Oxidation of 4a,4b-Dihydrophenanthrene. Part V.† Tunnelling Effect on the Kinetics of the Initiation Step

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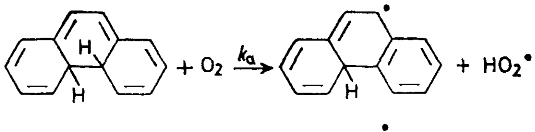
The rate constant k_a of the initiation step in the reaction of 4a,4b-dihydrophenanthrene (PH_2) with molecular oxygen: $PH_2 + O_2 \longrightarrow PH\cdot + HO_2\cdot$ was measured over the temperature range 263—191 K. A significant positive deviation from the Arrhenius dependence, $\ln k_a = \ln A - E_a/RT$, was observed, and is ascribed to quantum-mechanical tunnelling.

Quantum-mechanical tunnelling can play a considerable role in chemical reactions involving transfer of hydrogen atoms or ions.[1] An unusually large kinetic isotope effect of deuterium ($k_a^H/k_a^D = 95$ at 242 K) was recently reported for the initiation step (1) of the oxidation of 4a,4b-dihydrophenanthrene,[2-5] in which such a hydrogen transfer occurs.

The theoretical analysis of the potential surface for this step [4,5] indicates that the large kinetic isotope effect is due to an unusually large tunnelling factor which results in a very large calculated ratio of tunnelling factors for hydrogen and deuterium, $\Gamma_a^H/\Gamma_a^D = 11{\cdot}8$ at 242 K.[4]

The results of the theoretical calculation of the isotope effects due to zero-point energy difference and to tunnelling are in satisfactory agreement with the experimental data.[4,5] However, the unusual extent of quan-



(a)

PH_2 $PH^\bullet$

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† Part IV, ref. 5.

[1] E. F. Caldin, *Chem. Rev.*, 1969, **69**, 135.

[2] A. Bromberg and K. A. Muszkat, *J. Amer. Chem. Soc.*, 1969, **91**, 2860.

[3] A. Bromberg, K. A. Muszkat, and E. Fischer, *Chem. Comm.*, 1968, 1352.

[4] A. Warshel and A. Bromberg, *J. Chem. Phys.*, 1970, **52**, 1262.

[5] A. Bromberg, K. A. Muszkat, and A. Warshel, *J. Chem. Phys.*, 1970, **52**, 5952.

tum-mechanical tunnelling in step (a) has prompted us to look for additional experimental evidence to support the basic assumption about the role of tunnelling in this step. We now describe results of an investigation showing the dependence of the rate constant of step (a) on temperature. In the absence of tunnelling a linear dependence of ln k_a on $1/T$ is expected as the rate constant is quite accurately expressed by the Arrhenius equation (1)

$$\ln k = \ln A - E/RT \qquad (1)$$

Where quantum-mechanical tunnelling is important a considerable positive deviation from linearity is to be expected [1,5,6] at the lower temperatures and has been observed.[1,6] We found such a deviation and this result further confirms the previous conclusions.

EXPERIMENTAL

Rate Constant Measurements.—At high concentrations of the inhibitor (di-t-butyl-*p*-cresol or a thiol) the rate of oxidation of PH_2 becomes completely controlled by step (a). For a constant oxygen concentration this rate is given by the pseudo-first-order expression [2,3] (2) since the concentration

$$-d[PH_2]/dt = k_a[O_2][PH_2] \qquad (2)$$

of oxygen is kept constant during the experiment. The solvent used was 2,2,4-trimethylpentane. In previous work [2-5] the solubility of oxygen in this solvent at the required temperatures was deduced by interpolation and extrapolation of the experimental results of Kretschmer *et al.*[7] However, as Kretschmer *et al.*[7] reached only 248 K, this procedure introduced a definite uncertainty in the measured rate constants at temperatures much lower than 248 K. In the present investigation the temperature range over which the rate of step (a) was studied has been extended considerably and therefore it was necessary to eliminate this uncertainty altogether by measuring the solubility of oxygen in the solvent in the temperature range at which k_a was determined.

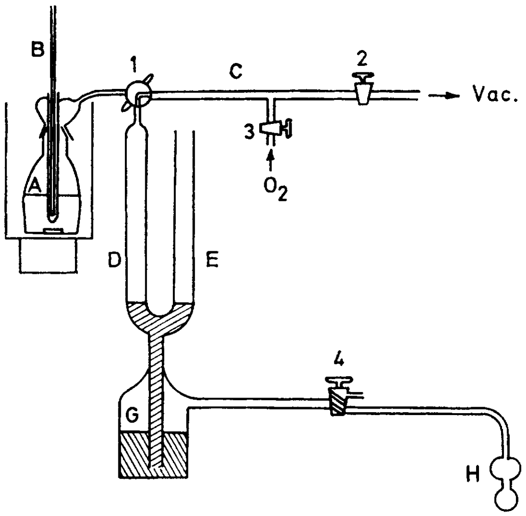

FIGURE 1 Apparatus for the determination of the solubility of oxygen in 2,2,4-trimethylpentane

The solubility of oxygen in 2,2,4-trimethylpentane was measured with the apparatus shown in Figure 1. A known volume of the solvent (determined by weight and from the known density [8]) is introduced into flask A. Following degassing of the solvent by repeated freezing and evacuation, a known volume of oxygen is introduced into A from burette D until constant pressure p is obtained.

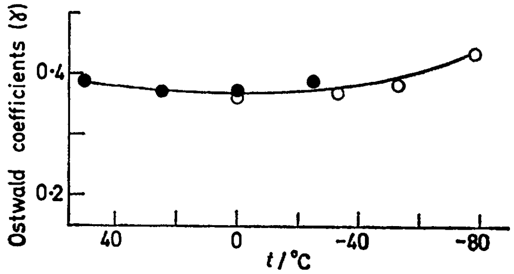

FIGURE 2 Solubilities (Ostwald coefficient) of oxygen in 2,2,4-trimethylpentane. ●, ref. 7; ○, this work

The Ostwald coefficient γ of the gas–solvent pair is then given by expression (3). Here V_T is the total volume of

$$\gamma = \frac{V_T \cdot T_D \cdot p}{V_S \cdot T_S \cdot (p - p_S)} - \left(\frac{V_F}{V_S} - 1\right) \qquad (3)$$

oxygen gas introduced, V_F is the volume of flask A, V_S is the volume of the solvent, p is the measured pressure, p_S is the vapour pressure of the solvent, and T_D and T_S are the respective temperature of burette D and of the solvent. The vapour pressure of the solvent is given in ref. 7. Our results (and those of Kretschmer *et al.*[7] for the higher temperature range) are given in Figure 2. We estimate that the relative error involved in this measurement is lower than ±5%.

The rates of reaction [step (a)] were measured spectrophotometrically as described previously.[2] Constant concentrations of oxygen were maintained by bubbling through the reaction cell a slow stream of oxygen presaturated with the solvent at the appropriate temperature. The results for the undeuteriated compound are listed in the Table.*

DISCUSSION

As shown in Figure 3 (curve A) the experimental value of k_a at the lowest temperature deviates by *ca.* 100% from the value extrapolated from the linear behaviour at the higher temperatures (curve B). We tend to disregard the remote possibility that this deviation from linearity at low temperatures could be due to a change of mechanism. The fact that equation (2) is accurately

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* At 221 K the present value of k_a, which is the mean of several experiments, is *ca.* 30% higher than the value given in the previous study,[3] which was based on only one determination. In the Table on p. 1353 of ref. 3, $k_a[O_2]$ at 221 K should read 0·094 and not 0·94 h^{-1}. At higher temperatures the slight deviation from the k_a values of previous work is due to different alues for the oxygen concentrations.

[6] (*a*) R. P. Bell, J. A. Fendley, and J. R. Hulett, *Proc. Roy. Soc.*, 1956, *A*, **235**, 453; (*b*) J. R. Hulett, *ibid.*, 1959, *A*, **251**, 274; (*c*) E. F. Caldin and M. Kasparian, *Discuss. Faraday Soc.*, 1965, **39**, 25; (*d*) E. F. Caldin, M. Kasparian, and G. Tomalin, *Trans. Faraday Soc.*, 1968, **64**, 2802.

[7] C. B. Kretschmer, J. Novakowska, and R. Wiebe, *Ind. Eng. Chem.*, 1946, **28**, 506.

[8] T. W. Richards, C. L. Speyers, and E. Carves, *J. Amer. Chem. Soc.*, 1924, **46**, 1196.

obeyed at every temperature investigated is an indication that the original mechanism [2-5] remains valid.

The least-squares fit of all the experimental points to equation (4) yields the results: $\ln A = 14{\cdot}7 \pm 0{\cdot}3$, $E_a = 5{\cdot}7 \pm 0{\cdot}1$ kcal mol^{-1}.

$$\ln k_a = \ln A - E_a/RT \qquad (4)$$

The small deviation of the experimental points from linearity above 211 K (Figure 3, curve A), and the minimal scatter of all the points indicate that the curvature in line A is not due to experimental error but rather represents an effect which cannot be described properly by equation (4).

The observed curvature is in quantitative agreement with that expected from the isotope effect reported previously.[1,4,5] We can show this by correcting the experimental rate constant values for the effects of tunnelling in the following way.

The expression for a rate constant (k) in a system where tunnelling is not negligible is given by [1,4,5] equation (5),

$$k = k' \,.\, \Gamma \qquad (5)$$

where k' is the classical rate constant and Γ is the tunnelling correction. Therefore the experimental rate constants (Table) were divided by the appropriate tunnelling corrections Γ^{H} (column 7) which were calculated according to the methods of refs. 4 and 5. The corrected rate constants, plotted according to equation (4) (Figure 3, curve C), show a much improved linearity. The uncertainties in $\ln A'$ ($22{\cdot}0 \pm 0{\cdot}2$) and E_a' ($11{\cdot}90 \pm 0{\cdot}06$ kcal mol^{-1}), compared with the values obtained if the correction is omitted, are now much smaller. The linearity achieved by applying the calculated Γ^{H} correction to the experimental k_a values is thus a convincing indication of the large extent of tunnelling in step (a).

Rate constants and tunnelling factors for the initiation step

T/K	[SH]/M	n [a]	$10^4 k_a[O_2]$/s^{-1} (average)	[O_2]/M	$10^4 k_a$/l mol^{-1} s^{-1}	Γ_H [b]	Γ_D [b]
263	0·136	5	2·55 ± 0·11	0·0171	149·4	120	15
253	0·136	3	1·64 ± 0·05	0·0181	90·3	180	19
242	0·136	6	0·92 ± 0·03	0·0191	48·1	290	25
232	0·136	4	0·58 ± 0·03	0·0202	28·9	500	34
221	0·136	5	0·33 ± 0·03	0·0218	15·3	970	51
211	0·136	3	0·19 ± 0·01	0·0237	8·1	1950	79
201	0·113	1	0·108 ± 0·003	0·0258	4·2	4400	130
201	0·090	2					
191	0·090	4	0·075 ± 0·005	0·0281	2·8	11,000	250

[a] Number of determinations. [b] Computed tunnelling factors for H and for D.

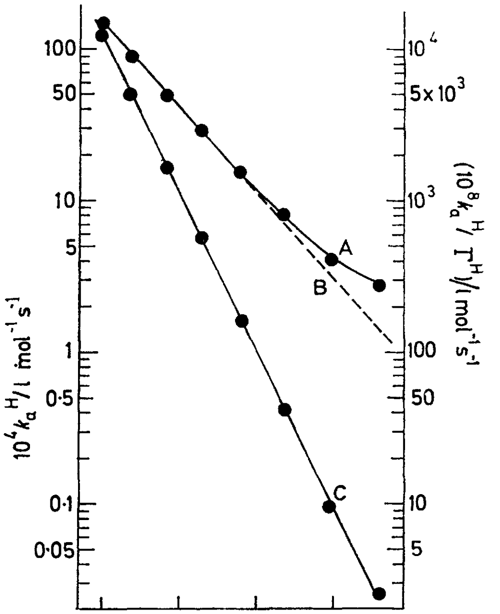

FIGURE 3 Curve A, left-hand scale: experimental plot of $\ln k_a$ against $1/T$. Curve B: extrapolation of linear behaviour. Curve C, right-hand scale: $\ln (k_a^{H}/\Gamma^{H})$ against $1/T$

The large tunnelling factor has two consequences which have not yet been fully discussed.[2-5]

(*a*) In previous papers [2,3,5] the low value for the experimental pre-exponential factor, $A_H = 10^{3\cdot8}$ l mol^{-1} s^{-1}, was ascribed only to the polarity and specific geometry of the transition state. To these two factors we add that the low value of the experimental pre-exponential factor for the reaction of PH_2 [3] is due in part to tunnelling.

The temperature-dependence of the tunnelling correction can be approximated by an exponential expression of the form [1] (6). For undeuteriated PH_2 in the temperature range 263—242 K the values of the parameters are

$$\Gamma = \Gamma^0 \exp (E_\Gamma/RT) \qquad (6)$$

$\Gamma_H^0 = 10^{-2\cdot32}$, and $E_\Gamma^{H} = 5{\cdot}33$ kcal mol^{-1}.[4,5] In order to obtain the classical Arrhenius parameters for k' of equation (5), *i.e.*, A'_H and E'_H, the experimental values ($E_B = 6{\cdot}85$ kcal mol],[1] $A_H = 10^{3\cdot8}$ l mol s^{-1}) are corrected according to equation (7) which is derived from equation (5). We thus obtain a value for the classical pre-exponential factor $A'_H = A_H/\Gamma^0_H = 10^{6\cdot1}$ l mol s^{-1}, which is much closer to the normal range (A = *ca.* 10^{10} s^{-1}) as defined by Laidler.[9] Apart from entropy of activation factors, the low apparent A

$$A_H \exp (-E_H/RT) = \Gamma^0_H \exp (E_\Gamma/RT) \,.\, A'_H \exp (-E'_H/RT) \qquad (7)$$

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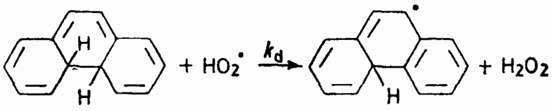
[9] K. J. Laidler, ' Chemical Kinetics,' 2nd edn., McGraw-Hill, New York, 1965, ch. 5.

value of step (a) is caused by the low value of the tunnelling pre-exponential factor.

(*b*) Kinetic isotope effects of deuterium much larger than measured till now (95 at 242 K) [3] should be expected for step (a) at low temperatures. The ratio of the classical rate constant of step (a), k'_H/k'_D [calculated from equation (5) and from the tunnelling factors in the Table] gives the predicted contribution of the zero-point energy difference to the experimental kinetic isotope effect. At 221 K, this effect amounts to a factor of 10, and at 191 K to a factor of 14. Multiplication of these factors by the calculated tunnelling factor ratios in the Table (Γ_H/Γ_D) yields the predicted overall kinetic isotope effects of deuterium. At 221 K the calculated value of k_H/k_D is 190, and at 191 K $k_H/k_D = 630$. The accurate experimental measurement of rate constants of the reaction of deuteriated PH_2 at these temperatures is difficult because of the very slow rate of reaction (*ca.* 1% per 24 h at 221 K). Nevertheless the experimental value obtained thus far, $k_H/k_D = ca.\ 2{\cdot}5 \times 10^2$ at 221 K for 15% reaction, is in good agreement with the above prediction.

In the propagation step (d), a kinetic isotope effect of normal magnitude [10] was observed ($k_d^H/k_d^D = 9{\cdot}9$ at 242 K).[5] According to our model both steps (a) and (d) involve similar isotope effect contributions due to differences in zero-point energy in the transition state. However, the tunnelling factor contributions are widely different. The main reason for this difference is that the potential barrier for step (a) is higher and on the whole narrower than for step (d).[5] The differences in the dimensions of the potential barriers may be qualitatively ascribed to the fact that while step (a) is essentially isoenergetic, step (d) is distinctly exothermic.[2]



(d)

[1/1227 *Received, 16th July, 1971*]

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[10] L. Melander, 'Isotope Effects on Reaction Rates,' Ronald, New York, 1960.