL.[13]

Compounds	K-region Bond	K-region Indices	L-region Carbons	L-region Indices	Carcinogenic activity
Naphthalene	1-2	3.56	1,4	5.98	-
Anthracene	1-2	3.43	9,10	5.33	-
Phenanthrene	9-10	3.365	-	-	-
Naphthacene	1-2	3.33	6,11	5.26	-
1,2-benzanthracene	3-4	3.29	9,10	5.53	-
Chrysene	1-2	3.38	-	-	-
3,4-benzphenanthrene	1-2	3.41	-	-	+
Pyrene	1-2	3.33	-	-	-
Triphenylene	1-2	3.81	-	-	-
1,2,5,6-dibenzanthracene	3-4	3.305	9,10	5.69	+ +
1,2,7,8-dibenzanthracene	3-4	3.31	9,10	5.66	+
3,4-benzpyrene	6-7	3.23	-	-	+ + + +
1,2,5,6-dibenzphenanthrene	7-8	3.41	-	-	+
1,2,3,4-dibenzphenanthrene	9-10	3.42	-	-	+

TABLE II (Continued - Page 2)

Compounds	K-region Bond	K-region Indices	L-region Carbons	L-region Indices	Carcinogenic activity
1,2-benzpyrene	6-7	3.37	-	-	-
1,2-benznaphthacene	3-4	3.20	6,11	5.25	-
Pentaphene	6-7	3.23	5,14	5.56	-
1,2,3,4-dibenzanthracene	5-6	3.51	9,10	5.67	-
Pentacene	1-2	3.27	6,13	5.03	-
3,4,5,6-dibenzphenanthrene	1-2	3.38	-	-	-
Picene	11-12	3.37	-	-	-
2,3,7,8-dibenzphenanthrene	9-10	3.27	1,4	5.47	-
2,3,5,6-dibenzphenanthrene	9-10	3.30	1,4	5.48	-
Perylene	-	-	-	-	-
Anthanthrene	1-2	3.20	-	-	-
1,2,3,4,5,6-tribenzanthracene	7-8	3.33	9,10	5.80	-
1,2,6,7-dibenzpyrene	-	-	-	-	-
1',2'-anthra-1,2-anthracene	3-4	3.30	9,10	5.45	-
2'-1'-anthra-1,2-anthracene	3-4	3.24	9,10	5.44	-

TABLE II (Continued - Page 3)

Compounds	K-region Bond	K-region Indices	L-region Carbons	L-region Indices	Carcinogenic activity
1,2-naphtho-3,4-pyrene	6-7	3.14	1,4	5.30	-
1,2,9,10-dibenznaphthacene	3-4	3.25	5,12	5.40	-
1,2,7,8-dibenznaphthacene	3-4	3.24	5,12	5.42	-
1,2,3,4-dibenzpyrene	6-7	3.24	-	-	+ + +
3,4,8,9-dibenzpyrene	6-7	3.175	-	-	+ + + +

TABLE III

ULTRA VIOLET ABSORPTION SPECTRA.[3] λ MAX. VALUES.

Compounds	ν (cm^{-1}) ($\nu = 1/\lambda$)	Carcinogenic Activity
Naphthacene	21120	-
1,2-benzanthracene	25970	?
3,4-benzphenanthrene	26880	+
Pyrene	26910	-
Chrysene	27780	-
Triphenylene	28570	-
Pentacene	17380	-
1,2-benznaphthacene	22100	-
Perylene	23040	-
Pentaphene	23640	-
3,4-benzpyrene	24810	+ + + +
2,3,5,6-dibenzphenanthrene	24940	-
1,2,7,8-dibenzanthracene	25320	+
1,2,5,6-dibenzanthracene	25320	+ +
2,3,7,8-dibenzphenanthrene	25450	-
1,2-benzpyrene	25770	-
1,2,5,6-dibenzphenanthrene	25910	+
3,4,5,6-dibenzphenanthrene	25910	-
Picene	26600	-
1,2,3,4-dibenzanthracene	26670	-
1,2,3,4-dibenzphenanthrene	26950	+
2,3-naphtho-3,4-pyrene	21830	-

TABLE III (Continued - Page 2)

Compounds	ν (cm^{-1}) ($\nu = 1/\lambda$)	Carcinogenic Activity
1,2,3,4-dibenzpyrene	22030	+ + +
3,4,8,9-dibenzpyrene	22170	+ + + +
1,2,7,8-dibenznaphthacene	23000	-
Anthanthrene	23090	-
1,2,9,10-dibenznaphthacene	23120	-
2,1-anthra-1,2-anthracene	23810	-
1,2,6,7-dibenzpyrene	25300	-
1,2,3,4,5,6-tribenzanthracene	25770	-

TABLE IV

RESONANCE ENERGY[3]

Compounds	Resonance Energy K cal./mole R (B=20)	Carcinogenic Activity
Pyrene	6.506	-
Naphthacene	6.932	-
1,2-benzanthracene	7.101	?
3,4-benzphenanthrene	7.187	+
Chrysene	7.190	-
Triphenylene	7.275	-
3,4-benzpyrene	8.222	+ + + +
Perylene	8.245	-
Pentacene	8.544	-
Pentaphene	8.763	-
1,2,7,8-dibenzanthracene	8.879	+
1,2,5,6-dibenzanthracene	8.880	+ +
1,2,3,4-dibenzanthracene	8.942	-
Picene	8.943	-
Anthracene	9.253	-
3,4,8,9-dibenzpyrene	9.928	+ + + +

TABLE V

IONIZATION POTENTIALS.[3]

Compounds	Energy of the highest occupied orbital	Activity
Triphenylene	0.5841	-
3,4-benzphenanthrene	0.4971	+
Chrysene	0.4603	-
1,2-benzanthracene	0.4064	?
Pyrene	0.4005	-
Naphthacene	0.2747	-
Picene	0.4460	-
1,2,3,4-dibenzanthracene	0.4437	-
1,2,5,6-dibenzanthracene	0.4434	+ +
1,2,7,8-dibenzanthracene	0.4379	+
Pentaphene	0.3941	-
3,4-benzpyrene	0.3379	+ + + +
Perylene	0.3196	-
Pentacene	0.2083	-
3,4,8,9-dibenzpyrene	0.2814	+ + + +
Anthanthrene	0.2712	-

TABLE VI

REDUCTION POTENTIALS, HIGHEST BOND ORDERS AND FREE VALENCY.

Compounds	Reduction[81] Potential (Volts)	Highest[83] Bond Order	Free Valency[83]	Carcino-genic Activity
Naphthalene	1.98	0.724(1-2)	0.452(1)	-
Phenanthrene	1.935	0.774(9-10)	0.451(10)	-
Anthracene	1.46			-
Triphenylene	1.97	0.690(1-2)	0.439(1)	-
Chrysene	1.805	0.712(1-2)	0.457(12)	-
3,4-benzphenanthrene	1.745	0.762(5-6)	0.451(5)	+
Pyrene	1.61	0.776(4-5)	0.468(3)	-
1,2-benzanthracene	1.53	0.783(5-6)	0.514(7)	?
Naphthacene	1.135	0.741(1-2)	0.529(12)	-
Picene	1.79	0.758(5-6)	0.457(5)	-
1,2,5,6-dibenzphenanthrene	1.73			+
1,2-benzpyrene	1.67			-
1,2,3,4-dibenzphenanthrene	1.645			+
1,2,7,8-dibenzanthracene	1.57	0.780(5-6)	0.510(7)	+

TABLE VI (Continued - Page 2)

Compounds	Reduction[81] Potential (Volts)	Highest[83] Bond Order	Free Valency[83]	Carcinogenic Activity
1,2,5,6-dibenzanthracene	1.545	0.778(5-6)	0.498(7)	+
1,2,3,4-dibenzanthracene	1.54	0.727(12-13)	0.499(14)	-
Pentaphene	1.525	1.790(6-7)	0.514(5)	-
2,3,7,8-dibenzphenanthrene	1.435			-
2,3,5,6-dibenzphenanthrene	1.40			-
3,4-benzpyrene	1.36	0.724(1-2)	0.452(1)	+ + + +
Perylene	1.25	0.707(2-3)	0.474(3)	-
1,2-benznaphthacene	1.19			-
Pentacene	0.86	0.737(1-2)	0.520(9)	-
1,2,6,7-dibenzpyrene	1.685			-
1,2,3,4,5,6-tribenzanthracene	1.57			-
1,2,7,8-dibenznaphthacene	1.25			-
Anthanthrene	1.19			-
3,4,8,9-dibenzpyrene	1.16			+ + + +

TABLE VI (Continued - Page 3)

Compounds	Reduction[81] Potential (Volts)	Highest[83] Bond Order	Free Valency[83]	Carcino-genic Activity
2',3'-naphtho-3,4-pyrene	1.15			-
1,2,3,4-dibenzpyrene	1.08			+ + +

For the values of highest bond orders and free valency, numbers shown in the brackets refer to the carbon atoms.

APPENDIX II

THE REACTIVITY OF POLYNUCLEAR HYDROCARBONS TOWARD METHYL METHACRYLATE RADICALS.

A few of these hydrocarbons were also investigated for their influence on the rate of polymerization of methyl methacrylate, using 2,2'-azo-bis-isobutyronitrile as an initiator. The experimental procedure and the reaction temperature for these studies was the same as described in this thesis. It was found that hydrocarbons like 2',3'-naphtho-3,4-pyrene which strongly retarded the rate of polymerization of styrene, and 3,4-benzpyrene that gave both inhibition and retardation effects with the above monomer, had no noticeable effect on the rate of polymerization of methyl methacrylate.

This was an unusual, but interesting behaviour. A compound that acts as an inhibitor or a retarder in vinyl polymerization would be expected to act as a more efficient chain stopping agent if the relative reactivity of the corresponding radical is greater. The order of reactivity of the two monomer radicals studied in these investigations is:

Styryl < methyl methacryl radical.

Thus, considering their relative reactivities, it would be expected that those compounds which acted as inhibitors and retarders of styrene polymerization should be more reactive toward methyl methacryl radicals. However, the experimental results were contrary to the expected behaviour. These results are listed in Table I.

TABLE I

SUMMARY OF EXPERIMENTAL RESULTS FROM DILATOMETRIC MEASUREMENTS.

Hydrocarbon	Hydrocarbon Conc.	$(AIBN)^{\frac{1}{2}}$	rate %/hr.	r_o	$r/r_o = \emptyset$
Naphthalene	16.5×10^{-3} M	4.24×10^{-2} M	1.62	1.42	1.14
	4.79 "	5.26 "	1.77	1.71	1.03
Phenanthrene	6.09 "	7.05 "	2.22	2.24	0.98
Anthracene	11.8 "	5.25 "	2.00	1.71	1.17
	8.26 "	5.74 "	2.10	1.86	1.13
	4.49 "	5.53 "	1.66	1.80	0.92
3,4-benzpyrene	3.52 "	5.80 "	1.77	1.88	0.94
	1.11 "	6.46 "	2.01	2.07	0.97
2,3-naphtho-3,4-pyrene	1.31 "	6.92 "	2.05	2.20	0.94
	0.432 "	6.92 "	2.10	2.20	0.96

In Table I r_o means the rate of uninhibited polymerization, r is the observed rate, and ϕ (r/r_o) is the efficiency of retardation.

For the unretarded runs the following relation for the rates was found to be:

$$r_o = 29.3\ (AIBN)^{\frac{1}{2}} + 0.18\%\ \text{per hour.}$$

Discussion of Results.

Ihrig[84] has provided an explanation for the "unexpected" reversal of the reactivities of the styryl and methyl methacryl radicals toward hydrocarbon retarders. In order to seek an elucidation of this behaviour, the following factors need to be considered:

Of the two monomers investigated, styrene is more reactive than methyl methacrylate while the reactivities of their radicals is reverse ie. styryl radical is less reactive than methyl methacryl radical.

On page 71 of this thesis, a new reaction step is postulated to account for shortening of inhibition periods:

$$Z^{\bullet} + M \rightarrow HM^{\bullet} + \overset{\cdot}{X}$$

This reaction was not found necessary in mechanistic studies of other types of retarders.

The polynuclear aromatic hydrocarbons, as a class of retarders of vinyl polymerization, are different from the usual retarders like quinones, nitro compounds etc. inasmuch as there are no "functional groups" present to interact with the chain-carrying radicals. The centers of reactivity of

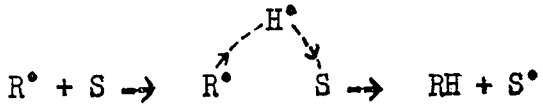
these molecules are the K and L-regions and these regions are merely loci of relatively high pi-electron density. Therefore, the postulation of a new sort of reaction step need not in itself be surprising.

A necessary consequence of the reaction ($Z^{\bullet} + M \rightarrow HM^{\bullet} + \dot{X}$) entering into the overall mechanism is that we can no longer consider only the reactivity of the radical as the sole criterion for prediction of inhibition or retardation by a given added hydrocarbon. The reactivity of the monomer from which the radical is derived is also important here. First, the radical must be reactive enough to form $Z^{\bullet}$ (probably as a complex), and then the monomer surrounding must be reactive enough to abstract the hydrogen atom from $Z^{\bullet}$ or its complex in order to stabilize it. Otherwise the $Z^{\bullet}$ radical will break down to form $R^{\bullet}$ and X, with a net result of no observable change in the rate of polymerization.

Since styrene monomer is considerably more reactive than methyl methacrylate monomer, while the reactivity difference in their radicals is less great, the styrene system probably combines the two features to a greater extent than the methyl methacrylate system. Thus, the anomoly observed tends to support the new mechanistic step introduced on page 71 for another reason.

In one sense, this newly proposed reaction is the opposite of conventional chain transfer in those cases where the transfer agent acts by shifting a labile H atom to the

growing chain and stopping the propagation reaction:



where S is the chain transfer agent and S• the radical formed from it by the removal of a H atom. Comparing this with the reaction

it is seen that in the first case H• transfer is from molecule to radical, while in the second it is from the radical to molecule.

We should expect that for this second reaction, a difference in reactivity between styrene and methyl methacrylate (when used as M) should be in the direction as their reactivity difference with a given chain transfer agent. Put another way, in chain transfer the more reactive <u>radical</u> abstracts the H atom from the chain transfer agent most readily and, in inhibitor stabilization the more reactive <u>monomer</u> should abstract the labile H atom most readily. Comparing the chain transfer constants of styrene and methyl methacrylate with n-butyl mercaptan as transfer agent, Walling[85] has found the styryl radical to be thirty three times as reactive in abstracting the H atom from sulfhydryl group as the methyl methacryl radical.

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