187. *The Retardation of Benzaldehyde Autoxidation. Part VII.* Further Studies of the Actions of Polycyclic Aromatic Hydrocarbons.*

By A. H. Turner and William A. Waters.

The work of Part VI * has been continued; kinetic results obtained with substituted anthracenes, 1 : 2-benzanthracenes, and other polycyclic aromatic hydrocarbons are reported and are reviewed critically. Too many anomalous results have now been obtained for it still to be possible to maintain the view that a numerically simple connection can be traced between the retarding power of a polycyclic aromatic compound and its maximum free valence number, $F_{\text{max.}}$, or between retarding power and carcinogenic action, without detailed knowledge of (*a*) the precise reaction mechanism and (*b*) the chemical natures of the reaction products.

Perylene is outstanding in being a strong retarder which has no carbon centre of high $F_{\text{max.}}$ whilst 9-methyl-1 : 2-benzanthracene, 9 : 10-dimethylanthracene, and 9 : 10-dimethyl-1 : 2-benzanthracene are exceptional in having scarcely any retarding action.

No simple connections can be traced between the induction period during which a compound retards benzaldehyde autoxidation and its chemical structure. For anthracene it has been established that all the hydrocarbon has been destroyed at the end of the induction period, but that its oxidation products comprise a complex mixture, including anthraquinone, dianthron-9-yl and dianthron-9-ylidene. It is therefore concluded that the retardation of benzaldehyde autoxidation by anthracene involves the consecutive addition of two $Ph{\cdot}CO{\cdot}O_2{\cdot}$ radicals to the *meso*-positions of anthracene or else the dimerisation of the primary single-radical adduct.

In Part VI of this series [1] it was shown that anthracene and 1 : 2-5 : 6-dibenzanthracene acted as retarders of the benzoyl peroxide-catalysed autoxidation of benzaldehyde by combining with benzoylperoxy-radicals, Ph•CO•O•O. For a number of other polycyclic aromatic hydrocarbons which were presumed to act in a similar manner it was found that their relative efficiencies as retarding agents could be correlated fairly satisfactorily with the " free valence numbers " of their centres of highest reactivity. Some hydrocarbons, such as anthracene (termed type A), ceased completely to be inhibitors after a time, others, such as 1 : 2-benzanthracene and 3 : 4-benzopyrene (termed type B), which included all the carcinogenic hydrocarbons that had then been tested, became, after a period, weaker but still evident retarders. It was tentatively suggested that the compounds of type B gave quinonoid oxidation products which still had some chain-stopping potency. A few of the hydrocarbons tested, such as chrysene (termed type C), were initially feeble autoxidation retarders, but became more effective as their oxidation products were formed.

Several further aromatic hydrocarbons, and a number of their substitution products, have now been examined in a similar way. In addition, a more detailed study has been made of the reactions which are involved when anthracene is added to autoxidising benzaldehyde. The following sections review critically the conclusions that may be drawn from this experimental evidence.

Efficiencies as Retarding Agents.—Tables 1—3 give the initial rates of oxygen uptake at 60° for systems containing equimolecular amounts of the various compounds tested in solution in 10 ml. of benzaldehyde containing 1·500 g. of benzoic acid and 0·150 g. of benzoyl peroxide as catalyst. Series I contain retarder equivalent to 5 mg. of anthracene, series II retarder equivalent to 10 mg., and series III that equivalent to 15 mg. The classification of reaction types as A, B, or C follows the system given above.

These collected results show that the earlier surmise that there might be a simple connection between the actions of aromatic molecules in retarding autoxidation and their carcinogenic potencies was based upon far too few observations. The highly carcinogenic

* Part VI, *J.*, 1954, 580.

[1] Dunn, Waters, and Roitt, *J.*, 1954, 580.

TABLE 1. *Retardation of the autoxidation of benzaldehyde by anthracene and acridine derivatives: initial rates of the oxidation at* 60°.

Anthracene deriv.	Ml. of O_2 per min. for 10 ml. of Ph·CHO		
	I	II	III
Unsubst.	(D) 0·12	0·059	v.s.
9-Methyl-	(D) 0·38	0·12	(D) 0·13
9-Ethyl-	—	0·22	—
9-Phenyl-	0·12	0·058	v.s.
9-Cyano-	—	0·11	—
9-Bromo-	—	0·14	—
9-Methoxy-	—	0·15	—
9-Benzoyloxy-	—	0·14	—
Anthrone	—	(0·8)	—
9 : 10-Dimethyl-	—	(v.l.)	—
9 : 10-Diethyl-	—	(0·31)	—
9 : 10-Diphenyl-	(3·35)	0·84	0·30
9 : 10-Diallyl-	—	(0·40)	—
9 : 10-Dichloro	—	(1·5)	—
9 : 10-Dichloromethyl-	—	(0·68)	—
9 : 10-Diacetoxy-	—	v.l.	—
9 : 10-Dibenzoyloxy-	—	v.l.	—
9-Ethyl-10-methyl-	—	(0·45)	—
9-Benzoyloxy-10-methyl	—	v.l.	—
Acridine deriv.			
Unsubst.	0·195	0·074	v.s.
5-Methyl-	—	0·43	—
5-Phenyl-	—	0·46	—

v.l. = very large rate; v.s. = very small rate.

For figures in parentheses the rate was increasing during the period of measurement, but has been extrapolated to zero time.

Results marked (D) are due to Dr. J. R. Dunn and are quoted from Part VI.

TABLE 2. *Retardation of the autoxidation of benzaldehyde by* 1 : 2*-benzanthracene derivatives: initial rates of the oxidation at* 60°.

Compound		Ml. of O_2 per min. for 10 ml. of Ph·CHO		
		I	II	III
1 : 2-Benzanthracene	(D)	1·04	0·42	0·19
3-Methyl-1 : 2-benzanthracene		0·27	0·17	v.s.
4-Methyl- „		1·17	0·34	—
5-Methyl- „	(D)	0·93	0·33	0·12
7-Methyl- „		—	0·096	—
9-Methyl- „		16·8	14·7	10·0
10-Methyl- „	(D)	1·31	0·42	0·22
10-*iso*Propyl- „	(D)	6·73	1·39	0·83
5-Pentyl- „		0·98	0·30	0·072
5 : 6-*cyclo*Pentano- „	(D)	0·45	0·15	0·097
9 : 10-Dimethyl- „		—	(v.l.)	—
9 : 10-Diphenyl- „		2·49	0·97	—
Cholanthrene		—	0·10	—
20-Methylcholanthrene	(D)	0·37	0·098	0·061

All benzanthracene derivatives give autoxidation curves of type B.

See also footnotes to Table 1.

hydrocarbon 9 : 10-dimethyl-1 : 2-benzanthracene, for instance, has scarcely any retarding action and resembles 9 : 10-dimethylanthracene. Again perylene, which is not carcinogenic, is a very potent inhibitor of autoxidation.

The correlation, *i.e.*, log R varies as $F_{\text{max.}}$, between initial retarding efficiency, R calculated as $1/\{n(-d[O_2]/dt-0{\cdot}002)\}$, and free valence number, $F_{\text{max.}}$, that was applied in Part VI, was previously noted as failing for pyrene; it is now seen to fail markedly also for perylene which has a relatively low free valence number, and for stilbene which has no retarding action. Nevertheless Fig. 1*A* indicates that the overall concordance of this relationship, originally due to Kooyman and Farenhorst,[2] is surprisingly good considering the approximations and assumptions that are inherent in the underlying theory. Critical inspection of the plot shows, however, that most of the consistency is found for molecules of the anthracene type for which a common reaction process, *i.e.*, addition to a *meso*-position, is presumably involved. For molecules of other shapes the correlation is poor and the criticism that support for the general relation depends mainly on artificially selected data cannot wholly be refuted. It may now be suggested that correlations of this type between structural calculations and experimental measurements of chemical reactivities hold only for groups of reactions that have exactly the same mechanism.

[2] Kooyman and Farenhorst, *Trans. Faraday Soc.*, 1953, **49**, 58.

TABLE 3. *Retardation of the autoxidation of benzaldehyde by other polycyclic hydrocarbons : initial rates of the oxidation at* 60°.

Compound		Class	Ml. of O_2 per min. per 10 ml. of Ph·CHO		
			I	II	III
Naphthacene		A	—	0·056	—
Chrysene	(D)	C	10·8	6·35	4·84
Pyrene	(D)	C	0·44	0·23	0·14
3 : 4-Benzopyrene	(D)	B	0·16	0·081	0·051
Picene		C	11·7	5·22	3·07
Perylene		B	0·08	0·02	v.s.
Stilbene				No inhibiting power	
Fluorene				No inhibiting power	
Fluoranthene		C	—	7·72	—
Acenaphthene		?C	1·78	1·26	—
1-Methylnaphthalene				No inhibiting power	
1 : 2-3 : 4-Dibenzanthracene		B	2·36	1·02	0·56
1 : 2-5 : 6-Dibenzanthracene	(D)	B	1·82	0·79	0·55
1 : 2-7 : 8-Dibenzanthracene	(D)	B	1·30	0·58	0·35
3′-Methyl-1 : 2-7 : 8-dibenzanthracene		B	0·98	0·32	0·18
3′-Methyl-1 : 2-5 : 6-dibenzanthracene	(D)	B	1·22	0·50	0·26
2-Methyl-3 : 4-benzophenanthrene	(D)	C	8·44	3·84	2·84
6-Methyl-3 : 4-benzophenanthrene		C	—	2·60	—
7-Methyl-3 : 4-benzophenanthrene		C	—	3·10	—
1 : 2-3 : 4-Dibenzophenanthrene	(D)	C	13·3	5·37	3·39
1 : 2-5 : 6-Dibenzophenanthrene		C	6·12	4·07	2·93
9-Benzoyloxy-1 : 2-5 : 6-dibenzanthracene		?	—	3·57	—
5-Benzoyloxy-3 : 4-benzopyrene		B	—	0·079	—
Benzanthrone				No inhibiting power	

See footnotes to Table 1.

TABLE 4. *Connections between the autoxidation-retarding powers* (R) *of aromatic hydrocarbons and calculated structural factors.*

$R = 1/\{n(-\,d[O_2]/dt - 0{\cdot}002)\}$. $F_{\text{max.}}$ = maximum free valence.
$E\,*$ = Singlet–triplet state excitation frequency (in cm.^{-1}).

Hydrocarbon	n	$F_{\text{max.}}$	$-\,d[O_2]/dt$	$\log_{10} R$	$E\,*$
3 : 4-Benzopyrene	1	0·212	0·081	1·092	—
Anthracene	2	0·202	0·059	0·928	14,850 [a]
1 : 2-Benzanthracene	1	0·196	0·42	0·377	16,500 [b]
3-, 4-, 5-, 7-, and 10-Methylbenzanthracene	1	—	0·1—0·4	0·4—0·7	16,250—17,000 [b]
9-Methylbenzanthracene	1	—	14·7	−1·17	16,260 [b]
1 : 2-5 : 6-Dibenzanthracene	2	0·180	0·79	−0·20	18,300 [c]
1 : 2-7 : 8-Dibenzanthracene	1	0·192	0·58	0·236	—
Pyrene	4	0·151	0·23	0·045	16,800 [d]
Chrysene	2	0·139	6·35	1·10	19,800 [d]
Phenanthrene	4	0·134	v.l.	− 2 ?	21,600 [d]
2-Methyl-3 : 4-benzophenanthrene	3 ?	—	3·84	−0·11	19,700 [b]
Naphthacene	4	0·212	0·056	0·65	10,250 [a]
1 : 2-3 : 4-Dibenzanthracene	2	0·181	1·02	−0·31	—
Picene	2	0·139	5·22	−1·02	—
Perylene	4	0·156	0·02	1·10	—
Stilbene	2	0·163	v.l.	−3 ?	21,700 [d]
Fluoranthene	2	0·152	7·72	−1·19	—
Acridine	1	—	0·074	1·14	—

$F_{\text{max.}}$ values are from sources cited by Kooyman and Farenhorst.[e]

[a] McGlynn, Pudhye, and Kasha, *J. Chem. Phys.*, 1955, **23**, 593. [b] Moodit and Reid, *ibid.*, 1954, **22**, 252. [c] McClure, *ibid.*, 1951, **19**, 670. [d] *Idem*, *ibid.*, 1949, **17**, 905. [e] Kooyman and Farenhorst, *Trans. Faraday Soc.*, 1953, **49**, 58.

Szwarc [3] and Levy and Szwarc [4] suggested that a more appropriate correlation may be that between the free-radical reactivity of a hydrocarbon and the energy required for its photochemical excitation to its lowest triplet state, since the latter presumably has the structure of a chemically reactive diradical form.[5] Fig. 1*B* shows that this correlation is somewhat more satisfactory than the correlation with maximum free valence number.

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[3] Szwarc, *J. Chem. Phys.*, 1955, **23**, 204.

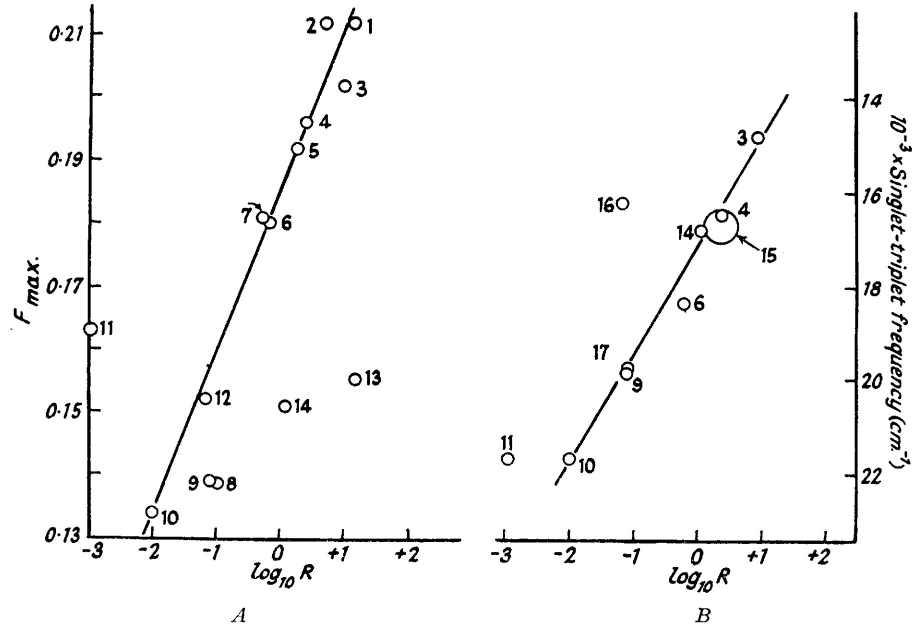
[4] Levy and Szwarc, *J. Amer. Chem. Soc.*, 1955, **77**, 1949.

[5] Lewis and Kasha, *ibid.*, 1944, **66**, 2100; Lewis and Calvin, *ibid.*, 1945, **67**, 1232.

It may be noted (Table 1) that acridine is a slightly poorer inhibitor than anthracene, though it has been suggested by Dewar [6] that it should be slightly more reactive to free-radical attack, just as pyridine is slightly more reactive than benzene.[7] The result accords with the finding by Levy and Szwarc [4] that acridine reacts with methyl radicals less easily than does anthracene.

Effects of substituents on the initial retarding actions of anthracene are shown in Table 1. Except for phenyl substitution the replacement of one *meso*-hydrogen atom of anthracene by any other group approximately halves the initial retarding power : with two substituents the retarding power becomes negligible, except again for the diphenyl derivative. In Table 5 the efficiencies of 9-substituted anthracenes as retarders of benzaldehyde autoxidation are compared with their reactivities towards the 2-cyano-2-propyl free radical, as determined by Kooyman and Farenhorst.[8] Neither series of figures can be correlated with either the polar or the electromeric properties of the substituents.

FIG. 1. *Connections between retarding powers of hydrocarbons and theoretical factors.*



A, Connections between log *R and* $F_{max.}$.
B, Connections between log *R and singlet–triplet excitation energy.*

Key :
1 = 3 : 4-Benzopyrene.
2 = Naphthacene.
3 = Anthracene.
4 = 1 : 2-Benzanthracene.
5 = 1 : 2-7 : 8-Dibenzanthracene.
6 = 1 : 2-5 : 6-Dibenzanthracene.
7 = 1 : 2-3 : 4-Dibenzanthracene.
8 = Picene.
9 = Chrysene.
10 = Phenanthrene.
11 = *trans*-Stilbene.
12 = Fluoranthene.
13 = Perylene.
14 = Pyrene.
15 = 3-, 4-, 5-, and 10-Methyl-1 : 2-benzanthracenes (large circle).
16 = 9-Methyl-1 : 2-benzanthracene.
17 = Methylbenzophenanthrenes.

With the substituted 1 : 2-benzanthracenes (Table 2) noticeable changes in reactivity occur only when alkyl groups occupy *meso*-positions. The effect of a methyl group in the reactive, sterically unhindered 10-position is similar to that of a methyl group in a single *meso*-position in anthracene, but substitution of a methyl in the sterically blocked 9-position (see I) is even more effective than methylation in both the 9- and the 10-position in destroying the antioxidant power of the aromatic molecule.

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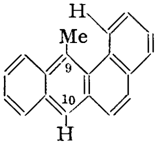
[6] Dewar, *ibid.*, 1952, **74**, 3361.
[7] Hey and Williams, *Discuss. Faraday Soc.*, 1953, **14**, 219; *J. Chem. Phys.*, 1955, **23**, 757.
[8] Kooyman and Farenhorst, *Nature*, 1955, **175**, 1949.

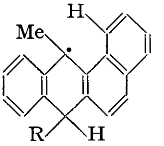
TABLE 5. *Reactivities of* 9-*substituted anthracene derivatives.*

	Relative rate constant for reaction with $Me_2C(CN)\cdot$ radicals at 55°	Reciprocal of initial rate of O_2 uptake in Ph·CHO at 60° (calc. on the basis of anthracene = 2·0
Anthracene	2·00	2·00
9-Methylanthracene	2·12	0·98
9-Ethylanthracene	1·54	0·54
9-Phenylanthracene	—	1·9
9-Methoxyanthracene	2·15	0·79
9-Cyanoanthracene	4·30	1·07
9-Bromoanthracene	1·39	0·84
9 : 10-Dimethylanthracene	0·24	Very small
9 : 10-Diphenylanthracene	—	0·14

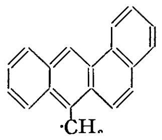
One tentative explanation of this marked positional effect is that the radical (II) from 9-methylbenzanthracene has its point of free valence so encumbered that it cannot take part in any further radical combinations but tends to dissociate back to the molecule (I) and the chain-propagating $Ph\cdot CO\cdot O_2\cdot$ radical.



(I)



(II)



(III)

The low retarding efficiencies of the *meso*-dimethylanthracenes and benzanthracenes may perhaps be due to the concurrent action of chain-transfer processes such as :

$$Ph\cdot CO\cdot\ (Ph\cdot CO\cdot O_2\cdot) + H\cdot CH_2\cdot Anth \longrightarrow Ph\cdot CO\cdot H\ (Ph\cdot CO\cdot O_2H) + CH_2\cdot Anth$$

$$\cdot CH_2\cdot Anth + O_2 \longrightarrow \cdot O_2\cdot CH_2\cdot Anth \text{ etc.}$$

since radicals, $\cdot CH_2\cdot Anth$, such as (III), are extended resonance systems which undoubtedly can be formed with great ease.[9] The marked difference between methyl and phenyl substitution could be explained in this way. However no satisfactory interpretation of all the present results can be offered.

Induction Periods and Oxidation Products.—All the anthracene derivatives tested belong to group A (see p. 879), and the benzanthracene and dibenzanthracene derivatives to group B giving eventual oxygen uptake rates of 10—20 times their initial values. As indicated in Part VI this final oxidation rate seems to be somewhat related to the redox potential of the corresponding *meso*-quinone (Table 6). Since for several of these compounds the duration of the " induction period " of markedly retarded autoxidation of the benzaldehyde is proportional to the amount of the material that has been added, it is reasonable to suggest that the induction period, measured by extrapolating to zero oxygen uptake the time of onset of fast oxidation, indicates the time taken to destroy all the initial retarder. This conclusion has been confirmed quantitatively in the case of anthracene by measuring fluorimetrically its change of concentration in the autoxidising system and showing (see Fig. 2) that the time required for its complete disappearance coincides with the time at which the retardation of the oxidation of benzaldehyde ceases.

TABLE 6.

Hydrocarbon	Redox potential (v) of quinone	Final rate of O_2 uptake of Ph·CHO (ml./min.)
Anthracene	0·150	Very large
1 : 2-Benzanthracene	0·224	8·2
5-Methyl-1 : 2-benzanthracene	0·168	8·0
3-Methyl-1 : 2-benzanthracene	0·208	6·57
7-Methyl-1 : 2-benzanthracene	0·209	5·55
1 : 2-5 : 6-Dibenzanthracene	0·255	5·1
1 : 2-7 : 8-Dibenzanthracene	0·238	4·1

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[9] Beckwith and Waters, *J.*, 1956, in the press.

Fig. 2 shows also that the rate of removal of the anthracene is a zero-order process. This is to be expected since in all the autoxidation mixtures benzoyl peroxide has been added in a constant large excess to act as the chain-starting catalyst. Since for the chain oxidation of benzaldehyde there should be a general relation (Rate of chain starting) = (Rate of chain termination), *i.e.*, $-\mathrm{d}[\mathrm{Anth}]/\mathrm{d}t = +\mathrm{d}[\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}}]/\mathrm{d}t$, it might be expected that equimolar quantities of different hydrocarbons would give identical, or numerically related, induction periods according to whether the aromatic compound was effective in stopping 1, 2, or more reaction chains. Tables 7 and 8 show that not only is this far from being the case, but also that the product (Initial oxygen uptake rate) × (Induction period) is not constant, as might happen if all the oxygen absorbed during the period of retarded autoxidation were used, as $\mathrm{Ph{\cdot}CO{\cdot}O_2{\cdot}}$, to destroy the polycyclic compound. Differences are marked even between closely related hydrocarbons; and the anomalous substances 9 : 10-dimethylanthracene, 9-methyl-1 : 2-benzanthracene, and 9 : 10-dimethyl-1 : 2-benzanthracene, exhibit very small induction periods except when added in very high concentration.

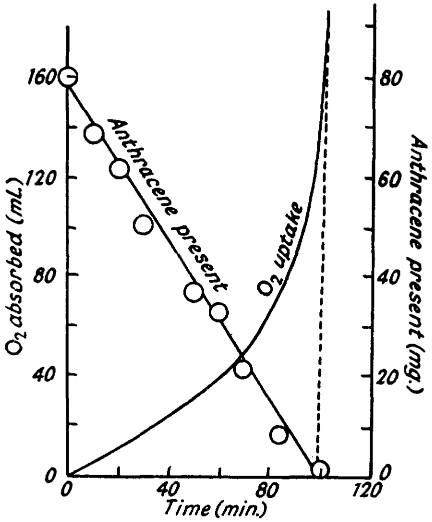

FIG. 2. *Retardation of benzaldehyde autoxidation by anthracene at 60°.*

Connection between disappearance of anthracene (fluorimetric determinations) and the rate of oxygen uptake.

Even the rate of destruction of anthracene is larger than was expected. From Fig. 2

TABLE 7. *Induction periods for the retardation of benzaldehyde autoxidation by anthracene derivatives.*

Anthracene deriv.	Induction period (min.) I	II	III	Ind. period (II) × init. rate
Unsubst.	56	119	174	7
9-Methyl- (D)	14·5	24·2	35·5	2·9
9-Ethyl-	—	25	—	5·5
9-Phenyl-	74	130	—	7·6
9-Cyano-	—	170	—	—
9-Bromo-	—	100	—	14·0
9-Methoxy-	—	33	—	5·0
9-Benzoyloxy-	—	76·5	—	10·7
Anthrone	—	59·5	—	48
9 : 10-Dimethyl-	—	7	—	v.l.
9 : 10-Diethyl-	—	15	—	(5)
9 : 10-Diphenyl-	13	36	65	30
9 : 10-Diallyl-	—	19	—	(8)
9 : 10-Dichloro-	—	(7)	—	—
9 : 10-Bischloromethyl-	—	24	—	(20)
9 : 10-Diacetoxy-	—	v.s.	—	—
9 : 10-Dibenzoyloxy-	—	v.s.	—	—

See footnotes to Table 1.

it can be seen that 10 mg. are consumed at 60° in about 100 min., when 0·150 g. of benzoyl peroxide catalyst is used. This corresponds to a rate of $5{\cdot}6 \times 10^{-7}$ mole/min. and from the data of Table 9 the activation energy of the measured reaction, which should be that of the formation of active radicals from the benzoyl peroxide, is 27·7 kcal. mole^{-1}. Bawn and Mellish,[10] who used the rate of destruction of the free radical *NN*-diphenyl-*N'*-picrylhydrazyl in a number of solvents to measure the rate of radical formation from benzoyl peroxide, give 29·6 kcal. mole^{-1} as the activation energy, and from their data it would be expected that the induction period for the 10 mg. of anthracene would be about 7 times what we found. However, other investigators have given higher values for the rate of decomposition of benzoyl peroxide, which depends to some extent on the polarity of the solvent and often is accelerated by a chain reaction involving solvent molecules.[11] Again, the efficiency of *NN*-diphenyl-*N'*-picrylhydrazyl as a radical collector has been doubted.[12]

Some of the oxidation of the anthracene may be due to the heterolytic action [13] of the perbenzoic acid formed, though Bäckström and Beatty [14] concluded that autoxidising benzaldehyde destroys anthracene at least 600 times more quickly than does perbenzoic acid; and with many of the other hydrocarbons destruction by the autoxidising system is undoubtedly much more rapid than destruction by the per-acid.

TABLE 8. *Induction periods for the retardation of benzaldehyde autoxidation by higher hydrocarbons.*

Hydrocarbon		Induction periods (min.) I	II	III	Ind. period (II) × init. rate
1 : 2-Benzanthracene	(D)	27	56·5	99	23·8
3-Methyl-1 : 2-benzanthracene		36	78·5	141	13·4
4-Methyl- ,,		34	71·5	—	24·3
5-Methyl- ,,	(D)	27·5	50	100	16·5
5-Pentyl- ,,		26	51	95	15·5
7-Methyl- ,,		—	73	—	7·0
9-Methyl- ,,		v.s.	v.s.	v.s.	—
10-Methyl- ,,	(D)	16·5	29·3	40	12
9 : 10-Dimethyl- ,,		?	?	v.s.	—
9 : 10-Diphenyl- ,,		24	43	79	41·8
Cholanthrene		79·5	109	—	11·0
20-Methylcholanthrene	(D)	33	68	120	6·7
1 : 2-3 : 4-Dibenzanthracene		14·5	35	49·5	36
1 : 2-5 : 6-Dibenzanthracene	(D)	34	71	105	56
1 : 2-7 : 8-Dibenzanthracene	(D)	47	108	205	63
3'-Methyl-1 : 2-5 : 6-dibenzanthracene	(D)	36	82	117	42
3'-Methyl-1 : 2-7 : 8-dibenzanthracene		49	128	160	42
10-*iso*Propyl-1 : 2-benzanthracene	(D)	7·3	15	23·5	20·9
5 : 6-*cyclo*Pentano-1 : 2-benzanthracene	(D)	21	56	90	8·4
3 : 4-Benzopyrene	(D)	52	115	165	9·3
Naphthacene		—	10·5	—	0·59
1 : 2-Benzonaphthacene		—	19·2	—	—

See footnotes to Table 1. Results marked (D) have not been reported previously.

TABLE 9. *Inhibition of benzaldehyde autoxidation by anthracene.*

Temp.	Initial rate of O_2 uptake (ml./min.)	Ind. period (min.) (extrap.)	Temp.	Initial rate of O_2 uptake (ml./min.)	Ind. period (min.) (extrap.)
60·0°	0·056	91	70·0°	0·25	26
62·4	0·069	66	72·5	0·37	21
65·0	0·12	52	75·0	0·51	15
67·5	0·15	39			

Measurements were made with 0·0100 g. of anthracene in 10 ml. of benzaldehyde containing 1·500 g. of benzoic acid and 0·150 g. of benzoyl peroxide (Series II of Tables 1 and 7).

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[10] Bawn and Mellish, *Trans. Faraday Soc.*, 1951, **47**, 1216.

[11] Tobolsky and Mesrobian, "Organic Peroxides," Interscience Publ. Inc., New York, 1954, pp. 72—88.

[12] Russell and Tobolsky, *J. Amer. Chem. Soc.*, 1954, **76**, 396; Hammond, Sen, and Boozer, *ibid.*, 1955, **77**, 3246; Walling, *J. Polymer Sci.*, 1954, **14**, 395.

[13] Roitt and Waters, *J.*, 1949, 3060.

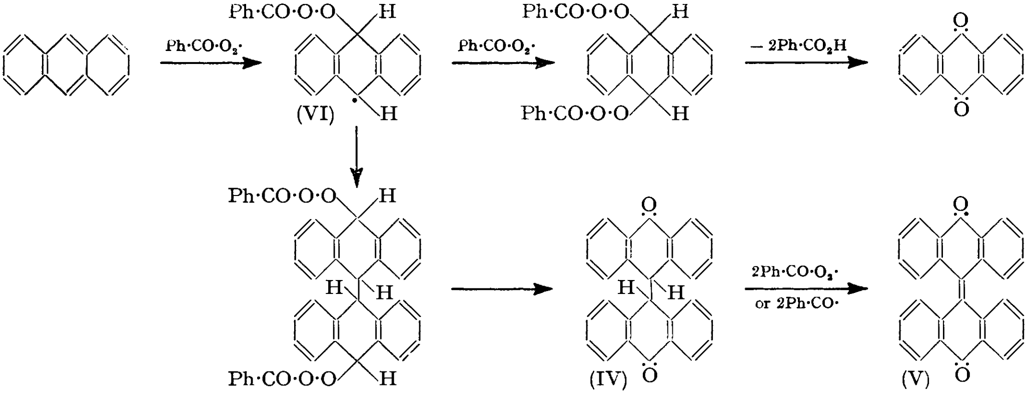
[14] Bäckström and Beatty, *J. Phys. Chem.*, 1931, **55**, 2530.

To obtain further experimental evidence concerning the mode of destruction of anthracene the products resulting from its autoxidation in the presence of both oxygen and benzoyl peroxide have been investigated. From air-blown benzaldehyde not containing added catalyst or inhibitor there has been isolated a trace of *s*-diphenylethylene dibenzoate $(Ph{\cdot}CO{\cdot}O{\cdot}CHPh{\cdot})_2$, which is also formed by the direct reaction of benzaldehyde with benzoyl peroxide or *tert.*-butyl peroxide [15] and is probably one of the chain-ending products of the unretarded autoxidation of benzaldehyde. In the presence of anthracene this substance does not appear to be formed. When the autoxidation is prolonged until the destruction of the anthracene is complete a dark tar is produced in which, besides anthraquinone, dianthron-9-yl (IV) and dianthon-9-ylidene (V) have been identified by their colour reactions and infrared spectra. The last product was also isolated in an experiment where only 60% of the anthracene had been destroyed; but in neither case could a quantitative separation of oxidation products be achieved.

The formation of the dianthronyl (IV) was suspected by Bäckström and Beatty,[14] who isolated a 90% yield of anthraquinone at room temperature but noted that this yield diminished as the temperature was raised.

The mechanism of oxidation of anthracene in benzaldehyde can now be extended to the scheme shown. Products (IV) and (V) evidently arise by reactions following dimerisation of the initial adduct (VI), the structure of which was indicated by the kinetic studies of Part VI. The formation of the dimeric products (IV) and (V) shows that the combination of anthracene with benzoylperoxy-radicals is a two-stage addition entirely analogous to its reactions with 2-cyano-2-propyl radicals [16] and with methyl radicals.[9]

Preliminary studies with 1 : 2-5 : 6-dibenzanthracene have given a still more complex mixture of oxidation products, containing some of the *meso*-dibenzanthraquinone, but there is no evidence, as yet, of any initial homolytic oxidation of either anthracene or dibenzanthracene at the positions in the side rings which are concerned in their biochemical oxidations.[17]



Evidently the products of the reactions of polycyclic aromatic hydrocarbons with the radicals formed in autoxidising benzaldehyde exhibit all the complexities associated with other homolytic reactions of aromatic compounds, and thus it is not surprising that the values of induction periods listed in Tables 7 and 8 show no simple consistency. Indeed it is remarkable that connections between reactivity and chemical structure can be traced as simply as Fig. 1 indicates. The hope that a broad survey of the effects of polycyclic hydrocarbons in retarding autoxidation might provide a guide to the possible behaviour of carcinogenic substances in biochemical metabolic processes has not been fulfilled, and it now must be recognised that the complexity of homolytic reactions *in vitro*, like those of biochemical reactions *in vivo*, are such that detailed studies of particular hydrocarbons are

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[15] Rust, Seubold, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 3258.

[16] Bickel and Kooyman *Rec. Trav. chim.*, 1952, **71**, 1137; Engelsma, Farenhorst, and Kooyman, *ibid.*, 1954, **73**, 878.

[17] See *Biochem. Soc. Symp.*, 1950, No. 5.

now needed rather than further attempts to derive analogies from considerations of structural formulæ alone.

EXPERIMENTAL

The kinetic measurements of oxygen uptake were carried out by the procedure described[1] in Part VI. Periodic tests of the retarding effect of pure anthracene were made to ensure that each batch of benzaldehyde had been purified to the state that reproducible data could be obtained.

The 1 : 2-benzanthracene, dibenzanthracene, and benzophenanthrene derivatives examined were pure specimens from the Chester Beatty Research Institute and were mainly compounds which had been prepared by Professor J. W. Cook, F.R.S. In view of its unexpected behaviour the sample of 9-methyl-1 : 2-benzanthracene was carefully examined. It still had m. p. 139° [picrate, m. p. 114—115° (decomp.)], as described originally,[18] and its ultraviolet spectrum corresponded exactly to that reported.[19] This spectrum shows a certain degree of blurring of the fine structure characteristic of the 1 : 2-benzanthracene system, which may indicate that the molecule is slightly strained. The anthracene derivatives were synthesised. 9-Methylanthracene, prepared from anthrone,[20] was purified through alumina and had m. p. 79·5—80°. The direct dimethylation of anthracene[21] gave very poor yields of 9 : 10-dimethylanthracene but the following procedure was far more satisfactory. 9-Methylanthracene was formylated with *N*-methylformanilide, and the resulting 10-methyl-9-anthraldehyde, m. p. 161—164°, was heated with 90% hydrazine hydrate and potassium hydroxide in ethylene glycol for 4½ hr. The product was converted into the picrate (purple leaflets, m. p. 170°) which was decomposed by passing its benzene solution through alumina. The pure 9 : 10-dimethylanthracene crystallised from benzene in yellow needles, m. p. 177·5—178·5°. Perylene was prepared by heating to dull red heat a mixture of di-β-naphthol, phosphorus pentachloride, and phosphoric acid as described by Brass and Tengler;[22] after crystallisation from benzene the yellow sublimate had m. p. 253°; from this was prepared the picrate, m. p. 224—226° (decomp.) (from benzene), and thence, by decomposition with aqueous ammonia, pure perylene, yellow plates, m. p. 263°. The main, more soluble, product of the pyrolysis gave a dark red picrate, m. p. 158°, and proved to be 1 : 1′-dinaphthyl-2 : 2′-ylene oxide, m. p. 152—153°; this was the only product obtained by heating dinaphthol with zinc dust and zinc chloride.[23] Other syntheses followed, and confirmed, accounts in the literature.

Isolation of Products from Benzaldehyde Autoxidations. Products from Anthracene.—Air was blown through a warm solution of anthracene in benzaldehyde (500 ml.) containing a little benzoyl peroxide until the material became pasty owing to separation of benzoic acid. The product was washed repeatedly with sodium hydrogen sulphite solution to remove benzaldehyde, and then with sodium hydrogen carbonate solution to remove benzoic acid. There remained a black tar which in part dissolved in benzene, leaving a residue of anthraquinone. By repeated crystallisation and chromatography of the solution there were also separated a light brown solid, m. p. 240—245°, and a yellowish-green solid, m. p. >360°. The latter crystallised from acetophenone in bright yellow needles and gave an intense cherry-red colour with concentrated sulphuric acid. The product of lower m. p. dissolved in warm alcoholic sodium hydroxide to a red solution, gave faint colours with alcoholic ferric chloride and diazotised *p*-nitroaniline, and was easily oxidised to the product of higher m. p. (dianthron-9-ylidene) by chloranil in hot nitrobenzene or *tert.*-butyl peroxide in tetrachloroethane. Treatment with acetic anhydride in hot pyridine gave 10 : 10′-diacetoxy-9 : 9-dianthryl. Both substances were synthesised by the method of Barnett and Matthews[24] and their identities confirmed by comparisons of infrared spectra.

From another oxidation mixture which had been aërated for a shorter period, 52% of unchanged anthracene was recovered together with 32% of anthraquinone and 2·5% of dianthronylidene, but no dianthronyl. From an air-blown sample of benzaldehyde to which

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[18] Cook, Robinson, and Goulden, *J.*, 1937, 393.
[19] Jones, *J. Amer. Chem. Soc.*, 1940, **62**, 148.
[20] Sieglitz and Marx, *Ber.*, 1923, **56**, 1619.
[21] Badger, Goulden, and Warren, *J.*, 1941, 18.
[22] Brass and Tengler, *Ber.*, 1931, **64**, 1648.
[23] Marschalk, *Bull. Soc. chim. France*, 1928, **43**, 1388; Lundin, *J. Gen. Chem.* (*U.S.S.R.*), 1939, **9**, 682; *Chem. Abs.*, 1940, **34**, 414.
[24] Barnett and Matthews, *J.*, 1923, 380.

neither anthracene nor benzaldehyde had been added there was isolated 0·002% of *s*-diphenylethylene dibenzoate, m. p. 246°, identical with a specimen prepared from benzaldehyde and *tert.*-butyl peroxide.[15]

Determination of Anthracene in Autoxidation Mixtures.—For recovery of anthracene, oxidations were carried out with mixtures of 0·080 g. of hydrocarbon, 1·200 g. of benzoyl peroxide, and 12·0 g. of benzoic acid in 80 ml. of benzaldehyde, which had approximately the same induction period at 60° as the mixtures of Series II of Tables 1 and 7. At 10 min. intervals the autoxidation was arrested and 1·0 ml. samples of the solution were withdrawn, diluted with 100 ml. of purified xylene, and shaken with 100 ml. of concentrated aqueous sodium hydrogen sulphite. After two further sulphite extractions the xylene solutions were treated with 50 ml. of a solution of sodium dithionite (3%) in aqueous potassium hydroxide (4%) and heated at 100° under nitrogen for an hour. After removal of quinones in this way the xylene solution was dried (Na_2SO_4) and then 2 ml. samples were diluted with 25 ml. of fresh xylene, and their fluorescence was measured by using a Hilger " Spekker " fluorimeter which had been calibrated with solutions obtained by serial dilution of a standard containing 0·128 g. of anthracene per l. in xylene. All the anthracene solutions were stored in the dark to prevent loss of hydrocarbon through photo-oxidation. Provided that the instrument was recalibrated regularly reproducible results were obtained.

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