Reactions at High Pressure. Part 5.[1] The Effect of Pressure on Some Primary Kinetic Isotope Effects

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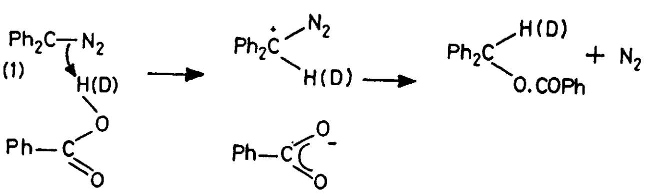
Primary kinetic isotope effects for the reactions; diphenyldiazomethane–benzoic [^{2}H]acid and [^{2}H]leuco-Crystal Violet–chloranil have been determined at pressures up to 2 kbar. The former shows $k_H/k_D < 5$, almost invariant with pressure while for the latter, believed to possess a significant tunnelling contribution, k_H/k_D falls from 11.5 to 7.5 at 2 kbar. It is suggested that increased solvation of the proton under pressure diminishes the extent of tunnelling.

PRIMARY kinetic isotope effects (k.i.e.s) may arise when hydrogen (H•, H^+, or H^-) undergoes transfer in a rate-determining step and may be attributable to differences in zeropoint energy of the isotopic bonds undergoing fission, to differences in various vibrational frequencies between reagent and transition state for the isotopic species [2] and occasionally to differences in the extent of quantum-mechanical tunnelling,[3] a highly mass-dependent property which has been implicated in a dozen hydrogen transfer reactions in solution.[4] Tunnelling is believed to be revealed by several criteria including abnormally large k.i.e.s ($k_H/k_D > 7$ at 25 °C for instance), isotopic dependence of the A-factor and curved Arrhenius plots.[5,6] The extent of tunnelling depends upon the shape of the potential barrier [7] and it seemed to us likely that this would be affected by the application of external pressure to a suitable reaction although in what direction such changes would occur was debatable. Zeropoint energies and vibrational frequencies however should not be significantly affected by moderate pressures and so it seemed likely that normal k.i.e.s would be independent of pressure while those deriving at least in part from tunnelling would be pressure dependent.

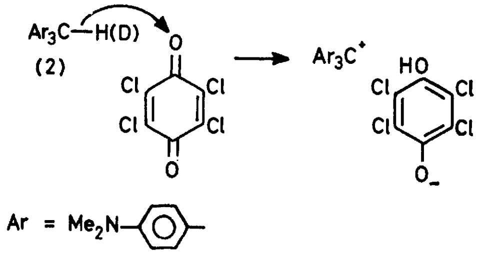
We have now examined this prospect with a view to obtaining a further criterion for the identification of tunnelling using one reaction showing a ' normal ' k.i.e. and one with a very high value. The first reactions was the decomposition of diphenyldiazomethane (1) by benzoic [^{2}H]acid for which $k_H/k_D = 4.5$ and which has been shown to occur by a slow proton transfer:[8,9]



The other reaction investigated was the hydride transfer between [^{2}H]leuco-Crystal Violet (2), and chloranil for which k_H/k_D has been found to be 11.2.[10]

EXPERIMENTAL

Diphenyldiazomethane was obtained by the method of Schroeder and Katz [11] and had m.p. 31—32 °C. Leuco-Crystal Violet was prepared as follows; dried Crystal Violet chloride (1.9 g) was dissolved in dry tetrahydrofuran (50 ml) and lithium aluminium hydride (0.19 g) in tetrahydrofuran (50 ml) was added dropwise to it with stirring. The reaction was then heated for 1 h at reflux temperature. The product was poured into deoxygenated water and extracted with ether (3 × 100 ml). The extracts were combined and dried ($MgSO_4$), and the ether removed; the residue was recrystallised twice from ethanol under nitrogen to give leuco-Crystal Violet (1.5 g) as colourless plates, m.p. 180—183 °C. The same method was used with lithium aluminium deuteride (0.21 g) in place of the hydride to obtain [^{2}H]leuco-Crystal Violet. The crystals of these compounds were quite stable in air and solutions only developed a slight purple colour over a period of weeks. Choranil was recrystallised from benzene–ethanol and had m.p. 290 °C. Solvents were dried and fractionated and middle fractions were collected according to published procedures.[12]



Both reactions were followed spectrophotometrically, by the disappearance of the red colour of diphenyldiazomethane ($\lambda_{max.} = 526$ nm) and the appearance of the purple colour of the Crystal Violet cation ($\lambda_{max.} = 590$ nm). Solutions containing diphenyldiazomethane (10^{-4}M) and benzoic acid (H or D) (0.03—0.04M) were placed in the reaction vessel

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(Figure 1) whose temperature was held to ±0.2 °C by an air thermostat. The vessel was closed and the pressure raised to the desired value by means of the intensifier and hand pump. Samples were periodically withdrawn through the needle valve, material being rejected which might have been resident in the valve itself, and analysed spectrophotometrically. It was established that temperature changes in the sample caused by pressurisation and pressure release disappeared within 1 min, the reactions usually being followed over several hours. Rates of the leuco-Crystal Violet–chloranil reaction were obtained in a similar fashion using initial concentrations of 10^{-5}M and 6 × 10^{-4}M respectively. In each case, second-order rate constants were evaluated to give an estimated uncertainty of 2—4% rising to 5—6% for the fastest reactions with a half-life of less than 1 h.

RESULTS AND DISCUSSION

Measured rates and isotope effects for the diphenyldiazomethane (DDM)–benzoic acid reaction are given in Table 1 and rates of the Crystal Violet–chloranil reaction in Table 2 with activation parameters and isotope effects in Tables 3 and 4. The pressure dependent data were fitted by a least-squares procedure to the quadratic function [equation (1)].

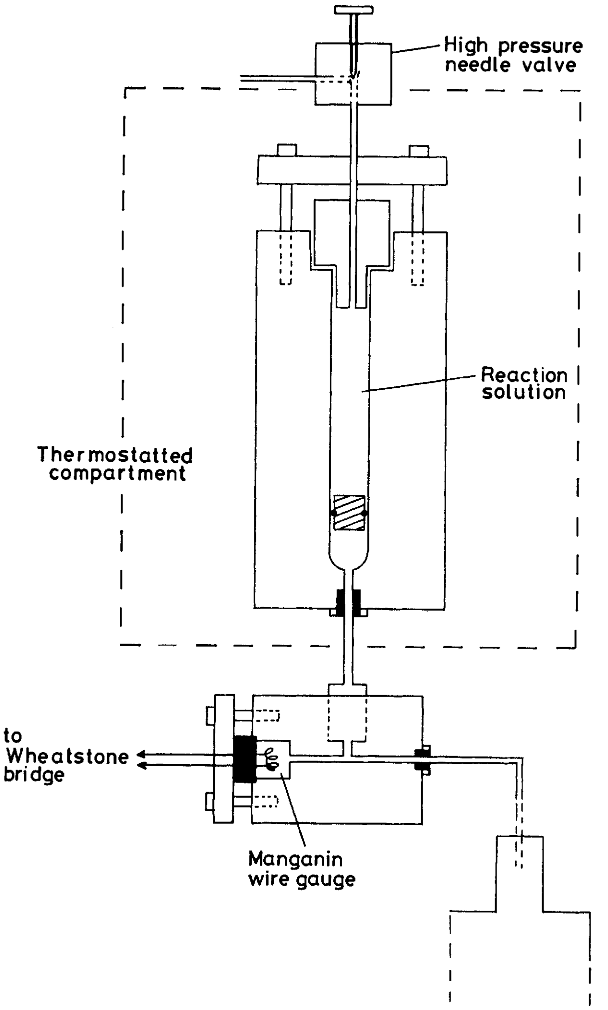

FIGURE 1 High-pressure sampling apparatus

$$\ln k = \mathrm{A} + \mathrm{B}P + \mathrm{C}P^2 \qquad (1)$$

Both reactions yielded negative volumes of activation, no doubt mainly on account of the electrostriction of solvent molecules brought about by the development of charges in the transition state.[13] The DDM–benzoic acid reaction yields activation volumes essentially identical for the two isotopic species, $\Delta V_0^{\ddagger}$ (H) = −13, $\Delta H_0^{\ddagger}$ (D) = 13 cm^3 mol^{-1}. Very little data is available with which to compare this value which is for a slow proton transfer. Caldin *et al.*[14] have measured the activation volume for proton transfer between (nitrophenyl)nitromethane and

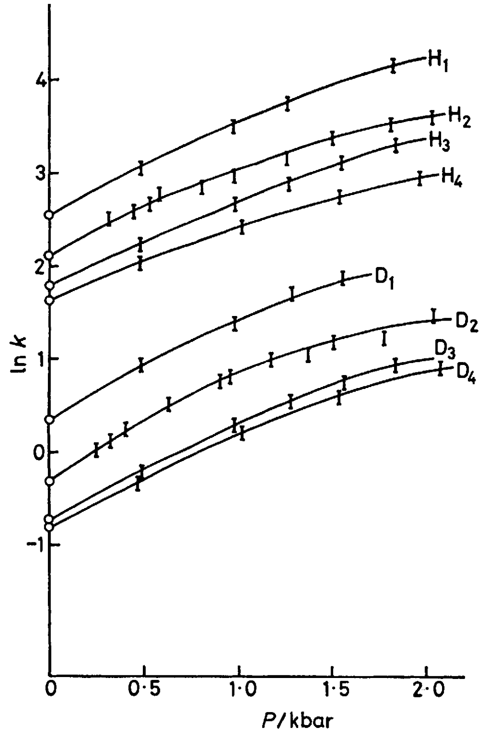

FIGURE 2 Pressure effects on rates of reaction of leuco-Crystal Violet (H and D) with chloranil: 1, 2, and 3 in acetonitrile at 40, 29, and 21 °C respectively; 4, in isobutyronitrile at 29 °C

TABLE 1

Rates of reaction of diphenyldiazomethane with benzoic acid (H,D) in dibutyl ether at 27.5 °C

P/atm	Benzoic acid 10^3k_2/ l mol^{-1} min^{-1}	Benzoic [^{2}H]acid 10^3k_2/ l mol^{-1} min^{-1}	k_H/k_D
1	40.7	9.14	4.5
200	45.5	9.95	4.6
600	53.0	11.3	4.7
800	57.3	12.3	4.7
1 090	61.4	12.9	4.7

$$\ln k_2(\mathrm{H}) = -3.194 + (5.502 \times 10^{-4})P - (1.65 \times 10^{-7})P^2$$
$$\ln k_2(\mathrm{D}) = -4.698 + (4.986 \times 10^{-4})P - (2.0 \times 10^{-7})P^2$$

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tetramethylguanidine, obtaining a value of −15 cm^3 which is clearly very similar to our result. The only other study of pressure effects in isotope effects has come from work by Palmer and Kelm [15] who have shown that there is no effect on the magnitude of k_H/k_D up to 2 kbar for many hydrogen atom transfers from phenols to the radical. All the examples studied had normal, quite small isotope effects.

TABLE 2

(a) Reaction rates of leuco-Crystal Violet with chloranil in acetonitrile

	k_2/l mol^{-1} min^{-1}		
P/bar	21.0	29.1	40.0
1	5.98	8.32	12.7
320		12.0	
460		13.0	
492	9.11		21.8
540		14.6	
589		16.1	
820		17.4	
985	14.4	19.3	33.4
1 240		23.1	
1 270		23.6	
1 280	17.9		42.6
1 505		29.4	
1 560	21.1		53.7
1 820		31.6	
1 850	24.4		
2 050		35.7	

(b) Reaction rates of [^{2}H]leuco-Crystal Violet with chloranil in acetonitrile

	k_2/l mol^{-1}min^{-1}		
P/bar	21.0	29.1	40.0
1	0.48	0.74	1.40
245		1.02	
330		1.14	
400		1.29	
490	0.78		2.53
550		1.60	
630		1.64	
850		2.17	
905		2.30	
985	1.32		4.03
1 180		2.76	
1 285	1.72		5.37
1 300		2.92	
1 370		2.97	
1 505		3.18	
1 560	2.12		6.58
1 780		3.54	
1 840	2.52		
2 050		4.31	

By contrast, activation volumes for the leuco-Crystal Violet–choranil reaction are isotope dependent, $\Delta V_0^{\ddagger}$ (H) $= -25$, $\Delta V_0^{\ddagger} = -35$ cm^3 mol^{-1} and the isotope effect diminishes from above 11 to near 8 at 2 kbar. While the data clearly show a higher activation energy for the deuterium reaction, there is insufficient precision to enable the pressure effect upon the Arrhenius parameters to be measured or the effect of pressure upon the barrier dimensions to be estimated. The very large p.k.i.e. at low pressure is attributed to a contribution to the rate from quantum mechanical tunnelling and it is significant that many such effects which are known [16] are found to occur in hydrogen transfers within highly hindered cage-like structures. In such a system it may be postulated that the motion of the atom being transferred would be relatively poorly coupled to solvent motions due to the exclusion of solvent molecules from the proximity of the reaction centre. Hence the effective mass of the hydrogen is more close to its atomic mass which is in the range for tunnelling to be significant. The rarity of reactions considered to show tunnelling may well be due to the ubiquity of the solvation effects. In our case we suggest that the effect of pressure is to force the solvent molecules into closer proximity with the reaction centre so increasing the translational coupling of motion with the hydride ion and thereby reducing the amount of tunnelling which can take place. In this connection we measured the isotope effect as a function of pressure in isobutyronitrile, a solvent with similar polar characteristics to acetonitrile but greater bulk. It was found (Table 4) that the reduction of isotope effect with pressure was slightly less rapid than with acetonitrile. It appears that, in both solvents, the isotope effect levels off at around 8 at pressures in excess of 2 kbar, that is, at a value which can be attributed to zero-point energy differences between C–H and C–D bonds. Further studies of tunnelling reactions will be needed to see whether anomalous values of ΔV are usual and can be used as a criterion for this phenomenon.

TABLE 3

Activation parameters for reaction of leuco-Crystal Violet with chloranil in acetonitrile

	H	D
E_A/kcal mol^{-1}		
1 bar	8.7 ± 0.5	10.3 ± 0.5
490	8.5	11.0
985	8.3	10.6
log A 1 bar	7.2	7.3
490	7.3	8.1
985	7.3	8.0
$\Delta V_0^{\ddagger}$/cm^3 mol^{-1}	-25 ± 2	-35 ± 2
A [equation (1)]	2.148	−0.2943
B	1.031×10^{-3}	1.476×10^{-3}
C	2×10^{-7}	3×10^{-7}
$\Delta V_0^{\ddagger}$/cm^3 mol^{-1} (in Pr^{i}CN)	−22	−29

TABLE 4

Isotope effects for the leuco-Crystal Violet–chloranil reaction

	k_H/k_D (MeCN)			k_H/k_D (Pr^{i}CN)
P/bar	21	29	40	29
0	12.3	11.2	9.1	11.5
500	11.6	9.5	8.6	10.3
1 000	10.8	8.5	8.2	9.0
1 500	10.1	8.2	7.8	8.2
2 000	9.3	8.0		(8.0)

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