The Relative Acidities of 4-Nitro-, 2,4-Dinitro-, and 2,4,6-Trinitro-toluene

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The rates of proton abstraction and carbanion protonation have been measured for the title compounds in methanolic dimethyl sulphoxide and, where possible, in aqueous dimethyl sulphoxide solutions. These data allow estimates of their pK_a values in water to be made, and provide a revised value for the pK_a of 4-nitrotoluene in dimethyl sulphoxide solution.

In recent years, numerous studies of the acidities of organic molecules have been reported and these have contributed greatly towards a better understanding of the influence of solvent, substituents *etc.* upon hydrocarbon acidities.[1-3] While 'acidity' traditionally refers to aqueous solution, this medium is obviously unsuitable for measurements on most organic compounds of interest and considerable use has therefore been made of amine solvents (*e.g.* cyclohexylamine) for studies of weakly acidic hydrocarbons,[4] and of dipolar aprotic solvents (*e.g.* dimethyl sulphoxide) for the (relatively) more acidic compounds ($pK_a \leqslant 32$).[1,5] Although the absence of a wealth of data for aqueous solutions makes comparisons difficult, it appears that simple (usually parallel) relationships exist between sets of p*K* values in different media,[6] and hence that useful comparisons can be made among compounds whose acidities render measurements in the same solvent difficult or impossible.

For studies of the quantitative effects of substitution upon acidity, pK_a values for a variety of simple compounds are required, and in some instances these are either unavailable, or scarce. In the course of our studies of the kinetic acidities of various nitroaromatic hydrocarbons we have recently examined the proton abstraction–carbanion protonation rates of 2,4-dinitrotoluene in aqueous and methanolic dimethyl sulphoxide (DMSO) mixtures for comparison with data for 4-nitro- and 2,4,6-trinitro-toluene. Such comparisons required us both to extend our previous measurements on 4-nitrotoluene[7] and, as a result, to revise the reported[8] value for the pK_a of this compound in DMSO, and also to make spectroscopic measurements to determine the pK_a of 2,4,6-trinitrotoluene in methanolic DMSO solutions. The results obtained are presented and discussed in this article.

Results

4-Nitrotoluene.—Because of the low acidity of this compound, measurements of the rates of proton abstraction by lyate bases (k_1^1), and of carbanion protonation by the protic solvent (k_1^p), can only be made in extremely highly basic media. Corresponding measurements in such media are not always possible for 2,4-dinitro- or 2,4,6-trinitro-toluene because of their markedly higher acidities, and therefore *direct* comparisons of the acidities of these three compounds are not possible, although *indirect* comparisons based upon assumed parallel log k_1^1–% DMSO relationships may be made[9] (*vide infra*). Values of k_1^1 and k_1^p in 98% DMSO–2% MeOH are shown in the Table, together with previously reported values in 95% DMSO–5% H_2O.[7] From

Table. Rate and equilibrium constants for proton abstraction–carbanion reprotonation reactions of substituted nitrotoluenes in methanolic and aqueous DMSO solutions at 25 °C[a]

%DMSO		0	40	50	60	70	80	90	95	98
A Methanol solutions										
2,4,6-Trinitrotoluene	k_1^1	13.3,[b] 20 ± 5[c]	225 ± 25[c]	530 ± 30[c]	1 000 ± 200[c]	~5 000[d]	$\sim 2 \times 10^4$[d]	$\sim 9 \times 10^4$[d]		
	k_1^p	1.07,[b] 1.6[e]		7.7×10^{-3}[f]	5.9×10^{-4}[f]	2×10^{-4}[f]	$\sim 9 \times 10^{-4}$[f]			
	K	12.4[b]		6.9×10^4	1.7×10^6	2.6×10^7	2.2×10^9			
	pK_a	15.6		12.67[g]	12.01[g]	11.5[g]	10.5[g]			
2,4-Dinitrotoluene	k_1^1				10.7	33.1	125	656	2 525	8 100
	k_1^p				0.23	0.06	*h*	*h*	*h*	*h*
	K				46.5	552				
	pK_a				16.6	16.2				
4-Nitrotoluene	k_1^1								7.6	35
	k_1^p								0.56	0.36
	K								13.6	97.2
	pK_a								21.6	25.7
B Aqueous solutions										
2,4-Dinitrotoluene	k_1^1				0.48	1.4	9.9	180	1 530	
	k_1^p				0.012	0.004	*h*	*h*	*h*	
	K				40	350				
	pK_a				15.0	15.2				
4-Nitrotoluene	k_1^1								17.4[i]	
	k_1^p								0.22[i]	
	K								79[i]	
	pK_a								22.1	

[a] Units k_1^1/dm^3 mol^{-1} s^{-1}; k_1^p/s^{-1}; $K = k_1^1/k_1^p$/dm^3 mol^{-1}. [b] Ref. 12. [c] Ref. 15. [d] Estimated from Figure 2. [e] Calculated assuming $K = 12.4$. [f] Calculated from $K = k_1^1/k_1^p$, using K values derived from equation (1). [g] Spectrophotometrically determined value (see Figure 1). [h] Too low for measurement. [i] Ref. 7.

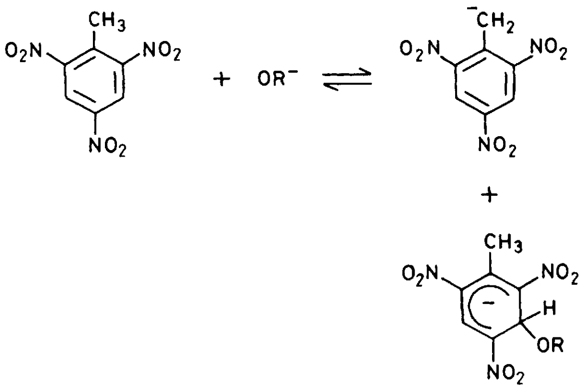
these values, together with the ionic products of the solvent mixtures,[10] pK_s, the pK_a values may be calculated from equation (1), where $K = k_1^1/k_1^p$ in the given medium. These

$$pK_a = pK_s - \log K \qquad (1)$$

values are also given in the Table.

2,4-*Dinitrotoluene*.—Values of k_1^1 and k_1^p (where measurable) for this compound in 60—98% DMSO–MeOH solutions and in 60—95% DMSO–H_2O solutions are also shown in the Table, together with the corresponding pK_a values derived from equation (1). The absorption spectrum of the 2,4-dinitrotoluene carbanion was identical to that obtained by Buncel *et al.* for this ion, formed by means of the thermal decarboxylation of the 2,4-dinitrophenylacetate ion in DMSO.[11] As the possibility of σ-complex formation by base attack on a ring carbon does not exist in their system, the spectral identity implies that no competing σ-complex formation interferes under the conditions employed in this study.

2,4,6-*Trinitrotoluene*.—In water or in aqueous DMSO solutions, the reaction of 2,4,6-trinitrotoluene with hydroxide ion yields two species, the anion and the σ-complex resulting from attack of hydroxide on C-3, as shown in equation (2).[12—15]



(2)

The kinetics of this system are mixed and no valid measurements of k_1^1 and k_1^p can be obtained in these media. In alcoholic solutions both the carbanion and the corresponding σ-complex are also formed by reaction with lyate base, but previous workers have shown that the rates of carbanion formation can be studied in methanolic DMSO solutions if the base concentration is maintained low (≤0.1M), when a sufficiently large difference between the rates of σ-complex and carbanion formation exists to allow the determination of $k^1{}_1$ values.[15] Reported[15] values of $k^1{}_1$ in 0—60% DMSO–MeOH solutions are summarized in the Table, whence it can be seen that *direct* comparison of the rates of carbanion formation from 2,4-dinitro- and 2,4,6-trinitro-toluene can be made.

Because of the stability of the 2,4,6-trinitrotoluene carbanion in solutions containing DMSO, values of k_1^p are low, and cannot normally be measured by the stopped-flow technique employed. Recourse has to be made to spectroscopic measurements of $K = k_1^1/k_1^p$, from which k_1^p may then be determined using the measured k_1^1 data. The final product from reaction (2) is the more stable anion, the σ-complex rapidly disappearing; equilibrium measurements for protonation of this anion are therefore uncomplicated by the presence of other species. For these measurements buffered solutions are used and several phenol buffers have been calibrated according to a previously described method;[16,17] the variation of the position of the equilibrium (3) was then followed as a function of pH at the wavelength of absorption of the anion (630 nm), by the overlapping buffer method. Excellent linear plots of log ([TNT⁻]/[TNT]) *versus* pH with unit slopes were obtained for equilibria in 50—80% DMSO–MeOH (Figure 1), from which values of pK_a may be readily obtained when log ([TNT⁻]/[TNT]) = 0 [equation (4)]. These pK_a values are shown in the Table,

$$\log([\mathrm{TNT}^-]/[\mathrm{TNT}]) = \log K_a + \mathrm{pH} \qquad (4)$$

together with the derived K and k_1^p values, calculated using equation (1), for equilibria in 50 and 60% DMSO–MeOH solutions.

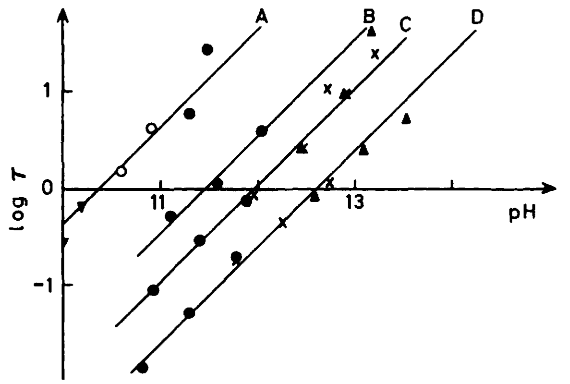
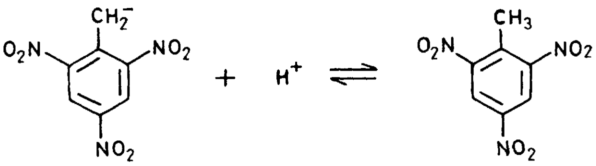


Figure 1. The variation of the ratio of ionized to un-ionized 2,4,6-trinitrotoluene as a function of pH in methanolic DMSO solutions at 25 °C, μ = 10^{-2}M. A 80% DMSO–20% MeOH; B 70% DMSO–30% MeOH; C 60% DMSO–40% MeOH; D 50% DMSO–50% MeOH. (Buffers used: ▲ 4-chlorophenol; ● 4-cyanophenol; × 2-bromophenol; ○ 2-cyanophenol; ▼ acetic acid)



(3)

Discussion

Kinetic Acidities.—Examination of the data for proton abstraction in methanolic DMSO solutions (Table) shows clearly the large range of kinetic acidity exhibited by the three compounds studied. Thus the ratio of k_1^1 values for proton abstraction from 2,4-dinitro- and 4-nitro-toluene is 230 in 98% DMSO–2% MeOH, and *ca.* 100 for proton abstraction from 2,4,6-trinitro- and 2,4-dinitro-toluene in 60% DMSO–40% MeOH. This translates into an increase in kinetic acidity resulting from the introduction of two *o*-nitro groups into 4-nitrotoluene of the order of 2 × 10^4 if the measured kinetic acidity differences between these pairs of compounds are not greatly solvent-dependent. That this is likely to be correct is supported by Figure 2, in which the log k_1^1 values for the ionization of 2,4,6-trinitro- and 2,4-dinitro-toluene in MeOH–DMSO mixtures, and for the latter compound in H_2O–DMSO mixtures, are plotted as a function of the mole fraction of DMSO.

As can be seen from Figure 2, approximate linear relationships between log k_1^1 and X_{DMSO} are found for solutions having $X_{\mathrm{DMSO}} < 0.7$ (*ca.* 90% DMSO by volume in both solvent mixtures). The slopes, d log k_1^1/d X_{DMSO}, of the linear plots are 4.6 and 6.7 for MeOH–DMSO and H_2O–DMSO mixtures,

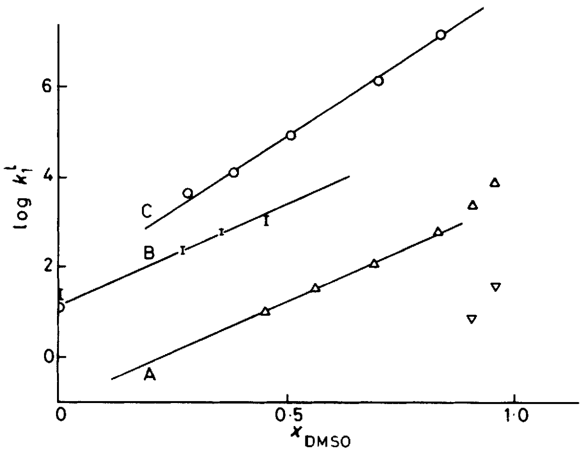


Figure 2. The variation of the rates of proton abstraction in methanolic media by lyate base from 2,4-dinitrotoluene (A) and from 2,4,6-trinitrotoluene (B) at 25 °C. The values for 4-nitrotoluene in 98% DMSO solution are indicated by ▽. The variation of proton abstraction rates, in aqueous media, from 2,4-dinitrotoluene is illustrated by (C) (for clarity 4 + log k_1^{l} values have been plotted as a function of X_{DMSO})

respectively, the former being identical to that observed recently in studies of proton abstraction from a variety of *ortho-* and/or *para*-nitro-substituted arylmethanes.[9]

Such linear correlations allow reliable estimates to be made of k_1^{l} values in solvent mixtures where they cannot be directly measured, and we have used Figure 2 to estimate k_1^{l} values for proton abstraction from 2,4,6-trinitrotoluene in 70 and 80% DMSO–MeOH mixtures. These are given in the Table, together with the corresponding k_1^{p} data calculated from K ($= k_1^{\mathrm{l}}/k_1^{\mathrm{p}}$) values, obtained from measured pK_a data *via* equation (1) (see Results section).

Thermodynamic Acidities.—In our studies of various nitroarylmethanes we have consistently found that their pK_a values decrease with increasing DMSO concentration,[7,9,18–20] in contrast to the majority of other classes of compounds studied.[21] Thus phenols,[22] carboxylic acids,[23] and nitroalkanes[1] are weaker acids in DMSO than in water, and many hydrocarbons[6] and amines[23] have almost identical pK_a values in these solvents. Other workers have also noted that those compounds yielding highly delocalized anions show decreased pK_a values in DMSO relative to water, *e.g.* trinitroarylamines.[24] Furthermore, the pK_a difference between water and DMSO is greater for the stronger acids (*e.g.* 2.5 units between 0 and 50% DMSO for 2,2′,4,4′-tetranitrodiphenylmethane) than for the weaker ones (*e.g.* 1 unit between 0 and 95% DMSO for 4-nitrodiphenylmethane).[9] The data for 2,4-dinitro- and 2,4,6-trinitro-toluene are in accord with these general observations (Table).

For comparisons of thermodynamic acidities, pK_a values in a common solvent are required, and water would be the medium of choice. For reasons referred to earlier, proton abstraction rates are not measurable for 2,4,6-trinitrotoluene in water or aqueous DMSO solutions. However, there is a close similarity between the k_1^{l}, k_1^{p}, and K values for this compound and for 2,2′,4,4′-tetranitrodiphenylmethane in methanol–DMSO solutions, the latter also lending itself to study in water.[18,19] If one assumes a similar acidity difference between these two compounds in water as is found in methanol (ΔpK_a 0.45)[18] then pK_a 13.6 for 2,4,6-trinitrotoluene in water is derived. This is 2 units lower than the measured value in methanol, as has been noted for several other nitroarylmethanes. This value is slightly lower than that obtained by an acidity function technique in aqueous ethylenediamine (pK_a 14.45).[25]

A similar examination of the k_1^{l} and k_1^{p} data for ionization of 4,4′-dinitrodiphenylmethane in aqueous and methanolic DMSO solutions shows values for this compound which are almost identical to those shown in the Table for 2,4-dinitrotoluene.[9] The pK_a value in water for the former, obtained by an acidity function method, is thus an excellent reference for that for 2,4-dinitrotoluene as it is unlikely that any significant change in this behaviour would be found in water, *i.e.* pK_a 16 ± 0.2. This is also *ca.* 2 units lower than the predicted pK_a in methanol, and 1 unit lower than the value reported in aqueous ethylenediamine solutions (17.12).[26]

Addition of DMSO to aqueous or methanolic solutions of 4-nitrotoluene would be expected to result in only a small change in acidity of this compound, as it is a relatively weak acid. Thus the measured value in 95% DMSO–5% H_2O might increase by, at most, 1.5 units (*cf.* 4-nitrodiphenylmethane)[9] to provide a value of pK_a 23.5 ± 0.5 in water for 4-nitrotoluene.

The small increase in thermodynamic acidity resulting from the addition of the third nitro group to toluene presumably reflects a saturation effect on the charge delocalization of the type noted by Bordwell.[27] The Δp$K_a^{\mathrm{H_2O}}$ 7.5 units for addition of a second nitro group to toluene may be compared with the recently determined value of 4.6 for the addition of a second nitro group to benzyl cyanide in 50% aqueous DMSO solution.[28] Assuming that these values may be compared (*i.e.* ignoring solvent differences), the smaller value for the benzyl cyanide system is in accordance with the suggestion that part of the charges in the corresponding carbanions are delocalized onto the nitrile group.[28] This would stabilize the anion from 4-nitrobenzyl cyanide relative to that from 4-nitrotoluene, and hence the influence of a further nitro group would be moderated.

Our experimental pK_a values of 22.1 in 95% DMSO–5% H_2O and 25.7 in 98% DMSO–2% MeOH for 4-nitrotoluene are both greater than the reported value of 20.4 in pure DMSO obtained by Bordwell.[8] Allowing for the possibility that greater error attaches to these measurements because of the inherent difficulties in making up and working with solutions of such high DMSO content, these data suggest that pK_a^{DMSO} for 4-nitrotoluene is greater than the currently accepted value, probably by at least 2 units. Such a value (*i.e.* 22—23) would be in far better agreement with that expected from considerations of $+R$ *para*-substituent effects in anilines and phenols, and higher than the pK_a^{DMSO} for 4-nitroaniline (20.9) as expected.[8,12]

Revision of the pK_a^{DMSO} value for 4-nitrotoluene does not alter the currently accepted value for the pK_a^{DMSO} of toluene (42), derived from the linear relationship between pK_a^{DMSO} values for *para*-substituted anilines and toluenes,[8] and suggests only a marginal decrease in the estimated ρ value for the ionization of toluenes in DMSO (12→11.5). However, such a revised value does decrease the free energy of ionization of 4-nitrotoluene in DMSO relative to that for toluene, to a value only *ca.* 8 kJ mol^{-1} greater than that found for the corresponding gas-phase reaction.[2,3] This difference is comparable in magnitude to those estimated for specific solvation by DMSO of highly charged-delocalized anions (*e.g.* diphenylmethyl, α-cyanotoluyl),[2] suggesting that the charge in the 4-nitrotoluyl anion is completely delocalized. This would imply that even larger substituent-solvation-assisted resonance effects in DMSO may be anticipated for toluenes than those recently noted for phenol and aniline acidities.[29]

Knowledge of a value for the pK_a of 4-nitrotoluene allows an estimate to be made for that of 2-nitrotoluene. It is well known that charge delocalization by an *o*-nitro group is less effective than that by a *p*-nitro group, recent calculations suggesting a ΔpK_a of *ca.* 1.5 units due to this difference.[30] The p$K_a^{\mathrm{H_2O}}$ for 2-nitrotoluene may thus be estimated to be at least 25.

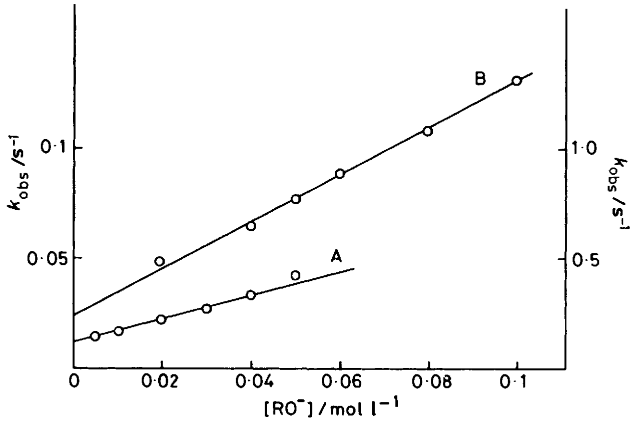


Figure 3. Typical plots of the variation of the observed rate constant, k_{obs}, as a function of base concentration for proton abstraction from 2,4-dinitrotoluene in solutions containing 60% DMSO by volume. A, aqueous solution, RO$^-$ = hydroxide ion, left-hand scale. B, methanolic solution, RO$^-$ = methoxide ion, right-hand scale

Experimental

Materials.—All compounds were commercial products, or synthesized according to standard procedures, recrystallized to constant literature m.p.s and carefully dried before use. Solutions of methanolic potassium methoxide or aqueous potassium hydroxide, in DMSO where required, were prepared as previously described.[31,32]

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 substrate concentrations in the range 3×10^{-5}—10^{-4}M and base concentrations in the range 10^{-3}—10^{-1}M. Under these conditions the observed first-order rate constants are given by equation (5), where k_1^1 is the

$$k_{obs} = k_1^1[\text{Base}] + k_1^{p} \qquad (5)$$

second-order rate constant for proton abstraction and k_1^{p} is the first-order rate constant for carbanion protonation. Plots of k_{obs} *versus* base concentrations were linear (Figure 3) and from these plots values of k_1^1 were determined (except for 2,4,6-trinitrotoluene – see Results section), and hence equilibrium constants $K(= k_1^1/k_1^{p})$. Rate constants are considered accurate to ±3%.

Equilibrium Measurements.—In the case of 2,4,6-trinitrotoluene the equilibrium protonation of the carbanion was followed by monitoring the changes in the absorbance at the absorption maximum, λ 630 nm, as a function of pH. The buffers used were the same as employed in previous studies in methanol–DMSO mixtures,[32] recalibrated at 25 °C. The measurements were carried out using a given buffer at several buffer ratios. A Beckman Acta 3 spectrophotometer with a thermostatted cell compartment at 25 ± 0.1 °C was used.

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