

The Retardation of Benzaldehyde Autoxidation. Part VI. The Actions of a Number of Polycyclic Aromatic Hydrocarbons of Carcinogenic Interest.*

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Kinetic study of the retardation of the benzoyl peroxide-catalysed autoxidation of benzaldehyde by anthracene and by 1:2-5:6-dibenzanthracene indicates that chain termination is initially effected by combination of benzoyl-peroxy-radicals, $\text{Ph}\cdot\text{CO}\cdot\text{O}\cdot\text{O}\cdot$, with the hydrocarbon. After longer periods of action polycyclic hydrocarbons of different structure show differences in type of behaviour and classification into the following groups is possible: *A*, hydrocarbons which are initially inhibitory but are oxidised to products having no such action; *B*, good initial inhibitors which are oxidised to products that are also inhibitors; *C*, very poor inhibitors which are oxidised to more effective inhibitors. Carcinogenic activity seems to be associated mainly with the hydrocarbons of group *B*.

The maximum free valency numbers, F_{max} , of polycyclic aromatic hydrocarbons can be correlated with their relative efficiencies as retarders of the initial stage of benzaldehyde autoxidation. Their eventual retarding efficiency can, to some extent, be correlated with the redox potentials of the corresponding quinones.

It is well known that certain polycyclic aromatic hydrocarbons can retard the autoxidation of benzaldehyde. Branch, Almquist, and Goldsworthy (*J. Amer. Chem. Soc.*, 1933, **55**, 4052) showed that anthracene was an effective initial inhibitor of this autoxidation and that the inhibiting action ceased when all the anthracene had been destroyed, presumably by oxidation to anthraquinone which Bäckström and Beatty (*J. Phys. Chem.*, 1950, **35**, 2530) had isolated in 80% yield from this same system. Benzaldehyde autoxidation was also chosen by Wasley and Rusch (*Cancer Res.*, 1942, **2**, 422) for studying both the inhibiting powers and the induced oxidations of anthracene, 1:2-benzanthracene, 1:2-5:6-dibenzanthracene, 20-methylcholanthrene, and 3:4-benzopyrene. They showed, *inter alia*, that 3:4-benzopyrene was thereby oxidised to a mixture of the 5:8- and the 5:10-quinone which are also autoxidation inhibitors (Muller and Rusch, *ibid.*, 1945, **5**, 480) and are toxic, though not carcinogenic (Berenblum and Schoental, *ibid.*, 1943, **3**, 145). Lisle (*ibid.*, 1951, **11**, 153), from a study of the effects of a number of compounds on the rate of decolorisation of an autoxidising solution of indigo-carmin in benzaldehyde, has placed polycyclic aromatic hydrocarbons in the order: 3:4-benzopyrene, 20-methylcholanthrene > anthracene, pyrene (all powerful inhibitors) \gg 1:2-5:6-dibenzanthracene (moderate) > chrysene, 2:3-benzophenanthrene (weak inhibitors).

Since the active carcinogenic agents can act as inhibitors of biological oxidations (cf. Boyland, *Nature*, 1932, **130**, 274; Joyet-Lavergne, *Compt. rend.*, 1944, **219**, 494), presumably by affecting certain types of enzyme oxidase systems (Rusch and Kline, *Cancer Res.*, 1941, **1**, 465), the possibility of correlating carcinogenic action with the inhibition of the chemical autoxidations of compounds of lipid type was naturally envisaged by Rusch and his colleagues, and Lisle had aimed at devising, on this basis, a simple colour test for carcinogenic potency. Magat and Bonême (*Compt. rend.*, 1951, **232**, 1657) have found that both carcinogenic and non-carcinogenic hydrocarbons can inhibit the polymerisation of styrene and emphasise the fact that this is due to reactions of the hydrocarbons with free radicals. From the foregoing results Kooyman and Heringa (*Nature*, 1952, **170**, 661) concluded that there can be no direct relation between neoplastic activity of hydrocarbons and their reactivity towards free radicals.

By 1950 it had become clear that the autoxidation of benzaldehyde can be retarded both by certain polycyclic hydrocarbons and by some of the quinones derived from them (cf.

* Part V, *J.*, 1953, 2993.

Part V, *loc. cit.*). In order to provide a much wider basis for tracing possible connections between carcinogenesis and the retardation of free-radical oxidations by polycyclic aromatic hydrocarbons and their various oxidation products it was then decided to make a fuller study of the whole subject. The kinetics of the retardation of benzaldehyde autoxidation by anthracene and by 1 : 2-5 : 6-dibenzanthracene have therefore been studied by us in some detail and a more general survey has been made of the behaviour of 16 other hydrocarbons, using the experimental methods of preceding Parts of this series of papers : the results are summarised below.

1. *Kinetics of Retardation of Autoxidation by Anthracene and by 1 : 2-5 : 6-Dibenzanthracene.*—For the benzoyl peroxide-initiated reaction at 60° it has been found that for both hydrocarbons the initial rate of oxygen uptake is proportional to

$$[\text{Benzoyl Peroxide}] \times ([\text{Benzaldehyde}] + a)/([\text{Hydrocarbon}] - b)$$

The two constants a and b are very small indeed in the case of anthracene and within the limits of experimental error in the case of dibenzanthracene. Moreover, in the pressure

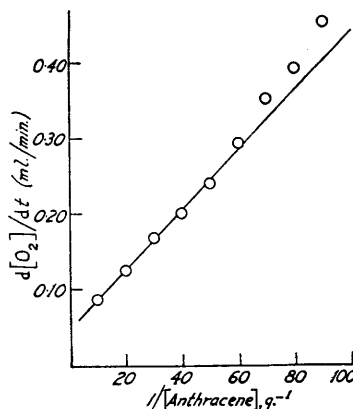
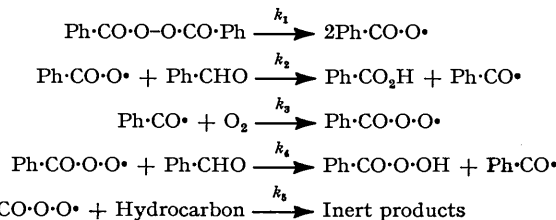


FIG. 1. The retardation of benzaldehyde autoxidation by anthracene.

Each mixture contained 1.00 g. of benzoyl peroxide and 1.50 g. of benzoic acid in 10 ml. of benzaldehyde.

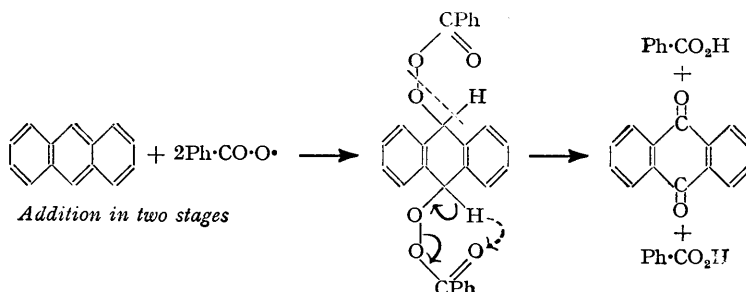
range 20—76 cm. Hg, the initial oxidation rate is independent of the oxygen pressure. With anthracene these relations hold only at high relative concentrations of inhibitor and low concentrations of initiator; under reverse conditions higher oxidation rates are found (see Fig. 1 and Table 4, p. 585), for the rate of destruction of hydrocarbon molecules is then such that their mean concentration in the system during the 12-minute period of observation is noticeably less than the initial concentration. Since 1 : 2-5 : 6-dibenzanthracene is a much less efficient inhibitor it was used in higher concentration and consequently no corresponding deviations from regularity could be observed. As explained in Parts I and III of this series (*J.*, 1951, 812; 1952, 2427), if it is assumed that initially all the benzaldehyde-oxygen reaction chains are terminated by reactions involving hydrocarbon molecules, then *only* the following kinetic scheme accords with the experimental observations :



whence $-d[\text{O}_2]/dt = 2k_1[(\text{Ph}\cdot\text{CO}_2)_2](1 + k_4[\text{Ph}\cdot\text{CHO}]/k_5[\text{Hydrocarbon}])$

Direct abstraction of hydrogen atoms from hydrocarbon molecules would leave radicals active enough to effect chain transfer, and this would be inconsistent with the observed

kinetics. It seems likely therefore that the benzoylperoxy-radicals *combine* with the hydrocarbon to give the chain-ending reaction product. Direct evidence of radical addition to the 9- and the 10-position of anthracene has been obtained by Bickel and Kooyman (*Rec. Trav. chim.*, 1952, **71**, 1137) using 2-cyano-2-propyl radicals and by Fieser and Putnam (*J. Amer. Chem. Soc.*, 1947, **69**, 1038) using acetate radicals. It may be suggested that quinone formation occurs as follows:



Until direct measurements of the rate of destruction of hydrocarbon have been made it is not possible to be sure that other reactions do not occur. Clear evidence of the occurrence of consecutive reactions has been obtained by studying the retarded autoxidations over

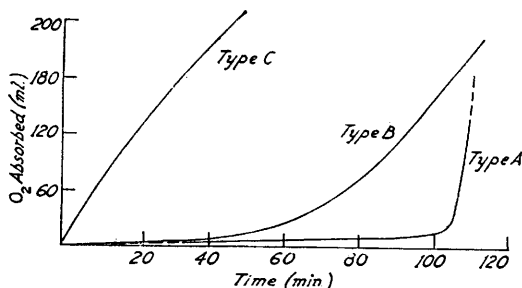


FIG. 2. Types of retarded autoxidation curves (cf. Table 1).

Curve A, plotted from data for anthracene.
Curve B, plotted from data for 20-methylcholanthrene.
Curve C, plotted from data for chrysene.

longer periods, with high catalyst : inhibitor ratios (see below), and in the case of 1 : 2 : 5 : 6-dibenzanthracene by investigating the nature of the final reaction product. In this instance the percentage yield of dibenzanthraquinone was very low, indicating that secondary reactions between quinone molecules and free radicals must occur.

2. *Types of Inhibiting Action shown in Prolonged Autoxidations.*—When the hydrocarbon retardation of the catalysed benzaldehyde autoxidation is examined over long periods of time, distinctive features of late stages of the reaction can be noted. From these it is evident that polycyclic aromatic hydrocarbons can, in general, be classified into three groups according to the type of oxygen uptake curve which can be obtained (A, B, and C of Fig. 2).

Class A includes those hydrocarbons which, though non-carcinogenic, are powerful inhibitors of autoxidation. Their oxygen uptake curves indicate that their oxidation products are incapable of inhibiting benzaldehyde autoxidation. Anthracene is a typical member of this group.

Class B, which includes the majority of the carcinogenic hydrocarbons, comprises the inhibitors which yield reaction products that also have inhibiting powers: 3 : 4-benzopyrene can be taken as typical of this class.

Class C comprises the weak inhibitors which became converted into oxidation products which have greater inhibiting power, so that the retardation of autoxidation becomes more evident after a long reaction period. This class includes chrysene, which is feebly carcinogenic (Steiner and Falk, *Cancer Res.*, 1951, **11**, 56), and also the more powerful carcinogens 2-methyl-3 : 4-benzophenanthrene and 1 : 2-3 : 4-dibenzophenanthrene. Pyrene is anomalous, for its marked inhibiting action varies but little with time over a remarkably long

period (see below). In broad outline therefore carcinogenic action does seem to be associated with hydrocarbons which, of themselves or *via* their oxidation products, can exert some inhibiting action upon benzaldehyde autoxidation over a prolonged period.

Table I lists the types of autoxidation curve found for each hydrocarbon examined, together with the initial and the final autoxidation rates, measured under standard conditions. Each sample was tested at 60° in 10 ml. of benzaldehyde containing 1.5 g. of benzoic acid and 0.1500 g. of pure benzoyl peroxide as catalyst. Series I contained inhibitor molecularly equivalent to 0.005 g. of anthracene, series II an amount equivalent to 0.010 g., and series III an amount equivalent to 0.0150 g. Further consideration is given below to the data of series II of this Table.

TABLE I.

Hydrocarbon	Type of curve	Series I.		Series II.		Series III.	
		init.	max.	init.	max.	init.	max.
Anthracene	A	0.12	—	0.06	—	v. small	—
9-Methylanthracene	A	0.38	—	0.12	—	0.13	—
Naphthacene	A	—	—	—	—	—	—
5 : 6-cycloPentano-1 : 2-benzanthracene	B	0.447	14.7	0.149	8.99	0.097	5.8
1 : 2-Benzanthracene	B	1.04	17.0	0.42	8.2	0.19	4.3
10-Methyl-1 : 2-benzanthracene	B	1.31	9.18	0.419	9.1	0.216	5.9
5-Methyl-1 : 2-benzanthracene	B	0.93	18.6	0.33	8.0	0.12	5.2
10-isoPropyl-1 : 2-benzanthracene	B	6.73	16.2	1.39	11.04	0.828	8.08
1 : 2-7 : 8-Dibenzanthracene	B	1.30	7.8	0.58	4.1	0.35	2.8
3'-Methyl-1 : 2-5 : 6-dibenzanthracene	B	1.22	5.6	0.50	2.6	0.26	1.6
1 : 2-5 : 6-Dibenzanthracene	B	1.82	10.7	0.79	5.1	0.55	2.7
Pyrene	C?	0.44	—	0.226	—	0.14	—
2-Methyl-3 : 4-benzophenanthrene	C	8.44	—	3.84	—	2.84	—
1 : 2-3 : 4-Dibenzophenanthrene	C	13.3	—	5.37	—	3.39	—
Chrysene	C	10.8	—	6.35	—	4.84	—
Phenanthrene	C	—	—	v. large	—	—	—
3 : 4-Benzopyrene	B	0.155	—	0.081	2.3	0.051	1.3
20-Methylcholanthrene	B	0.37	15.1	0.098	4.7	0.061	3.5

—d[O₂]/dt is given in ml. per min. (S.T.P.) per 10 ml. of benzaldehyde.

3. *Efficiency of the Initial Retardation of Autoxidation.*—If the kinetic equation of Section I above can be applied to the other polycyclic hydrocarbons, then since

$$k_5[\text{Hydrocarbon}] = \text{Constant}(-d[\text{O}_2]/dt - 2k_1[(\text{Ph}\cdot\text{CO}_2)_2]^{-1})$$

where k_1 is approximately $7 \times 10^{-5} \text{ min.}^{-1}$ (cf. Bawn and Mellish, *Trans. Faraday Soc.*, 1951, **47**, 1216), relative values of k_5 can be computed from the simplified equation

$$k_5[\text{Hydrocarbon}] = \text{Constant}(-d[\text{O}_2]/dt - 0.002)^{-1}$$

where $-d[\text{O}_2]/dt$ is measured in ml. per minute per 10 ml. sample of benzaldehyde.

Kooyman and Farenhorst (*Trans. Faraday Soc.*, 1953, **49**, 58), who measured the potencies of hydrocarbon inhibitors towards combination with trichloromethyl radicals, have satisfactorily correlated the logarithms of their reactivities with computed values of the maximum free valency numbers, F_{max} , of their hydrocarbons. The velocity constants k_5 above may similarly be related to maximum free valency numbers, and Table 2 has been constructed on this basis. It is supposed that for those hydrocarbons in which there is more than one position of maximum free valency the reactivity of only one of the equivalent positions should be related to F_{max} , and the reactivity of a hydrocarbon for radicals has therefore been computed as

$$R = \{n(-d[\text{O}_2]/dt - 0.002)\}^{-1}$$

where n is the number of positions of maximum free valency.

Following Coulson, Burkitt, and Longuet-Higgins (*Trans. Faraday Soc.*, 1951, **47**, 553), $F_{\text{max}} = N_{\text{max}} - N_r$, where N_{max} for a carbon atom bound only to two others, as in these polycyclic aromatic hydrocarbons, has the value of $(3 + \sqrt{2})$, and N_r is the sum of the orders of all bonds joining the atom r to the remainder of the system. Computations by earlier theorists, who had chosen other values for N_{max} , have been corrected to this scale. The

data for K_R given in Table 2 are the relative reactivity values found experimentally by Kooyma and Farenhorst.

Fig. 3 gives a plot of $\log R$ against F_{\max} for those hydrocarbons for which theoretical calculations of free valency numbers have been made. It affords striking support for the view of Kooyma and Farenhorst that the maximum free valency number of a hydrocarbon is a valid measure of its reactivity towards free radicals. Consequently the experimental data given in Table 2 could be used to indicate the maximum free valency numbers of hydrocarbons for which computations have not yet been made, as for instance those containing alkyl substituents. Thus the maximum free valency number of 20-methylcholanthrene should be *ca.* 0.21, *i.e.*, slightly less than that for 3:4-benzopyrene and decidedly greater than those for 1:2-benzanthracene or for the dibenzanthracenes.

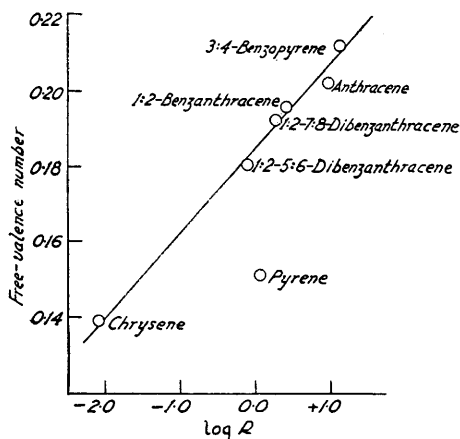


FIG. 3. The connection between $\log R$ and F_{\max} .

The only hydrocarbon having a much greater reactivity than would have been predicted is pyrene. Its strong inhibiting action has previously been reported by Lisle (*loc. cit.*) and by Wittig and Pieper (*Annalen*, 1947, 558, 207). Under conditions in which anthracene was completely oxidised to the quinone, the latter workers were able to recover pyrene

TABLE 2. The relation between retardation of autoxidation and F_{\max} .

Hydrocarbon	n	$-d[O_2]/dt$	R	K_R	F_{\max}
3:4-Benzopyrene.....	1	0.081	12.99	70.0	0.212 ¹
20-Methylcholanthrene.....	1	0.098	10.64	48.8	—
Anthracene.....	2	0.059	9.09	11.0	0.202 ²
9-Methylanthracene.....	1	0.120	8.62	—	—
5:6-cycloPentano-1:2-benzanthracene.....	1	0.149	6.90	—	—
5-Methyl-1:2-benzanthracene.....	1	0.33	3.07	—	—
10-Methyl-1:2-benzanthracene.....	1	0.42	2.41	—	—
1:2-Benzanthracene.....	1	0.42	2.40	20.0	0.196 ³
3'-Methyl-1:2-5:6-dibenzanthracene.....	1	0.50	2.02	—	—
1:2-7:8-Dibenzanthracene.....	1	0.58	1.74	—	0.192 ⁴
10-isoPropyl-1:2-benzanthracene.....	1	1.39	0.72	—	—
1:2-5:6-Dibenzanthracene.....	2	0.79	0.637	1.85	0.180 ⁴
Pyrene.....	4	0.226	1.13	0.3	0.151 ³
2-Methyl-3:4-benzophenanthrene.....	?3	3.84	?0.087	—	—
1:2-3:4-Dibenzophenanthrene.....	?4	5.37	?0.047	—	—
Chrysene.....	2	6.35	0.0435	3.3×10^{-2}	0.139 ³
Phenanthrene.....	4	v. large	v. small	4.0×10^{-2}	0.134 ²

¹ Kooyma and Farenhorst, *loc. cit.* ² Coulson, Burkitt, and Longuet-Higgins, *loc. cit.* ³ Berthier, Coulson, Greenwood, and Pullman, *Compt. rend.*, 1948, 226, 1906. ⁴ Baldock, Berthier, and Pullman, *ibid.*, 1949, 228, 931.

unchanged at the end of an autoxidation. Its action, which remains obscure, may therefore have no relevance to the radical-combination process to which we have attributed the inhibiting actions of all the other hydrocarbons tested. In contrast to this, 1:2-benzanthracene, which Kooyma and Farenhorst thought to be anomalous, exhibits the expected degree of reactivity.

From Fig. 3 it can be deduced that a decrease of 0.01 in F_{\max} corresponds to about a threefold decrease in the rate of radical combination at the position under consideration. Such a relation should also hold for the various F_{\max} values at different positions within one hydrocarbon, and inspection of calculated F values shows that they differ sufficiently to justify the hypothesis of exclusive reaction at the point of maximum free valency.

4. *The Final Retardation of Benzaldehyde Autoxidation.*—Curve B of Fig. 2 indicates that the primary reaction products of the autoxidations of the carcinogenic hydrocarbons are themselves retarders of autoxidation. A measure of the efficiency of the retarding actions of these products is given by the slopes of the steeper, secondary parts of the autoxidation curves. In the case of 3:4-benzopyrene this may measure the inhibiting power of the toxic benzopyrenequinones: in the case of anthracene inhibition ceases entirely since the oxidation product, anthraquinone, is inert, while in that of 1:2-5:6-dibenzanthracene definite inhibiting power remains. Earlier work (Part V, *loc. cit.*) indicated that there was some connection between inhibiting powers of quinones and oxidation-reduction potentials. Iball (*Amer. J. Cancer*, 1940, **38**, 372) has measured the redox potentials of a number of benzantraquinones, and Table 3 which gives his values indicates that there is some connection between the final autoxidation rates found for certain of the hydrocarbons and the redox potentials of the related quinones. The greater the redox potential of the final quinone the more is the retardation of the autoxidation of benzaldehyde after the initial action due to the chain-stopping by the hydrocarbon itself has ceased.

TABLE 3. *Suggested influences of quinones on final autoxidation rates.*

Hydrocarbon	$-d[O_2]/dt$ (max.)	π_0 for Quinone
1:2-5:6-Dibenzanthracene	3.70	0.255
1:2-7:8-Dibenzanthracene	3.57	0.238
1:2-Benzanthracene	2.33	0.224
5:6-cycloPentano-1:2-benzanthracene	1.77	0.173
5-Methyl-1:2-benzanthracene	1.92	0.168
Anthracene	0.00	0.150

We suggest that the general results discussed above have some relevance to the problem of carcinogenicity, but do not feel that our correlations can, as yet, do more than support the suggestion made under Section 2 of this discussion.

EXPERIMENTAL

Materials.—Anthracene was purified by Fieser's method ("Experiments in Organic Chemistry," D. C. Heath & Co., Boston, U.S.A., 1941, p. 345 footnote); commercial 1:2-5:6-dibenzanthracene (Messrs. L. Light & Co.) was crystallised to m. p. 261—262° after reaction with maleic anhydride (Cook *et al.*, *Proc. Roy. Soc.*, 1932, *B*, **111**, 469); pure pyrene was prepared for us at the laboratories of the Coal Tar Research Association, Gomersal, and the specimens of the carcinogenic hydrocarbons and their analogues were tested materials from the collection of the Chester Beatty Research Institute of the Royal Cancer Hospital.

The purifications of the benzaldehyde and benzoyl peroxide, and the kinetic measurements, were carried out as described in Part I, 60° being chosen for all comparative reactivity tests.

Kinetics of Retardation by Anthracene.—(i) Fig. 1 shows the variation of rate with concentration of anthracene. It can be seen that the initial rate, measured as the average for the first 12 min., increases unduly when the anthracene concentration is particularly low.

(ii) *Variation in benzoyl peroxide concentration.* Each mixture contained 1.50 g. of benzoic acid and 0.010 g. of anthracene in 10 ml. of benzaldehyde. The definite enhanced increase in reaction velocity at high benzoyl peroxide concentrations may be noted from Table 4.

TABLE 4.

Benzoyl peroxide (g.)	$-d[O_2]/dt$ (ml./min.)	$-[Bz_2O_2]d[O_2]/dt$	Benzoyl peroxide (g.)	$-d[O_2]/dt$ (ml./min.)	$-[Bz_2O_2]d[O_2]/dt$
0.2	0.083	0.415	0.8	0.328	0.410
0.3	0.137	0.443	0.9	0.388	0.431
0.4	0.154	0.385	1.0	0.457	0.457
0.5	0.205	0.410	1.1	0.503	0.462
0.6	0.243	0.405	1.2	0.631	0.526
0.7	0.272	0.389			

(iii) *Variation in benzaldehyde concentration.* Each system contained 1.000 g. of benzoyl peroxide, 0.010 g. of anthracene, 1.50 g. of benzoic acid, and 10.0 ml. of a benzaldehyde-chlorobenzene mixture. For ten rate determinations, with proportionate amounts from 1 to 10 ml. of benzaldehyde, the results could be expressed as

$$-d[\text{O}_2]/dt - 0.1 = 36.8 \times 10^{-3}, \pm 1.07 \times 10^{-3} \text{ ml. of oxygen per min. per ml. of benzaldehyde present.}$$

(iv) *Variation in oxygen pressure.* Each system contained 0.300 g. of benzoyl peroxide, 0.005 g. of anthracene, and 1.50 g. of benzoic acid in 10 ml. of benzaldehyde. The following measurements were made at 80°, the absorption rates being calculated as ml. of oxygen at S.T.P. per min.

O ₂ (mm.)	764	688	612	536	463	360	310	237	163
-d[O ₂]/dt	0.255	0.264	0.255	0.269	0.267	0.249	0.250	0.229	0.241

Kinetics of Retardation by 1:2-5:6-Dibenzanthracene.—(i) *Variation in hydrocarbon concentration.* Each mixture contained 0.050 g. of benzoyl peroxide and 1.50 g. of benzoic acid in 10 ml. of benzaldehyde. For 8 determinations, with 6.0—50 mg. of hydrocarbon

$$-d[\text{O}_2]/dt \text{ (ml./min.)} \times [\text{Dibenzanthracene}] \text{ (mg.)} = 4.32 \pm 0.14$$

For this amount of benzoyl peroxide the calculated intercept is less than the experimental error.

(ii) *Variation in benzoyl peroxide concentration.* For 9 experiments, each with 0.050 g. of dibenzanthracene, and 1.50 g. of benzoic acid in 10 ml. of benzaldehyde and amounts of benzoyl peroxide varying from 30.4 to 600 mg.

$$(-d[\text{O}_2]/dt - 0.018)/[\text{Benzoyl peroxide}] = 97.0 \times 10^{-5} \pm 2.8 \times 10^{-5} \text{ mg. ml./min.}$$

(iii) *Variation in benzaldehyde concentration.* Each mixture contained 0.5600 g. of benzoyl peroxide, 0.050 g. of dibenzanthracene, and 1.50 g. of benzoic acid in 10 ml. of a mixture of benzaldehyde and chlorobenzene. For 8 experiments, with from 1—10 ml. of benzaldehyde

$$(-d[\text{O}_2]/dt - 0.022)/[\text{Benzaldehyde}] = 59.0 \times 10^{-3} \pm 0.85 \times 10^{-3} \text{ ml. of O}_2 \text{ per min.}$$

(iv) *Variation in oxygen pressure.* Each mixture contained 0.050 g. of benzoyl peroxide, 0.0070 g. of dibenzanthracene, and 1.50 g. of benzoic acid in 10 ml. of benzaldehyde.

O ₂ pressure (mm.)	333	401	423	539	752
-d[O ₂]/dt (N.T.P.)	0.65	0.57	0.61	0.65	0.68

(v) *Oxidation products.* Air was aspirated for 36 hr. through a solution of dibenzanthracene (0.75 g.) and benzoyl peroxide (1.00 g.) in benzaldehyde (60 ml.) at 80°. Acids were removed by extraction with sodium hydrogen carbonate solution; no phenols could be removed by subsequent extraction with aqueous sodium hydroxide. The neutral remainder, after removal of benzaldehyde, was a dark red gum (1.73 g.) from which the only pure product which could be isolated chromatographically was 1:2-5:6-dibenzanthra-9:10-quinone, m. p. and mixed m. p. 248—249° (20 mg.).

The initial exploratory work, and the detailed study of 1:2-5:6-dibenzanthracene, were carried out by I.M.R., who thanks the British Empire Cancer Campaign for a Grant held during 1950—1952. J. R. D. thanks the Department of Scientific and Industrial Research for a Maintenance Grant held in 1951—1953. The authors thank Professors A. Haddow and F. Bergel of the Chester Beatty Research Institute for their help in providing most of the specimens of the hydrocarbons used in this investigation.