

[CONTRIBUTION FROM THE SCIENTIFIC LABORATORY, FORD MOTOR CO., DEARBORN, MICH.]

# Reactions of Peroxy Radicals with Polynuclear Aromatic Compounds. I. Reactivities of Anthracene, $\alpha$ -Benzoanthracene, and Tetracene toward Alkyl Aryl Peroxy Radicals

BY L. R. MAHONEY

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The kinetics of the competitive oxidation of anthracene in cumene have been examined over wide ranges of concentration. A single kinetic expression has been obtained which describes the rate of oxygen absorption and the rate of disappearance of anthracene by solutions containing up to  $15 \times 10^{-3} M$  anthracene. A mechanism consistent with the rate expression is proposed; the slow step is the attack of the peroxy radical on the polynuclear aromatic hydrocarbon. Similar results have been obtained for the competitive oxidation of  $\alpha$ -benzoanthracene and of tetracene with cumene and tetralin, respectively. Second-order rate constants for the attack of a cumyl or tetralylperoxy radical on  $\alpha$ -benzoanthracene, anthracene, and tetracene have been calculated as 4.3, 62, and 20,200 moles<sup>-1</sup> l. sec.<sup>-1</sup>, respectively. Correlation of these rate constants with various molecular orbital approximations have proved successful and the high selectivity of the alkyl aryl peroxy radical compared to other radicals is discussed in terms of the transition state for the reaction.

## Introduction

The reaction of radical species with polynuclear aromatic hydrocarbons is of considerable theoretical interest.<sup>1</sup> Kinetic experiments involving competitive techniques have been used to determine the relative reactivities of a number of such polycyclic substrata toward methyl,<sup>2</sup> trichloromethyl,<sup>3</sup> trifluoromethyl,<sup>2</sup> and benzoyl peroxy radicals.<sup>4</sup> Unfortunately, the studies on peroxy radicals used benzoyl peroxide as the initiator and benzaldehyde as the reference substrate. The benzoyl peroxide undergoes complex and inadequately understood reactions<sup>5,6</sup> which result in unpredictable rates of radical production; furthermore, benzaldehyde leads to products such as perbenzoic acid which may participate in nonradical reactions.<sup>7</sup> As a result, previous workers<sup>4</sup> were handicapped in their studies by their choice of initiator and solvent which was used as the reference substrate.

This Laboratory has initiated an extensive study of the relative reactivities of alkyl aryl peroxy radicals toward polynuclear aromatic hydrocarbons. A clearly defined oxidizing system has been used so that the rate data determined from the competitive oxidation can be interpreted unambiguously. Cumene and tetralin have been chosen as the reference hydrocarbons because their oxidation mechanisms have been extensively studied<sup>8,9</sup>; also, azobis-(2-methylpropionitrile) (AIBN) has been used as the initiator since it produces radicals at a predictable rate.<sup>10</sup>

The present paper describes the kinetic results of the competitive oxidation of anthracene in cumene over wide ranges of concentration and shows that anthracene,  $\alpha$ -benzoanthracene, and tetracene oxidize by the same mechanism.

## Results

In the current studies the rate of production of radicals from the initiator,  $R_i$ , was chosen as  $1.38 \times 10^{-5}$  mole l.<sup>-1</sup> sec.<sup>-1</sup> (AIBN). This value was adopted from the work of Russell<sup>8</sup>; it corresponds to  $2\epsilon k$  (AIBN) where  $\epsilon$ , the efficiency of radical production, was determined to be 0.60 by the 2,6-di-*t*-butyl-*p*-cresol inhibitor technique<sup>11</sup> and  $k$  is the first-order rate

(1) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 398-407.

(2) A. P. Stefani and M. S. Szwarc, *J. Am. Chem. Soc.*, **84**, 3661 (1962).

(3) E. C. Kooyman and E. Farenhorst, *Trans. Faraday Soc.*, **49**, 58 (1953).

(4) A. H. Turner and W. A. Waters, *J. Chem. Soc.*, 879 (1956).

(5) G. S. Hammond and U. S. Nandi, *J. Am. Chem. Soc.*, **83**, 1213 (1961).

(6) G. A. Russell, *ibid.*, **78**, 1044 (1956).

(7) S. L. Fries and A. Miller, *ibid.*, **72**, 2611 (1950).

(8) G. A. Russell, *ibid.*, **79**, 3871 (1957).

(9) C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc. (London)*, **A198**, 252 (1949).

(10) G. S. Hammond, C. H. S. Wu, O. D. Trapp, J. Warkentin, and R. T. Keep, *J. Am. Chem. Soc.*, **82**, 5394 (1960), and earlier papers.

constant for the decomposition of AIBN in chlorobenzene, *viz.*  $1.15 \times 10^{-6}$  at 60°.

All the measurements were conducted at 60° with oxygen pressures in excess of 375 mm. where the rates of oxygen absorption were independent of pressure. The rates were also independent of the rate of stirring (varied from 500 to 1300 r.p.m.) and were insensitive to the light of the laboratory.

**I. Anthracene and the Cumylperoxy Radical.**—Table I summarizes the data for the rate of oxygen absorption by solutions of AIBN and cumene in chlorobenzene which contained varying amounts of anthracene. As the concentration of anthracene was increased in these solutions, the rate of absorption of oxygen was initially unaffected, then decreased to a minimum, and finally increased. The effects observed within these different ranges of anthracene concentrations have been examined in detail and will be treated separately below.

TABLE I

RATE OF OXYGEN ABSORPTION BY 3.45 M CUMENE AND 0.10 M AIBN IN CHLOROBENZENE AT 60°

Anthracene, mole l. <sup>-1</sup>	$-\frac{dO_2}{dt} \times 10^6$ , moles l. <sup>-1</sup> sec. <sup>-1</sup>	Anthracene, mole l. <sup>-1</sup>	$-\frac{dO_2}{dt} \times 10^6$ , moles l. <sup>-1</sup> sec. <sup>-1</sup>
0.0000	10.2	0.0390	0.75
.00057	10.1	.0740	1.38
.0020	8.5	.1520	2.25
.0050	4.43	.232	3.45
.0150	1.47		

<sup>a</sup> All the rates of absorption of oxygen reported in this paper have been corrected for nitrogen evolution by AIBN and for oxygen absorption by the initiator fragments.

**A. Anthracene Concentrations below  $5 \times 10^{-4} M$ .**—Anthracene in this concentration range does not alter the rate of oxygen absorption by the solutions; however, the anthracene itself gradually disappears. A number of experiments were conducted in which the anthracene concentration was followed spectrophotometrically at 3790 Å. until at least 75% of it had disappeared. Excellent first-order plots were obtained in all cases. A typical plot of log absorbance *vs.* time is given in Fig. 1 and all the results are summarized in Table II. The rate law for the disappearance of anthracene is

$$-d(\text{An})/dt = a(R_i)^{1/2}(\text{An}) \quad (1)$$

where

$$a = \frac{k'}{(R_i)^{1/2}} = 2.20 \times 10^{-1} \left( \frac{\text{liters}}{\text{moles sec.}} \right)^{1/2}$$

Since the presence of small amounts of anthracene has no measurable effect on the rate of oxygen absorption and thus does not change the steady state concen-

(11) C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *ibid.*, **77**, 2233 (1955).

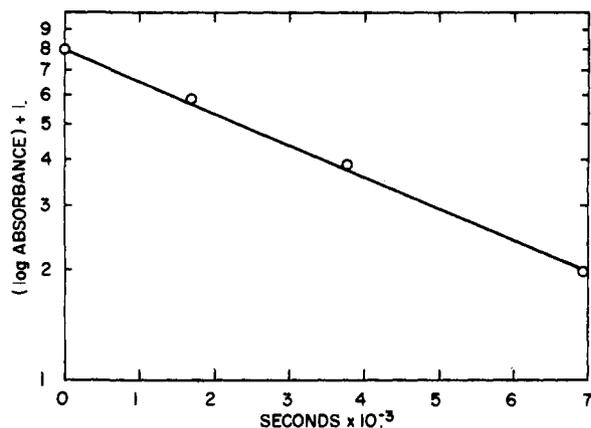
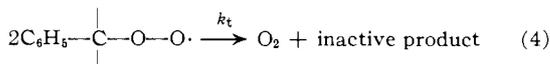
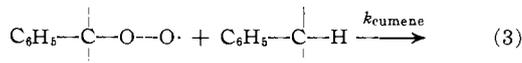
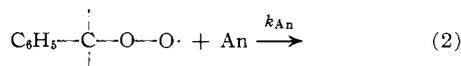


Fig. 1.—First-order plot for disappearance of anthracene; (AIBN) =  $56.4 \times 10^{-3} M$ ; (An) =  $5.4 \times 10^{-4} M$ ; (cumene) =  $2.07 M$ .

tration of cumylperoxy radicals, these results can be explained by considering the following reactions to be important in this concentration range



In this case, the radicals terminate *via* reaction 4 and thus

$$R_i = 2k_t(\text{RO}_2\cdot)^2; \quad (\text{RO}_2\cdot) = (R_i/2k_t)^{1/2}$$

$$-\frac{d(\text{An})}{dt} = k_{\text{An}}(\text{RO}_2\cdot)(\text{An}) = \frac{k_{\text{An}}}{(2k_t)^{1/2}} (R_i)^{1/2}(\text{An}) \quad (5)$$

in agreement with experiment (eq. 1).

Also

$$-d(\text{cumene})/dt = -d(\text{cumene})/dt = k_{\text{cumene}}(\text{RO}_2\cdot)(\text{cumene}) = \frac{k_{\text{cumene}}}{(2k_t)^{1/2}} (R_i)^{1/2}(\text{cumene}) \quad (6)$$

The data on the rates of oxygen absorption by these solutions agree with this expression. From Table III it is seen that  $k_{\text{cumene}}/(2k_t)^{1/2}$  has the value of  $2.54 \times$

TABLE II

DISAPPEARANCE OF ANTHRACENE IN SOLUTIONS OF ANTHRACENE AND CUMENE IN CHLOROENZENE AT  $60^\circ\text{a}$

(An) <sub>0</sub> , moles l. <sup>-1</sup> × 10 <sup>4</sup>	(R <sub>i</sub> ) <sup>1/2</sup> , (moles l. <sup>-1</sup> sec. <sup>-1</sup> ) <sup>1/2</sup> × 10 <sup>4</sup>	Cumene, moles l. <sup>-1</sup>	k', sec. <sup>-1</sup> × 10 <sup>4</sup>	k'/(R <sub>i</sub> ) <sup>1/2</sup> , 1. <sup>1/2</sup> mole <sup>-1/2</sup> sec. <sup>-1/2</sup> × 10 <sup>1</sup>
5.4	11.35	3.45	2.40	2.11
5.4	8.82	2.07	1.98	2.24
5.4	5.09	3.45	1.10	2.16
4.7	6.45	1.39	1.38	2.14
4.7	11.2	2.07	2.61	2.32
Mean 2.20 ± 0.07				

<sup>a</sup> (An)<sub>0</sub> is the initial concentration of anthracene, R<sub>i</sub> is the rate of initiation and k' is the first-order rate constant obtained from plots of log (anthracene) *vs.* time.

$10^{-3}$  (1. mole<sup>-1</sup> sec.<sup>-1</sup>)<sup>1/2</sup>. The ratio of *a* in eq. 1 to  $k_{\text{cumene}}/(2k_t)^{1/2}$  has the value of 87 and is the relative reactivity,  $k_{\text{An}}/k_{\text{cumene}}$ , of a cumylperoxy radical toward anthracene and cumene, respectively.

**B. Anthracene Concentration from  $2 \times 10^{-3}$  to  $15 \times 10^{-3} M$ .**—Within this concentration range, the rate of disappearance of anthracene follows a different expression from that given above for the more dilute solutions. The data presented in Table IV and Fig. 2 show that

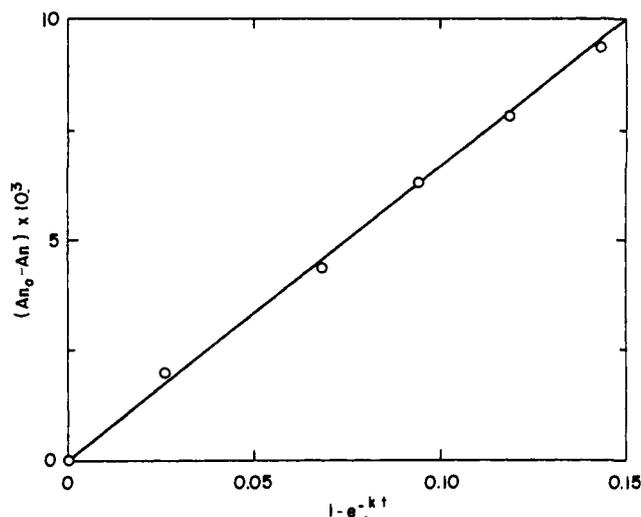


Fig. 2.—Determination of stoichiometric factor, *n*, for anthracene in cumene; (An)<sub>0</sub> =  $14.8 \times 10^{-3} M$ , (An)<sub>t</sub> =  $5.5 \times 10^{-3} M$ , (AIBN)<sub>0</sub> =  $125 \times 10^{-3} M$ , (cumene) =  $6.90 M$ .

$$\Delta(\text{An}) = 1/2 \Delta(\text{radicals formed})$$

and therefore

$$-d(\text{An})/dt = 1/2 R_i \quad (7)$$

Furthermore, within this range, the rate of oxygen absorption decreases as the concentration of anthracene

TABLE III

RATE OF ABSORPTION OF OXYGEN BY SOLUTIONS OF ANTHRACENE AND CUMENE IN CHLOROENZENE

(An) <sub>0</sub> , moles l. <sup>-1</sup> × 10 <sup>4</sup>	R <sub>i</sub> <sup>1/2</sup> , (moles l. <sup>-1</sup> sec. <sup>-1</sup> ) <sup>1/2</sup> × 10 <sup>4</sup>	Cumene, moles l. <sup>-1</sup>	-dO <sub>2</sub> /dt, moles l. <sup>-1</sup> sec. <sup>-1</sup>	$\frac{-d\text{O}_2/dt}{(R_i)^{1/2}(\text{RH})} \times 10^2$ 1. <sup>1/2</sup> mole <sup>-1/2</sup> sec. <sup>-1/2</sup>
0	11.8	3.45	10.2	2.51
5.7	11.8	3.45	10.1	2.49
5.4	11.35	3.45	10.3	2.64
4.7	6.45	1.39	2.32	2.58
Mean				2.54 ± 0.06

TABLE IV

STOICHIOMETRIC FACTOR (*n*) FOR ANTHRACENE INHIBITION OF CUMENE OXIDATION

(An) <sub>0</sub> , mole l. <sup>-1</sup> × 10 <sup>2</sup>	(An) <sub>t</sub> , moles l. <sup>-1</sup> × 10 <sup>2</sup>	(AIBN) <sub>0</sub> × 10 <sup>3</sup> , moles l. <sup>-1</sup>	Cumene, moles l. <sup>-1</sup>	<i>n</i> <sup>a</sup>
14.8	5.5	125.0	6.90	2.2
7.1	4.7	188.0	3.45	1.9
7.4	2.5	125.0	3.45	2.1

<sup>a</sup> *n* is defined as the number of radicals produced for each anthracene molecule consumed and is calculated from the expression  $(\text{An})_0 - (\text{An})_t = \frac{1.2(\text{AIBN})_0}{n} (1 - e^{-1.15 \times 10^{-5}t})$ .

is increased. The general expression for such an inhibited oxidation is given as

$$-\frac{d\text{O}_2}{dt} = \frac{c(R_i)^\alpha(\text{RH})^\beta}{(\text{An})^\gamma} \quad (8)$$

where  $\alpha$ ,  $\beta$ , and  $\gamma$  are appropriate exponents and *c* is a constant. Although the dependence of the rate of absorption of oxygen upon the concentration of anthracene, *i.e.*, the value of  $\gamma$ , can be estimated from the initial slopes of oxygen *vs.* time curves, a less tedious and more accurate method has been adopted in this work. A direct relationship has been established in this work between time and anthracene concentration. Therefore, combining eq. 7 and 8

$$-d\text{O}_2 = -2c \frac{(R_i)^\alpha(\text{RH})^\beta}{(R_i)} \times \frac{d(\text{An})}{(\text{An})^\gamma} \quad (9)$$

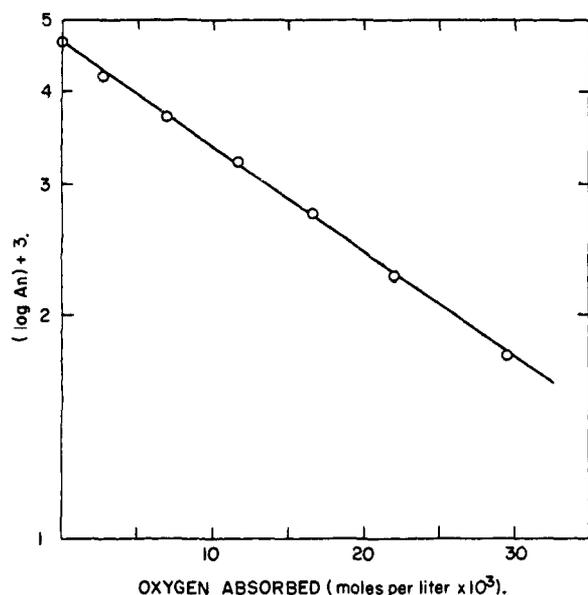


Fig. 3.—Logarithm of anthracene concentration vs. oxygen absorption;  $(An)_0 = 4.68 \times 10^{-3} M$ ,  $(AIBN) = 115 \times 10^{-3} M$ ,  $(cumene) = 3.45 M$ .

Within a given experiment, however, the initiator and the cumene are present in large excess and therefore  $R_i$  and  $R_H$  can be regarded as constant. Plots of  $\log(An)$  vs. oxygen absorbed yield straight lines as shown in Fig. 3. Therefore,  $\gamma = 1$  and

$$-dO_2 = 1/k''(d(An)/(An)) \quad (10)$$

The values of  $k''$  for a series of measurements are given in Table V and are shown to be independent of  $R_i$  so that  $\alpha = 1$ . Furthermore,  $k''(cumene)$  is a constant so that  $\beta$  must also be equal to 1.

TABLE V

ABSORPTION OF OXYGEN BY MIXTURES OF ANTHRACENE AND CUMENE

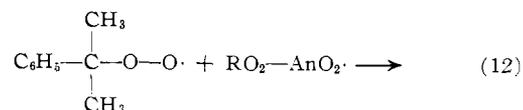
$R_i$ , moles $l.^{-1} sec.^{-1}$ $\times 10^8$	$(An)_0$ , moles $l.^{-1}$ $\times 10^3$	$PO_2$ , mm.	Cumene, moles $l.^{-1}$	$k''^a$ , moles $^{-1} l.$	$k''$ , (cumene)
96.6	3.28	750	3.45	30.1	104
146.0	7.76	490	3.45	29.2	101
146.0	7.76	378	3.45	29.6	102
146.0	7.76	750	3.45	29.7	102
161.5	4.68	750	3.45	32.2	111
181.5	4.68	750	3.45	31.0	107
292	7.76	750	3.45	30.3	105
154	4.65	750	1.39	76.0	107
96.6	4.94	750	2.78	36.3	100
418	15.6	750	6.90	16.5	114
161.5	7.76	750	3.45	30.1	104
Mean					105

<sup>a</sup>  $k'' = 0.693/(O_2)_{1/2}$  and was obtained from plots of  $\log(An)$  vs.  $O_2$  absorbed;  $(O_2)_{1/2}$  = amount of  $O_2$  absorbed when  $(An)$  decreased to  $1/2(An)_0$ .

The over-all rate expression for the oxygen absorption in this range of anthracene concentrations can therefore be summarized as

$$-dO_2/dt = c(R_i)(RH)/(An) \quad (11)$$

The kinetic results observed in this range can be interpreted by assuming that the concentration of the anthracenylperoxy radicals is sufficiently high that the slow bimolecular termination reaction of two cumylperoxy radicals is superseded by the very fast reaction of a cumylperoxy radical with an anthracenylperoxy radical



This system is thus analogous to the cumene tetralin system reported by Russell.<sup>12</sup> The slow step in the termination reaction is (2) and therefore

$$R_i = 2k_{An}(RO_2\cdot)(An)$$

$$(RO_2\cdot) = R_i/2k_{An}(An)$$

$$-d(An)/dt = k_{An}(RO_2\cdot)(An) = 1/2R_i \quad (13)$$

Also

$$- \frac{dO_2}{dt} = k_{cumenc}(RO_2\cdot)(cumene) = \frac{k_{cumenc}R_i(cumene)}{2k_{An}(An)} \quad (14)$$

These expressions agree with experimental ones (7) and (11). The relative reactivity of a cumylperoxy radical toward anthracene and cumene, *i.e.*,  $k''(cumene)$ , respectively, is 105 in comparison with the value of 87 obtained for the lower concentration ranges of anthracene described above.

**C. Rate Constant for Addition of a Cumylperoxy Radical to Anthracene.**—The mean value of the relative reactivities determined from the two concentration ranges above is 96. Multiplication of this ratio of  $k_{An}/k_{cumene}$  by the absolute value of  $k_{cumene}$  yields a value for  $k_{An}$ . The value of  $k_{cumene}$  from the literature (*viz.* 0.31 at 50° and 0.56 at 65°)<sup>13</sup> is open to question. Thomas and Tolman<sup>14</sup> found it necessary to adjust this value to 0.64 at 57° to obtain agreement with data they obtained on cumene. The value of  $k_{cumene}/(2k_t)^{1/2}$  obtained in this study (Table III) is about 25% higher than would be predicted from the literature value of  $k_{cumene}$  and consequently a value of 0.65 was adopted here for the value of  $k_{cumene}$  at 60°. Using this value  $k_{An}$  has been calculated to be 62 moles $^{-1} l. sec.^{-1}$ .

**D. Anthracene Concentration between  $5.0 \times 10^{-4}$  and  $2.0 \times 10^{-3} M$ .**—In the concentration ranges intermediate between those described above, the rate of anthracene disappearance is complex since termination takes place *via* two reactions [(4) and (2)]. Therefore

$$R_i = 2k_t(RO_2\cdot)^2 + 2k_{An}(RO_2\cdot)(An) \quad (15)$$

$$- \frac{d(An)}{dt} = k_{An}(An) \left[ \frac{-2k_{An}(An) + \sqrt{4k_{An}^2(An)^2 + 8R_i k_t}}{4k_t} \right] \quad (16)$$

This general equation, of course, describes the rate of disappearance of anthracene over the entire concentration range below  $15 \times 10^{-3} M$ . At high anthracene concentrations

$$-d(An)/dt \longrightarrow R_i/2$$

while at low anthracene concentrations

$$-d(An)/dt \longrightarrow k_{An}(An)(R_i)^{1/2}/(2k_t)^{1/2}$$

as was observed experimentally. Table VI compares the values of  $\Delta(An)/\Delta t$  observed for the rate of disappearance of anthracene in the concentration range  $0.60 \times 10^{-3}$  to  $2.4 \times 10^{-3} M$  with those calculated from eq. 16 where  $k_t = 3.2 \times 10^4 l. mole^{-1} sec.^{-1}$  and  $k_{An} = 62.0 l. mole^{-1} sec.^{-1}$ . Due to the inherent errors involved in the determination of instantaneous values of  $\Delta(An)/\Delta t$  in this intermediate range, the agreement must be considered satisfactory.

**E. Anthracene Concentration above about  $50 \times 10^{-3} M$ .**—The data in Table I indicate that the rate of oxygen absorption by the cumene solution reaches a

(12) G. A. Russell, *J. Am. Chem. Soc.*, **77**, 4583 (1955).

(13) H. W. Melville and S. Richards, *J. Chem. Soc.*, 944 (1954).

(14) J. R. Thomas and C. H. Tolman, *J. Am. Chem. Soc.*, **84**, 2079 (1962).

minimum at about  $40 \times 10^{-3} M$ . Above this level the rate increases as the anthracene concentration increases. This result suggests that anthracene undergoes a chain autoxidation, *i.e.*, it reacts with anthracenylperoxy radicals to propagate a chain.

TABLE VI  
RATE OF REACTION OF ANTHRACENE IN INTERMEDIATE  
CONCENTRATION RANGE

(An) $\times 10^3$ , moles l. <sup>-1</sup>	$R_i \times 10^3$ , moles l. <sup>-1</sup> sec. <sup>-1</sup>	$\Delta(\text{An})/\Delta t$ $\times 10^3$ , <sup>a</sup> moles l. <sup>-1</sup> sec. <sup>-1</sup> (exptl.)	$d(\text{An})/dt$ $\times 10^3$ , moles l. <sup>-1</sup> sec. <sup>-1</sup> (calcd.)	Cumene, moles l. <sup>-1</sup>
2.41	71.2	26.0	25.8	1.39
2.11	71.2	28.0	24.5	1.39
1.78	71.2	25.0	22.4	1.39
1.14	61.5	17.0	15.5	1.39
0.98	61.5	13.9	14.1	1.39
.79	61.5	13.4	12.0	1.39
.60	61.5	10.2	9.0	1.39
.96	92.2	18.0	19.0	1.39
.79	92.2	19.0	16.0	1.39

<sup>a</sup> Calculated from consecutive points  $(\text{An}_{t_n} - \text{An}_{t_{n+1}})/(t_{n+1} - t_n)$ .

II.  $\alpha$ -Benzoanthracene and the Cumylperoxy Radical.—The rate of absorption of oxygen by cumene solutions in chlorobenzene was not affected by the addition of up to  $10^{-2} M$   $\alpha$ -benzoanthracene. The  $\alpha$ -benzoanthracene, however, did disappear as was observed by a decrease in the absorbance at 3600 Å. Owing to the low reactivity, however, this disappearance was followed only to a maximum of about 30% (see Table VII) in order to minimize the effects of the

TABLE VII  
DISAPPEARANCE OF  $\alpha$ -BENZOANTHRACENE IN SOLUTIONS OF  
CUMENE IN CHLOROBENZENE

$\alpha$ -BAN, moles l. <sup>-1</sup> $\times 10^3$	$(R_i)^{1/2}$ (moles l. <sup>-1</sup> sec. <sup>-1</sup> ) <sup>1/2</sup> $\times 10^3$	Cumene, moles l. <sup>-1</sup>	$k'$ , sec. <sup>-1</sup> $\times 10^6$	$k'/(R_i)^{1/2}$ , (mole <sup>-1</sup> l. sec. <sup>-1</sup> ) <sup>1/2</sup> $\times 10^2$	% reac- tion followed
6.70	0.835	5.30	1.38	1.66	12.5
6.70	1.59	5.30	2.65	1.67	25.0
3.14	1.75	3.14	3.13	1.79	19.0
2.64	1.02	3.14	1.64	1.61	12.5
2.64	1.62	3.14	2.77	1.71	30.0
Mean				1.69 $\pm$ 0.04	

changes in rate of initiation and concentration of cumene. The rate expression for this disappearance is

$$-d(\alpha\text{-BAN})/dt = a(R_i)^{1/2}(\alpha\text{-BAN}) \quad (17)$$

in analogy to that for dilute solutions of anthracene. The value of  $k_{\alpha\text{-benzoanthracene}}/k_{\text{cumene}}$  is 6.6 and thus the rate constant for the addition of a cumylperoxy radical to  $\alpha$ -benzoanthracene is 4.3 l. mole<sup>-1</sup> sec.<sup>-1</sup>.

III. Tetracene and the Cumylperoxy and Tetralylperoxy Radical.—The relative reactivity of tetracene compared to cumene is so great that  $5 \times 10^{-6} M$  tetracene in 3.45  $M$  cumene disappears at a rate proportional to  $R_i$  and independent of tetracene concentration. As a result, a more reactive reference hydrocarbon, tetralin, was used. In Table VIII are presented the data from the spectrophotometric determination of tetracene concentration in oxidizing tetralin, and in Table IX are given the rates of oxygen absorption of solutions of tetralin in chlorobenzene with and without added tetracene. These results are analogous to those obtained with anthracene and  $\alpha$ -benzoanthracene in cumene at concentration levels below those of inhibition. From these results the value of  $k_{\text{tetracene}}/k_{\text{tetralin}}$ , that is, the relative reactivity of a tetralylperoxy

TABLE VIII  
DISAPPEARANCE OF TETRACENE IN SOLUTIONS OF TETRALIN IN  
CHLOROBENZENE AT 60°

Tetracene, moles l. <sup>-1</sup> $\times 10^4$	Tetralin, moles l. <sup>-1</sup>	$(R_i)^{1/2}$ , (moles l. <sup>-1</sup> sec. <sup>-1</sup> ) <sup>1/2</sup> $\times 10^3$	$k' \times 10^4$ , sec. <sup>-1</sup>	$k'/(R_i)^{1/2}$
1.30	2.72	5.6	1.82	3.25
1.62	1.36	11.2	3.76	3.36
2.03	3.28	3.12	1.06	3.40
2.03	2.72	7.0	2.66	3.79
Mean				3.42 $\pm$ 0.15

TABLE IX  
RATE OF OXYGEN ABSORPTION BY SOLUTIONS OF TETRACENE AND  
TETRALIN IN CHLOROBENZENE AT 60°

Tetracene, moles l. <sup>-1</sup> $\times 10^4$	Tetralin, moles l. <sup>-1</sup>	$(R_i)^{1/2}$ , moles l. <sup>-1</sup> $\times 10^4$	$-dO_2/dt$ $\times 10^6$ , moles l. <sup>-1</sup> sec. <sup>-1</sup>	$-dO_2/dt$ ( $R_i$ ) <sup>1/2</sup> (tetralin) $\times 10^3$
0.00	6.20	5.1	16.70	5.30
2.03	3.45	5.1	9.95	5.65
2.03	3.45	3.6	6.70	5.40
Mean				5.45 $\pm$ 0.15 $\times 10^{-3}$

radical toward tetracene and tetralin, respectively, is calculated as 630. From the data of Bamford and Dewar,<sup>15</sup>  $k_{\text{tetralin}}$  at 60° is calculated to be 32 mole<sup>-1</sup> l. sec.<sup>-1</sup>. Therefore, the rate constant for the addition of a tetralylperoxy radical to tetracene is 20,200 mole<sup>-1</sup> l. sec.<sup>-1</sup>.

### Discussion

In the work described above, the rate constants for the addition of the cumylperoxy radical to anthracene and to  $\alpha$ -benzoanthracene and of the tetralylperoxy radical to tetracene have been determined in a well defined system. The observed kinetics are consistent with the concept that the slow step in the reaction is the attack of the corresponding peroxy radical on the polynuclear aromatic hydrocarbon.

We turn now to a comparison of the relative reactivities of these different polynuclear aromatic hydrocarbons toward alkyl aryl peroxy radicals. In this discussion it is assumed that the cumylperoxy radical has the same reactivity toward tetracene as that observed for the tetralyl peroxy radical; this assumption seems justified since Russell<sup>12</sup> has shown that tetralylperoxy and cumylperoxy radicals have essentially the same reactivities toward tetralin and cumene. It is also assumed that the cumylperoxy radicals attack the polynuclear aromatic hydrocarbon exclusively at the *meso* positions and that therefore anthracene,  $\alpha$ -benzoanthracene, and tetracene have 2, 1, and 4 equivalent positions, respectively. This assumption is based on the observation in this laboratory that anthrone and anthraquinone accounted for more than 98% of the products resulting from the chain oxidation of anthracene. Using these assumptions, the rate constants per equivalent position are calculated to be 31, 4.3, and 5000 mole<sup>-1</sup> l. sec.<sup>-1</sup>, for these three hydrocarbons, respectively.

Other workers<sup>2,3</sup> have shown that the logarithms of the rate constants per equivalent position are linearly related to the radical localization energy of the hydrocarbons. Figure 4 shows that the present data follow such a straight line relationship and Table X compares the value of the slope,  $\beta$ , of this line with those obtained for other radicals. The high  $\beta$ -value from this work indicates that peroxy radicals have a much greater selectivity than methyl, trifluoromethyl, and trichloromethyl radicals.

(15) C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc. (London)*, **A198**, 252 (1949).

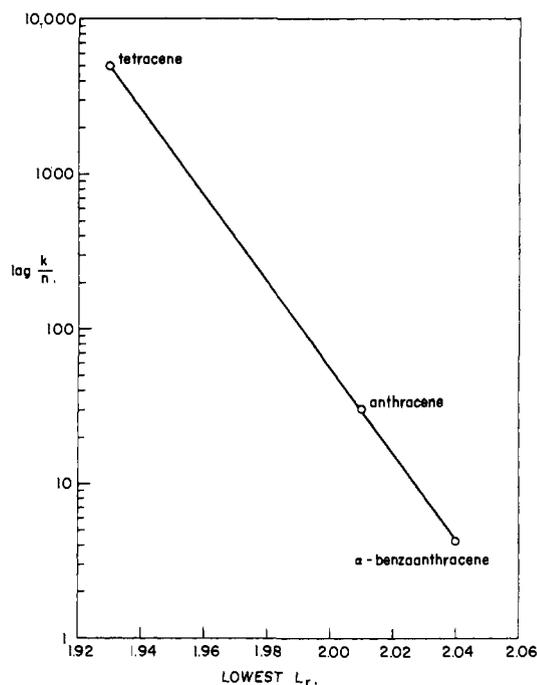


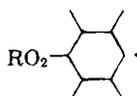
Fig. 4.—Logarithm of rate constants per equivalent position vs. radical localization energies.

It has been suggested<sup>1</sup> that the magnitude of  $\beta$  provides an indication of the structure of the transition state. The methyl and trifluoromethyl radicals show both a small  $\beta$ -value and a small secondary isotope effect and the  $\sigma$ -bond in the transition state is considered to be relatively long.<sup>16</sup> No data are yet available on

TABLE X  
VALUES OF  $\beta$ , THE BOND INTEGRAL, FOR VARIOUS RADICALS

Radical	$\beta$ , kcal./mole	Reference
CF <sub>3</sub>	-9	2
CH <sub>3</sub>	-11	2
CCl <sub>3</sub>	-20	3
RO <sub>2</sub>	-40	This work

the secondary isotope effects of the addition of peroxy radicals to polynuclear aromatic hydrocarbons; however, the high  $\beta$ -value implies that the  $\sigma$ -bond is relatively short, and therefore the product radical, *viz.*



may serve as a model for the transition state.

The present study was carried out in aromatic solvents and it is possible that the high selectivity of the peroxy radicals could be attributed, at least in part, to radical-solvent interactions such as those observed for chlorine atom reactions.<sup>17</sup> Further studies will be required to establish the magnitude of this effect.

### Experimental

**I. Material's.**—Anthracene (Eastman, m.p. 215–217°) was purified by distillation with ethylene glycol<sup>18</sup> or by chromatography on activated alumina. Anthracene from both techniques, m.p. 217°, was highly fluorescent and gave identical rates of reactions.

Azobis-(2-methylpropanitrile) (Eastman) was recrystallized twice from methanol and dried over phosphorus pentoxide; m.p. 106–107°.

(16) M. Feld, A. P. Stefani, and M. S. Swarc, *J. Am. Chem. Soc.*, **84**, 4451 (1962)

(17) G. A. Russell, *ibid.*, **80**, 4987 (1958).

(18) J. A. C. Yule, U. S. Patent 2,213,755, (Sept. 3, 1940); see also L. F. Fieser, "Experiments in Organic Chemistry," Part II, D. C. Heath and Co., New York, N. Y., 1941, p. 345.

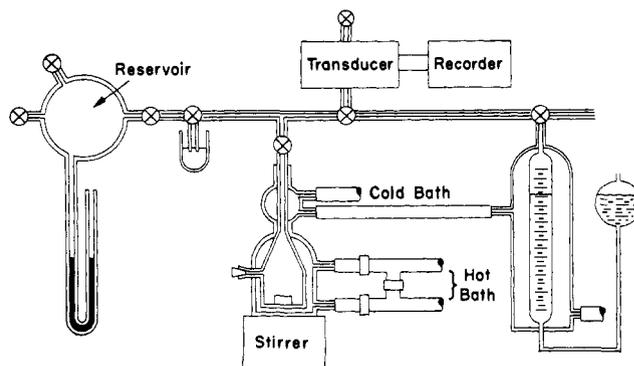


Fig. 5.—Oxygen absorption apparatus.

Chlorobenzene (Baker "Analyzed Reagent") was dried over anhydrous calcium sulfate and then was distilled through a column, 2.4 cm. i.d.  $\times$  50 cm. long, packed with  $3/32$ -in. glass helices. The center fraction, b.p. 132.5°, was used for this work.

Cumene (Eastman Practical grade) was shaken repetitively with concentrated sulfuric acid until the acid layer was colorless. After washing repeatedly with water and drying over sodium sulfate, the dried material was distilled in an atmosphere of nitrogen using the column described above. The center fraction, b.p. 151.5–152°, was stored at  $-5^\circ$ . Immediately prior to use in each of the experiments here, this material was passed through a bed of silica gel.

Tetracene (Terra Chemicals, Inc., 95% minimum) was recrystallized twice from *p*-xylene; m.p. 352° cor. (sealed tube, aluminum block).

$\alpha$ -Benzoanthracene (Terra Chemicals, Inc.) was purified by chromatography on alumina; m.p. 159°.

Tetralin (Eastman Practical) was purified by the technique used for cumene; b.p. 205.0°.

**II. Apparatus.**—The rates of absorption of oxygen were measured under both constant volume and constant pressure conditions using the apparatus diagrammed in Fig. 5.

The reaction cell was similar to that described by Bolland<sup>19</sup> and consisted of a glass vessel surrounded by a water jacket through which water was circulated at  $60.0 \pm 0.05^\circ$  from a constant temperature bath. A second water jacket at the top of the cell was held at  $31 \pm 0.1^\circ$  by an additional water jacket. The capillary portions of the system, 1.5 mm. i.d., were not water jacketed but were held at  $24 \pm 1^\circ$  by the ambient temperature of the laboratory.

In experiments made at constant pressures, the volume of the system was changed manually by raising or lowering a mercury leveling bulb attached to the gas buret. A differential pressure transducer (Dynamic Instrument Co., Model 6V984) coupled with a power supply and a recorder (Leeds and Northrup Azar recorder) was used as a null device to permit adjustment of volumes.

When it had been determined by prior experiments that changes of pressure produced no measurable effects upon the reaction rate, the changes in pressure at constant volume then were recorded directly by the transducer and recorder system. Using this system, a continuous record of oxygen absorption was obtained throughout the run. At the sensitivities used here it was possible to observe a change of pressure of 9 mm. or a change of volume of 1.52 ml. across the full chart width of the recorder. When the changes of volume exceeded 1.52 ml., the system was readily readjusted to zero on the recorder by momentarily opening the stopcock to the gas reservoir.

**III. Rates of Oxygen Absorption.**—Measured amounts of anthracene, AIBN, chlorobenzene, and cumene or tetralin were introduced into the reaction cell at room temperature. The system was degassed by evacuation, flushed several times with oxygen, and then adjusted to atmospheric pressure. During this operation and throughout the experiment, the solution was vigorously agitated using a magnetically driven Teflon-coated stirring bar. During the period at room temperature, the rate of oxygen absorption was negligible. As soon as the hot water ( $60^\circ$ ) was introduced into the water jacket of the reaction vessel (taken as "zero-time") instead of through the bypass, then oxygen absorption started. In about 2 min., temperature equilibration was established in the liquid.

The moles of oxygen absorbed per unit time were determined either from the recorder chart for pressure changes or from individual observations on the volume changes at constant pressure.

**IV. Rates of Hydrocarbon Disappearance.**—For measurements of the rate of disappearance of polynuclear aromatic hydrocarbons, separate experiments were made using the same reaction cell. Samples were withdrawn periodically through a hypodermic

(19) J. L. Bolland, *Proc. Roy. Soc. (London)*, **A186**, 218 (1946).

syringe inserted into the solution *via* the side arm of the cell. The samples were quenched to room temperature and aliquots were diluted to the desired volumes. No further reaction was noted in any of these cooled and diluted samples.

Ultraviolet spectra of the diluted solutions of anthracene from 6500 to 3000 Å. were recorded in either of two separate spectrophotometers. For solutions between  $1.5 \times 10^{-5}$  and  $20 \times 10^{-6}$  M a Beckman constant ratio instrument was used and for solutions below  $2 \times 10^{-5}$  M a Cary 14 spectrophotometer equipped with 5-cm. cell was used. The extinction coefficients were  $6.0 \times 10^3$  and  $7.2 \times 10^3$  on the two instruments, respectively, and accordingly, separate calibrations were made for each instrument. Beer's law was obeyed at 3790 Å. for all concentrations used on

both instruments and at this wave length no interfering absorptions from other reactants or products were observed.

The ultraviolet spectra for the other aromatics were measured on the Cary instrument. Beer's law was obeyed at all concentrations for  $\alpha$ -benzoanthracene at 3600 Å. ( $\epsilon 5.4 \times 10^3$ ) and for tetracene at 4760 Å. ( $\epsilon 7.7 \times 10^3$ ), and no interfering absorptions were observed.

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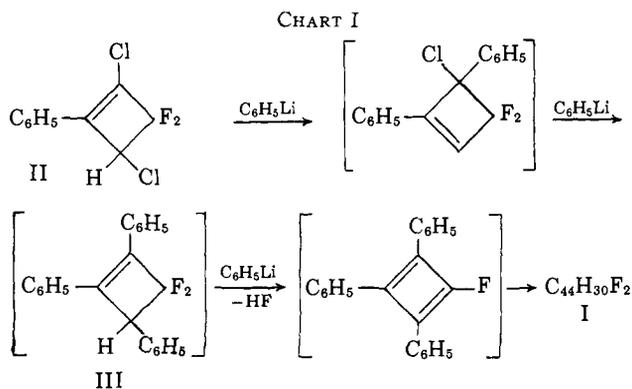
## Small-Ring Compounds. XXXX. The Structure and Properties of a Dimer of Triphenylfluorocyclobutadiene<sup>1</sup>

BY KUPPUSWAMY NAGARAJAN, MARJORIE C. CASERIO, AND JOHN D. ROBERTS

RECEIVED AUGUST 26, 1963

The chemistry of the previously described substance,  $C_{44}H_{30}F_2$ , from the reaction of 1,1-difluoro-2,4-dichloro-3-phenylcyclobutene and phenyllithium is described. The physical and chemical data presented are best interpreted in terms of an *anti*-tricyclo[4.2.0.0<sup>2,5</sup>]octadiene structure for the substance which could arise by dimerization of triphenylfluorocyclobutadiene. The recent X-ray diffraction study of the substance by Hughes and Fritchie has confirmed the proposed structure.

During a recent study in this laboratory of nucleophilic displacement reactions of some halophenylcyclobutenes,<sup>2</sup> a substance was isolated of composition  $C_{44}H_{30}F_2$  (I) from the reaction of phenyllithium with 1,1-difluoro-2,4-dichloro-3-phenylcyclobutene (II). We suggested that this substance could well be a dimer of triphenylfluorocyclobutadiene formed by the route outlined in Chart I. This route presumes attack of phenyllithium at the vinyl position of II in an  $SN2'$ -type of displacement reaction to give a product which is rapidly attacked further by phenyllithium in a similar  $SN2'$  reaction to give the triphenylcyclobutene derivative III; elimination of hydrogen fluoride from III would lead to triphenylfluorocyclobutadiene which could then dimerize to give I.

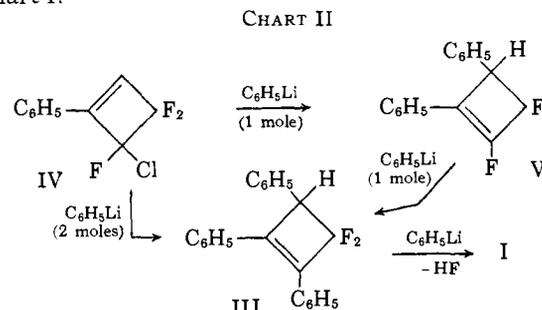


We have subsequently investigated in further detail the pathway by which the dimer I is formed, and the results of this work are described in this paper together with some of the interesting and unusual properties of the dimer.

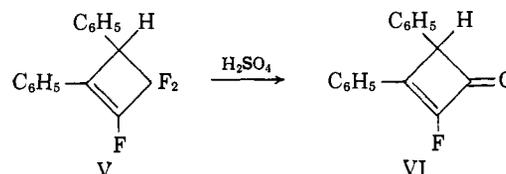
Formation of the dimer by the route given in Chart I involves, as the key intermediate, formation of 1,1-difluoro-2,3,4-triphenylcyclobutene (III). Evidence in support of the formation of III was obtained by the isolation of III from the reactions of phenyllithium with various other halophenylcyclobutenes, some of which

were prepared previously,<sup>3</sup> and the demonstration that III does indeed react with phenyllithium to give the dimer I.

Starting with 1,1,2-trifluoro-2-chloro-3-phenylcyclobutene (IV), it was found possible to prepare the dimer I by reaction of IV with a 3–4 M excess of phenyllithium. The route by which this reaction could take place is given in Chart II and is closely similar to that of Chart I.



A significant experiment is the reaction of IV with only one molar equivalent of phenyllithium which gave a compound (m.p. 65–67°) that has been assigned structure V on the basis of its ultraviolet, infrared, and nuclear magnetic resonance spectra and the fact that it could be hydrolyzed with sulfuric acid to a ketone identified as having structure VI.



Treatment of V with a further molar equivalent of phenyllithium resulted in the displacement of the vinyl fluorine of V to give a compound identified as the difluorotriphenylcyclobutene III on the basis of spectral evidence and hydrolysis to a ketone identified as VII. Like other cyclobutenones,<sup>4</sup> neither VI nor VII

(3) (a) J. D. Roberts, G. B. Kline, and H. E. Simmons, Jr., *ibid.*, **75**, 4765 (1953); (b) E. J. Smutny, M. C. Caserio, and J. D. Roberts, *ibid.*, **82**, 1793 (1960).

(4) E. F. Jenny and J. D. Roberts, *ibid.*, **78**, 2005 (1956).

(1) Supported in part by the National Science Foundation.

(2) Y. Kitahara, M. C. Caserio, F. Scardiglia, and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 3106 (1960).