Ionization of Nitrotriphenylmethanes. Remarkable Kinetic Evidence for Steric Inhibition to Resonance and F-strain

François Terrier,[*,a] **Hai-Qi Xie,**[a] **Jacques Lelievre,**[a] **Taoufik Boubaker,**[a] **and Patrick G. Farrell**[b]
[a] *Laboratoire de Physicochimie des Solutions, UA CNRS 403, ENSCP, 11 Rue Pierre et Marie Curie, 75231 Paris Cedex 05, France*
[b] *Department of Chemistry, Mac Gill University, 801 Sherbrooke St. West, Montreal, P.Q. Canada H3A 2K6*

Rate and equilibrium data for the reversible deprotonation of 2,2′,2″,4,4′,4″-hexanitro-, 2,2′,4,4′,4″-pentanitro-, 2,4,4′,4″-tetranitro-, 4,4′,4″,-trinitro-, 4,4′-dinitro- and 4-nitro-triphenylmethanes (**2a–f**) by hydroxide ion have been measured in various H_2O–dimethyl sulphoxide (DMSO) mixtures at 25 °C. The increase in acidity (pK_a) brought about by the introduction of a first *p*-nitro group in triphenylmethane (**2g**) to give (**2f**) is very large and equal to about 12 p*K* units while the acid-strengthening influence of each of the second and third *p*-nitro groups is only of the order of 2 p*K* units. This suggests that only one *p*-nitrophenyl ring of the 4,4′-dinitro- and 4,4′,4″-trinitro-triphenylmethyl anions [(C-**2e**), (C-**2d**)] is in a favourable position for effective conjugation with the exocyclic sp^2 carbon atom of these carbanions at any given time. Accordingly, the effects exerted by the additional *p*-nitrophenyl ring(s) are mainly inductive in nature. Support for these ideas is the observation that the increases in acidity observed on going from (**2f**) to (**2e**) to (**2d**) are essentially the result of the corresponding increases in the kinetic acidity (k_p^{OH}). Addition of a first *o*-nitro group to (**2d**) to form (**2c**) further increases the kinetic acidity but it also results in a large decrease in $k_{-p}^{H_2O}$, consistent with a preferential stabilization of the corresponding 2,4,4′,4″-tetranitrotriphenylmethyl carbanion (C-**2c**) by the 2,4-dinitrophenyl ring. Significantly the introduction of the second and third *o*-nitro groups enhances the thermodynamic acidity while it decreases markedly the k_p^{OH} and $k_{-p}^{H_2O}$ values. It is suggested that these anomalous variations are the reflection of unfavourable steric interactions arising from the accumulation of *o*-nitro groups in the triphenylmethane system.

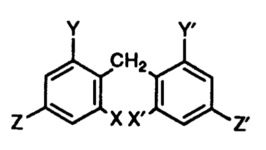
Kinetic studies of the ionization of nitroalkanes have played a major role in the development of current mechanistic notions about proton transfer at carbon.[1–12] This is because many features that are typical of proton transfers to or from carbon in general manifest themselves more dramatically with nitroalkanes than with other carbon acids.[12,13] In particular, it is these studies which have led to a good understanding of why many proton transfers at carbon are characterized by high intrinsic barriers and anomalous Brönsted correlations.[4,12–20] According to recent views, these two features are different manifestations of the same underlying phenomenon, namely, the fact that the development of resonance and solvation of a strongly stabilized carbanion lags behind the proton transfer at the transition state.[13,17,18]

In connection with our interest in the ionization of benzylic-type carbon acids,[16,21–23] we have recently reported a kinetic and thermodynamic study of a series of polynitrodiphenylmethanes in various H_2O–dimethyl sulphoxide (DMSO) mixtures.[24] A notable finding of this work was the observation of a marked disruption in the acidity and reactivity patterns upon introduction of a third *o*-nitro group in the diphenylmethane moiety. Based on the results of a concomitant NMR study,[21c] we demonstrated that this disruption was the reflection of steric effects. Mono-*o*-nitro- and di-*o*-nitro-diphenylmethyl carbanions, *e.g.* (C-**1d**) and (C-**1c**), are coplanar and have a highly delocalized negative charge. In contrast, no mutual coplanarity of the two phenyl rings can be achieved in carbanions (C-**1b**) and (C-**1a**), which have three and four *o*-nitro groups, respectively.[21c] Hence, the delocalization of the negative charge of such species can take place in only one of the two activated phenyl rings at a given time. Accordingly, the parent carbon acids, *i.e.* (**1b**) and (**1a**), behave as α-(2,4-dinitrophenyl)- and α-(2,4,6-trinitrophenyl)-substituted 2,4,6-trinitrotoluenes rather than polynitrodiphenylmethanes and this results in marked variations in acidity (pK_a) and intrinsic reactivity.[21c]

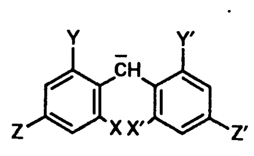
As a continuation of the above work, we now present thermodynamic and kinetic data for the ionization of a series of nitrotriphenylmethanes, (**2a–f**), by hydroxide ion in H_2O–DMSO mixtures of various compositions (Scheme 1). Notwithstanding the well-known fact that the unsubstituted triphenylmethyl carbanion itself is not planar—it has a propeller arrangement[25–27]—our results provide evidence that the accumulation of *o*-nitro groups in the three phenyl rings gives rise to an especially important steric effect which manifests itself by dramatic changes in reactivity. In addition, our results provide further evidence that a large number of carbon acids have kinetic acidities that respond similarly to solvent transfer from water to DMSO.[28]

Results

The rates of reversible deprotonation of (**2a–f**) were measured in aqueous DMSO solutions by monitoring the appearance of the corresponding carbanions (C-**2a**)–(C-**2f**) at or near λ_{max} in a stopped-flow apparatus. Intense and very large absorption maxima are centred at 720, 650, and 630 nm for (C-**2a**), (C-**2b**), and (C-**2c**), respectively, in 50% H_2O–50% DMSO and at 780, 800, and 540 nm for (C-**2d**), (C-**2e**) and (C-**2f**), respectively in 10% H_2O–90% DMSO. Kinetic experiments were first carried out under pseudo-first-order conditions with a large excess of OH^- (10^{-3}–10^{-2} mol dm^{-3}) over the substrate concentration (*ca.* 3×10^{-5} mol dm^{-3}), not at constant ionic strength. Under these experimental conditions, the observed first-order rate constant for the approach to the equilibrium in Scheme 1 is

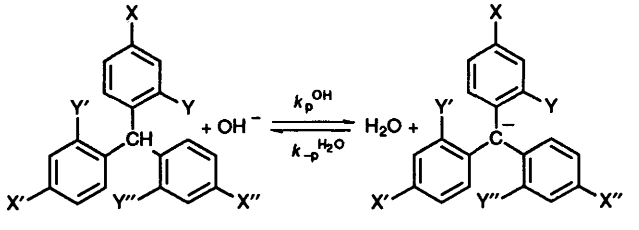


(1)



(C-1)

a; $X = X' = Y = Y' = Z = Z' = NO_2$
b; $X = X' = Y = Z = Z' = NO_2, Y' = H$
c; $X = X' = Z = Z' = NO_2, Y = Y' = H$
d; $X = Z = Z' = NO_2, X' = Y = Y' = H$
e; $Z = Z' = NO_2, X = X' = Y = Y' = H$
f; $Z = NO_2, X = X' = Y = Y' = Z' = H$
g; $X = X' = Y = Y' = Z = Z' = H$



(2) (C-2)

a; $X = X' = X'' = Y = Y' = Y'' = NO_2$
b; $X = X' = X'' = Y = Y' = NO_2, Y'' = H$
c; $X = X' = X'' = Y = NO_2, Y' = Y'' = H$
d; $X = X' = X'' = NO_2, Y = Y' = Y'' = H$
e; $X = X' = NO_2, X'' = Y = Y' = Y'' = H$
f; $X = NO_2, X' = X'' = Y = Y' = Y'' = H$
g; $X = X' = X'' = Y = Y' = Y'' = H$

Scheme 1.

simply given by equation (1). Plots of k_{obs} *vs.* $[OH^-]$ were all

$$k_{obs} = k_p^{OH}[OH^-] + k_{-p}^{H_2O} \qquad (1)$$

linear and, from these, values of the k_p^{OH} rate constants for deprotonation of (**2a**–**f**) were readily determined. Values of the rate constants $k_{-p}^{H_2O}$ for reprotonation of the carbanions (C-**2d**), (C-**2e**) and (C-**2f**) by the solvent were, in most cases, obtainable from the intercepts of the observed straight lines. In these instances, the equilibrium constants K_p were calculated from the ratios $k_p^{OH}/k_{-p}^{H_2O}$.

In the case of (**2a**, **b** and **c**) the intercepts of the k_{obs} *vs.* $[OH^-]$ plots were too small to allow reliable determination of $k_{-p}^{H_2O}$ and therefore of K_p. Thus, the thermodynamic acidity of (**2a**–**c**) was assessed by monitoring the changes in the equilibrium absorbance at the absorption maxima of the corresponding carbanions as a function of pH. Various phenol and carboxylic acid buffers, which were previously calibrated at 25 °C and an ionic strength I of 0.5 mol dm^{-3} maintained by NMe_4Cl, were used for this purpose in mixtures containing 50, 70 and 80% DMSO. In accordance with equation (2), excellent straight lines with unit slopes were obtained on plotting the ratio of ionized to un-ionized triphenylmethanes (**2a**–**c**) as a function of pH (Figure 1). These allowed the determination of the pK_a values and hence of the K_p and $k_{-p}^{H_2O}$ values by means of equation (3) and the ratio k_p^{OH}/K_p, respectively. In such instances, the k_p^{OH} values were also determined at I = 0.5 mol dm^{-3} to get homogeneous sets of rate and equilibrium data at this ionic strength. In equation (3), pK_s is the autoprotolysis constant of the solvent: pK_s = 15.83, 16.65, 18.02, 20.17 at 0.5 mol dm^{-3} NMe_4Cl in 50, 60, 70 and 80% DMSO, respectively.[16]

$$\log \frac{[(\text{C-}\mathbf{2a}\text{–}\mathbf{c})]}{[(\mathbf{2a}\text{–}\mathbf{c})]} = \log K_a + \text{pH} \qquad (2)$$

$$\text{p}K_a = \text{p}K_s - \log K_p \qquad (3)$$

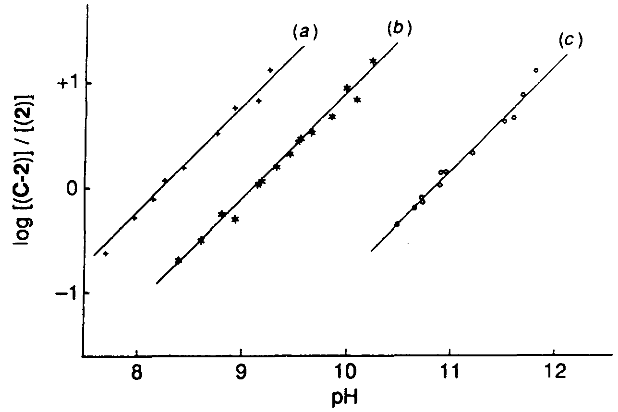


Fig. 1. The variation of the ratio of ionized to un-ionized triphenylmethanes (*a*) (**2a**), (*b*) (**2b**) and (*c*) (**2c**) as a function of pH in 50% H_2O–50% DMSO; T = 25 °C; I = 0.5 mol dm^{-3} NMe_4Cl.

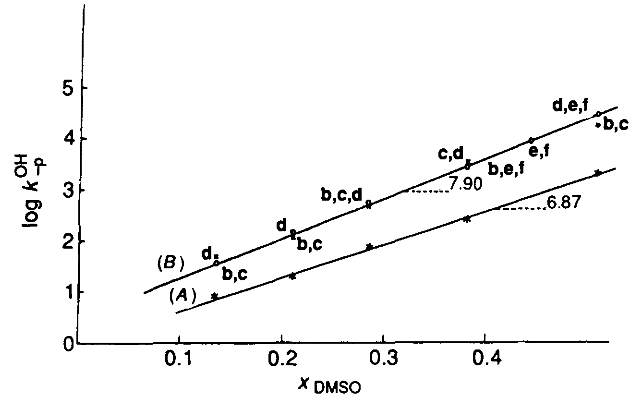


Fig. 2. Variation of $\log k_p^{OH}$ for proton abstraction from (**2a**–**f**) by hydroxide ion in aqueous DMSO mixtures with mole fraction of DMSO (x_{DMSO}). (*B*) The data for (**2b**–**f**) are normalized with respect to (**2c**) by means of Δ values for (**2b**) of 0.1, (**2c**) 0, (**2d**) 1.05, (**2e**) 2.58 (**2f**) 3.95. The data for (**2a**) [plot (*A*)] are not normalized.

All rate and equilibrium data obtained at 25 °C for the ionization of (**2a**–**f**) according to Scheme 1 are summarized in Tables 1 and 2. As can be seen, the effect of the ionic strength on k_p^{OH} is not large and consideration of this effect is omitted in the following discussion.

Discussion

Solvent Effects on Rates and pK_a *Values.*—Examination of the data in Tables 1 and 2 shows that the rates of proton abstraction (k_p^{OH}) for each of the nitrotriphenylmethanes (**2a**–**f**) increase with increasing the DMSO content of the solutions. These changes are similar to those reported in other studies of similarly activated carbon acids and are explicable in the same terms as those previously discussed.[9,11,28–31] However, it is interesting to note that nicely linear relationships with essentially similar slopes are obtained on plotting the $\log k_p^{OH}$ values for (**2a**–**f**) *vs.* the mole fraction of DMSO. This is illustrated in Figure 2 in which the $\log k_p^{OH}$ values at no constant ionic strength have been normalized with respect to 2,4,4′,4″-tetranitrotriphenylmethane (**2c**) by means of an increment, Δ, which is constant for a given compound. With the exception of those for (**2a**), these normalized data fall satisfactorily upon a single linear relationship [plot (*B*)] with a slope ($d\log k_p^{OH}/dN_{DMSO}$) = 7.90 which is, within experimental

Table 1. Rate and equilibrium data for the ionization of triphenylmethanes (**2a**), (**2b**) and (**2c**) in various H_2O–DMSO mixtures.[a]

(2a)

% Me_2SO	k_p^{OH}/dm^3 mol^{-1} s^{-1}	$k_{-p}^{H_2O}$/s^{-1} [d]	K_p/dm^3 mol^{-1} [e]	pK_a [f]
40[b]	8.4			
50[b]	21			
50[c]	23.8	6.26×10^{-7}	3.80×10^{7}	8.25
60[b]	76			
70[b]	293			
70[c]	304	4.6×10^{-9}	6.6×10^{10}	7.20
80[b]	2 090			
80[c]	2 220	5.09×10^{-11}	4.36×10^{13}	6.53
90[b]	32 400			

(2b)

% Me_2SO	k_p^{OH}/dm^3 mol^{-1} s^{-1}	$k_{-p}^{H_2O}$/s^{-1} [d]	K_p/dm^3 mol^{-1} [e]	pK_a [f]
40[b]	26.8			
50[b]	84.8			
50[c]	118	2.25×10^{-5}	5.25×10^{6}	9.11
60[b]	432			
70[b]				
70[c]	3 600	1.65×10^{-7}	2.18×10^{10}	7.68
80[b]	13 300			
80[c]	16 300	1.27×10^{-9}	1.28×10^{13}	7.06
90[b]				

(2c)

% Me_2SO	k_p^{OH}/dm^3 mol^{-1} s^{-1}	$k_{-p}^{H_2O}$/s^{-1} [d]	K_p/dm^3 mol^{-1} [e]	pK_a [f]
40[b]	35.5			
50[b]	122			
50[c]	131	1.40×10^{-3}	9.33 10^{4}	10.86
60[b]	515			
70[b]	3 400			
70[c]	3 620	2.94×10^{-5}	1.23×10^{8}	9.93
80[b]	14 700			
80[c]	15 200	9.38×10^{-8}	1.62×10^{11}	8.96
90[b]				

[a] T = 25 °C; k_p^{OH}, $k_{-p}^{H_2O}$ and K_p as defined by Scheme 1. [b] No constant ionic strength. [c] I = 0.5 mol dm^{-3}. [d] Calculated from $k_{-p}^{H_2O} = k_p^{OH}/K_p$. [e] Calculated from p$K_a$ by means of equation (3). [f] Determined from equilibrium measurements.

Table 2. Rate and equilibrium data for the ionization of triphenylmethanes (**2d**), (**2e**) and (**2f**) in various H_2O–DMSO mixtures.[a]

(2d)

% Me_2SO	k_p^{OH}/dm^3 mol^{-1} s^{-1}	$k_{-p}^{H_2O}$/s^{-1}	K_p/dm^3 mol^{-1}	pK_a [b]
40	3.1	0.02	155	13.69
50	6.7	0.02	335	13.30
60	41.8	~0.014	~2985	~ 13.17
70	266.5	1.98×10^{-3}	1.34×10^{5} [d]	12.89[e]
75	560	—	—	—
80	2 160	—	—	—
90	37 500	—	—	—

(2e)

% Me_2SO	k_p^{OH}/dm^3 mol^{-1} s^{-1}	$k_{-p}^{H_2O}$/s^{-1}	K_p/dm^3 mol^{-1}	pK_a [b]
40				
50				
60				
70	6.92	0.023	301	15.54
75	24	0.03	800	
80	72	—	—	—
90	1238	—	—	—

(2f)

% Me_2SO	k_p^{OH}/dm^3 mol^{-1} s^{-1}	$k_{-p}^{H_2O}$/s^{-1}	K_p/dm^3 mol^{-1}	pK_a [b]
40				
50				
60				
70	0.32	0.025	13	16.90
75	1	0.02	50	
80	3.43	0.037	93	18.20
90	18.8	0.038	495	

[a] T = 25 °C; no constant ionic strength; k_p^{OH}, $k_{-p}^{H_2O}$, and K_p as defined by Scheme 1. [b] Calculated from K_p by means of equation (3). [c] Calculated from $k_{-p}^{H_2O} = k_p^{OH}/K_p$. [d] Calculated from p$K_a$ by means of equation (3). [e] Determined from equilibrium measurements.

error, the same as that previously defined from the solvent dependence of k_p^{OH} for various nitrodiphenylmethane and nitrotoluene derivatives, (dlog k_p^{OH}/dN_{DMSO}) = 8.2.[28,31] This observation is significant since it confirms previous conclusions that the kinetic acidity of most benzylic-type carbon acids exhibit an identical response to a transfer from a protic solvent like water or methanol to a dipolar aprotic solvent like DMSO.[28] This behaviour is obviously of considerable interest because it allows reliable extrapolations, making it possible to compare the kinetic acidities of carbon acids exhibiting widely different thermodynamic acidities in a given reference solvent. In the case of (**2a**), it appears that the log k_p^{OH} values tend to fall below the line at high DMSO contents. In fact, the data exhibit a linear relationship with a somewhat more shallow slope (6.90). In this regard, it is useful to recall the finding that the slopes of the log k_p^{OH} *vs.* N_{DMSO} plots tend to decrease slightly when the carbon acid strength reaches pK_as of the order of those for nitroethane and phenylnitromethane.[28] In the present case, (**2a**) is the most acidic compound in the series and it has a pK_a value (8.25) which is close to that of phenylnitromethane (7.93) in 50% H_2O–50% DMSO.[11]

Increasing the DMSO content of the solutions leaves the $k_{-p}^{H_2O}$ values for the more basic carbanions (C-**2d**), (C-**2e**) and (C-**2f**) essentially unaffected but markedly decreases the $k_{-p}^{H_2O}$ values for the three less basic carbanions (C-**2a**), (C-**2b**) and (C-**2c**) which have at least one 2,4-dinitrophenyl ring. This behaviour is similar to that observed in our studies of polynitrodiphenylmethanes and toluenes.[24,31] As a result of a concomitant increase in k_p^{OH} and a decrease in $k_{-p}^{H_2O}$, the equilibrium constants K_p for formation of (C-**2a**), (C-**2b**) and (C-**2c**) according to Scheme 1 increase strongly with increasing DMSO concentration. In fact, the observed increase in K_p is greater than the decrease in the autoprotolysis product of the solvent (K_s), as evidenced by the observation that the pK_a values for (C-**2a**), (C-**2b**) and (C-**2c**) notably decrease on addition of the DMSO cosolvent. In the field of carbon acids, such a decrease in pK_a values in H_2O–DMSO mixtures is only observed for compounds giving rise to carbanions with highly delocalized negative charge, implying that this holds in (C-**2a**), (C-**2b**) and (C-**2c**). Contrasting with this behaviour, the pK_a value for the less acidic tris(4-nitrophenyl)methane (**2d**) is only slightly decreased on going from 40 to 80% DMSO but the observed trend is consistent with the pK_a value of 12.2 reported for this derivative in pure DMSO.[32] On the other hand, the pK_a values for the di- and mono-nitrotriphenylmethanes (**2e** and **f**) tend to increase with increasing the DMSO concentration.

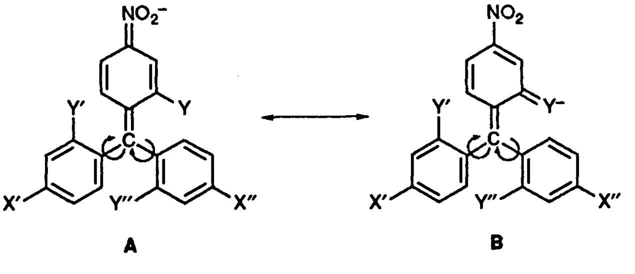
Table 3. Comparison of rates and equilibrium parameters for the reactions in Scheme 1 in 30% H_2O–70% DMSO at 25 °C.

Triphenylmethane	n[a]	k_p^{OH}/dm^3 mol^{-1} s^{-1}	$k_{-p}^{H_2O}$/s^{-1}	pK_a	ΔpK_a[b,c]
(2a)	6	304	4.6×10^{-9}	7.20	0.48
(2b)	5	3600	1.65×10^{-7}	7.68	2.25
(2c)	4	3620	2.94×10^{-5}	9.93	2.96
(2d)	3	266.5	1.98×10^{-3}	12.89	2.65
(2e)	2	6.92	0.023	15.54	1.36
(2f)	1	0.32	0.025	16.90	12.4
(2g)[d]	0	—	—	30.6[e]	
				27.2[f]	

[a] Number of nitro groups. [b] ΔpK_a = pK_a^n − pK_a^{n+1}. [c] Values calculated with respect to an average pK_a for **(2g)** of 28.9. [d] Data taken from ref. 33. [e] pK_a value in DMSO. [f] pK_a value in aqueous DMSO.

The Effects of Nitro Substitution on Equilibrium and Kinetic Acidities. Steric Effects.—The k_p^{OH} and pK_a values determined in 30% H_2O–70% DMSO for **(2a–f)** are compared, together with the $k_{-p}^{H_2O}$ values, in Table 3. Also given for purposes of comparison are the pK_a values reported for triphenylmethane **(2g)** with reference to DMSO and dilute aqueous solution as the standard states. We have used the average value of p$K_a^{(2g)}$ = 28.9 to estimate the ΔpK value for addition of a *p*-nitro group to triphenylmethane.

The ΔpK values measuring the effect of the successive introduction of three *p*-nitro and then three *o*-nitro groups on the thermodynamic acidity of triphenylmethane call for several comments. Firstly, the increase in acidity (ΔpK = 12.4) brought about by the introduction of one *p*-nitro group in **(2g)** is not appreciably less than that caused by a similar introduction in diphenylmethane **(1g)** where ΔpK = 12 or 13.4, depending upon the reported pK_a value for **(1g)**.[24] This indicates that the *p*-nitro group contributes very effectively to the resonance stabilization of the carbanion (C-**2f**) [resonance structure (A) (Scheme 2); X′ = X″ = Y = Y′ = Y″ = H] despite the non-planar structure of this triphenylmethyl anion. In this context, it is perhaps worth recalling that X-ray crystallography studies have revealed that the three phenyl rings of (C-**2g**) adopt a propeller arrangement around the central sp^2 carbon atom with torsion angles of *ca.* 20, 30 and 45°, respectively, in a lithium salt.[25]



Scheme 2.

In contrast with the large effect of the first *p*-nitro group, the acid-strengthening influence of each of the second and third *p*-nitro groups is only approximately 1.5 and 2.5 pK units respectively. This is considerably less than that brought about by the introduction of a second nitro group in the diphenylmethane system (ΔpK = 5).[24] This can be readily understood in terms of only one *p*-nitrophenyl ring of such 'propeller' carbanions as (C-**2d**) and (C-**2e**) being in the most favourable position for effective conjugation with the exocyclic sp^2 carbon atom at any given time. Accordingly, the effects exerted by the additional *p*-nitrophenyl rings must be mainly inductive in nature and this may account for the similar ΔpK changes observed on going from **(2f)** to **(2e)** and **(2e)** to **(2d)**. This interpretation is also consistent with the ΔpK pattern obtained on accumulating *o*-nitro groups in (C-**2d**). The transition from (C-**2d**) to (C-**2c**) is accompanied by a relatively strong increase in acidity (ΔpK ~3) and this is certainly a reflection of the preferential stabilization of the negative charge of (C-**2c**) by the more activated 2,4-dinitrophenyl ring [structures (A)–(B), X′ = X″ = Y = NO_2]. Effective conjugation with more than one 2,4-dinitrophenyl ring is not possible in these carbanions, and a reduced contribution of the other *o*-nitro groups to the acidity would be expected. As can be seen from Table 3, much reduced ΔpK values are actually observed: $\Delta pK_{a(2c)}^{(2b)}$ = 2.25, $\Delta pK_{(2b)}^{(2a)}$ = 0.48.

It is instructive to analyse these changes in pK_a in terms of the variations in the rate constants k_p^{OH} and $k_{-p}^{H_2O}$. As can be seen in Table 3, the increases in acidity brought about by the introduction of the second and third *p*-nitro groups in **(2f)** to form **(2e)** and **(2d)**, respectively are essentially the result of the corresponding increases in the kinetic acidity: $k_{p(2e)}^{OH}/k_{p(2f)}^{OH}$ = 21.6, $k_{p(2d)}^{OH}/k_{p(2e)}^{OH}$ = 38.5. Concomitantly, there is virtually no change in $k_{-p}^{H_2O}/S$ on going from **(2f)** to **(2e)** and only a tenfold decrease in $k_{-p}^{H_2O}$ on going from **(2e)** to **(2d)**. Since it is known that such $k_{-p}^{H_2O}$ rate constants for carbanion reprotonation by the solvent in H_2O–DMSO mixtures are largely governed by the extent of charge delocalization, the above observations support our suggestion that the carbanions (C-**2f**), (C-**2e**) and (C-**2d**) are resonance-stabilized to similar extents.[21,24]

Addition of the first *o*-nitro group to **(2d)** to form **(2c)** further increases the kinetic acidity but it also results in an approximately seventyfold decrease in the $k_{-p}^{H_2O}$ value in 70% DMSO solution. This important decrease is certainly associated with the much larger charge stabilization by a 2,4-dinitrophenyl ring than by a *p*-nitrophenyl ring. While not *directly* comparable, because of the coplanarity of the two rings in the diphenylmethyl carbanions (C-**1d**) and (C-**1e**), it is interesting to note that a decrease in $k_{-p}^{H_2O}$ of the same order of magnitude was found upon the introduction of one *o*-nitro group into 4,4′-dinitrodiphenylmethane **(1e)** to form 2,4,4′-trinitrodiphenylmethane **(1d)**: [$k_{-p}^{H_2O}$ **(1e)**/$k_{-p}^{H_2O}$ **(1d)**] ≈ 20.86 in 50% DMSO solutions.* However, the most significant finding of this work is perhaps provided by the observed changes in k_p^{OH} and $k_{-p}^{H_2O}$ caused by the introduction of further *o*-nitro groups into **(2c)** to form **(2b)** and **(2a)**. As can be seen in Table 3, k_p^{OH} remains unchanged on going from **(2c)** to **(2b)** and decreases by a factor of 7.1 on going from **(2b)** to **(2a)**. Concomitantly, there are very large decreases in the $k_{-p}^{H_2O}$ values ($k_{-p(2c)}^{H_2O}/k_{-p(2b)}^{H_2O}$ = 178; $k_{-p(2b)}^{H_2O}/k_{-p(2a)}^{H_2O}$ = 36 in 70% DMSO) and these cannot be understood in terms of an increased resonance

---

* Values of k_{-p} for (C-**1e**) and (C-**1d**) in 70% DMSO solutions were too small to measure directly.

stabilization of the carbanions (C-**2a**) and (C-**2b**). We therefore suggest that the above anomalous variations are the result of additional unfavourable steric interactions arising from the accumulation of *o*-nitro groups in the triphenylmethane system. Based on the observed variations in k_p^{OH} and $k_{-p}^{H_2O}$, these steric interactions will operate both in the starting carbon acids and in the carbanions, and can be viewed mainly as steric hindrance to the approach of hydroxide ion or water to exocyclic carbon (F-strain).

Experimental

Materials.—Solvents were purified and solutions made up as described previously.[16,21b,31] 2,2′,2″,4,4′,4″-Hexanitro-, 4,4′,4″-trinitro-, 4,4′-dinitro-, and 4-nitrotriphenylmethanes [(**2a**), (**2d**), (**2e**), (**2f**)] were synthesized according to previously reported methods: (**2a**) m.p. 256 °C (lit.,[34] m.p. 256–258 °C); (**2d**) m.p. 213 °C (lit.,[35] m.p. 212–213 °C); (**2e**) m.p. 171 °C (lit.,[36] m.p. 169–170 °C); (**2f**) m.p. 92 °C (lit.,[37] m.p. 92–93 °C).

2,4,4′,4″-Tetranitrotriphenylmethane (**2c**) *and 2,2′,4,4′,4″-Pentanitrotriphenylmethane* (**2b**). Compound (**2d**) (5 g) was slowly added at −25 °C to a solution of concentrated nitric acid ($d = 1.52$; 40 cm^3) and concentrated sulphuric acid ($d = 1.83$; 10 cm^3). The mixture was stirred at −25 °C for 3 h and then poured on to ice. This yielded a crude precipitate which was filtered, washed several times with water, and chromatographed on a silica gel column with benzene as the eluant to afford 1 g of (**2c**) together with a similar amount of (**2b**) and small amounts of (**2d**) and (**2e**). An additional recrystallization from 95% ethanol–5% water gave analytically pure yellow crystals of (**2c**) or (**2b**).

For (**2c**): m.p. 178–179 °C (Found: C, 53.8; H, 2.85; N, 12.95. Calc. for $C_{19}H_{12}N_4O_8$: C, 53.78; H, 2.85; N, 13.20%); δ_H($CDCl_3$; Me_4Si) 8.80 (1 H, d, *J* 2.4 Hz, 3-H), 8.35 (1 H, dd, *J* 2.4, 8.6 Hz, 5-H), 7.22 (1 H, d, *J* 8.6 Hz, 6-H), 8.17 and 7.18 (8 H, AA′BB′, J_{AB} 8.6 Hz, 2′,2″,3′,3″,5′,5″,6′,6″-H) and 6.50 (1 H, s, CH).

For (**2b**): m.p. 200–201 °C (Found: C, 48.2; H, 2.2; N, 14.5. Calc. for $C_{19}H_{11}N_5O_{10}$: C, 48.62; H, 2.36; N, 14.92%); δ_H($CDCl_3$) 8.87 (2 H, d, *J* 2.5 Hz, 3-, 3′-H), 8.51 (2 H, dd, *J* 2.5, 8.6 Hz, 5-, 5′-H), 8.27 and 7.52 (4 H, AB, J_{AB} 8.7 Hz, 2″-, 3″-, 5″-, 6″-H), 7.43 (2 H, d, *J* 8.6 Hz, 6-, 6′-H) and 7.0 (1 H, s, CH).

Measurements.—Kinetic studies were made using a Durrum stopped-flow spectrophotometer, with a thermostatted cell compartment (25 ± 0.2 °C). Slow kinetic measurements were made using a Shimadzu UV-160 spectrophotometer.

Thermodynamic determinations of pK_a values of the most acidic compounds were made in buffered solutions according to a previously reported method.[16,22,31]

References

1 J. R. Jones, *The Ionization of Carbon Acids*, Academic Press, London, 1971.

2 E. Buncel, *Carbanions: Mechanistic and Isotopic Aspects*, Elsevier, Amsterdam, 1975.

3 A. J. Kresge, *Can. J. Chem.*, 1975, **52**, 1897.

4 F. G. Bordwell and W. J. Boyle, *J. Am. Chem. Soc.*, 1971, **93**, 511; 1972, **94**, 3907; 1975, **37**, 4447.

5 F. G. Bordwell, J. E. Bartmess and J. A. Hautala, *J. Org. Chem.*, 1978, **43**, 3107, 3113, 3116; F. G. Bordwell, J. E. Bares, J. E. Bartmess, G. J. McCollum, M. Van der Puy, N. R. Vanier and W. S. Matthews, *J. Org. Chem.*, 1977, **42**, 321; F. G. Bordwell, G. E. Drucker and G. J. McCollum, *J. Org. Chem.*, 1982, **47**, 2504, and references cited therein.

6 B. G. Cox and A. Gibson, *Chem. Commun.*, 1974, 638.

7 R. P. Bell and R. L. Tranter, *Proc. R. Soc. London, Ser. A*, 1974, **337**, 518.

8 J. R. Keeffe and N. H. Munderloch, *Chem. Commun.*, 1974, **17**; J. R. Keeffe, J. Morey, C. A. Palmer and J. C. Lee, *J. Am. Chem. Soc.*, 1979, **101**, 1295.

9 C. D. Slater and Y. W. Chan, *J. Org. Chem.*, 1978, **43**, 2423.

10 P. Y. Bruice, *J. Am. Chem. Soc.*, 1984, **106**, 5959.

11 C. F. Bernasconi, D. A. V. Kliner, A. S. Mullin and J. X. Ni, *J. Am. Chem. Soc.*, 1988, **53**, 3342.

12 R. P. Bell, *The Proton in Chemistry*, 2nd edn., Cornell University, Ithaca, NY, 1973; A. J. Kresge, *Chem. Soc. Rev.*, 1973, **2**, 475; F. Hibbert, *Compr. Chem. Kinet*, 1977, **8**, 97; C. F. Bernasconi, *Pure Appl. Chem.*, 1982, **54**, 2335.

13 C. F. Bernasconi, *Tetrahedron*, 1985, **41**, 3219.

14 R. P. Bell and S. Grainger, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1367.

15 N. Agmon, *J. Am. Chem. Soc.*, 1980, **102**, 2164.

16 F. Terrier, P. G. Farrell, J. Lelievre and A. P. Chatrousse, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1479.

17 C. F. Bernasconi, *Acc. Chem. Res.*, 1987, **20**, 301.

18 C. F. Bernasconi and S. A. Hibdon, *J. Am. Chem. Soc.*, 1983, **105**, 4343; C. F. Bernasconi and R. D. Bunnell, *Isr. J. Chem.*, 1985, **26**, 420; C. F. Bernasconi and P. Paschalis, *J. Am. Chem. Soc.*, 1986, **108**, 2969; C. F. Bernasconi and F. Terrier, *J. Am. Chem. Soc.*, 1987, **109**, 7115; C. F. Bernasconi, R. D. Bunnell and F. Terrier, *J. Am. Chem. Soc.*, 1988, **110**, 6514.

19 J. P. L. Cox, M. R. Crampton and P. Wight, *J. Chem. Soc., Perkin Trans. 2*, 1988, 25.

20 J. W. Bunting and D. Stefanides, *J. Am. Chem. Soc.*, 1988, **110**, 4008.

21 (*a*) A. P. Chatrousse, F. Terrier, P. G. Farrell and F. M. Fouad, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1243; (*b*) P. G. Farrell, P. Fogel, A. P. Chatrousse, J. Lelievre and F. Terrier, *J. Chem. Soc., Perkin Trans. 2*, 1985, 51; (*c*) M. P. Simonnin, H. Q. Xie, F. Terrier, J. Lelievre and P. G. Farrell, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1553.

22 F. Terrier, A. P. Chatrousse, E. Kizilian, N. V. Ignatev and L. M. Yagupolskii, *Bull. Soc. Chim. Fr.*, 1989, 623.

23 F. Terrier, J. Lelievre, A. P. Chatrousse, R. Schaal and P. G. Farrell, *Can. J. Chem.*, 1987, **65**, 1980.

24 F. Terrier, H. Q. Xie and P. G. Farrell, *J. Org. Chem.*, 1990, **55**, 2610.

25 J. F. Brooks and G. D. Stucky, *J. Am. Chem. Soc.*, 1972, **94**, 7333.

26 W. Clegg and J. C. Lockhart, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1621.

27 S. E. Browne, S. E. Asher, E. H. Cornwall, J. K. Frisoli, I. J. Harris, E. A. Salot, E. A. Sauter, M. A. Trecoske and P. S. Veale, Jr., *J. Am. Chem. Soc.*, 1984, **106**, 1432.

28 P. Fogel, P. G. Farrell, J. Lelievre and F. Terrier, *J. Chem. Soc., Perkin Trans. 2*, 1985, 711.

29 R. P. Bell and B. G. Cox, *J. Chem. Soc. B*, 1971, 783.

30 E. A. Walters, *J. Phys. Chem.*, 1978, **82**, 1219.

31 J. Lelievre, P. G. Farrell and F. Terrier, *J. Chem. Soc., Perkin Trans. 2*, 1986, 333.

32 C. D. Ritchie and R. E. Ushold, *J. Am. Chem. Soc.*, 1967, **89**, 1721; 1968, **90**, 2821.

33 A. Streitwieser, Jr., E. Juaristi and L. Nebenzahl, in *Comprehensive Carbanion Chemistry*, eds. E. Buncel and T. Durst, Elsevier, Amsterdam, 1980, p. 323.

34 J. D. Margerum, L. J. Miller, E. Saito, M. J. Brown, H. S. Mosher and R. Hardwick, *J. Phys. Chem.*, 1962, **66**, 2434.

35 K. Bowden and R. Stewart, *Tetrahedron*, 1965, **21**, 261.

36 T. J. Adley and R. D. Clarke, *Can. J. Chem.*, 1969, **47**, 505.

37 D. Y. Curtin and K. Auer, *J. Org. Chem.*, 1960, **25**, 880.

Paper 0/02491K
Received 4*th June* 1990
Accepted 15*th June* 1990