The Oxidation of 4a,4b-Dihydrophenanthrenes: a Large Kinetic Isotope Effect of Deuterium in the Initiation Step of the Thermal Reaction with Oxygen

By A. BROMBERG,† K. A. MUSZKAT, and E. FISCHER*

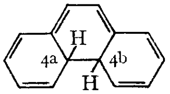
(*Department of Chemistry, The Weizmann Institute of Science, Rehovoth, Israel*)

WE have found that deuterium has an unusually large kinetic isotope effect [$k_1^H/k_1^D = 95$ (at $-31°$)] on the rate constant of the self-initiation step of the thermal reaction of 4a,4b-dihydrophenanthrene (PH_2), (I) with oxygen. Other results[1-3] show that PH_2 reacts thermally with oxygen at low temperatures through the self-initiated $HO_2\cdot$ chain. The products are phenanthrene (P) and hydrogen peroxide. The reaction is inhibited by 4-methyl-2,6-di-t-butylphenol (SH)

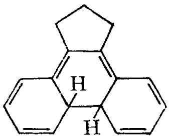
---

† Part of a Ph.D. Thesis to be submitted by A. Bromberg to the Graduate School of the Weizmann Institute.

which combines with the $HO_2\cdot$ radicals. At high inhibitior concentrations, [SH] > 0·04M, the reaction chain is as follows:[1,2]



(I)



(II)

1. $Ph_2 + O_2 \xrightarrow{k_1} PH\cdot + HO_2\cdot$ (self initiation)
2. $PH\cdot + O_2 \xrightarrow{k_2} P + HO_2\cdot$
3. $HO_2\cdot + SH \xrightarrow{k_3}$ inactive products

where PH· denotes the species obtained by the 4a-hydrogen abstraction from PH_2. Under such conditions the rate of disappearance of PH_2 (determined spectrophotometrically)[1,3] is controlled by step 1 and is first-order[1,2] with respect both to $[O_2]$ and to $[PH_2]$:

$$\frac{d[PH_2]}{dt} = -k_1\,[O_2][Ph_2].$$

The substrates we investigated, as 2—3 × 10^{-4}M solutions, were formed by the u.v. irradiation[3] of 2,2,4-trimethylpentane solutions of either normal *trans*-stilbene (Eastman, Scintillation grade) or perdeuterio-*trans*-stilbene (Merck, Sharp, and Dohme of Canada, 98·3% deuteriation on benzene rings, 92·7% on ethylene bridge). The oxidation of the perdeuterio-compound fits the first-order curve well, except for an initial deviation, which is due to the fast reaction of the small amount of light compound present. Experiments with a different sample having 96% deuteriation on the benzene rings gave similar results, except that the initial deviation was larger. Further purification had no effect. The inhibitor concentration was 0·136M. A constant concentration of oxygen was maintained during oxidation by saturating the solution with the gas at 1 atmos. pressure.‡ The self-initiation rate constants, k_1^H and k_1^D (see Table) were obtained by correcting the apparent overall rate constants $*k_1^H$ and $*k_1^D$ for the effect of the much slower first-order thermal ring-opening reaction,[3] $PH_2 \xrightarrow{k_0}$ *cis*-stilbene.

The isotopic effect in step 1 is probably the largest so far reported,[5-10] and is due to a difference of *ca.* 2·5 kcal./mole in the activation energies, $E_1^H = 7$ and $E_1^D = 9{\cdot}5$ kcal./mole, while the pre-exponential factors are almost equal, $A_1^H = 10^4$ and $A_1^D = 10^{4\cdot2}$ l.mole^{-1} sec.$^{-1}$.

The exceptional magnitude of this isotope effect necessitates an examination of possible sources of errors, in particular the presence of an adventitious impurity in the deuteriated compounds, acting as an inhibitor. The following facts indicate that this is not the case. (a) The effect was observed with samples from different sources; (b) the experiments were all carried out in the presence of the inhibitor SH at concentrations above those needed to reach saturation of the inhibition; and (c) experiments with the deuteriated compound in the absence of inhibitor[1] fitted the oxidation kinetics developed and observed for the uninhibited oxidation of the light compound. The reproducibility of reaction rates in individual experiments is within 10%, *i.e.* far beyond the effect described.

In analogy with simpler systems which are amenable to a detailed analysis,[5] the large kinetic isotope effect observed in the present study is necessarily due to both a considerable loss of zero-point energy of stretching and bending vibrations in the transition state and a large contribution from quantum-mechanical tunnelling. As in the reaction[5] $CF_3\cdot + CD_3H$, the A^H and A^D factors in our work are about equal. These findings contrast with the criterion suggested for tunnelling by Bell, Fendley, and Hulett,[11] $A^D \gg A^H$, and observed in the bromination of

Rate constants[a] *of the self-initiation reaction of* PH_2 *and of* $[^2H_{12}]PH_2$[b] *with oxygen*, k_1, *and the thermal ring-opening reaction*, k_0

T(°C)	k_0 (hr.$^{-1}$)	$*k_1^H\,[O_2]$ (hr.$^{-1}$)	$*k_1^D\,[O_2]$ (hr.$^{-1}$)	k_1^H (l. mole^{-1} hr.$^{-1}$)	k_1^D (l. mole^{-1} hr.$^{-1}$)	$[O_2]$[3] mole/l.
−10	0·0040	0·90	0·0180	52	0·81	0·0173
−31	0·00027	0·32	0·00365	16	0·17	0·0198
−52	negligible	0·94		4·2		0·0226

[a] The rate constants are reproducible within 5—10%.
[b] No correction for hydrogen content of $[^2H_{12}]PH_2$ was applied to k_1^D.

---

‡ The concentration of oxygen under these conditions were extrapolated from the published data.[4]

2-ethoxycarbonylcyclopentanone[11] and in the ionization of nitroparaffins[6–9] in the presence of various bases.

The self-initiation step in the oxidation of normal 9,10-cyclopentano-4a,4b-dihydrophenanthrene (II) has the same activation energy ($E_1 = 7$ kcal./mole) but a slightly higher pre-exponential factor ($A_1 = 10^{4.5}$ l. mole^{-1}. sec^{-1}),[1] than PH_2.

The equality of the activation energies indicates that in the present case changes in the mass of the molecule at positions distant from the reaction site have no influence on the k^H/k^D values.

The immediate conclusion from the large value of k^H/k^D is that the rate-determining process in step 1 is the transfer of a hydrogen atom from PH_2 to O_2. The low pre-exponential factor indicates that the reaction takes place in only one specific configuration of the transition state.

(*Received, August 12th,* 1968; *Com.* 1116.)

---

[1] A. Bromberg and K. A. Muszkat, submitted for publication.

[2] A. Bromberg, K. A. Muszkat, and E. Fischer, in preparation.

[3] K. A. Muszkat and E. Fischer, *J. Chem. Soc.* (*B*), 1967, 662. The kinetic isotope effect mentioned in the Journal refers to experiments carried out in the absence of inhibitors.

[4] C. B. Kretschmer, J. Novakowska, and R. Wiebe, *Ind. Eng. Chem.*, 1946, **38**, 506.

[5] T. E. Sharp and H. S. Johnston, *J. Chem. Phys.*, 1962, **37**, 1541.

[6] E. S. Lewis and J. D. Allen, *J. Amer. Chem. Soc.*, 1964, **86**, 2022.

[7] E. S. Lewis and L. H. Funderburk, *J. Amer. Chem. Soc.*, 1967, **89**, 2322.

[8] L. Funderburk and E. S. Lewis, *J. Amer. Chem. Soc.*, 1964, **86**, 2531.

[9] R. P. Bell and D. M. Goodall, *Proc. Roy. Soc.*, 1966, *A*, **294**, 273.

[10] R. Stewart and R. Van der Linden, *Discuss. Faraday Soc.*, 1960, **29**, 211.

[11] R. P. Bell, J. A. Fendley, and J. R. Hulett, *Proc. Roy. Soc.*, 1956, *A*, **235**, 453; J. R. Hulett, *ibid.*, 1959, *A*, **251**, 274.