Kinetic Isotope Effects in Various Solvents for the Proton-transfer Reactions of 4-Nitrophenylnitromethane with Bases

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Summary The kinetic isotope effect for the proton-transfer reactions between 4-nitrophenylnitromethane and the bases tetramethylguanidine, tri-n-butylamine, and triethylamine is markedly dependent on the solvent; for the reaction with tetramethylguanidine in toluene, exceptionally large values are found for the rate ratio at 25° ($k^{H}/k^{D} = 45 \pm 2$) and for the ratio of the Arrhenius A-factors ($A^{D}/A^{H} = 31 \pm 8$), and quantum-mechanical tunnelling is used to explain them.

4-Nitrophenylnitromethane and its deuteriated analogue react with strong bases (B) in aprotic solvents by a proton-transfer or deuteron-transfer reaction producing an ion-pair[1] (equations 1 and 2). The rates lie conveniently in

$$NO_2{\cdot}C_6H_4{\cdot}CH_2NO_2 + B \rightleftharpoons NO_2{\cdot}C_6H_4{\cdot}CHNO_2^{-}HB^{+} \tag{1}$$

$$NO_2{\cdot}C_6H_4{\cdot}CD_2NO_2 + B \rightleftharpoons NO_2{\cdot}C_6H_4{\cdot}CDNO_2^{-}DB^{+} \tag{2}$$

the stopped-flow range. The most important results are shown in the Table; a full account will be published elsewhere. The secondary isotope effect due to the second deuteron will be quite small.[2a,b]

TABLE

Kinetic isotope effect and Arrhenius parameters for the reaction of 4-nitrophenylnitromethane with bases

	Tetramethylguanidine		Tri-n-butylamine		Triethylamine	
Quantity	Toluene[a]	Dichloromethane	Toluene	Acetonitrile	Toluene	Acetonitrile
ΔH°/kcal mol^{-1}	$-10{\cdot}6 \pm 0{\cdot}1$	$-8{\cdot}7 \pm 0{\cdot}6$	$-8{\cdot}5 \pm 0{\cdot}2$	—	$-10{\cdot}2 \pm 0{\cdot}2$	—
k^{H}/k^{D} at 25°	45 ± 2	$11{\cdot}7 \pm 0{\cdot}2$	14 ± 1	$2{\cdot}2 \pm 0{\cdot}1$	$11{\cdot}0 \pm 0{\cdot}7$	$3{\cdot}1 \pm 0{\cdot}3$
E_{obs}^{H}/kcal mol^{-1}	$4{\cdot}2 \pm 0{\cdot}1$	$3{\cdot}9 \pm 0{\cdot}1$	$5{\cdot}6 \pm 0{\cdot}4$	$6{\cdot}6 \pm 0{\cdot}1$	$4{\cdot}1 \pm 0{\cdot}1$	$7{\cdot}2 \pm 0{\cdot}1$
E_{obs}^{D}-E_{obs}^{H}/kcal mol^{-1}	$4{\cdot}3 \pm 0{\cdot}2$	$1{\cdot}9 \pm 0{\cdot}2$	$2{\cdot}0 \pm 0{\cdot}8$	$0{\cdot}8 \pm 0{\cdot}2$	$2{\cdot}0 \pm 0{\cdot}5$	$1{\cdot}0 \pm 0{\cdot}2$
$\Delta S_{H}^{\ddagger}$/cal K^{-1} mol^{-1}	$31 \pm 0{\cdot}2$	$-30{\cdot}5 \pm 0{\cdot}2$	-34 ± 1	$-25{\cdot}2 \pm 0{\cdot}3$	$-37{\cdot}0 \pm 0{\cdot}2$	$-22{\cdot}1 \pm 0{\cdot}4$
A_{obs}^{D}/A_{obs}^{H}	31 ± 8	$2{\cdot}2 \pm 0{\cdot}2$	$2{\cdot}2 \pm 0{\cdot}7$	$1{\cdot}7 \pm 0{\cdot}4$	$2{\cdot}4 \pm 0{\cdot}4$	$1{\cdot}8 \pm 0{\cdot}2$
a/Å	$0{\cdot}40 \pm 0{\cdot}01$	$0{\cdot}461 \pm 0{\cdot}01$	$0{\cdot}48 \pm 0{\cdot}01$	—	$0{\cdot}50 \pm 0{\cdot}01$	—
E^{H}/kcal mol^{-1}	$8{\cdot}6 \pm 0{\cdot}1$	$4{\cdot}6 \pm 0{\cdot}1$	$6{\cdot}7 \pm 0{\cdot}1$	—	$5{\cdot}2 \pm 0{\cdot}1$	—
ν^{*}/cm^{-1}	1420					

[a] Corrected for change of density with temperature.

With tetramethylguanidine [$HN{=}C(NMe_2)_2$] as base, in toluene as solvent, the isotopic rate ratio k^{H}/k^{D} has the high value 45 ± 2. This is much larger than the maximum value of 17 that can be explained by loss of vibrational degrees of freedom in the transition state, and suggests that tunnelling is important. The importance of tunnelling is confirmed by the high value of the ratio of the Arrhenius A-factors; $A^{D}/A^{H} = 31 \pm 8$, compared with the maximum value of 2 for any model that ignores tunnelling.[2] Preliminary calculations for tunnelling through an unsymmetrical parabolic energy-barrier, taking the first four terms of Bell's equation,[2,3] give the barrier height as $E^{H} = 8{\cdot}6$ kcal mol^{-1} and the width as $2a = 0{\cdot}89$ Å. The exceptionally large effects of tunnelling are thus attributable to an unusually small apparent barrier width, compared with that calculated for most other reactions.[4a,b] (Incidentally, such effects could not be explained for this reaction in terms of solvent lag.[4b,5])

The isotope effect for this reaction is remarkably sensitive to the solvent. In dichloromethane, $k^{H}/k^{D} = 11{\cdot}4$ and $A^{D}/A^{H} = 2{\cdot}2$; both these values are much nearer the 'classical' range. Application of Bell's equation gives the preliminary values $E^{H} = 4{\cdot}6$ kcal mol^{-1} and $2a$ *ca.* $0{\cdot}9$ Å; thus the apparent barrier height is less than in toluene and the apparent width somewhat greater. Sensitivity to solvent is also shown in the results for tri-n-butylamine and triethylamine. For each of these bases, on changing the solvent from acetonitrile to toluene the isotopic rate ratio rises to over 10, and A^{D}/A^{H} to over 2.

It appears that these ratios are determined not only by the energy-barrier for the motion of the proton alone, which would be independent of solvent, but by solvation changes also. Any motion of heavier atoms accompanying the motion of the proton will reduce the apparent effects of tunnelling, because it will increase the effective mass, to which the tunnel correction is very sensitive. If the solvation changes accompanying the formation of the transition state involve the rotation of solvent molecules, they will reduce the values of k^{H}/k^{D} and A^{D}/A^{H}. This may well be the case for dipolar molecules such as CH_2Cl_2 and CH_3CN, which will rotate in the field of the incipient ion-pair. In toluene, it is conceivable that this field leads mainly not to rotation but to polarisation of the solvent molecules, involving motion only of electrons; this would explain why the largest effects are found for toluene. The unusually large isotope effects recently observed for hydrogen atom-transfer reactions[6] may likewise be connected with the small solvation changes in these reactions.

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