The Acidity of Weak Carbon Acids. Part 4.[1] The Kinetic Acidities of 4-Nitro-, 4,4′-Dinitro and 4,4′,4″-Trinitrotriphenylmethanes

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Rate coefficients for the base-catalysed detritiation of 4,4′,4″-trinitro-, 4,4′-dinitro- and 4-nitrotriphenylmethanes in dimethyl sulphoxide have been measured at 25.0 °C. The bases are a series of secondary aliphatic amines and tetramethylguanidine and of benzoate anions. For 4,4′-dinitrophenylmethane and piperidine, the rate coefficients for detritiation at 55.0 °C and, for α-[$^2H_1$]-4,4′-dinitrotriphenylmethane and piperidine, dedeuteriation at 25.0 °C were also measured. The kinetic isotope effect and activation parameters indicate the rate-determining step to be the ionisation process. Brønsted coefficients, β, have been calculated using the known or previously measured pK_a values of the conjugate acids of the bases in dimethyl sulphoxide. The β values for both carbon acids are significantly greater for the benzoate anion than for the nitrogen base catalysis, and those for the dinitro-carbon acid are less than those for the trinitro-acid. No reactivity-selectivity relationship exists. This behaviour is discussed in relation to Marcus and related theories.

The acidity of triphenylmethanes (TPMs) has been studied by a variety of techniques and in various systems.[2–4] Thus, the pK_a values of some TPMs have been measured using H_- acidity function methods in aqueous and alcoholic dimethyl sulphoxide (DMSO)-containing base[5] and using indicator methods in DMSO.[6] The kinetic acidities of some TPMs and related carbon acids have been studied using exchange methods, *e.g.* the deuteriation catalysed by methoxide in deuteriated methanol–DMSO[7] and detritiation catalysed by methoxide in methanol.[8]

The discussion of structure-activity relationships in proton-transfer processes involving carbon acids in terms of their 'intrinsic reactivities' has been developed,[9] based on the formulation of Marcus theory. The relatively acidic 2,2′,4,4′-tetranitro- and 2,4,4′-trinitrodiphenylmethane (TENDPM and TRNDPM) have been studied in their rates of reversible proton abstraction by a variety of bases in 50% aqueous DMSO.[10] The Brønsted α and β values were considered to show a charge imbalance in the transition states.

In the present study we report the rates of detritiation of 4,4′,4″-trinitrotriphenylmethane (TNTPM), 4,4′-dinitrotriphenylmethane (DNTPM), and 4-nitrotriphenylmethane (NTPM) in DMSO by a series of nitrogen bases and benzoate anions. The activation parameters have been evaluated for the detritiation of DNTPM by piperidine. The rate of dedeuteriation of α-[$^2H_1$]-DNTPM by piperidine has also been measured. The pK_a values of the conjugate acids of the bases are known. The results are discussed in terms of reactivity-selectivity and the structure of the transition state.

Results

The rate coefficients, k_2, for the base-catalysed detritiation of the nitrotriphenylmethanes in DMSO at 25.0 °C are shown in Table 1. The reactions were found to be first order in the substrate and the base. The base was always in large excess and is not consumed, thus the reactions approximated to first-order behaviour. The rate coefficients, k_2, were calculated by dividing the base concentration into the observed first-order rate coefficients. The rate coefficient for the piperidine-catalysed dedeuteriation of DNTPM under similar conditions (see Experimental) is also shown in Table 1. The rate coefficients for the piperidine-catalysed detritiation in DMSO were measured at both 25.0 and 55.0 °C and are shown in Table 1. Table 1 also shows the pK_a values of the conjugate acids of the bases in DMSO.[1,11] The Hammett equation (1) has been used to correlate the rates of detritiation catalysed by the m-substituted benzoate anions using the known σ values.[12] The results for the latter are shown in Table 2.

Table 1. Rate coefficients, k_2, for the detritiation of DNTPM, TNTPM and NTPM catalysed by sodium *meta*-substituted benzoates and aliphatic amines and tetramethylguanidine in DMSO at 25.0 °C.[a]

		$k_2/10^{-4}$ dm^3 mol^{-1} s^{-1}		
		DNTPM	TNTPM	pK_a[e]
Substituent R[f]	Me	26.2	3670	11.26
	H	21.2	2730	11.02
	Cl	6.45	712	9.82
	Br	5.94	682	9.91
	NO_2	2.24	168	9.20
Iminodipropiononitrile		0.279	0.817	5.0
Morpholine		1.25	26.4	8.6_5
Diethanolamine		1.58	31.9	9.5
Diethylamine		1.68	40.0	10.4
Piperidine[b]		6.05[c,d]	200	10.6
Tetramethylguanidine		15.3	974	13.0

[a] Rate coefficients are reproducible to ±3%. [b] For NTPM at 25.0 °C, $10^4 k_2$ for detritiation is 0.10 (±0.02) dm^3 mol^{-1} s^{-1}. [c] At 55.0 °C, k_2 is 0.009 62 (±0.000 25) dm^3 mol^{-1} s^{-1}. [d] At 25.0 °C, k_2 for dedeuteriation is 0.0012 (±0.0002) dm^3 mol^{-1} s^{-1}. [e] Refs. 1, 11. [f] In sodium *meta*-substituted benzoates m-$RC_6H_4CO_2^-Na^+$.

$$\log (k/k_0) = \rho\sigma \qquad (1)$$

Discussion

The kinetic acidities of the nitro-substituted triphenylmethanes have been studied in DMSO. The reactions were all overall second order, being first order in both base and substrate.

Table 2. Reaction constants, ρ, for benzoate-catalysed detritiation of DNTPM and TNTPM in DMSO at 25.0 °C.[a]

Substrate	ρ	s	$\log k_0$	r	n
DNTPM	−1.377	0.011	−2.678	1.000	5
TNTPM	−1.686	0.022	−0.544	0.998	5
pK_a values of benzoic acids	−2.702	0.204	11.00	0.992	5

[a] s = standard deviation, r = correlation coefficient and n = number of points.

Table 3. Brønsted coefficients, β, and pK_a values of DNTPM and TNTPM in DMSO at 25.0 °C.[a]

Substrate	β	s	$\log G_b$	r	n	pK_a[b,e]
DNTPM[c]	0.215	0.035	−5.724	0.951	6	12.70
DNTPM[d]	0.501	0.037	−8.198	0.992	5	12.70
TNTPM[c]	0.379	0.041	−5.985	0.978	6	14.48
TNTPM[d]	0.610	0.063	−7.263	0.984	5	14.48

[a] See Table 1. [b] Reference 6. [c] Using nitrogen bases. [d] Using benzoate anions. [e] For NTPM, pK_a is 16.77.

Kinetic isotope effects are very important in establishing the nature of the rate-determining step in base-catalysed isotope exchange reactions. The importance of internal return was established by the early studies of Cram *et al.*[13] and has been more recently discussed in detail.[14] For DNTPM, the rate coefficients of detritiation, k_t, and dedeuteriation, k_d, catalysed by piperidine have been measured. The Swain–Schaad relation[15] in the form of eqn. (2) below has been used for the

$$k_h/k_d = (k_d/k_t)^{2.257} \qquad (2)$$

conversion of the observed k_d/k_t of 2.0 (±0.5) to the more familiar k_h/k_d of 5 (±1). The uncertainties in k_d, in particular, and a contribution to k_h/k_d by a secondary effect[16] make this result less useful. However, it remains diagnostic in indicating that the rate-determining step is the ionisation process itself. The activation parameters may be calculated for DNTPM, catalysed by piperidine, from the rates at 25.0 and 55.0 °C as $\Delta H^\ddagger$ and $\Delta S^\ddagger$ at 25.0 °C equal to 17.4 (±0.3) kcal mol^{-1} and −15 (±2) cal mol^{-1} K^{-1}, respectively. These values compare closely with those for benzyl cyanide in our previous study[1] and for other carbon acids of similar acidity in aprotic solvents having rate-determining ionisation.[17]

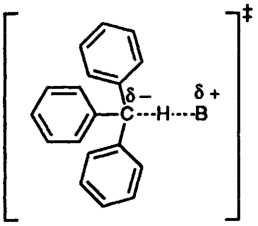
Bordwell *et al.*[6] have studied the equilibrium acidities of the nitrotriphenylmethanes in DMSO. The strengths of the bases or their conjugate acids have been measured either by ourselves[2] or others[11] previously. The strengths of the nitrogen bases, catalysing the reaction, varies by 8.0 pK_a units and of the carboxylate anions by *ca.* 2.0 pK_a units; whereas the kinetic basicity changes by *ca.* 10^2 and 20, respectively. The effect of changing the base strength can be estimated by use of the Brønsted eqn. (3) below. The results for the nitrogen bases

$$\log k_b = \beta \log k_b + \log G_b \qquad (3)$$

give reasonably linear relations and the β values are shown in Table 3. Alternatively the Hammett equation (1) can be used to correlate the results for the reactions catalysed by the benzoate anions, and the pK_a values of the benzoic acids in DMSO as shown in Table 2. Eqn. (4) below would then give the Brønsted

$$\beta = \rho_{k_2}/\rho_{K_a} \qquad (4)$$

β values. The values shown in Table 3 are calculated using eqn. (3) to be consistent, but are almost the same as those calculated using eqn. (4). The β values for the nitrogen bases and benzoate anions are significantly different (Δβ *ca.* 0.3). In both cases, the β values of TNTPM are significantly greater than those of DNTPM. However, if these values are considered as a 'rough' measure of charge development in the transition state,[18] those for the benzoate anions indicate a 'half-formed' carbanion; whereas, these for the nitrogen bases point to a transition state which is less advanced. A likely cause of this result is the fairly intense steric 'bulk' interactions to be expected in the transition state **1** when the base is either a secondary aliphatic amine or tetramethylguanidine and the acid a triphenylmethane. The steric 'bulk' interactions will be minimised by extending the bonds being made in the transition state[19] and reducing the advance of that state. The benzoate anions are relatively unhindered bases in steric 'bulk' terms.



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A very interesting result found in this study is that the more acidic TNTPM has greater β values, for both types of bases, than those for DNTPM. Both triphenylmethanes will have almost identical steric 'bulk' effects in the reaction. This is clearly 'anti-Hammond' behaviour in which the more reactive and acidic system shows greater selectivity.[20] There appears to be no evidence in this study for a reactivity-selectivity relation.

The intrinsic rate coefficients, k'_0, as defined by Bernasconi[9] in eqn. (5) have been tabulated for the rates of deprotonation of

$$\log k'_0 = \log k_1 - \log K_1 \qquad (5)$$

a number of carbon acids. Basing the calculation here on TNTPM and either piperidine or benzoate, $\log k'_0$ is given as 0.10 and 1.50, respectively, assuming a tritium isotope effect of 10. Likewise, the calculations for DNTPM and either piperidine or benzoate gives $\log k'_0$ as −1.09 and 0.11, respectively. These values are considerably less than that calculated for benzyl cyanide/piperidine, 9.76, in our previous study[1] and are much closer to the values for TENDPM and TRNDPM, with carboxylates or secondary amines, in 50% aqueous DMSO of *ca.* −0.10, −0.60 and −0.55, −1.10, respectively.

Triphenylmethyl carbanions can be considered to be considerably delocalised with a 'propeller-like' conformation, giving maximum delocalisation possible with the steric inhibition of the rings to full coplanarity, *cf.* ref. 21. The *para*-nitro groups can also be considered to be very capable of resonance stabilisation of this charge. Bernasconi[9] has considered that reactions with strongly imbalanced transition states also have large intrinsic barriers. Such a transition state in this study would require the negative charge to be relatively localised on the ionisable carbon atom which would possess considerable sp^3 character. The structural reorganisation would considerably lag behind the proton transfer.

It is possible to calculate a tentative value for α for the carbon acids by use of the Brønsted eqn. (6). α has been interpreted

$$\log k_a = \alpha \log K_a + \log G_a \qquad (6)$$

as a measure of the extent to which the transition state resembles reactants or products.[22] Unfortunately, NTPM was too slow in the detritiation reaction to be measured for all bases and the measurement shown in Table 1 for NTPM and piperidine is rather uncertain. However, the α value for piperidine, based on three points, is given as 0.81 (0.85 for DNTPM and TNTM alone) as shown in eqn. (7) below.

$$\log k = 0.81 \log K_a + 8.55 \qquad n = 3, r = 1.00, s = 0.02 \tag{7}$$

The value of α is significantly greater than β, as well as having $\alpha + \beta > 1$. Values of Brønsted coefficients greater than unity have been found in the reaction of nitroalkanes.[18,23] The latter compounds have a quite different structure to the ring-substituted nitro triphenylmethanes studied here. Bell[24] has proposed a general central force model which would account for differences between α and β; in particular the finding that $\alpha > \beta$ and that for uphill reactions $\alpha + \beta > 1$. However, the model does not account for $\alpha > 1$. Other explanations have been offered for such observations.[25] The preliminary results for α in this study will require confirmation and extension before detailed examination is possible.

The Brønsted coefficient can be calculated from eqn. (8) which has been developed from Marcus.[26] It is useful to

$$\beta = \frac{\Delta G^{\ddagger}}{\Delta G^{\circ}} - \left[\left(\frac{\Delta G^{\ddagger}}{\Delta G^{\circ}}\right)^2 - \left(\frac{\Delta G^{\ddagger}}{\Delta G^{\circ}}\right)\right]^{\frac{1}{2}} \tag{8}$$

compare the calculated and observed values for β using this relation. Using TNTPM and DNTPM and either piperidine or benzoate, β can be calculated as 0.52, 0.52 and 0.53, 0.53 respectively. The observed values of β are 0.38, 0.62 and 0.22, 0.51, respectively. Eqn. (9) has been developed by Lewis–More

$$\beta = (2 - \Delta G^{\circ}/\Delta G^{\ddagger})^{-1} \tag{9}$$

O'Ferrall[26] and β can be similarly calculated as 0.54, 0.53 and 0.57, 0.56, respectively. The severe discrepancy between the calculated and observed β values from the carbon acids and piperidine indicate a failure in this treatment. The cause of this could be the major influence of steric 'bulk' factors in determining β for this system.

It has been realised for some time that interactions can be both present and important in the transition state for acid- or base-catalysed reactions that are neither present and/or important in the initial or final states, *cf.* ref. 25. The triphenylmethanes, on ionising, have a situation in which steric and resonance effects are interrelated. The involvement of sp^3-hybridised character in the carbonionic transition state appears likely. The bond-breaking process would then precede resonance stabilisation without synchronisation.

Experimental

Materials.—4-Nitrotriphenylmethane was prepared by modifying the procedure of Baeyer and Lohr,[27] as described by Curtin and Kaver.[28] 4,4′-Dinitrotriphenylmethane was prepared by the oxidation[29] of the corresponding diamino compound.[30] Nitration of triphenylmethane gave 4,4′,4″-trinitrotriphenylmethane.[31] All these compounds were recrystallised to give m.p.s in good agreement with literature values and had IR and ^1H and ^{13}C NMR spectra confirming their structure. The aliphatic amines and guanidines were prepared and/or purified as described previously.[1] The sodium salts of the *meta*-substituted benzoic acids were prepared in the following manner. The acids were available commercially and purified if necessary. The benzoic acid (0.1 mol) was dissolved in aqueous sodium hydroxide (90 cm^3; 1 mol dm^{-3}) and stirred for 30 min, maintaining a small excess of the acid. The solution was then washed with ether (3 × 100 cm^3). After evaporation to dryness, the colourless powders were dried under reduced pressure for 24 h. The sodium salts were assayed titrimetrically using hydrochloric acid. The triphenylmethanes were tritiated as described previously for benzyl cyanides,[1] but extracting the solution with dichloromethane (3 × 15 cm^3). The deuteriation was completed in the same way as tritiation, using sodium deuteroxide in D_2O and [$^2H_6$]DMSO. The exchange was repeated (×3) to give the product, α-[$^2H_1$]dinitrotriphenylmethane, >98% deuteriated in the side-chain, as monitored by ^1H NMR spectroscopy. The tritiated or deuteriated products were then recrystallised from benzene, having m.p.s in agreement with the substrates.

Kinetic Measurements.—The rates of detritiation and dedeuteriation were followed by the method described previously.[1] Ion association occurs for sodium benzoates in DMSO,[32] which can be minimised by addition of an equivalent of [2.2.2] cryptand.[33]

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