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TEMPERATURE DEPENDENCE OF THE DEUTERIUM ISOTOPE EFFECT IN THE DEPROTONATION OF SOME NITROALKANES BY ANIONIC BASES

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The temperature dependences of rates and deuterium isotope effects were determined for the deprotonation of 1-phenyl-1-nitroethane (1), its analogue 1-*d*, 1-phenyl-2-nitropropane (2) and its analogue 2-*d* by methoxide in methanol, ethoxide in ethanol, hydroxide/methoxide in 50% (v/v) methanol–water and hydroxide in water. The isotope effects varied little with substrate or solvent–base combination. k_H/k_D at 30 °C was between 6·0 and 7·1 in all cases. The temperature dependences varied considerably [$A_{aH}/A_{aD} = 0\cdot14$–$1\cdot35$ and $E_{aD} - E_{aH}$ 0·95–2·29 kcal mol^{-1} (1 kcal = 4·184 kJ)]. A_{aH}/A_{aD} was lower with 1-phenyl-1-nitroethane than with 1-phenyl-2-nitropropane, but there was no consistent variation with solvent/base.

INTRODUCTION

We have been interested for some time in the role of tunneling in proton transfer processes. The most common method of detecting tunneling has been the temperature dependence of deuterium and tritium isotope effects. In the presence of tunneling the temperature dependence of the isotope effect is unusually steep, leading to low ratios of apparent Arrhenius pre-exponential factors, A_H/A_D or A_H/A_T. In the absence of tunneling, these ratios are expected to be within a range of *ca* 0·7–1·3.[1]

We have applied this test to elimination reactions proceeding by the *E*2 mechanism, and have found tunneling to be ubiquitous.[2–4] The observed temperature dependences can be fitted to the Bell equation for tunneling to give an estimate of the tunnel correction, Q_{tH}/Q_{tD} or Q_{tH}/Q_{tT}.[5] The range of tunnel corrections is disappointingly narrow, ranging from 1·0 for no tunnel correction up to 2·1 for the largest correction for deuterium transfer and 2·5 for the largest correction for tritium transfer. There were no obvious trends with reactant structure or solvent–base combination.

We decided to seek systems where a wider range of tunnel corrections might be observed so as to obtain a clearer picture of structural and environmental effects on tunneling. Deprotonation of 4-nitrophenylnitromethane in aprotic solvents was reported some time ago to give unusually large deuterium isotope effects.[6–8] Later investigations revealed that the isotope effects were apparently not as large as previously reported, but they were still larger than most values in the literature.[9–12] Likewise, deprotonation of 2-nitropropane by 2,6-disubstituted pyridines was found to occur with unusually large deuterium and tritium isotope effects.[13,14] Later work showed that there was also an unusually large 2-^{14}C isotope effect in the reaction.[15] Deprotonation of 1-aryl-1-nitroethanes and 1-aryl-2-nitropropanes by a variety of bases was found to be conveniently measurable.[16,17] Deuterium isotope effects at 25 °C for the former substrate were not unusually large but substantial (6·5–10·3).[18] We therefore concluded that this was a promising area to explore in our efforts to elucidate the causes of tunneling.

RESULTS AND DISCUSSION

We began our exploration by determining the effect of solvent–base combination and temperature on the rates of deprotonation of 1-phenyl-1-nitroethane (**1**) and 1-phenyl-2-nitropropane (**2**) and also **1**-*d* and **2**-*d*. The syntheses were straightforward and are described in the Experimental section. The rate constants and isotope effects are recorded in Tables 1 and 2. The effect of

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solvent on rate shows similar patterns for **1** and **2**, with ethanol the fastest and methanol the slowest, although the total range at 30 °C is only 10·7 for the former and 14·8 for the latter substrate. Again at 30 °C, **1** reacts consistently faster than **2**, but the **1**/**2** rate ratio only varies between 3·1 and 6·8. The k_H/k_D values are also relatively insensitive to the solvent–base combination and substrate structure, remaining within the range 6·0–7·1 at 30 °C in all cases. They are higher for **1** than for **2**.

The activation parameters (Tables 3 and 4) do not shed much light on the causes of these variations. $\Delta H^{\neq}$ is high and $\Delta S^{\neq}$ least negative in methanol, whereas $\Delta H^{\neq}$ is lowest in ethanol. The consistently negative $\Delta S^{\neq}$ values could arise simply from the loss of vibrational and rotational degrees of freedom of a bimolecular reaction, although changes in internal structure and in solvation between reactant and transition state undoubtedly also contribute. It is surprising that the reactivity should be lowest in methanol, although the differences between methanol on the one hand and water or methanol–water on the other are not large.

The Arrhenius parameters (Tables 3 and 4) suggest significant tunneling in three of four solvents for **1**, but only in ethanol for **2**. Thus our hope that tunneling might be sufficiently pronounced for the effects of solvent–base combination and reactant to become more easily interpretable has been disappointed. The only generalizations one can draw are that tunneling is insignificant in methanol for both substrates, and consistently greater for **1** than for **2**. Judging from these results, tunneling is less significant for the deprotonation of aliphatic nitro compounds than it is in *E*2 reactions.[2–4] It would appear that heavy-atom motion contributes more to the reaction coordinate motion in

Table 1. Rate constants for the deprotonation of $PhCL(NO_2)CH_3$[a]

Solvent[b]	Temperature (°C)	k_2^H(l mol^{-1} s^{-1})	k_2^D(l mol^{-1} s^{-1})	k_H/k_D
MeOH	0·0	0·3545 ± 0·0026[c]	0·0415 ± 0·0009[c]	8·54
	10·0	0·9406 ± 0·0114[c]	0·1156 ± 0·0020[c]	8·14
	10·0	1·072 ± 0·009[d]	0·1280 ± 0·0018[d]	8·38
	20·0	2·413 ± 0·039[c]	0·3326 ± 0·0040[c]	7·25
	20·0	2·702 ± 0·028[d]	0·4087 ± 0·0160[d]	6·61
	30·0	5·898 ± 0·186[c]	0·9963 ± 0·0122[c]	5·92
	30·0	6·146 ± 0·084[e]	0·8824 ± 0·0178[e]	6·96
	40·0	14·97 ± 0·361[c]	2·362 ± 0·066[c]	6·34
	40·0	13·92 ± 0·325[e]	2·041 ± 0·020[e]	6·82
	50·0	29·72 ± 0·265[e]	4·708 ± 0·078[e]	6·31
EtOH	0·0	5·619 ± 0·020[f]	0·5982 ± 0·0081	9·39
	10·0	13·63 ± 0·03[f]	1·585 ± 0·012[f]	8·60
	20·0	30·67 ± 0·50[f]	3·924 ± 0·011[f]	7·82
	30·0	64·16 ± 0·72[f]	9·579 ± 0·073[f]	6·70
	40·0	114·2 ± 1·6[f]	21·18 ± 0·17[f]	5·39
$MeOH–H_2O$[g]	0·0	1·063 ± 0·005[c]	0·1182 ± 0·0007[c]	8·99
	10·0	2·581 ± 0·011[c]	0·3161 ± 0·0009[c]	8·16
	20·0	5·938 ± 0·009[c]	0·7992 ± 0·0017[c]	7·43
	30·0	12·34 ± 0·04[c]	1·831 ± 0·002[c]	6·74
	40·0	25·62 ± 0·15[c]	4·069 ± 0·040	6·29
H_2O	5·0	1·556 ± 0·006[h]	0·1686 ± 0·0011[h]	9·23
	15·0	3·519 ± 0·030[h]	0·4447 ± 0·0016[h]	7·91
	25·0	7·789 ± 0·086[i]	1·029 ± 0·017[i]	7·58
	35·0	15·88 ± 0·18[i]	2·406 ± 0·027[i]	6·60
	45·0	28·69 ± 0·09[j]	4·950 ± 0·043[j]	5·79

[a] Each rate constant is the average of five runs; L = H or D; substrate concentration = 0·75 × 10^{-4} M.

[b] The base is the sodium salt of the conjugate base of the solvent (RONa, or in the mixed solvent NaOH–MeONa).

[c] Base concentration = 0·2225 M.

[d] Base concentration = 0·166 M.

[e] Base concentration = 0·083 M.

[f] Base concentration = 0·075 M.

[g] 50% (v/v).

[h] Base concentration = 0·3754 M.

[i] Base concentration = 0·2252 M.

[j] Base concentration = 0·1501 M.

Table 2. Rate constants for the deprotonation of $PhCH_2CL(NO_2)CH_3$[a]

Solvent[b]	Temperature (°C)	k_2^H(1 mol^{-1} s^{-1})	k_2^D(1 mol^{-1} s^{-1})	k_H/k_D
MeOH	10·0	0·2091 ± 0·0036[c]	0·0268 ± 0·0020[d]	7·80
	20·0	0·5589 ± 0·0134[c]	0·0750 ± 0·0010[d]	7·45
	30·0	1·410 ± 0·005[e]	0·1995 ± 0·0037[d]	7·07
	40·0	3·254 ± 0·051[e]	0·4860 ± 0·0138[d]	6·69
	50·0	6·521 ± 0·318[f]	1·073 ± 0·0139[e]	6·08
EtOH	0·0	1·772 ± 0·007[g]	0·2082 ± 0·0014[g]	8·51
	10·0	4·351 ± 0·052[g]	0·5551 ± 0·0036[g]	7·84
	20·0	9·813 ± 0·215[g]	1·419 ± 0·046[g]	6·91
	30·0	20·80 ± 0·20[h]	3·227 ± 0·007[h]	6·44
	40·0	42·46 ± 0·18[h]	6·969 ± 0·060[h]	6·09
$MeOH-H_2O$[m]	10·0	0·4075 ± 0·0026[i]	0·0554 ± 0·0009[i]	7·36
	20·0	1·046 ± 0·0035[i]	0·1495 ± 0·0036[i]	7·00
	30·7	2·514 ± 0·016[i]	0·3893 ± 0·0025[i]	6·46
	40·0	4·842 ± 0·191[j]	0·7672 ± 0·0110[j]	6·31
	50·0	10·55 ± 0·02[j]	1·768 ± 0·006[j]	5·97
H_2O	10·0	0·2909 ± 0·0017[k]	0·0437 ± 0·0010[k]	6·65
	20·0	0·7363 ± 0·0055[k]	0·1163 ± 0·0016[l]	6·33
	30·0	1·736 ± 0·018[k]	0·2904 ± 0·0290[k]	5·98
	40·0	3·989 ± 0·010[k]	0·6962 ± 0·0115[k]	5·73
	50·0	8·075 ± 0·054[k]	1·571 ± 0·017[k]	5·14

[a] Each rate constant is the average of five runs; L = H or D; substrate concentration = $1·5 \times 10^{-4}$ M.
[b] The base is the sodium salt of the conjugate base of the solvent (RONa, or in the mixed solvent NaOH–MeONa).
[c] Base concentration = 0·2149 M.
[d] Base concentration = 0·2315 M.
[e] Base concentration = 0·178 M.
[f] Base concentration = 0·167 M.
[g] Base concentration = 0·174 M.
[h] Base concentration = 0·087 M.
[i] Base concentration = 0·2595 M.
[j] Base concentration = 0·1038 M.
[k] Base concentration = 0·3114 M.
[l] Base concentration = 0·2955 M.
[m] 50% (v/v).

Table 3. Activation parameters for the deprotonation of $PhCL(NO_2)CH_3$[a]

	Solvent			
Parameter	MeOH	EtOH	$MeOH-H_2O$	H_2O
$A_{aH} \times 10^{11}$	10·11 ± 0·17	1·225 ± 0·614	0·668 ± 0·086	0·224 ± 0·074
$A_{aD} \times 10^{11}$	10·10 ± 0·39	8·489 ± 1·153	1·265 ± 0·127	0·828 ± 0·185
A_{aH}/A_{aD}	1·00 ± 0·39	0·144 ± 0·080	0·528 ± 0·028	0·270 ± 0·081
E_{aH}[b]	15·55 ± 0·10	12·89 ± 0·29	13·48 ± 0·07	12·91 ± 0·19
E_{aD}[b]	16·71 ± 0·23	15·18 ± 0·08	15·02 ± 0·06	14·86 ± 0·13
k_H/k_D (20 °C)[c]	7·17	7·31	7·43	7·68
Q_{tH}/Q_{tD} (20 °C)[c,d]	–	2·21 ± 0·28	1·49 ± 0·03	1·95 ± 0·18
$(k_H/k_D)_{sc}$ (20 °C)[c]	7·17	3·30	4·99	3·93
$\Delta H_H^{\neq}$[b]	14·96 ± 0·10	12·31 ± 0·29	12·90 ± 0·07	12·33 ± 0·19
$\Delta S_H^{\neq}$[e]	−5·60 ± 0·34	−9·79 ± 1·00	−10·99 ± 0·25	−13·17 ± 0·66

[a] From linear regression fits of experimental rate constants to the Arrhenius equation.
[b] kcal mol^{-1}.
[c] Calculated from the Arrhenius parameters.
[d] Error limits calculated from the error in A_{aH}/A_{aD} by standard methods for propagation of error.
[e] cal mol^{-1} K^{-1}.

Table 4. Activation parameters for the deprotonation of $PhCH_2CL(NO_2)CH_3$[a]

Parameter	Solvent			
	MeOH	EtOH	MeOH–H_2O	H_2O
$A_{aH} \times 10^{11}$	3·014 ± 1·282	1·076 ± 0·105	0·826 ± 0·284	1·508 ± 0·299
$A_{aD} \times 10^{11}$	2·650 ± 0·590	1·909 ± 0·374	0·613 ± 0·245	1·617 ± 0·117
A_{aH}/A_{aD}	1·137 ± 0·237	0·564 ± 0·092	1·347 ± 0·142	0·933 ± 0·213
E_{aH}	15·74 ± 0·25	13·46 ± 0·06	14·63 ± 0·21	15·16 ± 0·12
E_{aD}	16·83 ± 0·13	14·94 ± 0·11	15·58 ± 0·24	16·28 ± 0·04
k_H/k_D (20 °C)[c]	6·24	7·16	4·93	6·38
Q_{tH}/Q_{tD} (20 °C)[c,d]	–	1·45 ± 0·11	–	1·07 ± 0·21
$(k_H/k_D)_{sc}$ (20 °C)[c]	6·24	4·94	4·93	5·96
$\Delta H^{\neq}_{H}$[b]	15·15 ± 0·25	14·35 ± 0·11	15·00 ± 0·24	15·69 ± 0·04
$\Delta S_H^{\neq}$[c]	−8·00 ± 0·84	−10·05 ± 0·19	−10·57 ± 0·68	−9·37 ± 0·39

[a–e] See Table 3.

these deprotonations than it does in *E*2 reactions. There is considerable evidence that heavy-atom reorganization is less advanced than proton transfer in the transition states for deprotonation of aliphatic nitro compounds.[16–20] The present results suggest that there is enough reorganization to increase significantly the effective mass along the reaction coordinate and thereby attenuate tunneling. The same conclusion was reached on the basis of sizable carbon isotope effects at the 2-position in the deprotonation of 2-nitropropane by pyridine bases.[15] Calculations showed that carbon isotope effects of the observed magnitude resulted only when motion of the carbon atom was coupled with motion of the transferred proton.

A referee suggested that kinetic complexity might be responsible for the mixed results on tunneling. For example, Bordwell and Boyle[18] proposed that the reaction has two steps, the first the deprotonation to a pyramidal carbanion and the second a rearrangement to a planar carbanion. One can think of other versions of kinetic complexity, such as the formation of a complex between the reactants followed by deprotonation. In any event, partial rate control by each of two successive steps could in principle explain the puzzling variation in tunnel corrections. We do not consider such an explanation very likely. Incursion of partial rate control by a step insensitive to isotopic substitution should depress not only the tunnel correction but also the isotope effect. Isotope effects are slightly higher for **1** than for **2**. The comparison that should be made, however, is between the semi-classical isotope effects [without tunneling, $(k_H/k_D)_{SC}$ in Tables 3 and 4]. Once the tunnel correction is factored out, the semi-classical isotope effects are larger in cases where there is no tunnel correction than in cases where there is.

EXPERIMENTAL

Boiling points are uncorrected. NMR spectra were measured on a General Electric QE-300 multinuclear spectrometer. Ultraviolet absorbances were recorded on a Varian DMS 200 UV–visible spectrophotometer.

Distilled water was redistilled. Dimethylformamide was dried over KOH at room temperature for several hours, decanted and distilled at reduced pressure. Ethanol was refluxed over magnesium and a catalytic amount of iodine for several hours and distilled. Methanol was dried in the same way. The alkoxide bases were obtained by dissolving the clean metal in the appropriate alcohol under nitrogen. Alkoxide concentrations were determined by titration with standard sulfuric acid to the bromthymol blue end-point.

1-Phenylnitroethane. This was prepared from 1-phenylethyl bromide by the procedure of Kornblum *et al.*[21] except that toluene was used instead of benzene in the work-up. A 40% yield resulted of product of b.p. 51–52 °C (0·025 mmHg) [lit.[21] b.p. 61–62 °C (1 mmHg)]; ^{1}H NMR, $\delta(CDCl_3)$ 7·40–7·52 (m, 5H, aromatic), 5·63 (q, 1H, CH), 1·91 (d, 3H, CH_3).

*1-Phenyl-1-*d*-nitroethane.* This was prepared from 1-phenylnitroethane by repeated exchanges with deuterium oxide in the presence of tetra-*n*-butylammonium bromide and potassium carbonate. The mixture containing 1-phenylnitroethane (10·15 g, 0·067 mol), D_2O (4·0 g, 0·2 mol), potassium carbonate (1·5 g, 0·005 mol) and tetra-*n*-butylammonium bromide (1·5 g, 0.005 mol) was stirred under nitrogen for 10–12 h. It was extracted with methylene chloride (3 × 5 ml) and the extract dried over sodium sulfate. The solvent was removed first with a Rotovap and finally with an oil pump. The ^{1}H NMR spectrum indicated *ca* 50% deuteration at the 1-position. The process was repeated 4–5 times with fresh deuterium oxide and potassium carbonate (the phase-transfer catalyst remains in the organic layer and need not be replenished). The final product was purified by distillation. A 65% yield was obtained of material of b.p.

51–52 °C (0·025 mmHg), containing 1% ^{1}H at the 1-position by ^{1}H NMR.

1-Phenylpropan-2-ol. This was prepared from 1-phenylacetaldehyde by the procedure of Smith and Amin[22] in a yield of 95%, b.p. 48–50 °C (0·27 mmHg) [lit.[23a] b.p. 219–221 °C (760 mmHg)]; ^{1}H NMR, δ($CDCl_3$) 7·15–7·45 (m, 5H, aromatic), 3·97–4·12 (m, 1H, CH), 2·65–2·85 (m, 2H, CH_2), 1·7 (broad s, 1H, OH), 1·3 (d, 3H, CH_3).

2-Bromo-1-phenylpropane. To 13·6 g (0·1 mol) of 1-phenylpropan-2-ol were added dropwise with constant stirring 13·5 g (0·05 mol) of phosphorus tribromide over 0·5 h, followed by 2 h heating on a steam-bath. The resulting mixture was cautiously poured over 50 g of ice, the organic layer separated and the aqueous layer further extracted with 3 × 25 ml of diethylether. The combined extracts were washed with 3 × 25 ml of 10% sodium carbonate solution, dried over sodium sulfate and the solvent was removed with a Rotovap. The residue was distilled under reduced pressure to obtain a colorless liquid in 88·5% yield, b.p. 39–41 °C (0·15 mmHg) [lit.[23b] b.p. 107–109 °C (16 mmHg)]; ^{1}H NMR, δ($CDCl_3$) 7·2–7.5 (m, 5H, aromatic), 4·25–4·42 (m, 1H, CH), 3·05–3·35 (m, 2H, CH_2), 1·75 (d, 3H, CH_3).

2-Nitro-1-phenylpropane. In a 500 ml three-necked flask equipped with a magnetic stirrer were placed 22·7 g (0·38 mol) of urea (dried, at 110 °C) and 16·7 g (0·24 mol) of sodium nitrite in 250 ml of dimethylformamide under nitrogen. The solution was heated to 50 °C and 2-bromo-1-phenylpropane (33·2 g, 0·17 mol) rapidly added to the stirred solution. The reaction mixture was protected from light and the stirring continued for 12 h at 50 °C. It was then poured into 600 ml of ice–water and extracted with light petroleum (b.p. 35–60 °C) (5 × 100 ml). A solid which formed between the layers was removed by filtration of the organic layer. The extracts were combined, dried over sodium sulfate and concentrated with a Rotovap and an oil pump. The residue (13–15 g) was added to 50 ml of 20% NaOH solution, heated at 50–55 °C for 0·5 h and cooled to room temperature. The mixture was extracted with light petroleum (5 × 50 ml) and the aqueous layer neutralized by slow addition of glacial acetic acid, followed by extraction with light petroleum (5 × 50 ml). The light petroleum extracts were dried over sodium sulfate and concentrated with a Rotovap and an oil pump. The crude product was purified by column chromatography on silica gel (1 : 5 diethylether–hexane as eluent) and then distilled under reduced pressure. A 20% yield was obtained, b.p. 71–72 °C (0·4 mmHg) [lit.[24] b.p. 103–104 °C (4 mmHg)]; ^{1}H NMR, δ($CDCl_3$) 7·1–7·4 (m, 5H, aromatic), 4·7–4·9 (m, 1H, CH), 2·95–3·45 (m, 2H, CH_2), 1·6 (d, 3H, CH_3).

*2-Nitro-2-*d*-1-phenylpropane.* This was prepared from 2-nitro-1-phenylpropane by repeated exchanges with deuterium oxide in the same way as described for 1-phenyl-1-*d*-nitroethane in 68–70% yield. The product contained 3·5% ^{1}H at the 2-position by ^{1}H NMR analysis.

Kinetic procedures. The rates of reaction of the nitroalkanes with sodium ethoxide in ethanol, sodium methoxide in methanol, sodium hydroxide in water and sodium hydroxide in 50% (v/v) methanol–water were determined spectrophotometrically on a Hi-Tech SF-3L stopped-flow spectrophotometer interfaced to a Macintosh II computer. The nitronate ions have characteristic UV spectra in different solvents with λ_{max} 280–305 nm for 1-phenyl-1-ethanenitronate and 230–240 nm for 1-phenyl-2-propanenitronate. In the latter case, a wavelength of 245 nm was used for methanol, which absorbed significantly in the 230–240 nm region. All other reactions were followed at the λ_{max} of the anion. The molar absorptivities of the nitronates ranged from $0{\cdot}84 \times 10^4$ to $1{\cdot}36 \times 10^4$ l mol^{-1} cm^{-1} in the various solvents. The reactions were carried out under pseudo-first-order conditions with nitroalkane concentrations of *ca* $0{\cdot}75 \times 10^{-4}$ M for 1-phenylnitroethane and $1{\cdot}5 \times 10^{-4}$ M for 2-nitro-1-phenylpropane. The bases were used at concentrations several hundred times greater than those of the nitroalkanes. Data acquisition and treatment used LabView2 (National Instruments, Austin, TX, USA) and Igor (Wave Metrics, Lake Oswego, OR, USA) software. Data through four half lives were used in evaluation of the rate constants. All reactions were shown to be second order by varying the concentration of the base at a constant concentration of substrate. No consistent variation in either rate or isotope effect was found (compare entries 2–3, 4–5, 6–7 and 8–9 in Table 1, where the rates decrease with increasing base concentration in five cases and increase in three others), although differences were larger than the error limits for runs at a constant concentration. In order to minimize any uncertainties from these variations, isotope effects were calculated only from k_H and k_D values determined at common concentrations.

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REFERENCES

1. L. Melander and W. H. Saunders, Jr, *Reaction Rates of Isotopic Molecules*, pp. 75, 144–147. Wiley–Interscience, New York (1980).

2. S. B. Kaldor and W. H. Saunders, Jr, *J. Am. Chem. Soc.* **101**, 7594–7599 (1979).
3. S. B. Kaldor, M. E. Fredenburg and W. H. Saunders, Jr, *J. Am. Chem. Soc.* **102**, 6296–6299 (1980).
4. D. J. Miller and W. H. Saunders Jr, *J. Org. Chem.* **46**, 4247–4252 (1981).
5. L. Melander and W. H. Saunders, Jr, *Reaction Rates of Isotopic Molecules*, pp. 147–151. Wiley–Interscience, New York (1980).
6. E. F. Caldin and C. J. Wilson, *Faraday Symp. Chem. Soc.* **10**, 121–131 (1975).
7. E. F. Caldin and S. Mateo, *J. Chem. Soc., Faraday Trans. 1* **71**, 1876–1904 (1975).
8. E. F. Caldin and S. Mateo, *J. Chem. Soc., Faraday Trans. 1* **72**, 112–121 (1976).
9. J. H. Blanch and O. Rogne, *J. Chem. Soc., Faraday Trans. 1* **74**, 1254–1262 (1978).
10. I. Heggen, J. Lindstrøm and O. Rogne, *J. Chem. Soc., Faraday Trans. 1* **74**, 1263–1267 (1978).
11. O. Rogne, *Acta Chem. Scand., Ser. A* **32**, 559–563 (1978).
12. A. J. Kresge and M. F. Powell, *J. Phys. Org. Chem.* **3**, 55–61 (1990).
13. E. S. Lewis and L. H. Funderburk, *J. Am. Chem. Soc.* **89**, 2322–2327 (1967).
14. E. S. Lewis and J. K. Robinson, *J. Am. Chem. Soc.* **90**, 4337–4344 (1968).
15. J. C. Wilson, I. Källsson and W. H. Saunders, Jr, *J. Am. Chem. Soc.* **102**, 4780–4784 (1980).
16. F. G. Bordwell, W. J. Boyle, Jr, and K. C. Yee, *J. Am. Chem. Soc.* **92**, 5926–5932 (1970).
17. F. G. Bordwell and W. J. Boyle, Jr, *J. Am. Chem. Soc.* **94**, 3907–3911 (1972).
18. F. G. Bordwell and W. J. Boyle, Jr, *J. Am. Chem. Soc.* **97**, 3447–3452 (1975).
19. A. J. Kresge, *Chem. Soc. Rev.* **2**, 475–503 (1973).
20. W. J. Albery, C. F. Bernasconi and A. J. Kresge, *J. Phys. Org. Chem.* **1**, 29–31 (1988).
21. N. Kornblum, W. D. Gurowitz, H. O. Larson and D. E. Hardies, *J. Am. Chem. Soc.* **82**, 3099–3102 (1960).
22. P. J. Smith and M. Amin, *Can. J. Chem.* **67**, 1457–1467 (1989).
23. *Aldrich Chemical Catalog 1990–91*, (a) p. 1045; (b) p. 213. Aldrich Chemical, Milwaukee, WI (1990–91).
24. R. T. Gilsdorf and F. F. Nord, *J. Am. Chem. Soc.* **74**, 1837 (1952).