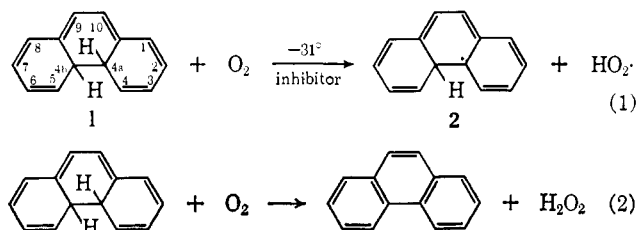# Oxidation of 4a,4b-Dihydrophenanthrenes. I. Kinetics of the Thermal Reaction of 9,10-Cyclopentano-4a,4b-dihydrophenanthrene with Oxygen[1]

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Abstract: The thermal reaction of 9,10-cyclopentano-4a,4b-dihydrophenanthrene (PH_2) with oxygen, both in the presence and in the absence of 2,6-di-*t*-butyl-4-methylphenol (SH), acting as inhibitor, takes place through the self-initiated $HO_2 \cdot$ chain. The products are hydrogen peroxide and phenanthrene (P). The following distinct steps were recognized: initiation, $PH_2 + O_2 \rightarrow PH \cdot + HO_2 \cdot$ (k_a); propagation, $PH \cdot + O_2 \rightarrow P + HO_2 \cdot$ (k_b); $PH_2 + HO_2 \cdot \rightarrow PH \cdot + H_2O_2$ (k_d); termination, $SH + HO_2 \cdot \rightarrow$ inactive products (k_c); $2HO_2 \cdot \rightarrow H_2O_2 + O_2$ (k_e). Three types of kinetics were found, according to the concentration of the inhibitor. (I) At high concentrations of the inhibitor, [SH] > 0.04 M, the reaction chain is composed of steps a, b, and c. The rate of the reaction of PH_2 is then controlled by step a and is of the first order with respect to both [O_2] and [PH_2]. At $-31°$, k_a is 0.65 l. mole^{-1} min^{-1}. The activation energy for step a is 6.2 kcal/mole. The preexponential factor is $10^{3.7}$ l. mole^{-1} sec^{-1}. Step a is accelerated in polar solvents, indicating a polar transition state. (II) In the absence of inhibitor the reaction is represented by steps a, b, d, and e. The rate expression for the disappearance of PH_2 is then to a good approximation of order $^1/_2$ with respect to [O_2], and of order $^3/_2$ with respect to [PH_2]. (III) At intermediate concentrations of the inhibitor, [SH] < 0.04 M, the rate of disappearance of PH_2 is to a good approximation of the second order with respect to [PH_2], of the first order with respect to [O_2], and inversely proportional to [SH]. The exact kinetic expressions (differential and integrated) in cases II and III were confirmed experimentally. The ratio $k_d/\sqrt{k_e}$ is 3×10^2 and does not vary with the temperature. The ratio k_c/k_d is 1.08×10^{-2} at $-31°$ and 1.57×10^{-2} at $-52°$. Steps b–e and probably step a are exothermic. The dissociation energy of the PH–H bond is estimated as equal to or lower than 47 kcal/mole.

We have recently observed[2] an unusually large kinetic isotope effect of deuterium ($k_H/k_D = 95$, at $-31°$) for the first stage (reaction 1) of the thermal oxidation of 4a,4b-dihydrophenanthrene (**1**) (reaction

2). In the present paper we wish to describe the mechanism and the kinetics of the over-all reaction (reaction 2).[3] The substrate for this study was 9,10-cyclopentano-4a,4b-dihydrophenanthrene (**3**), chosen because of its efficient formation from diphenylcyclopentene (**4**).[4]
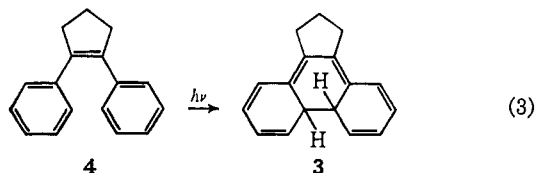
Photocyclization of the type represented by reaction 3 and subsequent oxidation (or photooxidation[4])

of the dihydro product have been observed in several systems derived from *cis*-1,2-diphenylethylene, such as substituted stilbenes,[5] bianthrones, helianthrones, hypericin, and 14-phenyldibenzoxanthylium salts.[6]

This aromatization scheme has been frequently applied to the synthesis of various polycyclic systems.[7] We expect the dihydro intermediates observed (or postulated) in all those studies to have rather similar reactivities. Thus the present conclusions about the mechanism and the kinetics of the oxidation of **3** should probably apply in many of the other cases.

Experimental Section

The thermal oxidation of **3** was investigated by following the absorbance changes at the maximum of the visible absorption band (460 mμ, ϵ 7600). The solvents used were isooctane (Fluka, spectroscopic grade), anhydrous ethanol (Fluka, analytical grade), and 1-butanol (BDH, analytical grade). A constant concentration of oxygen was achieved by bubbling continuously a slow stream of either oxygen or air through the reaction cell. The gases, dried by cooling to $-80°$, were presaturated with the solvent at the temperature of the experiment. The solubility of oxygen in these solvents at atmospheric pressure and at several temperatures was determined by Kretschmer, Novakowska, and Wiebe.[8] From these data the solubilities were extrapolated to lower temperatures as required in the present work (Table I). The solubilities of oxygen in solutions at equilibrium with air (O_2 at 0.21 atm[9]) were also

(1) Part of a Ph.D. thesis to be submitted by A. Bromberg to the Graduate School of the Weizmann Institute of Science.

(2) (a) Part II in the present series: A. Bromberg, K. A. Muszkat, and E. Fischer, *Chem. Commun.*, 1352 (1968); (b) part III: A. Warshel and A. Bromberg, in preparation; (c) part IV: A. Bromberg, K. A. Muszkat, and E. Fischer, in preparation.

(3) For a preliminary account see ref 4.

(4) K. A. Muszkat and E. Fischer, *J. Chem. Soc., B*, 662 (1967).

(5) F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Am. Chem. Soc.*, **86**, 3094 (1964).

(6) For a recent review see F. R. Stermitz in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 247.

(7) (a) W. Carruthers, *J. Chem. Soc., C*, 1525 (1967); (b) C. E. Loader and C. J. Timmons, *ibid.*, 1343, 1457 (1967); (c) H. Wynberg, H. Van Driel, R. M. Kellog, and J. Buter, *J. Am. Chem. Soc.*, **89**, 3487 (1967); (d) A. Padwa and R. Hartman, *ibid.*, **88**, 3759 (1966).

(8) C. B. Kretschmer, J. Novakowska, and R. Wiebe, *Ind. Eng. Chem.*, **38**, 506 (1946).

(9) "Handbook of Chemistry and Physics," 47th ed, R. C. Weast, Ed., The Chemical Rubber Co., Cleveland, Ohio, 1966, pp F-119, F-123.

Table I. Extrapolated Concentrations of Oxygen at Equilibrium with Oxygen or Air at 1 Atm Pressure

		2,2,4-Isooctane[8]		
t, °C		−31	−52	−80
O_2, mole/l.	(0.21 atm of O_2)	0.00416	0.00475	0.00564
	(1 atm of O_2)	0.0198	0.0226	0.0268
		Ethanol[8]		
t, °C		−31	−52	
O_2, mole/l.	(1 atm of O_2)	0.0119	0.0130	
		1-Butanol[8]		
t, °C		−31	−52	
O_2, mole/l.	(1 atm of O_2)	0.0104	0.0110	

extrapolated, assuming ideal behavior. Diphenylcyclopentene (4) was freshly recrystallized from methanol. The inhibitor used throughout this study was 2,6-di-*t*-butyl-4-methylphenol (BMP, Fluka, pure grade).

The reactions were carried out in a 1-cm spectrophotometric cell with elongated (30 cm) neck, contained in a windowed copper block surrounded by an optical dewar flask. A stream of either cold air or liquid air was circulated through holes bored in the copper block. The temperature was regulated by a Wheelco controller–thermocouple assembly. In a typical experiment a 1×10^{-3} M solution of 4 (3 ml) was cooled to the required temperature and freed from dissolved oxygen by purging for 15 min with nitrogen gas (100 ml/min, dried by cooling at −80°) bubbled through the liquid. The dihydrophenanthrene derivative (3) at a $2–3 \times 10^{-4}$ M concentration was formed by a 5-min irradiation with 220–330-mμ light from a 125-W Philips mercury spectral lamp, isolated with a $CoSO_4$–$NiSO_4$ solution filter.[4] After the irradiation, 1 ml of a solution of the inhibitor at a suitable concentration was added. Oxygen or air, dried by cooling at −80°, was bubbled through the solution at a rate of about 150 ml/min, and a continuous curve of the absorbance at 460 mμ vs. time was recorded on a Cary 14 spectrophotometer. At the end of the experiment all unreacted dihydrophenanthrene was reconverted into 4 by irradiation with 436-mμ light,[4] and the absorbance was measured to ascertain that no change occurred in the base line. Data from some 15–20 points from each experiment were processed on a computer according to a suitable equation (see below). Every experiment was repeated several times to check reproducibility. Considerable efforts were required to find the best experimental conditions necessary for obtaining a satisfactory reproducibility.

Hydrogen peroxide was determined colorimetrically by the pertitanic acid method[10a] (ϵ 730 at 410 mμ[10b]). Reaction mixtures in water-immiscible solvents (isooctane, chlorobenzene) were extracted with 1 ml of the aqueous reagent solution (400 mg/l. of TiO_2 in 7% w/v H_2SO_4). Solutions in ethanol were mixed directly with with the reagent.

Results and Their Analysis

Qualitative Observations. The following account gives the qualitative observations on the course of the reaction. These support the interpretation deduced from the quantitative results described subsequently.

In 2,2,4-isooctane solutions the rate of the oxidation reaction is considerable even at −90°. The reaction proceeds by a free-radical mechanism (HO_2· chain) and does not require external initiation with compounds serving as free-radical sources. Several compounds were examined for their inhibitory effect (in a 2,2,4-isooctane solution at −31°, unless stated otherwise). Stsong inhibition is shown by 2,6-di-*t*-butyl-4-methylphenol (BMP) and by aniline. Addition of excess α-naphthol, *p*-cresol, or hydroquinone had no effect.

Hydrogen peroxide or *t*-butyl hydroperoxide in coniiderable excess (added before or following admission of oxygen) do not react with 3 and are without any effect on the kinetics. The rate of reaction increases
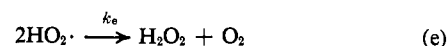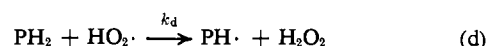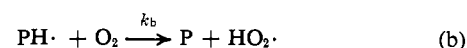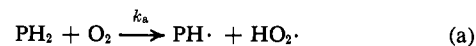
(10) (a) A. C. Egerton, A. J. Everett, G. J. Minkoff, S. Rudrakanchano, and K. C. Salooja, *Anal. Chim. Acta*, 10, 422 (1954); (b) R. Bailey and D. F. Boltz, *Anal. Chem.*, 31, 117 (1959).

with the oxygen concentration, and in several cases is proportional to it, at all inhibitor concentrations studied.

It was possible to recover only small amounts of hydrogen peroxide from thermally oxidized solutions of 3 in isooctane. We believe that this outcome is due to the extremely low solubility of hydrogen peroxide in isooctane, resulting in an absorption and subsequent decomposition of hydrogen peroxide on the walls of the reaction cell. In ethanol, 1 mole of hydrogen peroxide is formed per mole of 3 oxidized.[4] However, because of a difference in the kinetics of the thermal oxidation in isooctane and in ethanol, hydrogen peroxide was also determined in a reaction mixture in chlorobenzene, which dissolves hydrogen peroxide to a sufficient extent for the present purpose. In this solvent (at −31°, no inhibitor added) the kinetics of the thermal oxidation of 3 with oxygen are essentially as in isooctane, and a quantitative yield of hydrogen peroxide was found (1 mole of H_2O_2 per mole of 3). The only hydrocarbon product of the oxidation of 3 is cyclopentanophenanthrene.[4]

Quantitative Observations. Three different types of kinetics of the thermal oxidation of 3 in 2,2,4-isooctane were observed, according to the concentrations of the inhibitor (BMP). These are described separately, as follows (sections I, II, and III).

I. Kinetics in the Absence of Inhibitor. In the absence of inhibitors the following reaction sequence was found to apply.

$$PH_2 + O_2 \xrightarrow{k_a} PH\cdot + HO_2\cdot \qquad (a)$$

$$PH\cdot + O_2 \xrightarrow{k_b} P + HO_2\cdot \qquad (b)$$

$$PH_2 + HO_2\cdot \xrightarrow{k_d} PH\cdot + H_2O_2 \qquad (d)$$

$$2HO_2\cdot \xrightarrow{k_e} H_2O_2 + O_2 \qquad (e)$$

PH_2 denotes 3; PH· denotes the free radical formed by the abstraction of a hydrogen atom from 3, and P is cyclopentanophenanthrene. It is assumed that steps b, d, and e are much faster than step a, and that PH· and HO_2· do not recombine under the present conditions (*cf.* Discussion). Assuming steady-state concentrations for HO_2· and PH·, the following expressions are obtained.

$$[HO_2\cdot] = \sqrt{\frac{2k_a}{k_e}[O_2][PH_2]} \qquad (4)$$

$$\frac{d[PH_2]}{dt} = -k_a[O_2][PH_2] - k_d[PH_2]\sqrt{\frac{2k_a}{k_e}[O_2][PH_2]} \qquad (5)$$

Table II. Experimental Values for $k_d \sqrt{(2k_a/k_e)[O_2]}$ and for $k_d/\sqrt{k_e}$

t, °C ([O₂], mole/l.)	−31 (0.0198)	−31 (0.00416)	−52 (0.0226)
$k_d\sqrt{(2k_a/k_e)[O_2]}$	53	20	27
$k_d/\sqrt{k_e}$	330	260	290

At a constant oxygen concentration eq 5 may be integrated, giving

$$t = \frac{2}{k_a[O_2]} \times$$

$$\ln\left\{\sqrt{\frac{[PH_2]_0}{[PH_2]}}\left(\frac{k_a[O_2] + k_d\sqrt{\frac{2k_a}{k_e}[O_2][PH_2]}}{k_a[O_2] + k_d\sqrt{\frac{2k_a}{k_e}[O_2][PH_2]_0}}\right)\right\} \quad (6)$$

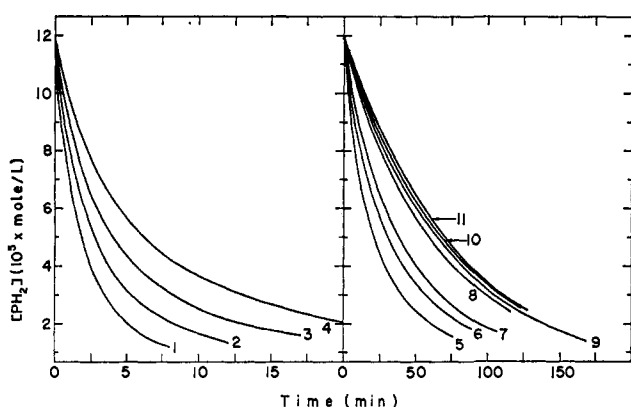Curve 1, Figure 1, shows a typical dependence of $[PH_2]$ $vs.$ time.

Figure 1. Graphs of $[PH_2]$ $vs.$ time at −31°, 1 atm of O₂, in isooctane: curve 1, no inhibitor added; curves 2–11, BMP added to give respectively final concentrations of 2.27, 6.82, 15.9, 68.2, 117, 171, 455, 911, 1360, and 2730 × 10⁻⁴ M.

The term $k_a[O_2]$ which is required in the following treatment of the experimental data is available from the results at high concentrations of the inhibitor (section III). In the absence of inhibitor, $d[PH_2]/dt \gg k_a[O_2][PH_2]$ in eq 5 ($i.e.$, 42–19 times larger at −31° with oxygen saturation, 72–28 times larger at −31° with air saturation, and 63–19 times larger at −52°, with oxygen saturation, the first value giving the initial ratio and the second giving the final ratio of these quantities). Equation 5 therefore reduces to

$$\frac{d[PH_2]}{dt} \cong -k_d[PH_2]\sqrt{\frac{2k_a}{k_e}[O_2][PH_2]} \quad (7)$$

Equation 7 predicts that in the absence of inhibitor the order of the reaction will be $^3/_2$ with respect to $[PH_2]$ and $^1/_2$ with respect to $[O_2]$. However, as the $k_a[O_2]$ values are known ($cf.$ section III), this approximation is not essential. Equation 5 gives the following expression after transposition and logarithmization.

$$\log\left(-\frac{d[PH_2]}{dt} - k_a[O_2][PH_2]\right) =$$

$$\frac{3}{2}\log[PH_2] + \log\left(k_d\sqrt{\frac{2k_a}{k_e}[O_2]}\right) \quad (8)$$

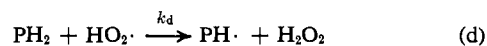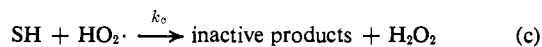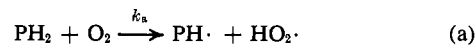At a constant concentration of oxygen, eq 8 predicts a slope of $^3/_2$ for log $\{-(d[PH_2]/dt) - k_a[O_2][PH_2]\}$ $vs.$ log $[PH_2]$. Very good linear plots were obtained with the following slopes: 1.55 (−31°, 1 atm and 0.21 atm of O₂) and 1.47 (−52°, 1 atm of O₂).

For each experiment the values of $k_a[O_2]$ (section III) of $[PH_2]_0$ and of $[PH_2]$ (as a function of time) were substituted into eq 6. The value of the product, $k_d\sqrt{(2k_a/k_e)[O_2]}$, calculated by means of this equation was constant within 10% during the course of every experiment. Values from different experiments differ at most by 10%. Mean values for this quantity obtained from ten experiments are given in Table II. The ratio of the terms $k_d\sqrt{(2k_a[O_2]/k_e)}$ at −31° at a partial pressure of O₂ of 1 atm and of 0.21 atm (Table II) is 2.61, 20% higher than the predicted value, $\sqrt{4.76}$ = 2.18.

Thus within the experimental uncertainty, eq 5–8 are satisfactorily obeyed. The ratio $k_d/\sqrt{k_e}$ (Table II) was calculated from the $k_d\sqrt{(2k_a/k_e)[O_2]}$ values and from the experimental $k_a[O_2]$ values listed in section III. A 25% difference is noted between the values for air and for oxygen saturation at −31°. $k_d/\sqrt{k_e}$ changes only little with the temperature, probably because the exponential factors in this fraction cancel out.

The present work does not allow one to determine k_d and k_e independently. However, the range of values which could be assumed by k_e may be estimated. Its lower limit would be $ca.$ 5 × 10⁶ l. mole⁻¹ sec⁻¹, measured at room temperature in water solutions at pH 2.[11] The value in nonpolar solvents[12] is probably somewhere between the value in water and the value for the diffusion-controlled rate constant ($ca.$ 1 × 10¹⁰ l. mole⁻¹ sec⁻¹). This range of 5 × 10⁶–10¹⁰ for k_e corresponds to a range of 6 × 10⁵–3 × 10⁷ l. mole⁻¹ sec⁻¹ for k_d.

II. Kinetics at Low Concentrations of Inhibitor. At low concentrations of the inhibitor ($i.e.$, below 2 × 10⁻² M), the reaction chain consists of the following steps

$$PH_2 + O_2 \xrightarrow{k_a} PH\cdot + HO_2\cdot \quad (a)$$

$$PH\cdot + O_2 \xrightarrow{k_b} P + HO_2\cdot \quad (b)$$

$$SH + HO_2\cdot \xrightarrow{k_c} \text{inactive products} + H_2O_2 \quad (c)$$

$$PH_2 + HO_2\cdot \xrightarrow{k_d} PH\cdot + H_2O_2 \quad (d)$$

where SH denotes the inhibitor. From the steady-state condition for the species PH· and HO₂·, we obtain

$$[HO_2\cdot] = \frac{2k_a[O_2][PH_2]}{k_c[SH]} \quad (9)$$

This result, when substituted into the rate expression for the disappearance of PH_2, gives the following equation

(11) G. Czapski and B. H. J. Bielski, $J. Phys. Chem.$, **67**, 2180 (1963), and literature cited therein.
(12) J. A. Howard and K. U. Ingold, $Can. J. Chem.$, **45**, 785 (1967).

Table III. k_c/k_d Values Computed from the B_i Values Obtained from Eq 11

[SH], 10^4 mole/l.	2.27	6.82	15.9	68.2	117	171
$10^2 k_c/k_d$ ($-31°$, O_2 at 1 atm)	2.19	1.36	0.87	0.99	1.10	1.14
$10^2 k_c/k_d$ ($-31°$, O_2 at 0.21 atm)	2.08	1.74	1.05	0.99	1.20	1.10
$10^2 k_c/k_d$ ($-52°$, O_2 at 1 atm)	1.70	1.37	1.50	1.40	1.65	1.62

$$\frac{d[PH_2]}{dt} = -k_a[O_2][PH_2] - 2k_a[O_2]\frac{k_d[PH_2]^2}{k_c[SH]} =$$

$$-k_a[O_2][PH_2] - \frac{k_a}{B_i}[O_2][PH_2]^2 \quad (10)$$

The corresponding integrated form is (at constant $[O_2]$ and $[SH]$)

$$t = \frac{1}{k_a[O_2]} \ln \left\{ \frac{[PH_2]_0}{[PH_2]} \left(\frac{B_i + [PH_2]}{B_i + [PH_2]_0} \right) \right\} \quad (11)$$

Here B_i denotes the term $k_c[SH]/2k_d$.

The effect of the inhibitor was examined at the following concentrations: 2.27, 6.82, 15.9, 68.2, 117, and $171 \times 10^{-4}\ M$. Typical experimental curves of $[PH_2]$ vs. time are shown in Figure 1, curves 2–7.

Equations 10 and 11 were applied to these results and fitted them satisfactorily. In eq 10, at the three lowest concentrations of the inhibitor, the term $k_a[O_2][PH_2]$ may be neglected compared to $d[PH_2]/dt$ ($k_a[O_2]$ is known from the results of section III). Thus at $-31°$, 1 atm of O_2, $6.82 \times 10^{-4}\ M$ BMP

$$7 \leqslant \frac{d[PH_2]}{dt} \Big/ k_a[O_2][PH_2] \leqslant 21$$

Under these conditions $d[PH_2]/dt$ is therefore *second* order with respect to $[PH_2]$ (*cf.* eq 10).

$$\frac{d[PH_2]}{dt} = -2k_a[O_2]\frac{k_d[PH_2]^2}{k_c[SH]} \quad (12)$$

At a constant concentration of oxygen eq 12 is integrable and gives the usual second-order form

$$\frac{1}{[PH_2]} - \frac{1}{[PH_2]_0} = \frac{2k_a[O_2]k_d}{k_c[SH]}t \quad (13)$$

This equation was obeyed experimentally with good accuracy.

A general relationship for $[SH] < 1.7 \times 10^{-2}\ M$, suitable for a graphical treatment, may be obtained by the logarithmization of eq 10.

$$\log \left(-k_a[O_2][PH_2] - \frac{d[PH_2]}{dt} \right) =$$

$$\log \left(\frac{2k_a k_d[O_2]}{k_c[SH]} \right) + 2 \log [PH_2] \quad (14)$$

The graphical treatment of the experimental data by this equation, plotting $\log \{ -k_a[O_2][PH_2] - (d[PH_2]/dt) \}$ vs. $\log [PH_2]$, gives straight lines as required. The slopes fall within the range 1.94–2.19, most of the values being very close to 2.

The terms B_i were computed from eq 11 for every point of each experiment. The constancy of B_i within 10% throughout all the points of each experiment served as a criterion for recognizing trustworthy experiments. This condition was fulfilled by all the experiments at concentrations of BMP larger than $6.82 \times 10^{-4}\ M$ (see below) referred to in the present section. It implies considerable accuracy under these conditions,

as then the term $[O_2][PH_2]^2/B_i$ in eq 10 is often only a correction term to $k_a[O_2][PH_2]$, especially toward the end of the reaction. Thus at $-31°$, 1 atm of O_2, and $[SH] = 0.0171\ M$, the fraction $\{[O_2][PH_2]^2/B_i\}/k_a[O_2][PH_2]$ has an initial value of 1.2 which declines to 0.12 at the last experimental point.

By definition, B_i is directly proportional to $[SH]$ and not dependent on $[O_2]$. This behavior was indeed observed, and the following k_c/k_d values were obtained from the slope of B_i vs. $[SH]$: 1.04×10^{-2} ($-31°$, 1 atm of O_2) and 1.12×10^{-2} (0.21 atm of O_2); mean value, 1.08×10^{-2}. At $-52°$, $k_c/k_d = 1.57 \times 10^{-2}$. Therefore the activation energies for steps d and c are not much different. The value of k_c/k_d indicates that at $-31°$ PH_2 is about 100 times more reactive toward $HO_2\cdot$ than the inhibitor.

The computed values for k_c/k_d ($\equiv 2B_i/[SH]$) from each set of conditions are given in Table III. At $-31°$ and $[SH] = 2.27$ and $6.82 \times 10^{-4}M$, the k_c/k_d values deviate from the values observed at higher inhibitor concentrations (Table III). At $-31°$, $[SH] = 2.27 \times 10^{-4}\ M$ and O_2 at 1 atm, the apparent initial k_c/k_d values are higher by 50% than the final values (observed during the last 30% of the reaction). In Table III the final values are listed for this case.

This deviation stems probably from several assumptions made in the above development, which may not always be justified. (A) Step e, $2HO_2\cdot \rightarrow H_2O_2 + O_2$, was excluded from the present scheme. (B) It was assumed that the reaction product of the inhibitor (step c) does not react further with $HO_2\cdot$ (which might not be the case, see below). (C) It was assumed that $[SH]$ is constant during the whole course of the oxidation. This assumption is true provided $[SH] \gg [PH_2]$, but not at the lower $[SH]$ values, where $[SH]$ and $[PH_2]$ are of similar magnitude. This approximation, however, has an effect which is opposite to the effect found.

A possibility considered in the present investigation was that traces of some internal inhibitor at a concentration equivalent to $[SH]_0$ were active even in experiments carried out in the absence of BMP. The following approach was used to test this point. Step e was introduced into the reaction scheme of the present section. The original assumptions lead to a kinetic expression of the form

$$\frac{d[PH_2]}{dt} = -k_a[O_2][PH_2] -$$

$$X\frac{k_c[SH]_0}{2k_d}\left(-1 + \sqrt{1 + \frac{2k_a[O_2][PH_2]}{Xk_c^2[SH]_0^2/4k_d^2}} \right) \quad (15)$$

where $X = k_d^2/k_e$, and $[SH]_0$ is the equivalent concentration of internal inhibitor. The experiments performed in the absence of inhibitor were analyzed by means of eq 15. Experimental values of $k_a[O_2]$ and k_c/k_d were introduced. Values of $[SH]_0$ and X minimizing the deviation between the experimental values of $d[PH_2]/dt$ and those calculated by eq 15 were chosen by iteration.

The results of this analysis show that the equivalent concentration of the internal inhibitor is at most 6×10^{-5} M, i.e., about one-third of the lowest inhibitor concentration investigated. In all experiments at $-52°$ and in some of those at $-31°$, no evidence for such internal inhibition was found. The value calculated for $\sqrt{X} = k_d/\sqrt{k_e}$ was 310 ± 20. These values are very similar to those found experimentally in section I (Table II). This fact indicates that the reaction schemes in sections I, II, and III are self-consistent to a considerable extent.

III. Kinetics at High Concentrations of the Inhibitor.

The kinetics of the thermal oxidation of 3 assume a particularly simple form at sufficiently high concentrations of the inhibitor, higher than ca. 2×10^{-2} M. The reaction chain under these conditions is composed of the three steps a, b, and c. The $HO_2 \cdot$ radical formed in the self-initiation step a and in step b reacts only with the inhibitor (step c) and not with PH_2 because $k_c[SH] >> k_d[PH_2]$. Steps b and c are assumed to be much faster than step a which involves oxygen and a closed-shell molecule.

The rate of disappearance of PH_2 is therefore given by

$$d[PH_2]/dt = -k_a[O_2][PH_2] \tag{16}$$

Equation 16 is obtainable, alternatively, as a limiting case of eq 10. At a constant oxygen concentration, eq 16 may be integrated, giving

$$\ln [PH_2]/[PH_2]_0 = -k_a[O_2]t \tag{17}$$

$[PH_2]_0$ is the initial concentration at time $t = 0$.

Under these conditions the rate of oxidation of PH_2 should be of the first order both with respect to the concentrations of oxygen and of PH_2, and should not depend on the concentration of the inhibitor. A typical experimental curve of $[PH_2]$ vs. time (at $-31°$, 1 atm of O_2) is shown in Figure 1 (curve 11). Curves 7–11 (Figure 1) illustrate the approach to the limit at high inhibitor concentrations, [SH] increasing from 0.045 (curve 8) to 0.27 M (curve 11), which is close to the solubility limit of BMP. The gradual approach to the first-order limit was carried out only for the case of the highest stationary concentrations of $HO_2 \cdot$ (1 atm of O_2, $-31°$). The same concentrations of the inhibitor which produced this limit were assumed to be equally effective for lower stationary concentrations of $HO_2 \cdot$ (i.e., 0.21 atm of O_2 at $-31°$; 1 atm of O_2 at $-52°$).

Equation 17 is accurately obeyed under the conditions of the present section. At $-31°$, the value of $k_a[O_2]$ is 1.3×10^{-2} min^{-1} for oxygen-saturated solutions and 3.0×10^{-3} min^{-1} for air-saturated solutions. The ratio of these values is 4.33. As the partial pressure of oxygen in air is 0.21 atm,[9] and assuming an ideal behavior for oxygen solutions in 2,2,4-isooctane, a value of 4.76 would be expected from eq 16. The agreement between these values is satisfactory for the present purpose. One of the reasons for the 10% difference in the above ratio could well be a deviation of these solutions from ideality. The $k_a[O_2]$ values are reproducible within less than 10%. From the results for oxygen-saturated solutions at $-31°$ ([O_2] = 1.98×10^{-2} M), the value obtained for k_a is 0.65 1. mole^{-1} min^{-1}. At $-52°$ ([O_2] = 2.26×10^{-2} M) $k_a[O_2]$ was found to be 0.043 ± 0.002 min^{-1}, leading to $k_a = 0.19$ 1. mole^{-1} min^{-1}. From these two values of k_a

the activation energy for step a was calculated as $E_a = 6.2$ kcal/mole, and the preexponential factor as $A = 10^{3.7}$ 1. mole^{-1} sec^{-1}.

The half-life time for the thermal ring opening reaction, $3 + \triangle \rightarrow 4$, is 140 hr at $-31°$ and 800 hr at $-52°$. These values have been extrapolated from the previously reported data at higher temperatures.[4] Thus the contribution of the thermal ring opening to the over-all reaction (i.e., the disappearance of PH_2) is entirely negligible even under the conditions of the present section, and of course even more so at low inhibitor concentrations.

IV. Effect of Polar Solvents on Step a.

The rate constants of step a at a high concentration of the inhibitor (0.136 M) were also measured in anhydrous ethanol and in 1-butanol solutions. These results are listed in Table IV. The reaction rates are then strictly

Table IV. Rate Constants, Activation Energies, and Preexponential Factors for Step a in Polar Solvents

	t, °C	$k_a[O_2]$, 10^5 min^{-1}	k_a, 1. mole^{-1} min$^-$	E_a, kcal mole^{-1}	A, 1. mole^{-1} sec^{-1}
Ethanol	-31	1600 ± 60	1.5	6.6	$10^{4.4}$
	-52	460 ± 6	0.42		
1-Butanol	-31	1960 ± 40	1.7	6.3	$10^{4.2}$
	-52	617 ± 8	0.48		

first order in $[PH_2]$, as required by eq 16. The concentration of oxygen in these measurements is given in Table I. The k_a values in these solvents are thus larger than in isooctane solutions. This result indicates that the low preexponential factor for step a might be due in part to a polar transition state (cf. Discussion).[13]

Discussion

1. **The Initiation.** One of the unusual aspects of the present work is the initiation. This reaction is a case of a fast self-initiation. In this respect 4a,4b-dihydrophenanthrenes differ markedly from less reactive hydrocarbons undergoing oxidation. In the latter compounds the reaction

$$RH + O_2 \longrightarrow R \cdot + HO_2 \cdot \tag{18}$$
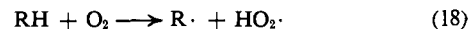
is strongly endothermic, has a high activation energy,[14a,b] and takes place only at high temperatures. Exothermic hydrogen-abstraction reactions of the type $R_1 \cdot + R_2H \rightarrow R_1H + R_2 \cdot$ proceed usually with low activation energies ($E < 10$ kcal/mole).[14c] The low (6.2 kcal/mole) value for E_a observed now[14d] strongly indicates that the activation energy of stage a is due to a potential barrier between products and reactants and not to the energy to be invested in an endothermic reaction. These considerations place an upper limit on the dissociation energy of the 4a C–H bond in 4a,4b-dihydrophenanthrenes, $D°(PH–H)$. Since $D°$ for the O_2–H bond is 47 kcal/mole,[15] it follows that

(13) We are indebted to one of the referees for suggesting this possibility.

(14) (a) K. U. Ingold, Chem. Rev., 61, 563 (1961); (b) S. W. Benson, J. Am. Chem. Soc., 87, 972 (1965); (c) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, Chapter 12. (d) A slightly different set of values ($E_a = 7$ kcal/mole, $A = 10^{4.5}$) has been reported previously[2a] due to an inaccurate calculation.

(15) S. N. Foner and R. L. Hudson, J. Chem. Phys., 36, 2681 (1962).

$D°(PH-H)$ is smaller than 47 kcal/mole. The reason for this low value is the considerable resonance stabilization of the PH· radical. According to this approach the stabilization energy of the PH· radical is approximately $D°((CH_3)_3C-H) - D°(PH-H) = 44$ kcal/mole $[D°((CH_3)_3C-H) = 91$ kcal/mole].[16]

The preexponential factor $A = 10^{3.7}$ l. mole^{-1} sec^{-1} observed for the rate constant k_a of step a is unusually low (cf. with $A = 10^{10}$ for a normal second-order reaction[17]). We believe for the following reasons that this low value is authentic. (A) Preexponential factors of similar magnitude (and similar activation energies) were observed for the parallel reactions of both light and perdeuterated dihydrophenanthrene[2] and also of dihydrophenanthrenes variously substituted at the 3 and 4 positions.[2c]

(B) The kinetics of the oxidation in alcohols were measured in the presence of a high concentration of BMP (Table IV). The rate constants were enhanced noticeably, but otherwise complete resemblance was found to the behavior in 2,2,4-isooctane. In particular the results of Table IV show that the assumption that initiation is provided by step a is correct.

(C) The experimental error in the measurement of rate constants and the uncertainty in the oxygen concentration are much too small to be considered as factors determining the low A values.

The low value of the preexponential factor for step a is due probably to two effects: polarity of transition state and strongly negative entropy of activation. The enhancement of the rate constants k_a in alcohols (Table IV) shows that the transition state of step a is more polar (and more strongly solvated) than the reactants. This type of behavior, whereby a "slow reaction"[17] having a low preexponential factor is accelerated in more polar solvents, has been observed in such reactions as alkylation of tertiary amines, benzoylation of m-nitroaniline, and the addition of cyclopentadiene to benzoquinone.[17] However, the effect in the present case is rather limited. Thus the most important single factor here is the strongly negative entropy of activations of step a $(\Delta S^{\neq} \approx -25$ eu). The low A value of step a indicates that PH_2 and O_2 react only when both are in a closely determined configuration.[2] Such reactions are rather well known.[17]

2. The Propagation. Two propagation stages, steps b and d, are involved in the present scheme.

$$PH· + O_2 \longrightarrow P + HO_2· \qquad (b)$$

$$PH_2 + HO_2· \longrightarrow PH· + H_2O_2 \qquad (d)$$
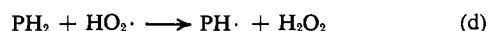
Both reactions involve hydrogen abstractions, and both probably have small activation energies. These reactions are strongly exothermic. Assuming that the estimate for the bond dissociation energy of the C-H bond in the cyclohexadienyl radical, $D°$(cyclohexadienyl) = 24 kcal/mole[16] applies in the present case and gives an upper limit for $D°(P-H)$, we have for the energy change of step b $-\Delta H° = D°(O_2-H) - D°(P·-H) \approx 25$ kcal/mole. This is actually a very conservative estimate. Very probably the P·-H bond is still weaker than the C-H bond in the cyclohexadienyl radical as two aromatic rings are formed when the P·-H bond is homolytically broken.

(16) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).
(17) K. J. Laidler, "Chemical Kinetics," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1965, Chapter 5.

The bond dissociation energy of the second hydrogen in H_2O_2 is $D°(HO_2-H) = 90$ kcal/mole.[15]

The energy change of step d is thus $-\Delta H° = D°(HO_2-H) - D°(PH-H) \approx 43$ kcal/mole.

Hydrocarbons of normal reactivity are oxidized slightly above room temperature only through the low-temperature path,[14b] $R + O_2 \rightarrow RO_2·$; $RO_2· + RH \rightarrow RO_2H + R·$. Organic peroxides and their decomposition products are formed under such conditions. The oxidation proceeds by the high-temperature path (HO$_2·$ chain), $RC·HCH_2R' + O_2 \rightarrow RCH=CHR' + HO_2·$; $RCH_2CH_2R' + HO_2· \rightarrow RC·HCH_2R' + H_2O_2$, only at considerably higher temperatures.[14b] 4a,4b-Dihydrophenanthrenes (as well as 1,4-cyclohexadiene and 1,4-dihydronaphthalene) are an exception in this respect. In the case of 4a,4b-dihydrophenanthrenes the oxidation proceeds through the high-temperature path because of the exothermicity of steps b and d and because of the instability of the hypothetical $PHO_2·$ radical. The $R-O_2·$ bond in allyl- or benzylperoxy radicals is known to be very weak $(D°(R-O_2·) \approx 13-15$ kcal/mole), and the more extended activation in $PHO_2·$ would make it still weaker in this radical.
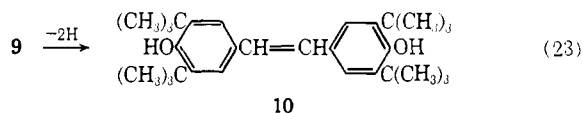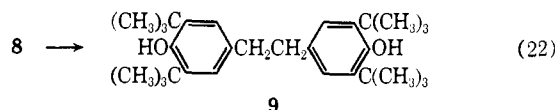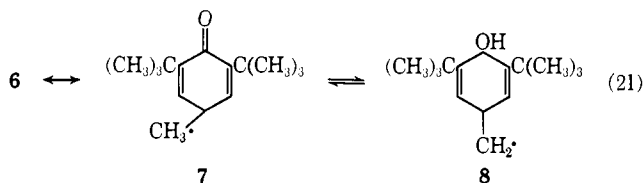
3. The Termination. Termination of the reaction chain is provided by steps c and e. BMP reacts with a *large excess* of the HO$_2·$ radicals as follows.[12,18,19]

$$2HO_2· + BMP \longrightarrow H_2O_2 + (CH_3)_3C\underset{HOO\quad CH_3}{\overset{O}{\bigcirc}}C(CH_3)_3 \qquad (19)$$
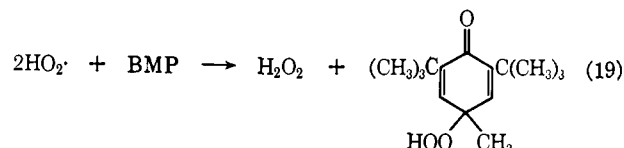
The first stage of reaction 19 is the formation of the S· radical by hydrogen abstraction from the hydroxy group.[19]

$$HO_2· + BMP \longrightarrow (CH_3)_3C\underset{CH_3}{\overset{O·}{\bigcirc}}C(CH_3)_3 + H_2O_2 \qquad (20)$$
$$\mathbf{6}$$
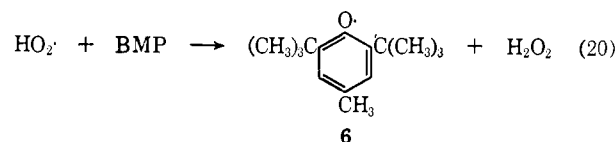
BMP reacts with other hydrogen-abstracting agents, such as the t-butoxy radical or lead dioxide, as follows.[19-21]

$$\mathbf{6} \longleftrightarrow (CH_3)_3C\underset{CH_3·}{\overset{O}{\bigcirc}}C(CH_3)_3 \rightleftharpoons (CH_3)_3C\underset{CH_2·}{\overset{OH}{\bigcirc}}C(CH_3)_3 \qquad (21)$$
$$\qquad\qquad \mathbf{7} \qquad\qquad\qquad\qquad \mathbf{8}$$

$$\mathbf{8} \longrightarrow \underset{(CH_3)_3C}{(CH_3)_3C}HO\bigcirc CH_2CH_2 \bigcirc\underset{C(CH_3)_3}{\overset{C(CH_3)_3}{OH}} \qquad (22)$$
$$\mathbf{9}$$

$$\mathbf{9} \xrightarrow{-2H} \underset{(CH_3)_3C}{(CH_3)_3C}HO\bigcirc CH=CH \bigcirc\underset{C(CH_3)_3}{\overset{C(CH_3)_3}{OH}} \qquad (23)$$
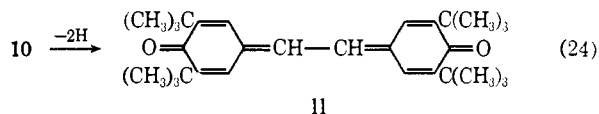$$\mathbf{10}$$

(18) G. M. Coppinger, *J. Am. Chem. Soc.*, **79**, 2758 (1957).
(19) K. U. Ingold, *Can. J. Chem.*, **41**, 2807 (1963).
(20) A. L. Buchachenko and M. B. Neiman, *Dokl. Akad. Nauk SSSR*, **139**, 916 (1961).
(21) V. D. Pokhodenko, L. N. Ganyuk, and A. I. Brodskii, *ibid.*, **145**, 815 (1962).

$$10 \xrightarrow{-2H} \quad (CH_3)_3C \text{—} O=\!\!\!\bigcirc\!\!\!=CH\text{—}CH=\!\!\!\bigcirc\!\!\!=O \text{—} C(CH_3)_3 \qquad (24)$$

11

Compounds 9–11 were isolated from the reaction with *t*-butoxy radicals.[18] Although in the present study the products formed from BMP were not characterized, we assume that the reaction followed the course described above (reactions 20–22). BMP was always kept at a large excess in the present work. Therefore it is very likely that reaction 19 is only of minor importance. The possibility of multiple and repeating hydrogen abstractions (reactions 23 and 24) could explain the observations made at the lowest concentrations of the inhibitor (see Results) where the apparent [SH] had twice the experimental value.

The O–H bond dissociation energy of phenol is $D°(C_6H_5O\text{–}H) = 85$ kcal/mole.[15] *p*-Cresol is expected to have the same $D°(O\text{–}H)$ value. However, this compound (see Results) is inactive as an inhibitor. Thus we come to the conclusion that the O–H bond dissociation energy in BMP is lower than 85 kcal/mole. Step c is therefore exothermic by more than 5 kcal/mole $[D°(HO_2\text{–}H) - D°(S\text{–}H)]$.

Step e, the disproportionation of the $HO_2\cdot$ radical, should be considered whenever the $HO_2\cdot$ radical is at a considerable concentration.

Howard and Ingold have found that this reaction is responsible for the termination of the $HO_2\cdot$ chain in the α,α'-azobisisobutyronitrile initiated oxidations of 1,4-cyclohexadiene and of 1,4-dihydronaphthalene.[12] In aqueous solutions, where the $HO_2\cdot$ radical may undergo considerable hydrogen bonding, the activation energy of step e is 5.9 kcal/mole.[22] In nonaqueous solutions this value is probably smaller.

The recombination of $PH\cdot$ and of $HO_2\cdot$

$$PH\cdot + HO_2\cdot \longrightarrow P + H_2O_2 \qquad (25)$$

was not considered in the present scheme. Both $PH\cdot$ and $HO_2\cdot$ are at low stationary concentrations. In step b $PH\cdot$ reacts in a radical–radical reaction with O_2, a triplet ground-state molecule at a relatively high concentration. On the other hand, $HO_2\cdot$ reacts with the closed-shell molecule PH_2 in a much slower radical-molecule reaction (step d). Thus the following inequalities hold: $k_b \gg k_d$; $[O_2] > [PH_2]$; and therefore $k_b[O_2] \gg k_d[PH_2]$.[13] Therefore the stationary concentration of $PH\cdot$ is much lower than that of $HO_2\cdot$. As a consequence, reaction 25 may be excluded from our scheme while reactions such as step e have to be considered.

As a cage effect[23] (*i.e.*, step a followed by reaction 25), reaction 25 could possibly take place at high viscosities, but then the sterical factor would be exceedingly low as the two 4a and 4b hydrogen atoms in PH_2 are probably on different sides of the molecular plane. Under such conditions the $HO_2\cdot$ radical would have to move from one side of the molecule to the other.

(22) B. H. J. Bielski and E. Saito, *J. Phys. Chem.*, **66**, 2266 (1962).
(23) For a case where a cage effect is observed, see R. Hiatt and T. G. Traylor, *J. Am. Chem. Soc.*, **87**, 3766 (1965).