Proton Abstraction from Bis-(2,4-dinitrophenyl)methane by Methoxide Ion

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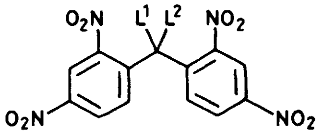
Rate constants for hydrogen or deuterium abstraction from bis-(2,4-dinitrophenyl)methane by methoxide ion have been determined in methanol, methanol–dimethyl sulphoxide, and deuteriated methanol solutions, together with the temperature variation of proton abstraction and carbanion protonation for the hydrogen-containing substrate in methanol. Isotope and solvent effects confirm the rate-limiting proton transfer.

The relative acidities of carbon acids have been studied extensively in recent years in efforts to rationalize and quantify the influence of substituents upon carbanion stabilities.[1] For such studies, arylmethanes bearing nitro groups upon the exocyclic and/or *ortho*-, *para*-carbon atoms have been chosen by various authors because of the facility with which such molecules can delocalize a negative charge. The general insolubility of arylalkanes in water has resulted in the majority of studies of their acidity being carried out in alcoholic or alcoholic–dipolar aprotic media, in which nucleophilic attack by the lyate base upon a ring carbon atom to yield a Meisenheimer complex may also occur.[2] Rates of both base and nucleophilic attack on suitably substituted arylmethanes have therefore been measured in various solvents, and their values discussed in terms of molecular structure, base strengths, isotopic substitution, ease of oxidation, proton tunnelling, solvent effects, *etc.*

There are, however, some difficulties in attempting to compare data for carbanion formation from different nitro-substituted aromatics, owing to the variety of solvent systems and bases used. Studies in a single solvent, or overlapping studies in mixed solvent systems, are desirable to allow direct comparisons of acid strengths. Various studies of proton abstraction from, or nucleophilic addition to, nitroaromatics in methanol–dimethyl sulphoxide (DMSO) solutions have revealed that these molecules exhibit identical, or closely similar, behaviour as a function of solvent composition.[2-9] This should facilitate comparisons of acid strengths between molecules and we have therefore measured the acidity of bis-(2,4-dinitrophenyl)methane (I) in methanol and methanol–DMSO mixtures for comparison with some other nitroaromatics. In addition we have measured kinetic and solvent isotope effects for proton abstraction and carbanion reprotonation of (I) in methanol, together with the corresponding thermodynamic parameters, and report here these and related results. The value of solvent-effect studies in such systems is confirmed.

Experimental

Materials.—Compound (**Ia**) was synthesized according to the standard procedure, recrystallized at least twice from acetic acid, and dried carefully before use, m.p. 182 °C.[10]

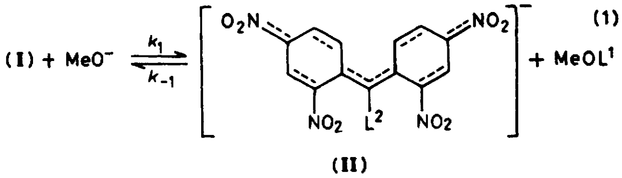


(**Ia**) $L^1 = L^2 = H$
(**Ib**) $L^1 = L^2 = D$
(**III**) $L^1 = H, L^2 = D$

Compound (**Ib**) was prepared from (**Ia**) by means of two successive base-catalysed exchanges at 80 °C using a two-phase system (benzene–D_2O) with dicyclohexyl-18-crown-6 as the transfer reagent. Quenching with deuterium chloride followed by extraction and recrystallization from benzene gave the desired product, m.p. 182 °C. High-resolution ^1H n.m.r. showed no trace of remaining exocyclic hydrogen atoms.

Solutions of methanolic potassium methoxide, in DMSO where required, were prepared as previously described using [^{2}H]methanol where appropriate.[5,7]

Rate Measurements.—Kinetic studies were carried out using a Durrum stopped-flow spectrophotometer fitted with a thermostatted cell compartment (±0.5 °C). All runs were performed under first-order conditions, with a substrate concentration of *ca.* 3×10^{-5}M and base concentrations in the range 10^{-3}—2×10^{-1}M. For proton abstraction from (**I**) and reprotonation of the generated carbanion (**II**),‡ according to equation (1), the observed first-order rate constant will be given by equation (2), where k_1 is the second-order rate constant for proton abstraction and k_{-1} is the first-order rate constant for carbanion reprotonation. Plots of $k_{obs.}$ *versus* base concentration were linear and, from these, values of k_1 and k_{-1} were determined, and hence equilibrium constants $K(=k_1/k_{-1})$ calculated. Rate constants are considered accurate to ±3%.



(1)

(**II**)

$$k_{obs.} = k_1[\text{Base}] + k_{-1} \quad (2)$$

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‡ The designation of (**II**) as a delocalized carbanion is not intended to preclude its initial formation as a charge-localized species.

Results

Rate Constants.—Proton-transfer rates from (**Ia**) to methoxide ion in methanol at various temperatures, together with the corresponding rates of reprotonation of the carbanion (**IIa**) by methanol, are shown in Table 1. Derived activation enthalpies and entropies, with the corresponding equilibrium values, are also shown in Table 1. From the values of k_1 and k_{-1} at 25 °C a value for the pK_a^{MeOH} of (**Ia**) in methanol may be derived from equation (3), assuming $pK_S = 16.7$ for methanol.

$$pK_a^{MeOH} = pK_S - \log_{10}k_1/k_{-1} \qquad (3)$$

In Table 2 are shown values of k_1 and k_{-1} (where measurement was possible) for reactions of (**Ia**) with methoxide ion in methanol–DMSO mixtures, and in [^{2}H]methanol solutions to yield solvent isotope effects. Corresponding values for measurements with (**Ib**) in methanol and 20% DMSO–methanol solutions are also shown in this Table, from which primary kinetic hydrogen isotope effects upon proton abstraction may be determined.

For reactions of (**Ia**) in [^{2}H]methanol the equilibrium constants of Table 2 refer to the 'pseudo-equilibrium' shown in equations (4) and (5). The number of exchangeable deuterium

$$(\mathbf{Ia}) + \text{MeO}^- \xrightarrow[\text{MeOD}]{k_1} (\mathbf{IIa}) + \text{MeOH} \xrightarrow[\text{MeOD}]{k_1} (\mathbf{III}) + \text{MeO}^- \qquad (4)$$

$$K' = k_1/k_{-1} \qquad (5)$$

atoms of the solvent is in such vast excess over the hydrogen atoms abstracted from (**Ia**) that re-attachment of hydrogen to (**IIa**) can be ignored. [Even in the event that proton abstraction from (**Ia**) leads to an initial sp^3-hybridized carbanion in which the exocyclic carbon atom is hydrogen-bonded to, or 'solvated' by the generated methanol molecules, the relative stability of (**IIa**) and the normal exchange of solvent molecules should lead to the deuteriated product (**III**).] Proton abstraction from (**III**) should occur at a lower rate than from (**Ia**) by the secondary hydrogen isotope effect of the deuterium atom, and considerably faster than deuterium abstraction. Such secondary isotope effects are small, but the stopped-flow method should be sufficiently sensitive to detect any interference by such an 'exchange reaction'. However, no deviations from first-order kinetic plots were experimentally observed,[11] and the solvent isotope effects obtained from the data of Table 2 are consistent with those reported by numerous authors.

Table 1. Rate constants and derived enthalpies and entropies for reaction of bis-(2,4-dinitrophenyl)methane with methoxide ion in methanol[a]

Temp. (°C)	15	20	25	30	36
k_1/dm^3 mol^{-1} s^{-1}	14.7	26.2	35.6	51.3	82.5
k_{-1}/s^{-1}	0.51_5	0.73	1.00	1.40	1.92
K_1/dm^3 mol^{-1}	28.5	35.9	35.4	36.6	43.2

$\Delta H_1^{\neq}$ 54.7 kJ mol^{-1}; $\Delta H_{-1}^{\neq}$ 46.5 kJ mol^{-1}; ΔH° 8.2 kJ mol^{-1}; $\Delta S_1^{\neq}$ -30.7 J mol^{-1} K^{-1}; $\Delta S_{-1}^{\neq}$ -91.0 J mol^{-1} K^{-1}; ΔS° 60.3 J mol^{-1} K^{-1}.

[a] Estimated errors: rate constants ±3%; ΔH values ±1.5 kJ mol^{-1}; ΔS values ±5 J mol^{-1} K^{-1}; $K_1 = k_1/k_{-1}$.

Discussion

p*K Values.*—Because of the limited solubility of most organic compounds in water, various 'p*K*' scales have been determined in aqueous mixtures of organic solvents (*e.g.* sulpholane, dimethyl sulphoxide) to determine relative acidities of carbon acids (in particular), and their relationship to the pK_a scale discussed.[12] In many cases, p*K* values derived in aqueous–organic solvent mixtures can be easily related to the pK_a values.

The influence of α-phenyl substitution upon the acidities of methanes and ethanes bearing electron-withdrawing groups was discussed recently by Bordwell *et al.* in terms of charge delocalization by resonance, and the effects of 'resonance saturation'.[13] This latter concept was introduced to account for the attenuation of the acidifying effect of a substituent by existing charge delocalization. Similar consideration of the data of Table 3 allows an estimation of the $pK_a^{H_2O}$ of (**I**) to be made, for comparison with the pK_a^{MeOH} value derived from the data of Table 1.

Thus, assuming that the replacement of an α-hydrogen of 4-nitrotoluene by a phenyl group will increase the acidity by *ca.* 2 p*K* units, as has been shown for various α-phenyl-substituted carbon acids,[13] a p*K* of 18.4 may be estimated for 4-nitrodiphenylmethane. The influence of an *o*-nitro group may then be calculated as $\Delta pK_{o\text{-NO}_2}$ *ca.* -1 from the p*K* difference between 2,4′-dinitrodiphenylmethane and 4-nitrodiphenylmethane, leading to an estimated $pK_a^{H_2O}$ for (I) given by $pK_a^{H_2O} = pK_{4,4'\text{-dinitrodiphenylmethane}} + 2\Delta pK_{o\text{-NO}_2}$ *ca.* 13.8. The data of Table 1 at 25 °C yield a value of $pK_{a(\mathrm{I})}^{MeOH} = 15.15$ which would suggest a $pK_a^{H_2O}$ value of *ca.* 13.1, allowing for the often observed $\Delta pK = 2$ between water and methanol values.[14]

Table 2. The effects of solvent composition and of isotopic substitution upon proton abstraction by methoxide ion from bis-(2,4-dinitrophenyl)methane at 20 °C in methanol–DMSO mixtures[a]

% DMSO	0	0[b]	20	20[b]	40	60	80
(**Ia**)							
k_1/dm^3 mol^{-1} s^{-1}	26.2	42.2	151	200	494	3 280	32 000
k_{-1}/s^{-1}	0.73	0.13_5	0.05	*c*	*c*	*c*	*c*
K/dm^3 mol^{-1}	35.9	313[d]	3 020				
(**Ib**)							
k_1/dm^3 mol^{-1} s^{-1}	2.5	5.5	12.2_5	27.2			
k_{-1}/s^{-1}	0.07_4			*c*			
K/dm^3 mol^{-1}	74.3						

[a] Estimated errors in rate constants ±3%; $K = k_1/k_{-1}$. [b] Values for deuteriated methanol, CH_3OD. [c] Too low for measurement. [d] Value refers to the 'pseudo-equilibrium' of equation (4).

Table 3. The influence of substitution upon the p*K* of toluene[a]

Acid	p*K*
Toluene	42[b]
4-Nitrotoluene	20.4[b]
2,4′-Dinitrodiphenylmethane	17.38[c]
4,4′-Dinitrodiphenylmethane	15.85[c]

[a] Values taken from ref. 12. [b] DMSO value. [c] DMSO–EtOH value.

An estimation of the $pK_a^{H_2O}$ of (I) from kinetic measurements in water containing 1% dioxane yielded a value of 13.2, in excellent agreement with the measured value in methanol, and with the above prediction.

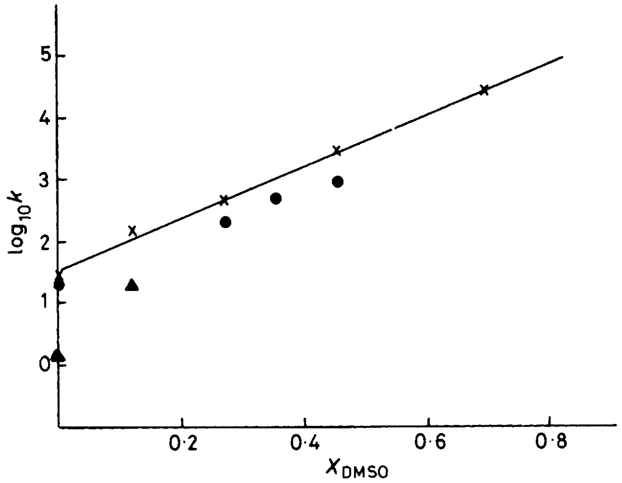
The inherent assumption in the derivation of the $pK_{a(I)}^{H_2O}$ value is that an *o*-nitro group is significantly less effective at resonance stabilization of a nitroarylmethyl carbanion than is a *p*-nitro group. Considerations of both steric hindrance to coplanarity in the carbanion, which is increased by *o*-nitro substitution, and the 'extended' conjugation deriving from charge delocalization onto the *p*-nitro groups would support that assumption.[15] Quantitative measures of the greater stabilization of Meisenheimer complexes by *p*-nitro substitution, relative to *o*-nitro substitution, show a 12-fold greater stabilization by the former.[2] Although not directly analogous because of the different steric factors *etc.* operative in nucleophilic attack upon a ring atom, these data support the assumptions made regarding resonance delocalization of the negative charge.

The pK_a^{MeOH} value measured for (I) may be also compared with that for 2,4,6-trinitrotoluene (TNT) for which an experimental value of $pK_a^{MeOH} = 15.6$ may be calculated.[16] The influence of substitution by a 2,4-dinitrophenyl group on the exocyclic carbon of 2,4-dinitrotoluene is thus comparable to that arising from the introduction of a second *o*-nitro group, from the viewpoint of *thermodynamic acidity*. The extensive charge delocalization possible in the carbanions obtained by proton abstraction from (I) and TNT would suggest that both ionization and reprotonation must be accompanied by considerable structural and solvent reorganization in each case, and hence should occur at comparable rates. In agreement with this argument, values of k_1 for (**Ia**) and TNT in methanolic methoxide solution at 25 °C are 35.6 and 13.3 $dm^3\ mol^{-1}\ s^{-1}$, respectively, and the corresponding k_{-1} values are 1.00 and 1.07 s^{-1}.[16] The reasonable assumption that these structurally similar carbon acids follow the same acidity function also requires that their proton abstraction rates vary in a similar manner with change of solvent.

Solvent Effects.—The influence of added DMSO upon the rates of proton abstraction from (I) is shown in Table 2 and, in accord with other studies of proton abstraction from carbon acids and with studies of nucleophilic attack upon suitably substituted aromatics to yield Meisenheimer-type complexes, results in an increase of k_1 with increasing percentage of DMSO.[2] The stabilizing effect of DMSO on a delocalized carbanion is a result of an increase in carbanion formation rate and a concomitant decrease in its rate of destruction (reprotonation, rearrangement, nucleophile elimination). The low values of rates of reprotonation of (I) make them difficult to measure, and hence relatively inaccurate, in methanol–DMSO mixtures, but there is a decrease in rate of reprotonation in 20% DMSO–methanol–methoxide relative to methanol–methoxide solution.

In the Figure, a comparison of proton abstraction and carbanion reprotonation rates for (**Ia**) and TNT in methanol–DMSO is shown.[6] It is immediately evident that values of log k_1 for proton abstraction from (**Ia**) are greater than those for TNT by an approximately constant amount, in accord with the lower pK_a^{MeOH} value of (**Ia**). In addition, the slopes of the linear relationships of the Figure between log k_1 and X_{DMSO} are approximately, though not exactly, equal confirming the suggestion that (**Ia**) and TNT will respond similarly to changing solvent composition.

These comparable effects of the second *o*-nitro group of TNT and of the α-(2,4-dinitrophenyl) group of (**Ia**) suggest that the introduction of the second *o*-nitro group into 2,4-dinitrotoluene causes little, or no, additional *steric* hindrance to proton abstraction by methoxide ion. Ease of solvent reorganization around the developing carbanionic centre will be decreased, however, by each of these substituents.



The influence of added DMSO (expressed as mole fraction) upon the proton abstraction rates from (**Ia**) (×) and TNT (●), and upon the protonation of (**IIa**) (▲, expressed as $-\log k_{-1}$), in methanol solutions

In a comparison of the rates of proton abstraction from TNT and 2,4,6-trinitrobenzyl chloride, Crampton noted only a small increase (*ca.* 20%) in rate for the latter compound in methanolic methoxide solutions and suggested that this low acid-enhancing effect of the chlorine atom may result from greater steric interaction between an *o*-nitro group and the chlorine atom.[17] This would affect both base attack and solvent rearrangement around the exocyclic carbon atom. An alternative explanation would be that the resonance saturation effect in TNT is already large, and only very little, if any, of the charge in the 2,4,6-trinitrobenzyl chloride anion would be delocalized onto the chlorine atom, *i.e.* the influence of this substituent upon the nature and energy of the transition state is small (*cf.* 4-nitrobenzyl chloride k_1 331 $dm^3\ mol^{-1}\ s^{-1}$ and 4-nitrotoluene k_1 *ca.* 1.5 $dm^3\ mol^{-1}\ s^{-1}$ in 90% DMSO–H_2O[18]).

The relatively high acidity of (I) and extensive charge delocalization in the carbanion (II) renders this reaction one in which '*solvent lag*' is likely to occur during deprotonation.[19] This concept has recently been discussed by several authors, in relation to the formation of highly delocalized carbanions, and used to explain the transition-state imbalances ($\alpha + \beta \neq 1$) often found in the ionization of carbon acids.[20–26] In this context, solvent lag expresses the possibility that solvent reorganization may not be synchronous with the electronic and structural reorganization occurring during ionization–protonation. Evidence for the essentially complete charge delocalization in (**IIa**) is provided by the value of $J_{\alpha\text{-CH}}$ of 163 Hz in DMSO solution,[27] a medium in which solvent-separated ions are also known to predominate. This value implies that the exocyclic carbon atom of (**IIa**) is olefin-like and hence that extensive structural reorganization of the molecule has occurred during carbanion formation. Such structural reorganization must be accompanied by corresponding solvent reorganization and the exocyclic 'olefinic' carbon atom will not be significantly solvated by methanol. In an attempt to find evidence of solvent lag in this reaction we have therefore studied isotope effects.

Solvent and Kinetic Isotope Effects.—Rate constants for reactions of (**Ia** and **b**) in deuteriated methanol (and k_1 values in 20% DMSO–MeOD) are shown in Table 2, from which solvent isotope effects on proton abstraction of $k_1^{\mathrm{MeOD}}/k_1^{\mathrm{MeOH}} = 1.6$, 1.3 (20% DMSO) for (**Ia**) and $k_1^{\mathrm{MeOD}}/k_1^{\mathrm{MeOH}} = 2.2$, 2.2 (20% DMSO) for (**Ib**) can be calculated. The corresponding data for reactions of TNT and [$^2H_3$]TNT with ethoxide ion in ethanol also show a greater solvent isotope effect for the deuteriated substrate, $k_1^{\mathrm{EtOD}}/k_1^{\mathrm{EtOH}} = 1.81$ and 1.97 for TNT and [$^2H_3$]TNT respectively.[28] A value of $k_{-1}^{\mathrm{MeOH}}/k_{-1}^{\mathrm{MeOD}} = 5.4$ may also be calculated for (**Ia**). For proton abstractions in methanol the origin of the solvent isotope effect is well established, and values of the fractionation factors for the exchangeable hydrogens involved in the proton transfer predict $k_1^{\mathrm{MeOD}}/k_1^{\mathrm{MeOH}}$ *ca.* 2.5 for a transition state which is essentially product-like.[29] Our values are in accord with other studies of proton abstraction in methanol solutions which suggest product-like, rather than reactant-like, transition states, particularly for (**Ib**). Although some authors have used the relative magnitude of the solvent isotope effect to predict the position of the transition state on the reaction pathway, this seems to us, as to others, to be an unreliable procedure and we do not attempt to draw such conclusions from the data presented.

That values of $k_{-1}^{\mathrm{MeOH}}/k_{-1}^{\mathrm{MeOD}} > 1$ are normally found has been shown by Eaborn and his co-workers in extensive studies of methoxide-ion-catalysed cleavages of aryltrialkylsilanes and -stannanes in methanol and [^{2}H]methanol solutions.[30] Thus a value of $k_{-1}^{\mathrm{MeOH}}/k_{-1}^{\mathrm{MeOD}} = 10$ was found for both *o*- and *p*-nitrobenzyl anions, generated from the corresponding trimethylsilanes, but much lower values of 1.3 and 1.5 for the diphenylmethyl carbanion generated from either the corresponding trimethylsilane or trimethylstannane respectively. These authors noted that the value of $k_{-1}^{\mathrm{MeOH}}/k_{-1}^{\mathrm{MeOD}}$ should exhibit a maximum value for carbanions derived from carbon acids of pK_a in the region of that of methanol. The pK_a^{MeOH} values for *o*- and *p*-nitrotoluenes lie above that for methanol while the value for (**Ia**) lies below it, and hence they span the $\Delta pK_a^{\mathrm{MeOH}} = 0$ region. The 'maxima' found in all studies of isotope effect variation with pK_a tend to be very broad and thus the $k_{-1}^{\mathrm{MeOH}}/k_{-1}^{\mathrm{MeOD}}$ values found in this work and the studies of Eaborn are in good qualitative agreement with the expected pK_a dependence.[30]

In Table 2 data for reactions of (**Ia** and **b**) in methanol and [^{2}H]methanol lead to values of the primary kinetic hydrogen isotope effect. Numerous studies of secondary isotope effects arising from the presence of α-deuterium atoms agree upon an average value of *ca.* 1.15 per atom, and we assume that value in this study.[31] Thus, in methanol and 20% DMSO–methanol solutions, corrected values of $k_1^{(\mathbf{Ia})}/k_1^{(\mathbf{Ib})}$ are 9.1 and 10.7, respectively, whereas in the corresponding [^{2}H]methanol solutions the values are 6.7 and 6.4. Gold and Grist also noted a lower primary kinetic isotope effect in the deuteriated medium in their study of proton abstraction from 2-nitropropane in methanol,[29] as did Russell *et al.* for the similar reaction of TNT in ethanol.[28]

These fairly large primary isotope effects on k_1 in methanol are of the same order of magnitude as those found for related nitroaromatics in various media. Thus values of 6.4—8.6 (after correction for the secondary deuterium effect) were obtained for the reactions of bis-(4-nitrophenyl)methane with t-butoxide in various toluene–t-butyl alcohol mixtures are 20 °C,[32] and values of 8.4, 8.9, and 20.5* respectively, at 25 °C, for the reactions of tris-(4-nitrophenyl)methane with toluene–alcoholic solutions of ethoxide, isopropoxide, and t-butoxide ions.[22] In the reaction of 4-nitrophenylphenylcyanomethane with tetramethylguanidine to form ion pairs in acetonitrile or benzonitrile at 20 °C, values of 10.5 and 14.5, respectively, were recorded.[33]

The most common explanations invoked to account for large primary kinetic isotope effects (*ca.* 8 or greater) are either proton tunnelling or solvent lag. Some proton tunnelling contribution has been suggested to account for the results obtained for tris-(4-nitrophenyl)methane[22] and 4-nitrophenylphenylcyanomethane,[33] particularly for reaction with the bulky t-butoxide ion, but evidence for tunnelling in proton abstraction from bis-(4-nitrophenyl)methane or from tris-(4-nitrophenyl)methane by smaller alkoxide bases is inconclusive.[22,32] In the present study, using methanolic methoxide ion and a relatively acidic substrate, proton tunnelling is unlikely to play a significant role. In contrast, the observed isotope effect may be accounted for by formation of the planar delocalized carbanion *via* a predominantly tetrahedral transition state, followed by rapid structural–electronic–solvational reorganization.[21,24] In this case, the intrinsic energy barrier, and hence the primary isotope effect, should decrease with increasing mole fraction of DMSO,[21] whereas an increase from 9.1 to 10.7 is found for (**Ia**) for only a small increase (0.122) in mole fraction of DMSO present. It is thus difficult to conclude unambiguously from the k_1 values that this system exhibits solvent lag.

However, we note that the reprotonation of (**IIa** and **b**) (measured in [^{2}H]methanol) shows a small isotope effect of $k_{-1}^{(\mathbf{IIa})}/k_{-1}^{(\mathbf{IIb})} = 1.8$. This value is considerably less than the values of 24 and 8.1 for reprotonation of the tris-(4-nitrophenyl)methyl anion in ethanol–15% toluene and isopropyl alcohol–15% toluene respectively,[22] but is the same as the (less reliable) value for reprotonation of this anion in t-butyl alcohol–15% toluene — values observed for reactions which would be expected to show isotope effects of unity. These latter values were explained on the basis of an initially formed hydrogen-bonded species, with slow equilibration of the hydrogen-bonding proton and the solvent, an intermediate proposed by other workers in studies of acidities of carbon acids, and which is still the subject of much debate.[21,24,34] However, the consequence of such an intermediate is the same as was discussed above, *i.e.* a pyramidal transition state. The deuterium atom of (**IIb**) would be expected to increase its basicity, relative to (**IIa**), and the small observed isotope effect would be consistent with the initial formation of such a weakly hydrogen-bonded species.

Thermodynamic Parameters.—Activation and equilibrium enthalpy and entropy values for the reaction of (**Ia**) with methoxide ions in methanol are shown in Table 1. As expected from the greater solvation energies of the smaller bases, $\Delta H^{\neq}$ for proton abstractions from nitro-compounds by methoxide or ethoxide ions are higher ($40 < \Delta H_1^{\ddagger} < 75$ kJ mol^{-1}), than those found for reactions with larger alkoxide ions ($28 < \Delta H_1^{\neq} < 45$ kJ mol^{-1}) and $\Delta H_1^{\neq}$ *ca.* 55 kJ mol^{-1} for ionization of (**Ia**) accords with this.[22,27,35,36] Correspondingly, $\Delta S_1^{\neq}$ values tend to be less negative for reactions with the smaller alkoxide ions ($\Delta S_1^{\neq} > -75$ J mol^{-1} K^{-1}), because of the entropically favourable differential solvation between the charge-localized alkoxide ions and the less solvated larger carbanions, and the value of Table 1 ($\Delta S_1^{\neq}$ -31 J mol^{-1} K^{-1}) lies in the expected range. It is of interest to note also that cleavages of carbon–silicon bonds by methoxide ions, to yield arylmethyl carbanion intermediates, have $\Delta S^{\neq}$ values of similar magnitude ($-40 < \Delta S^{\neq} < -80$ J mol^{-1} K^{-1}) to those for proton abstractions, in accord with the suggestion that desolvation of the alkoxide ion is of special importance in such cleavages.[30]

Relatively small reaction enthalpies and positive ΔS° values are commonly found for reactions of this type, reflecting the

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* The value of 20.5 is calculated from the rate constants reported by Caldin *et al.*,[22] and differs from that quoted by these authors in their summary table of data.

predominance of solvent reorganization in the reaction, especially in the carbanion protonation, and the data of Table 1 reflect this pattern. The position of the entropy-controlled equilibrium shifts towards the carbanion with increasing temperature.

Conclusions.—The reactions of (**I**) and (**II**) with methanolic methoxide ion thus occur at similar rates to those of TNT with this base, as expected from their similar $\mathrm{p}K_a$ values and the extensive charge delocalization possible in their respective carbanions. Evidence for the accompanying solvent lag expected for the ultimate formation of a highly delocalized, structurally reorganized anion such as (**II**) is not entirely conclusive.

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