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# Thermodynamic nitration rates of aromatic compounds. Part 4. Temperature dependence in sulfuric acid of $\text{HNO}_3 \rightarrow \text{NO}_2^+$ equilibrium, nitration rates and acidic properties of the solvent †

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The protonation–dehydration equilibrium of nitric acid ( $\text{HNO}_3 + \text{H}^+ \rightleftharpoons \text{H}_2\text{O} + \text{NO}_2^+$ ) has been studied in the range 80–94 wt%  $\text{H}_2\text{SO}_4$  as a function of temperature and the variations of  $[\text{NO}_2^+]/[\text{HNO}_3]$  ratios have been analysed to evaluate the dissociation constants ( $\text{p}K_{\text{NO}_2^+}$ ) and the enthalpy of dissociation of the process.

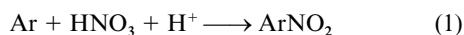
The nitration rates of some aromatic compounds, related both to the stoichiometric concentration of nitric acid (rate =  $k_{2\text{obs}}[\text{Ar}][\text{HNO}_3]$ ) and to the effective concentration of electrophilic species (rate =  $k_2[\text{Ar}][\text{NO}_2^+]$ ), have been investigated in the range 50–100 wt%  $\text{H}_2\text{SO}_4$  and the dependence upon acidity and temperature of the different rate profiles is discussed.

Activation energies determined by  $k_{2\text{obs}}$  and  $k_2^\circ$  nitration rates are reported. The  $k_2^\circ$  values are found to be independent of medium acidity and allow one to obtain consistent activation energies as expected for activated and deactivated aromatic substrates as well as for an encounter limited reaction.

Equilibria and rates in sulfuric acid have been analysed using the *Mc* activity coefficient functions whose values have been estimated over a range of temperature between 25 °C and 90 °C. The general trend observed in the acidic properties of the medium is reported. It is shown that the temperature has a small influence on the *Mc* function.

## Introduction

The nitration of aromatic compounds in concentrated strong acids [eqn. (1)] is an acid catalysed reaction widely used in theoretical studies and industrial applications.<sup>1–10</sup>

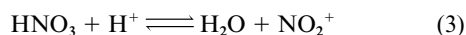


From a practical point of view aqueous sulfuric acid appears to be the most commonly used solvent<sup>6–8</sup> because of its catalytic efficiency, between 50–100 wt%, in the nitration process of activated and deactivated aromatic compounds. The acidity dependence of nitration rates and the equilibria between nitric acid and solvent, the latter involved in the formation process of the reacting species, are thus the key parameters which need to be known in order to carry out a reaction under the optimal experimental conditions.

Nitration rates of a large number of compounds, related to the stoichiometric concentrations of reagents by eqn. (2),<sup>6,7</sup>

$$\text{rate} = k_{2\text{obs}}[\text{Ar}]_{\text{st}}[\text{HNO}_3]_{\text{st}} \quad (2)$$

and equilibrium data of  $\text{NO}_2^+$ , formed from nitric acid by equilibrium (3),<sup>11–14</sup> are now available at 25 °C together with



new parameters accounting for the acidity properties of the medium.<sup>15–17</sup>

In this paper measurements of equilibria and rates, carried out in sulfuric acid at different temperatures, are reported. In particular,  $[\text{NO}_2^+]/[\text{HNO}_3]$  ratios of nitric acid, nitration rates

of aromatics and the protonating ability of sulfuric acid–water mixtures used as solvent are analysed. These results allow one to obtain additional knowledge of the effects of temperature in a chemical process characterized by a high exothermicity and by critical regions in which thermal runaway occurs.<sup>18</sup>

## Experimental

### Materials

Nitric acid was purified by vacuum distillation from concentrated sulfuric acid and was stored at –50 °C. Samples distilled once or twice did not give different results in the kinetic and equilibrium data.

Aromatic substrates were purified from the commercially available products (99%). Sulfuric acid was Analar grade. The aqueous solutions of various strengths were prepared by diluting concentrated acids and their percentage compositions were determined by weighing and/or by automatic potentiometric titrations against standard solutions of NaOH. Nitric acid solutions in sulfuric acid were prepared by weighing both reagent and solvent.

### Kinetic measurements

Separate solutions of the aromatic and nitric acid in sulfuric acid of appropriate concentrations were prepared using weighed samples of solvent and reagents. A small volume of the aromatic solution was transferred by micrometric syringe to an optical cell containing a weighed sample of nitric acid in sulfuric acid. The cell was kept at the fixed temperature by a digital thermostat and the change of absorbance with time at selected wavelengths was followed.

Second-order rate coefficients ( $k_{2\text{obs}}$ ) have been determined by eqn. (2) using either excess nitric acid or equimolar concentrations of nitric acid and the aromatic. The results obtained

† For Part 3, see ref. 10.

**Table 1** Second-order rate constants ( $k_{2\text{obs}}/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ) for nitration in aqueous sulfuric acid at 40 °C, 60 °C and 75 °C

Compound	40 °C		60 °C		75 °C	
	wt% H <sub>2</sub> SO <sub>4</sub>	log $k_{2\text{obs}}$	wt% H <sub>2</sub> SO <sub>4</sub>	log $k_{2\text{obs}}$	wt% H <sub>2</sub> SO <sub>4</sub>	log $k_{2\text{obs}}$
Benzene <sup>a,b</sup>	63.47	-2.37	63.00	-1.73		
	64.18	-2.16	63.48	-1.63		
	64.81	-1.98	64.18	-1.44		
	65.38	-1.78	64.79	-1.22		
	66.13	-1.62	65.36	-1.05		
	67.50	-1.17	66.14	-0.83		
	68.97	-0.67	66.17	-0.83		
	70.42	-0.10	67.47	-0.50		
		68.94	0.00			
		70.41	0.54			
<i>o</i> -Chloronitrobenzene <sup>a,c</sup>	80.45	-3.05	80.45	-2.34		
	81.34	-2.61	81.24	-1.99		
	82.15	-2.29	82.11	-1.60		
	84.72	-1.43	82.11	-1.61		
	84.76	-1.42	84.73	-0.82		
	88.76	-0.16	88.76	0.42		
	89.88	-0.10	88.78	0.49		
	90.66	-0.09	89.88	0.62		
	92.99	-0.18	90.66	0.61		
	94.85	-0.28	92.97	0.58		
	96.32	-0.39	94.85	0.43		
	96.32	-0.39	96.32	0.38		
	98.82	-0.54	98.82	0.22		
<i>p</i> -Chloronitrobenzene <sup>a,d</sup>	83.70	-3.16	83.70	-2.44	93.29	-0.37
	84.56	-2.96	84.56	-2.25	95.90	-0.49
	86.26	-2.29	86.26	-1.61	98.68	-0.64
	87.30	-1.89	87.30	-1.24		
	88.25	-1.82	88.25	-1.13		
	88.77	-1.75	89.57	-0.94		
	89.57	-1.60	91.11	-0.83		
	91.11	-1.56	92.11	-0.88		
	91.13	-1.61	93.30	-0.88		
	92.11	-1.63	94.06	-0.95		
	93.29	-1.65	95.93	-1.04		
	94.07	-1.74	98.68	-1.17		
	95.88	-1.93				
	95.93	-1.88				
	98.68	-2.04				

<sup>a</sup> [Aromatic]  $10^{-4}$ – $10^{-5} \text{dm}^{-3}$ ; [HNO<sub>3</sub>]  $10^{-2}$ – $10^{-3} \text{mol dm}^{-3}$ . <sup>b</sup>  $E_a/\text{kcal mol}^{-1} = 18.3$  (at 64 wt%), 14.6 (at 71 wt%). <sup>c</sup>  $E_a/\text{kcal mol}^{-1} = 16.5$  (at 84 wt%), 16 (at 87 wt%), 15.8 (at 91 wt%), 19.2 (at 98 wt%). <sup>d</sup>  $E_a/\text{kcal mol}^{-1} = 17.8$  (at 84 wt%), 17.4 (at 87 wt%), 16.9 (at 91 wt%), 20.1 (at 98 wt%).

at 40 °C and 60 °C for benzene, *o*- and *p*-chloronitrobenzenes are reported in Table 1. Nitration rates of *p*-chloronitrobenzene at 75 °C, in the range 90–100 wt% H<sub>2</sub>SO<sub>4</sub>, are also given.

### UV measurements

Aqueous solutions of sulfuric acid at selected concentrations were weighed in a UV cell and a small volume of pure nitric acid (or a solution of it in sulfuric acid) was added by using a micrometric syringe. The nitric acid concentrations, calculated from the density of unmixed solutions, were between  $10^{-3}$ – $10^{-2} \text{mol dm}^{-3}$ .

A change of the [NO<sub>2</sub><sup>+</sup>] in time and, in particular, a net increase of the absorbance with time has been observed. This required an extrapolation back to the time at which the reagents were mixed. This spectral behaviour is analogous to that previously reported at 25 °C for measurements of [NO<sub>2</sub><sup>+</sup>]/[HNO<sub>3</sub>] ratios in sulfuric<sup>11,12</sup> and trifluoromethanesulfonic acid<sup>14</sup> of different strengths.

In Table 2 the normalized molar extinction coefficients ( $\epsilon_N$ ) and the [NO<sub>2</sub><sup>+</sup>]/[HNO<sub>3</sub>] ionization ratios determined by UV measurements at 40 °C and 60 °C are reported. The change of absorbance was followed at 260 nm. Previous studies at 25 °C<sup>12</sup> have shown that Raman and UV data at this fixed wavelength are in fair agreement, in spite of the observed experimental complications and of some uncertainty of the experimental  $\epsilon_{\text{BH}^+}$  values at acidities >91% sulfuric acid.<sup>11</sup>

### Determination of the *Mc*(i) activity coefficient function

The dependence on temperature of the “activity coefficient term of solutes” (or *Mc*(i) activity coefficient function<sup>15–17</sup>) has been estimated from the available (log [BH<sup>+</sup>]/[B]) ionization ratios of some indicators (B), essentially nitroanilines. The values have been obtained by studying the corresponding protonation equilibria (B + H<sup>+</sup> ⇌ BH<sup>+</sup>) in sulfuric acid at different temperatures.<sup>19,20</sup> The log [BH<sup>+</sup>]/[B] ratios of nitroanilines in HClO<sub>4</sub><sup>21</sup> and the log [R<sup>+</sup>]/[ROH] ratios of triphenylmethanols (ROH) in sulfuric acid,<sup>22</sup> the latter related to the protonation–dehydration equilibrium of ROH (ROH + H<sup>+</sup> ⇌ R<sup>+</sup> + H<sub>2</sub>O), have also been analysed for comparison.

Even though the mathematical treatment of the experimental data is analogous to that already reported in the study of equilibria of indicators in aqueous acid solutions at 25 °C,<sup>15–17</sup> additional procedures have also been used. Intercepts ( $\text{p}K_{\text{BH}^+}$ ) and slopes (*n*) of the indicators (B) have been obtained by plotting: (i) {log [BH<sup>+</sup>]/[B] – log [H<sup>+</sup>]} = log  $Q_B$  (at *T* °C) vs. *Mc*(i) (at 25 °C); (ii) log  $Q_B$  (at *T* °C) vs. log  $Q_B$  (at 25 °C); (iii) log  $Q_B$  (at *T* °C) vs. log  $Q_{B'}$  (at *T* °C) (where B and B' are two different overlapping indicators). For triphenylmethanols, {log [R<sup>+</sup>]/[ROH] – log [H<sup>+</sup>] + log [H<sub>2</sub>O]} = log  $V_R$  (at *T* °C) has been used in the different plots.

Taking into account the new parameters, the *Mc* (*T* °C) functions at a given temperature have been estimated and referred to

**Table 2** Equilibrium  $\text{HNO}_3 \rightarrow \text{NO}_2^+$  in aqueous sulfuric acid by UV spectroscopy: normalized extinction coefficients ( $\epsilon_N$ ) and ionization ratios ( $\log [\text{NO}_2^+]/[\text{HNO}_3]$ ) at 40 °C and 60 °C<sup>a</sup>

$\text{H}_2\text{SO}_4$ (wt%)	40 °C		$\text{H}_2\text{SO}_4$ (wt%)	60 °C	
	$\epsilon_N$	$\log [\text{NO}_2^+]/[\text{HNO}_3]$		$\epsilon_N$	$\log [\text{NO}_2^+]/[\text{HNO}_3]$
83.74	1.68	-1.77	83.77	2.02	-1.68
83.76	1.26	-1.89	83.82	2.07	-1.67
84.90	2.76	-1.55	83.88	1.98	-1.69
85.56	5.29	-1.25	84.92	3.38	-1.45
85.69	5.65	-1.22	85.49	4.93	-1.28
86.58	12.47	-0.85	85.54	4.40	-1.34
86.77	14.25	-0.78	85.54	4.46	-1.33
86.78	15.31	-0.74	85.60	4.59	-1.32
86.93	15.37	-0.74	86.46	10.07	-0.95
87.09	18.46	-0.64	86.58	10.81	-0.92
87.26	20.10	-0.60	86.64	12.72	-0.84
87.56	22.61	-0.53	86.77	13.10	-0.82
87.68	24.24	-0.49	86.92	13.90	-0.79
88.44	39.44	-0.19	87.09	16.91	-0.69
88.49	40.82	-0.16	87.20	18.76	-0.64
88.53	41.43	-0.15	87.43	21.43	-0.56
88.63	43.75	-0.11	87.69	26.28	-0.45
88.84	48.86	-0.02	88.42	34.31	-0.28
89.00	56.41	0.11	88.54	39.93	-0.18
89.06	60.72	0.19	88.57	36.38	-0.24
89.41	65.80	0.28	88.65	38.65	-0.20
89.43	66.81	0.30	88.81	46.97	-0.05
89.76	73.33	0.44	89.20	51.12	0.02
90.02	74.74	0.47	89.72	63.40	0.24
90.03	76.32	0.51	90.05	67.90	0.32
90.62	83.64	0.71	90.17	72.16	0.41
90.81	85.58	0.77	90.36	74.88	0.47
90.89	87.43	0.84	90.42	76.00	0.50
91.63	90.70	0.99	90.96	80.83	0.62
91.67	91.53	1.03	90.98	82.20	0.66
			91.07	83.04	0.69
			91.07	84.18	0.72
			91.63	88.15	0.87
			91.68	88.98	0.91

<sup>a</sup>  $\epsilon$  Values determined at 260 nm; wt%  $\text{H}_2\text{SO}_4$  (at half-protonation) = 88 (at 25 °C); 88.8 (at 40 °C); 89.2 (at 60 °C).

$\log Q_{B^*}$  values (at  $T$  °C) of 2-nitroaniline ( $B^*$ ), the latter being used as standard indicator.<sup>15-17</sup>

By using the plots  $Mc(T$  °C) vs.  $Mc(25$  °C), the appropriate slopes or the appropriate factors for temperature dependence of the  $Mc(i)$  functions,  $[n(T$  °C)], have been derived at some fixed temperature. The observed values between 25–90 °C are given by eqn. (4), where  $n(T$  °C) = 0.957 (at 40 °C), 0.918 (at 60 °C),

$$Mc(i)^T = [n(T$$
 °C)]  $\times$   $Mc(i)^{25}$  (4)

0.888 (at 80 °C) and 0.875 (at 90 °C). Using the plots  $n(T$  °C) vs.  $1/T$  [ $T$  = temperature (K)], the empirical relationship (5) has been obtained, which is valid at 15–90 °C. It has been found that these parameters are, essentially, related to the temperature dependence of 2-nitroaniline, used as standard indicator ( $B^*$ ). Indeed, the slope of eqn. (5) turns out to be the slope observed

$$Mc(T$$
 °C) =  $(200 \times 1/T + 0.3292) \times Mc(25$  °C) in  $\text{H}_2\text{SO}_4$  (5)

in the plot of  $n(T$  °C) vs.  $1/T$  [ $T$  = temperature (K)] of ( $B^*$ ). The constant of eqn. (5) is the slope value observed in the plot  $n(T$  °C) vs.  $pK_{BH^+}(T$  °C) of ( $B^*$ ).

Analogous treatment of experimental data in  $\text{HClO}_4$  gives the empirical relationship (6) which is valid between 15 °C and 45 °C.

$$Mc(T$$
 °C) =  $(220 \times 1/T + 0.262) \times Mc(25$  °C) in  $\text{HClO}_4$  (6)

For the treatment of these data,  $\log [H^+]$  values at 25 °C were used because previous studies in sulfuric acid<sup>23,24</sup> show minimal variations on the degrees of dissociation ( $\alpha$ ) of aqueous acid

solutions with temperature. Furthermore, new experimental investigations in aqueous  $\text{HClO}_4$  between 25 and 90 °C, the latter ones performed by Raman measurements of integrated intensities of the  $\text{ClO}_4^-$  band at  $930\text{ cm}^{-1}$ , show an analogous behaviour.<sup>25</sup>

The problem of the errors affecting the results has already been discussed.<sup>15c</sup> However, the new studies related to the equilibria of solutes and solvents and in particular the studies of analogous solutes in different solvents<sup>16</sup> show that uncertainties in the experimental  $\log [BH^+]/[B]$  values or inconsistent data of different authors for the same indicator, are the main sources of errors.

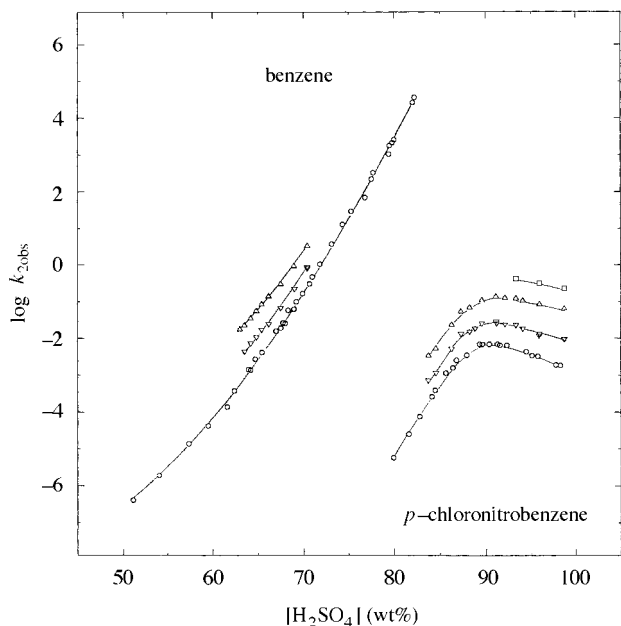
## Results and discussion

### Nitration rate profiles of the observed rate constants ( $\log k_{2\text{obs}}$ )

The temperature as well as the acidity dependence of nitration rate constants for benzene and *p*-chloronitrobenzene in the range 50–100 wt%  $\text{H}_2\text{SO}_4$  is shown in Fig. 1.

As is well known for nitration of aromatic compounds in  $\text{H}_2\text{SO}_4$ , the profiles of the observed rate constants ( $\log k_{2\text{obs}}$ ) vs. the medium composition show a large increase up to 90 wt%  $\text{H}_2\text{SO}_4$  and a small decrease in 90–100 wt%  $\text{H}_2\text{SO}_4$ .<sup>6,10,30</sup>

Obviously, on raising the temperature, an increase in rate is observed as a general trend, but the activation energies ( $E_a$ ) exhibit values with a different dependence on acidity in acidic media below and above 90 wt%. For instance, the activation energies of benzene are seen to decrease with increasing acidity and the values are 18.3 and 14.6 kcal mol<sup>-1</sup> at 64 wt% and 71 wt%, respectively. Analogous dependence of  $E_a$  on acidity has been found for *o*- and *p*-chloronitrobenzenes (see Table 1) as



**Fig. 1** Nitration in aqueous sulfuric acid of benzene and *p*-chloronitrobenzene. Values of  $\log k_{2,\text{obs}}$  vs.  $\text{H}_2\text{SO}_4$  wt% at (○) 25 °C; (▽) 40 °C; (△) 60 °C; (□) 75 °C. (Experimental data at 40 °C, 60 °C, 75 °C from this work; at 25 °C for benzene from refs. 26–28; for *p*-chloronitrobenzene from ref. 29).

well as for nitrations of activated and deactivated compounds carried out below 90 wt%.<sup>27,29,31</sup>

In the range between 90 and 100 wt%, the compounds exhibit activation energies which are seen to increase with increasing acidity.<sup>10,29,32,33</sup> The observed  $E_a$  values for *o*- and *p*-chloronitrobenzenes are between 15.8–16.9 at 91 wt% and 19.2–20.4 at 98 wt%. It has been suggested that, at high acidity, interactions between ions giving  $\text{HSO}_4^- \text{NO}_2^+$  ion pairs can affect the dissociation process of electrophilic species, with a decrease in rate for all substrates.<sup>10,30</sup> The kinetic dependence on temperature above 90 wt% supports the involvement of analogous species. As appears in Fig. 1 the decreasing factor of rates becomes smaller with the rise in temperature.

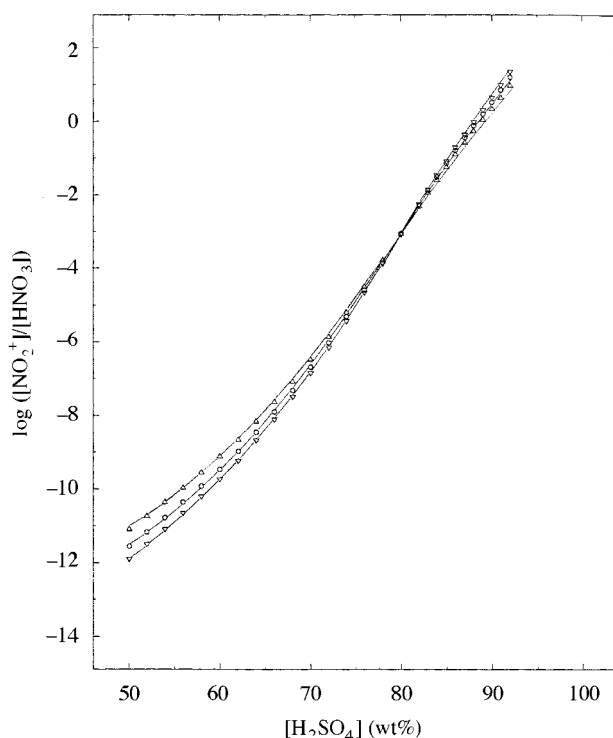
Further experimental observations obtained at different temperatures are discussed in the next sections where the acidity dependence of the equilibrium  $\text{HNO}_3 \rightarrow \text{NO}_2^+$  and theoretical nitration rate constants of aromatic compounds are reported.

#### Equilibrium $\text{HNO}_3 \rightarrow \text{NO}_2^+$

Spectroscopic studies by Raman, UV and NMR, show that the protonation–dehydration equilibrium of nitric acid to give  $\text{NO}_2^+$  [equilibrium (3)] can be studied in concentrated solutions of strong acids such as  $\text{H}_2\text{SO}_4$ <sup>11–13</sup> and  $\text{CF}_3\text{SO}_3\text{H}$ .<sup>14</sup> The range between 80 and 94 wt% has been found to be suitable for the evaluation of  $[\text{NO}_2^+]$  and the results observed in  $\text{H}_2\text{SO}_4$  at different temperatures are reported in Table 2. As expected, the temperature variations change the degrees of ionization of  $\text{NO}_2^+$  and the points of 50% conversion are between 88 and 89.2 wt%  $\text{H}_2\text{SO}_4$  as the temperature increases from 25 °C to 60 °C.

The evaluation of  $[\text{NO}_2^+]$  outside the actual range of observations requires the knowledge of two additional parameters, *i.e.* the equilibrium constant ( $\text{p}K_{\text{NO}_2^+}$ ) and the activity coefficient term  $[\log (f_{\text{HNO}_3} f_{\text{H}^+} / f_{\text{NO}_2^+} f_{\text{H}_2\text{O}})]$  that appear in the thermodynamic eqn. (7). In the studies carried out in  $\text{H}_2\text{SO}_4$ <sup>11,12</sup>

$$\text{p}K_{\text{NO}_2^+} = \log \{ [\text{NO}_2^+][\text{H}_2\text{O}]/[\text{HNO}_3][\text{H}^+] \} - \log (f_{\text{HNO}_3} f_{\text{H}^+} / f_{\text{NO}_2^+} f_{\text{H}_2\text{O}}) \quad (7)$$



**Fig. 2** Protonation–dehydration equilibrium of nitric acid in aqueous sulfuric acid (range 50–100 wt%  $\text{H}_2\text{SO}_4$ ). Values of  $\log [\text{NO}_2^+]/[\text{HNO}_3]$  at (▽) 25 °C; (○) at 40 °C; (△) at 60 °C; range 50–82 wt%  $\text{H}_2\text{SO}_4$ , estimated values; range 85–92 wt%  $\text{H}_2\text{SO}_4$ , experimental data from ref. 12 at 25 °C, from present work for  $T > 25$  °C.

and in  $\text{CF}_3\text{SO}_3\text{H}$ <sup>14</sup> at 25 °C, the  $\text{p}K_{\text{NO}_2^+}$  values have been estimated by eqn. (8), following a procedure suitable for solutes protonating in non ideal acid solutions.<sup>15–17</sup>

$$\text{p}K_{\text{NO}_2^+} = \log \{ [\text{NO}_2^+][\text{H}_2\text{O}]/[\text{HNO}_3][\text{H}^+] \} + n_{\text{NO}_2^+} Mc(i) \quad (8)$$

In this equation the “activity coefficient term” (a.c.) is evaluated by means of the “activity coefficient function” (or *Mc* function<sup>15–17</sup>), defined normally by eqn. (9) where reactants and products pertain to a reference compound.

$$Mc(i) = \log (\text{product of reactants' a.c.}) - \log (\text{product of products' a.c.}) \quad (9)$$

The parameters that have been found at 25 °C according to eqn. (8) are:  $\text{p}K_{\text{NO}_2^+} = -17.3$ ,  $n_{\text{NO}_2^+} = 2.46$  (in  $\text{H}_2\text{SO}_4$ );  $\text{p}K_{\text{NO}_2^+} = -17.3$ ,  $n_{\text{NO}_2^+} = 3.37$  (in  $\text{CF}_3\text{SO}_3\text{H}$ ). They are related, respectively, to intercepts ( $\text{p}K_{\text{NO}_2^+}$ ) and slopes ( $n_{\text{NO}_2^+}$ ) of the plots  $\{ \log [\text{NO}_2^+][\text{H}_2\text{O}]/[\text{HNO}_3][\text{H}^+] \} = \log V_N$  vs. the corresponding *Mc* “activity coefficient functions”<sup>15–17</sup> also determined at 25 °C.

An analogous procedure applied in the studies of equilibrium (3) at different temperatures allows one to obtain the following parameters, using  $\log V_N$  and *Mc* values at the defined temperature:  $\text{p}K_{\text{NO}_2^+} = -16.7$ ,  $n_{\text{NO}_2^+} = 2.445$  (at 40 °C);  $\text{p}K_{\text{NO}_2^+} = -15.9$ ,  $n_{\text{NO}_2^+} = 2.43$  (at 60 °C). The enthalpy of dissociation of 18.3 kcal mol<sup>-1</sup> has been estimated for the protonation–dehydration equilibrium of nitric acid.

The acidity dependence of  $[\text{NO}_2^+]/[\text{HNO}_3]$  ratios, in the range of sulfuric acid where the nitration can occur, is reported in Fig. 2. Experimental and estimated values are shown. These data are necessary for the study of the nitration process at acidities where the effective concentrations of  $\text{NO}_2^+$  are required.

#### Theoretical nitration rates ( $\log k_2^\circ$ )

The equilibrium data of nitric acid have been used for determin-

**Table 3** Theoretical rate constants ( $\log k_2^\circ/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ) and activation energies<sup>a</sup> ( $E_a^\circ/\text{kcal mol}^{-1}$ ) for nitration in aqueous sulfuric acid

Mesitylene <sup>b</sup>							
$T/^\circ\text{C}$				25	35.2	45.1	53.1
$\log k_2^\circ$				7.87	8.10	8.36	8.44
$E_a^\circ/\text{kcal mol}^{-1}$	7.3						
Toluene <sup>c</sup>							
$T/^\circ\text{C}$		15	20	25	30	35	
$\log k_2^\circ$		7.22	7.35	7.44	7.59	7.70	
$E_a^\circ/\text{kcal mol}^{-1}$	8.4						
Benzene <sup>d</sup>							
$T/^\circ\text{C}$				25	40	60	75
$\log k_2^\circ$				6.05	6.35	6.75	6.98 <sup>e</sup>
$E_a^\circ/\text{kcal mol}^{-1}$	9.2						
Chlorobenzene <sup>f</sup>							
$T/^\circ\text{C}$		20	25	30	35	40	45
$\log k_2^\circ$		4.94	5.05	5.19	5.31	5.46	5.54
$E_a^\circ/\text{kcal mol}^{-1}$	11.1						5.77
<i>o</i> -Chloronitrobenzene <sup>d</sup>							
$T/^\circ\text{C}$				25	40	60	70
$\log k_2^\circ$				-0.60	-0.05	0.70	1.10 <sup>e</sup>
$E_a^\circ/\text{kcal mol}^{-1}$	15.8						
<i>p</i> -Chloronitrobenzene <sup>d</sup>							
$T/^\circ\text{C}$				25	40	60	75
$\log k_2^\circ$				-2.10	-1.55	-0.78	-0.35
$E_a^\circ/\text{kcal mol}^{-1}$	16.9						

<sup>a</sup> Values of  $E_a^\circ$  determined by the  $k_2^\circ$  rate constants [see eqn. (10)]. <sup>b</sup> Values of  $\log k_{2\text{obs}}$  at 67.1 wt%  $\text{H}_2\text{SO}_4$  from ref. 34. <sup>c</sup> Values of  $\log k_{2\text{obs}}$  at 70.2 wt%  $\text{H}_2\text{SO}_4$  from ref. 35a. (Values of  $\log k_{2\text{obs}}$  at 77.3 wt%  $\text{H}_2\text{SO}_4$  and at 78.45 wt%  $\text{H}_2\text{SO}_4$  from ref. 35b give analogous estimates of  $E_a^\circ$ .) <sup>d</sup> Values of  $\log k_{2\text{obs}}$  from present work. <sup>e</sup> Estimated value. <sup>f</sup> Values of  $\log k_{2\text{obs}}$  at 70.2 wt%  $\text{H}_2\text{SO}_4$  from ref. 36a. (Values of  $\log k_{2\text{obs}}$  at 79.8 wt%  $\text{H}_2\text{SO}_4$  from ref. 36b and values of  $\log k_{2\text{obs}}$  at 67.5 wt%  $\text{H}_2\text{SO}_4$  from ref. 31 give analogous estimates of  $E_a^\circ$ .)

ing, from the  $k_{2\text{obs}}$ , the corresponding  $k_2^\circ$  rate constants of aromatic compounds. They are related to the stoichiometric concentration of nitric acid and to the effective concentration of electrophilic species by eqn. (10).

$$k_{2\text{obs}}[\text{Ar}]_{\text{st}}[\text{HNO}_3]_{\text{st}} = k_2^\circ[\text{Ar}][\text{NO}_2^+] \quad (10)$$

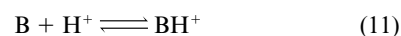
The new parameters, already determined for nitrations in  $\text{H}_2\text{SO}_4$ <sup>30</sup> and  $\text{CF}_3\text{SO}_3\text{H}$ <sup>10</sup> at 25 °C, allow one to obtain the separation of solvent effects involved in the equilibria of reagents from solvent effects involved in the kinetic behaviour of the reacting species. Indeed, in the range below 90 wt%  $\text{H}_2\text{SO}_4$ , the  $k_2^\circ$  values obtained by taking into account the actual concentrations of  $\text{NO}_2^+$  were found to be practically independent of medium acidity. In the range 89–91%, where  $[\text{HNO}_3]_{\text{st}} \approx [\text{NO}_2^+]$ , the condition  $k_{2\text{obs}} \approx k_2^\circ$  is satisfied.

In Table 3, the  $k_2^\circ$  rates at 25 °C, 40 °C, 60 °C and 75 °C estimated by eqn. (10) for benzene, *o*- and *p*-chloronitrobenzenes are reported, together with the corresponding activation energies ( $E_a^\circ$ ). Analogous data for mesitylene, toluene and chlorobenzene are given using literature data. The  $E_a^\circ$  values, obtained from the Arrhenius plots on the basis of theoretical rate constants, are in perfect agreement with the expected reactivity of activated and deactivated aromatic substrates. Furthermore, for mesitylene, the typical value expected for an encounter limited reaction has also been found.<sup>6,37</sup>

The linear relationship between  $k_2^\circ$  rates that has been observed for analogous compounds undergoing nitration in aqueous acid media (*i.e.*  $\text{H}_2\text{SO}_4$ ) and in the gas phase<sup>10</sup> or in different aqueous acids (*i.e.*  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$ ,  $\text{CF}_3\text{SO}_3\text{H}$ ),<sup>10,30</sup> strongly supports the validity of the above results.

**The temperature variation of the *Mc* activity coefficient function**  
Concentrated aqueous solutions of strong acids have been

extensively studied by the Hammett procedure<sup>38–42</sup> to determine the “acidity” of the medium in going from diluted to concentrated acids. In these studies the protonation of weak bases (B), whose equilibria [equilibrium (11)] are described by



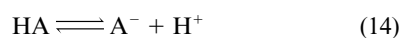
thermodynamic eqn. (12), has been analysed and the acidic

$$pK_{\text{BH}^+} = \log [\text{BH}^+]/[\text{B}] - \log [\text{H}^+] - \log (f_{\text{B}}f_{\text{H}^+}/f_{\text{BH}^+}) \quad (12)$$

strength of the aqueous mixtures between 25–90 °C has been determined by the ( $H_x$ ) acidity functions [see eqn. (13)].

$$H_x = \log [\text{H}^+] - \log (f_{\text{B}}f_{\text{H}^+}/f_{\text{BH}^+}) \quad (13)$$

New progress in our understanding of the properties of strong acids has been obtained by comparing the protonation process of B [eqns. (11) and (12)] and the dissociation process of aqueous monoprotic acids (HA)<sup>16</sup> [equilibrium (14)], the



latter described by the thermodynamic eqn. (15). The results

$$pK_{\text{HA}} = \log [\text{HA}]/[\text{A}^-] - \log [\text{H}^+] - \log (f_{\text{A}^-}f_{\text{H}^+}/f_{\text{HA}}) \quad (15)$$

obtained at 25 °C have shown that the protonation of B can be linearly related to the dissociation of HA by using: (i) the corresponding “activity coefficient functions” of solutes [ $Mc(i)$ ] and of solvents [ $Mc(s)$ ] [see eqn. (16) rewritten as (16a)]; (ii) the

$$-\log (f_{\text{B}}f_{\text{H}^+}/f_{\text{BH}^+}) = -n_{\text{is}} \log (f_{\text{A}^-}f_{\text{H}^+}/f_{\text{HA}}) \quad (16)$$

$$Mc(i) = n_{\text{is}} Mc(s) \quad (16a)$$

corresponding  $Ac(i)$  and  $Ac(s)$  functions, defined respectively by eqns. (17) and (18). The  $Ac(s)$  function, determined by the

$$Ac(i) = \{-n_{is} \log [H^+] + Mc(i)\} \quad (17)$$

$$Ac(s) = \{-\log [H^+] + Mc(s)\} \quad (18)$$

parameters of the solvent, is "the extension of the pH scale" in concentrated aqueous acid solutions.

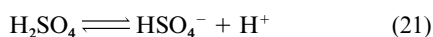
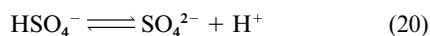
The studies of B in HA (HA = CH<sub>3</sub>SO<sub>3</sub>H, HBr, HClO<sub>4</sub>, CF<sub>3</sub>SO<sub>3</sub>H, HNO<sub>3</sub>) have shown that the observed  $n_{is}$  values are 3.3 for CH<sub>3</sub>SO<sub>3</sub>H; 2.80 for HBr; 2.35 for HClO<sub>4</sub>; 2.10 for CF<sub>3</sub>SO<sub>3</sub>H; 1.55 for HNO<sub>3</sub> when 2-nitroaniline is used as the reference indicator of  $Mc(i)$  scale.<sup>16</sup> The above relationships suggest that the protonation of a solute in concentrated strong acids is related, by the  $n_{is}$  value, to the proton transfer process from the solvent to the solute (*i.e.* from H<sub>3</sub>O<sup>+</sup>A<sup>-</sup> to BH<sup>+</sup>A<sup>-</sup>). It allows the description of equilibrium (11) by the empirical eqn. (19) or by eqn. (19a) for aqueous acid systems with unknown  $Mc(s)$  values. [In the eqn. (19a)  $n_{is} = 1 = n_{bb^*}$  for 2-nitroaniline used as the reference indicator of  $Mc(i)$  scale.]

$$pK_{BH^+} = \log [BH^+]/[B] - \log [H^+] + n_{is} Mc(s) \quad (19)$$

$$pK_{BH^+} = \log [BH^+]/[B] - \log [H^+] + n_{bb^*} Mc(i) \quad (19a)$$

The observed  $n_{is}$  values, that are found to be very different from unity, also suggest that the  $H_x$  acidity functions are not suited to describe the "acidity" of strong acids in the range outside the pH. Two additional observations support an analogous conclusion: (i) an "extension of the pH scale" in concentrated aqueous acid solutions can properly be determined by using the parameters of the solvent<sup>16</sup> [*i.e.* by the corresponding  $Ac(s)$  functions]; (ii) the  $H_x$  values are found to be unrelated to  $Ac(s)$  functions. As appears from eqns. (13) and (17), the  $H_x$  and  $Ac(i)$  functions differ by the  $n_{is}$  values, *i.e.* for the parameters expressing the interactions between solutes and solvents.

An extension of the previous studies in sulfuric acid, characterised from two dissociation equilibria of the solvent below and above 80 wt% [equilibria (20) and (21)], has also been



attempted.<sup>17</sup> In this case, the variation of both a.c. terms that appear in the thermodynamic eqns. (22) and (23) has been

$$pK_{H_2SO_4} = \log [H_2SO_4]/[HSO_4^-] - \log [H^+] - \log (f_{HSO_4^-} f_{H^+} / f_{H_2SO_4}) \quad (22)$$

$$pK_{HSO_4^-} = \log [HSO_4^-]/[SO_4^{2-}] - \log [H^+] - \log (f_{SO_4^{2-}} f_{H^+} / f_{HSO_4^-}) \quad (23)$$

estimated, taking into account the distribution of [SO<sub>4</sub><sup>2-</sup>], [HSO<sub>4</sub><sup>-</sup>] and [H<sub>2</sub>SO<sub>4</sub>] species observed at 25 °C in the range 0.1–100 wt% H<sub>2</sub>SO<sub>4</sub>.<sup>43,44</sup>

Application of the  $Mc$  procedure to the above equilibria allows one to obtain the corresponding  $pK_{H_2SO_4}$  and  $pK_{HSO_4^-}$  values and to compare the results with the available data. For instance,  $pK_{HSO_4^-} = -2$  has been found to be in accord with the known thermodynamic value.<sup>44</sup> The  $Mc(s)$  function of the solvent [defined by eqn. (24) or (24a)] has also been estimated, as

$$Mc(s) = \{[-\log (f_{SO_4^{2-}} f_{H^+} / f_{HSO_4^-})] + [-\log (f_{HSO_4^-} f_{H^+} / f_{H_2SO_4})]\} \quad (24)$$

$$Mc(s) = \{Mc(HSO_4^-) + Mc(H_2SO_4)\} \quad (24a)$$

this parameter can be used to compare the behaviour of solutes and of solvent *via* the corresponding  $Mc(i)$  and  $Mc(s)$  functions. The results have shown that the  $Mc(i)$  can be linearly related to the  $Mc(s)$  provided that the equilibria (20) and (21) are taken into account; a normalization factor relating the activity coefficient terms of the equilibria is used.<sup>17</sup>

It follows that the  $\log (f_B f_{H^+} / f_{BH^+})$  term of an indicator in sulfuric acid can be related by eqn. (25), where  $Mc^*(s)$  is given

$$Mc(i) = n_{is} Mc^*(s) \quad (25)$$

by eqns. (26) or (27), to the corresponding standard states of

$$Mc^*(s) = \{Mc^\circ(HSO_4^-) + Mc(H_2SO_4)\} \quad (26)$$

$$Mc^*(s) = \{Mc(HSO_4^-) + Mc^\circ(H_2SO_4)\} \quad (27)$$

the solvent, which can be normalized by an appropriate factor. The normalized  $Mc^*(s)$  functions and the corresponding  $n_{is}$  values of 2-nitroaniline used as standard indicator are given in eqns. (28) and (29).

$$Mc^*(s) = \{Mc/0.33(HSO_4^-) + Mc(H_2SO_4)\} \quad (n_{is} = 1) \quad (28)$$

$$Mc^*(s) = \{Mc(HSO_4^-) + Mc \times 0.33(H_2SO_4)\} \quad (n_{is} = 3) \quad (29)$$

The presence of two equilibria in sulfuric acid causes two distinct behaviours of indicators for a series of closely related compounds undergoing protonation.<sup>17</sup> This can be seen in the plots of slopes ( $n$ ) and equilibrium constants ( $pK_{BH^+}$ ), referred to  $pK_w$  of water, when analogous nitroanilines in H<sub>2</sub>SO<sub>4</sub> and in monoprotic acids at 25 °C are compared. Indeed, a linear dependence between  $n$  and  $pK_{BH^+}$  has been found in CF<sub>3</sub>SO<sub>3</sub>H, HClO<sub>4</sub>, HCl, HBr, CH<sub>3</sub>SO<sub>3</sub>H and HNO<sub>3</sub> [this feature is characterized by the corresponding slope (or  $N$  value) and is typical for each acid], as well as a progressive increase in the  $n$  values for increasingly weaker bases<sup>16</sup> (see Fig. 3, Table 4). As expected, two different linear dependences ( $N_1$  and  $N_2$ ) have been observed in H<sub>2</sub>SO<sub>4</sub> for the compounds whose protonation process occurs below and above 80 wt% H<sub>2</sub>SO<sub>4</sub>.<sup>17</sup> In Fig. 4 the results for nitroanilines and triarylcaminols are shown.

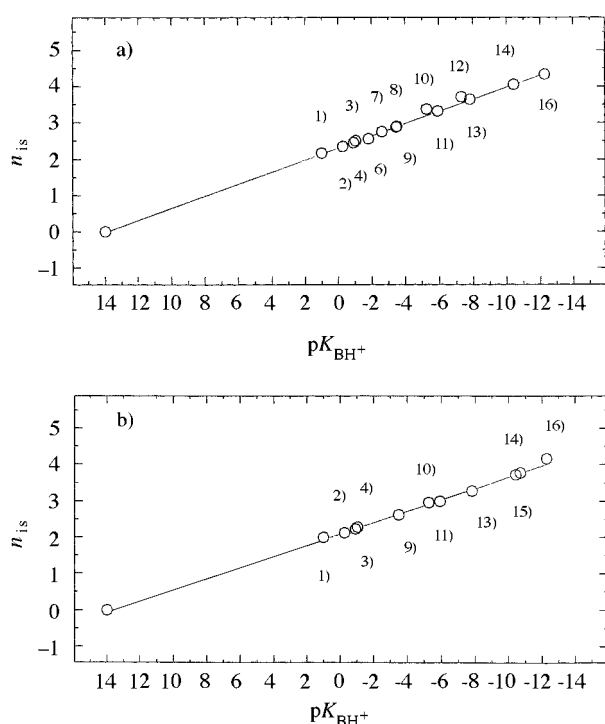
There is a reasonable consistency between the behaviour of indicators observed at 25 °C and the behaviour deduced from analogous studies at  $T$  °C  $\neq$  25 °C. It appears from the data in Tables 5–7, where slopes and equilibrium constants of nitroanilines and triphenylmethanols, analysed in sulfuric and perchloric acids between 15–90 °C, are given. Detailed observations related to temperature dependence of the equilibria of indicators are:

(i) On the plots  $pK_{BH^+}$  vs.  $1/T$  (for nitroanilines) and  $pK_R$  vs.  $1/T$  (for triphenylmethanols), linear relationships have been observed. For nitroanilines in sulfuric and perchloric acids, the trend related to the variations of equilibrium constants with temperature is reversed on going from stronger to weaker bases (see Tables 5 and 6). For triphenylmethanols the same general trend is observed (see Table 7). The behaviour is analogous to that previously reported in thermodynamic studies of analogous compounds by acidity functions.<sup>19–22</sup> It follows that  $\Delta G^\circ$  vs.  $\Delta H^\circ$  values are linearly related for all the triphenylmethanols, with a slope = 0.85. Two different linear dependences, with slopes = 1.5 and 0.6 are found for anilines, with decreasing and increasing  $pK_{BH^+}$  values *versus* temperature, respectively.

**Table 4** Slopes ( $n_{is}$ ,  $n_{bb^*}$ )<sup>a</sup> and intercepts ( $pK_{BH^+}$ )<sup>b</sup> for the protonation equilibria of nitroanilines in concentrated aqueous solutions of HClO<sub>4</sub>, CF<sub>3</sub>SO<sub>3</sub>H and H<sub>2</sub>SO<sub>4</sub> at 25 °C

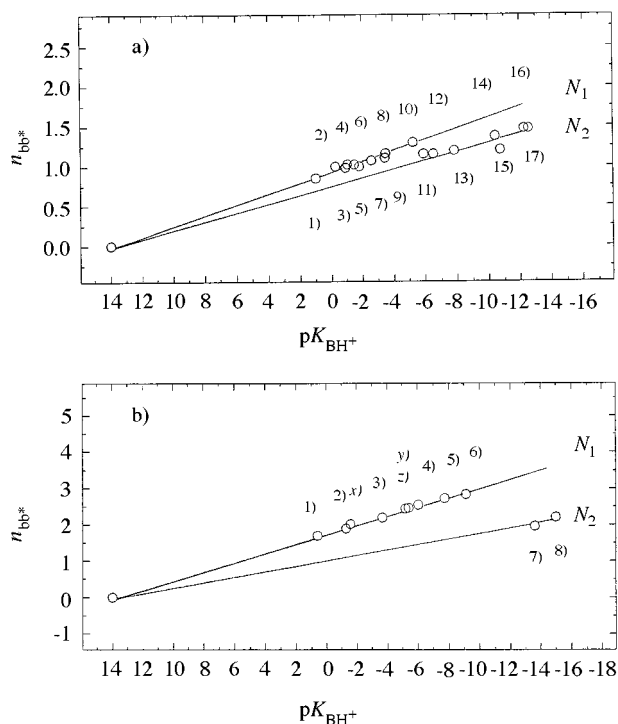
Nitroanilines <sup>c</sup>	HClO <sub>4</sub>		CF <sub>3</sub> SO <sub>3</sub> H		H <sub>2</sub> SO <sub>4</sub>	$pK_{BH^+}$
	$n_{is}$	$n_{bb^*}$	$n_{is}$	$n_{bb^*}$	$n_{bb^*}$	
1) 4-NO <sub>2</sub>	2.17	0.95	2.00	0.95	0.85	1.00
2) 2-NO <sub>2</sub>	2.35	1.00	2.12	1.00	1.00	-0.27
3) 2-Cl-4-NO <sub>2</sub>	2.45	1.04	2.23	1.04	0.98	-0.90
4) 4-Cl-2-NO <sub>2</sub>	2.50	1.07	2.28	1.05	1.02	-1.05
5) 5-Cl-2-NO <sub>2</sub>					1.02	-1.50
6) 2,5-Di-Cl-4-NO <sub>2</sub>	2.55	1.10			1.00	-1.80
7) 2-Cl-6-NO <sub>2</sub>	2.75	1.23			1.07	-2.60
8) 2,6-Di-Cl-4-NO <sub>2</sub>	2.87	1.28			1.10	-3.45
9) 2,4-Di-Cl-6-NO <sub>2</sub>	2.90	1.27	2.62	1.25	1.16	-3.50
10) 2,4-Di-NO <sub>2</sub>	3.37	1.44	2.95	1.40	1.30	-5.25
11) 2,6-Di-NO <sub>2</sub>	3.32	1.45	3.00	1.45	1.15	-5.90
12) 4-Cl-2,6-Di-NO <sub>2</sub> <sup>d</sup>	3.72	1.62				-7.30
13) 2-Br-4,6-Di-NO <sub>2</sub> <sup>e</sup>	3.64	1.57	3.28	1.60	1.19	-7.80
14) 3-Me-2,4,6-Tri-NO <sub>2</sub>	4.05	1.73	3.73	1.75	1.37	-10.40
15) 2,4,6-Tri-NO <sub>2</sub>			3.78	1.79	1.20	-10.70
16) 3-Br-2,4,6-Tri-NO <sub>2</sub>	4.33	1.84	4.16	1.96	1.47	-12.25
17) 3-Cl-2,4,6-Tri-NO <sub>2</sub>					1.47	-12.50

<sup>a</sup> ( $n_{is}$ ) slopes of the plots  $\log [BH^+]/[B][H^+]$  vs.  $Mc(s)$  [see eqn. (19)]; ( $n_{bb^*}$ ) slopes of the plots  $\log [BH^+]/[B][H^+]$  vs.  $Mc(i)$  [see eqn. (19a)]. <sup>b</sup> Intercepts of the plots  $\log [BH^+]/[B][H^+]$  vs.  $Mc$  functions;  $Mc(s)$  and  $Mc(i)$  in HClO<sub>4</sub> and CF<sub>3</sub>SO<sub>3</sub>H from ref. 16; in H<sub>2</sub>SO<sub>4</sub> from ref. 17. <sup>c</sup> For experimental data in HClO<sub>4</sub> and CF<sub>3</sub>SO<sub>3</sub>H (see ref. 16); in H<sub>2</sub>SO<sub>4</sub> (see ref. 17). <sup>d</sup>  $pK_{BH^+}$  value in H<sub>2</sub>SO<sub>4</sub> = -6.50 (see ref. 17). <sup>e</sup> The protonation of 2-Br-4,6-di-NO<sub>2</sub> in H<sub>2</sub>SO<sub>4</sub> shows two sets of values (see ref. 17):  $pK_{BH^+} = -6.60$ ,  $n_{bb^*} = 1.04$  (by exp. data in the range 65–80 wt%);  $pK_{BH^+} = -7.80$ ,  $n_{bb^*} = 1.20$  (by exp. data in the range 75–94 wt%).



**Fig. 3** (a) Nitroanilines in HClO<sub>4</sub> at 25 °C. Plot of  $n_{is}$  vs.  $pK_{BH^+}$ , slope ( $N_{is}$ ) = 0.170 ( $n_{is}$  and  $pK_{BH^+}$  values of indicators in Table 4). (b) Nitroanilines in CF<sub>3</sub>SO<sub>3</sub>H at 25 °C. Plot of  $n_{is}$  vs.  $pK_{BH^+}$ , slope ( $N_{is}$ ) = 0.150 ( $n_{is}$  and  $pK_{BH^+}$  values of indicators in Table 4).

(ii) In the studies of indicators at 25 °C it has been shown that the trend of the slopes is of interest. On going from 25 °C to 90 °C, decreasing slope values are observed by comparing an indicator at different temperatures. The results are given in Tables 5a and 6a for nitroanilines in H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub> and in Table 7a for triarylcannabinols in H<sub>2</sub>SO<sub>4</sub>. Moreover, analysis of data by using slopes and equilibrium constants shows that the ( $pK_{BH^+}/n_{bb^*}$ ) and ( $pK_{R^+}/n_{bb^*}$ ) ratios vs.  $1/T$  exhibit a linear dependence with temperature. However, the new



**Fig. 4** (a) Nitroanilines in H<sub>2</sub>SO<sub>4</sub> at 25 °C. Plot of  $n_{bb^*}$  vs.  $pK_{BH^+}$ , slopes:  $N_1 = 0.066$ ,  $N_2 = 0.056$  at 25 °C ( $n_{bb^*}$  and  $pK_{BH^+}$  values at 25 °C in Table 4); slopes:  $N_1 = 0.066$ ,  $N_2 = 0.056$  at 60 °C; slopes:  $N_1 = 0.066$ ,  $N_2 = 0.056$  at 90 °C ( $n_{bb^*}$  and  $pK_{BH^+}$  values at 60 °C and 90 °C in Table 5b). (b) Triphenylmethanols in H<sub>2</sub>SO<sub>4</sub> at 25 °C. Plot of  $n_{bb^*}$  vs.  $pK_{BH^+}$ , slopes  $N_1 = 0.066$ ,  $N_2 = 0.056$  at 25 °C; slopes  $N_1 = 0.066$ ,  $N_2 = 0.056$  at 60 °C; slopes  $N_1 = 0.066$ ,  $N_2 = 0.056$  at 80 °C ( $n_{bb^*}$  and  $pK_{BH^+}$  values in Table 7b).

plots, both for nitroanilines and triphenylmethanols, are found to be essentially linear and parallel. It suggests an analogous influence of temperature on the parameters of indicators whose protonation occurs both in dilute and in concentrated acid solutions.

(iii) By using the corresponding  $Mc$  functions at  $T$  °C,

**Table 5a** Thermodynamic data for the protonation equilibria of nitroanilines in aqueous sulfuric acid

Nitroanilines <sup>a-c</sup>		25 °C <sup>c</sup>	40 °C	60 °C	80 °C	90 °C	$\Delta G^{\circ f}$	$\Delta H^{\circ f}$
2) 2-NO <sub>2</sub> <sup>g</sup>	$pK_{\text{BH}^+}$	-0.27	-0.405	-0.515	-0.606	-0.645	-0.37	2.74
	$n_{\text{bb}}^{T, T_2}$	1.00	0.957	0.918	0.887	0.874		
	$R$	-0.27	-0.423	-0.561	-0.683	-0.738		
4) 4-Cl-2-NO <sub>2</sub>	$pK_{\text{BH}^+}$	-1.05	-1.10	-1.18	-1.21	-1.25	-1.43	1.88
	$n_{\text{bb}}^{T, T_2}$	1.00	0.95	0.88	0.86	0.82		
	$R$	-1.05	-1.16	-1.34	-1.40	-1.52		
6) 2,5-Di-Cl-4-NO <sub>2</sub>	$pK_{\text{BH}^+}$	-1.80	-1.85	-1.91	-1.95	-1.99	-2.45	1.28
	$n_{\text{bb}}^{T, T_2}$	1.00	0.98	0.94	0.91	0.90		
	$R$	-1.80	-1.88	-2.03	-2.14	-2.21		
7) 2-Cl-6-NO <sub>2</sub>	$pK_{\text{BH}^+}$	-2.60	-2.55	-2.60	-2.63	-2.62	-3.55	0.46
	$n_{\text{bb}}^{T, T_2}$	1.00	0.94	0.89	0.87	0.85		
	$R$	-2.60	-2.71	-2.92	-3.02	-3.08		
8) 2,6-Di-Cl-4-NO <sub>2</sub>	$pK_{\text{BH}^+}$	-3.45	-3.35	-3.40	-3.36	-3.29	-4.71	-1.37
	$n_{\text{bb}}^{T, T_2}$	1.00	0.92	0.91	0.87	0.83		
	$R$	-3.45	-3.64	-3.74	-3.86	-3.96		
10) 2,4-Di-NO <sub>2</sub>	$pK_{\text{BH}^+}$	-5.25	-5.01	-4.75	-4.63	-4.48	-7.16	-5.49
	$n_{\text{bb}}^{T, T_2}$	1.00	0.93	0.85	0.81	0.76		
	$R$	-5.25	-5.39	-5.59	-5.72	-5.89		
11) 2,6-Di-NO <sub>2</sub>	$pK_{\text{BH}^+}$	-5.90	-5.67	-5.33	-5.12	-4.92	-8.05	-7.32
	$n_{\text{bb}}^{T, T_2}$	1.00	0.93	0.86	0.79	0.76		
	$R$	-5.90	-6.10	-6.20	-6.48	-6.48		
14) 3-Me-2,4,6-Tri-NO <sub>2</sub>	$pK_{\text{BH}^+}$	-10.40	-10.20	-10.08	-9.91	-9.74	-14.19	-4.80
	$n_{\text{bb}}^{T, T_2}$	1.00	0.96	0.94	0.91	0.88		
	$R$	-10.40	-10.62	-10.72	-10.89	-11.07		
16) 3-Br-2,4,6-Tri-NO <sub>2</sub>	$pK_{\text{BH}^+}$	-12.25	-12.05	-11.90	-11.80	-11.65	-16.71	-5.03
	$n_{\text{bb}}^{T, T_2}$	1.00	0.97	0.94	0.92	0.90		
	$R$	-12.25	-12.42	-12.66	-12.83	-12.94		

<sup>a</sup> Progressive no. of nitroanilines as in Table 4. <sup>b</sup> Intercepts ( $pK_{\text{BH}^+}$ ) and slopes ( $n_{\text{bb}}^{T, T_2}$ ) estimated by  $\log [\text{BH}^+]/[\text{B}][\text{H}^+] = \log Q_{\text{B}}$  (at  $T$  °C) vs.  $\log Q_{\text{B}}$  (at 25 °C). <sup>c</sup>  $\log Q_{\text{B}}$  and  $pK_{\text{BH}^+}$  (at 25 °C) used as reference values;  $n_{\text{bb}}^{T, T_2} = 1.00$  (at 25 °C). <sup>d</sup>  $R$  (ratio) = ( $pK_{\text{BH}^+}/n_{\text{bb}}^{T, T_2}$ ). <sup>e</sup> Experimental data from ref. 19;  $pK_{\text{BH}^+}$  at 25 °C from ref. 17. <sup>f</sup>  $\Delta G^{\circ}$  estimated by  $2.303 RT pK_{\text{BH}^+}$  (at 25 °C);  $\Delta H^{\circ}$  estimated by plots of  $pK_{\text{BH}^+}$  vs.  $1/T$ ; ( $T$  = temperature (K) for  $\Delta G^{\circ}$  and  $\Delta H^{\circ}$  values); slopes of  $\Delta G^{\circ}$  vs.  $\Delta H^{\circ}$  are 1.5 (for indicators no. 2, 4, 6, 7) and 0.6 (for indicators no. 8, 10, 11). <sup>g</sup>  $pK_{\text{BH}^+}$ ,  $n_{\text{bb}}^{T, T_2}$  and  $R$  values of 2-nitroaniline, using experimental data from ref. 20 are: at 15 °C (-0.247, 1.025, -0.241); at 35 °C (-0.391, 0.958, -0.408); at 45 °C (-0.435, 0.94, -0.463); at 55 °C (-0.50, 0.922, -0.542).

**Table 5b** Intercepts ( $pK_{\text{BH}^+}$ )<sup>a</sup> and slopes ( $n_{\text{bb}}^{T}$ )<sup>a</sup> for the protonation equilibria of nitroanilines in aqueous sulfuric acid (at  $T$  °C)

Nitroanilines <sup>b-c</sup>		25 °C <sup>d</sup>	40 °C <sup>d</sup>	60 °C <sup>d</sup>	80 °C <sup>d</sup>	90 °C <sup>d</sup>
2) 2-NO <sub>2</sub>	$pK_{\text{BH}^+}$	-0.27	-0.405	-0.515	-0.606	-0.645
	$n_{\text{bb}}^{T}$	1.00	1.00	1.00	1.00	1.00
4) 4-Cl-2-NO <sub>2</sub>	$pK_{\text{BH}^+}$	-1.05	-1.10	-1.18	-1.21	-1.25
	$n_{\text{bb}}^{T}$	1.02	0.93	0.98	0.96	0.98
6) 2,5-Di-Cl-4-NO <sub>2</sub>	$pK_{\text{BH}^+}$	-1.80	-1.85	-1.91	-1.95	-1.99
	$n_{\text{bb}}^{T}$	1.00	1.00	1.00	1.04	1.01
7) 2-Cl-6-NO <sub>2</sub>	$pK_{\text{BH}^+}$	-2.60	-2.55	-2.60	-2.63	-2.62
	$n_{\text{bb}}^{T}$	1.07	1.05	1.05	1.09	1.07
8) 2,6-Di-Cl-4-NO <sub>2</sub>	$pK_{\text{BH}^+}$	-3.45	-3.35	-3.40	-3.36	-3.29
	$n_{\text{bb}}^{T}$	1.10	1.06	1.06	1.06	1.08
10) 2,4-Di-NO <sub>2</sub>	$pK_{\text{BH}^+}$	-5.25	-5.01	-4.75	-4.63	-4.48
	$n_{\text{bb}}^{T}$	1.30	1.26	1.23	1.23	1.17
11) 2,6-Di-NO <sub>2</sub>	$pK_{\text{BH}^+}$	-5.90	-5.67	-5.33	-5.12	-4.92
	$n_{\text{bb}}^{T}$	1.15	1.17	1.12	1.10	1.09
14) 3-Me-2,4,6-Tri-NO <sub>2</sub>	$pK_{\text{BH}^+}$	-10.40	-10.20	-10.08	-9.91	-9.74
	$n_{\text{bb}}^{T}$	1.37	1.39	1.42	1.42	1.41
16) 3-Br-2,4,6-Tri-NO <sub>2</sub>	$pK_{\text{BH}^+}$	-12.25	-12.05	-11.90	-11.80	-11.65
	$n_{\text{bb}}^{T}$	1.47	1.50	1.53	1.55	1.53

<sup>a</sup> Intercepts ( $pK_{\text{BH}^+}$ ) and slopes ( $n_{\text{bb}}^{T}$ ) estimated by  $\log [\text{BH}^+]/[\text{B}][\text{H}^+] = \log Q_{\text{B}}$  (at  $T$  °C) vs.  $M_{\text{c}}$  (at  $T$  °C) (see eqn. 19a);  $M_{\text{c}}$  (at  $T$  °C) referred to 2-nitroaniline (at  $T$  °C) as standard indicator (B\*). <sup>b</sup> Progressive no. of nitroanilines as in Table 4. <sup>c</sup> Experimental data from ref. 19;  $pK_{\text{BH}^+}$ ,  $n_{\text{bb}}^{T}$ ,  $M_{\text{c}}$  (at 25 °C) from ref. 17;  $M_{\text{c}}$  (at  $T$  °C) from this work. <sup>d</sup> The slopes of  $n_{\text{bb}}^{T}$  vs.  $pK_{\text{BH}^+}$  (or  $N$  values) (at  $T$  °C) are referred to the corresponding  $pK_{\text{w}}^T$  of water (at  $T$  °C), ( $pK_{\text{w}}^T = 14$  at 25 °C; 13.55 at 40 °C; 13 at 60 °C; 12.50 at 80 °C; 12.25 at 90 °C).

progressively weaker bases at a given temperature have been compared. The results are given in Tables 5b and 6b for nitroanilines in H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub> and in Table 7b for triphenylmethanols in H<sub>2</sub>SO<sub>4</sub>. The plots  $n_{\text{bb}}^{T}$  vs.  $pK_{\text{BH}^+}$  (and  $n_{\text{bb}}^{T}$  vs.  $pK_{\text{R}}$ ) show that the new  $N$  values obtained at  $T$  °C, and referred to the corresponding  $pK_{\text{w}}$  values of water at the same temperature, are higher or not very different from the  $N$  values that can be estimated for  $T = 25$  °C (see Fig. 4). Indeed, the variations of  $N$  values are found to be proportional to temper-

ature variations of the slopes of  $M_{\text{c}}$  functions, whose changes between 25 °C and 90 °C are not very large.

The new results are consistent with the view that the deviations from ideality (determined by the  $M_{\text{c}}$  activity coefficient functions) and the interactions between solutes and solvents (determined by the  $n_{\text{is}}$  or  $n_{\text{bb}}^{T}$  values) are the parameters of interest when equilibria and rates in concentrated aqueous acid solutions are analysed. A number of results obtained in the studies of equilibria and rates using solid acid



**Table 6a** Thermodynamic data for the protonation equilibria of nitroanilines in aqueous perchloric acid

Nitroanilines <sup>a-e</sup>		15 °C	25 °C <sup>c</sup>	35 °C	45 °C	$\Delta G^{\circ f}$	$\Delta H^{\circ f}$
2) 2-NO <sub>2</sub>	$pK_{BH^+}$	-0.247	-0.27	-0.391	-0.435	-0.37	2.74
	$n_{bb}^{T_1, T_2}$	1.025	1.00	0.958	0.945		
	<i>R</i>	-0.241	-0.27	-0.408	-0.46		
6) 2,5-Di-Cl-4-NO <sub>2</sub>	$pK_{BH^+}$	-1.76	-1.80	-1.83	-1.88	-2.45	1.28
	$n_{bb}^{T_1, T_2}$	1.02	1.00	1.00	1.00		
	<i>R</i>	-1.72	-1.80	-1.83	-1.88		
9) 2,4-Di-Cl-6-NO <sub>2</sub>	$pK_{BH^+}$	-3.53	-3.50	-3.46	-3.41	-4.77	-1.37
	$n_{bb}^{T_1, T_2}$	1.03	1.00	0.97	0.93		
	<i>R</i>	-3.42	-3.50	-3.57	-3.67		
10) 2,4-Di-NO <sub>2</sub>	$pK_{BH^+}$	-5.36	-5.25	-5.07	-4.98	-7.16	-5.49
	$n_{bb}^{T_1, T_2}$	1.04	1.00	0.95	0.91		
	<i>R</i>	-5.15	-5.25	-5.34	-5.47		
11) 2,6-Di-NO <sub>2</sub>	$pK_{BH^+}$	-6.08	-5.90	-5.73	-5.59	-8.05	-7.32
	$n_{bb}^{T_1, T_2}$	1.04	1.00	0.97	0.91		
	<i>R</i>	-5.85	-5.90	-5.91	-6.14		

<sup>a</sup> Progressive no. of nitroanilines as in Table 4. <sup>b</sup> Intercepts ( $pK_{BH^+}$ ) and slopes ( $n_{bb}^{T_1, T_2}$ ) estimated by  $\log [BH^+]/[B][H^+] = \log Q_B$  (at  $T$  °C) vs.  $\log Q_B$  (at 25 °C). <sup>c</sup>  $\log Q_B$  and  $pK_{BH^+}$  (at 25 °C) used as reference values; ( $n_{bb}^{T_1, T_2} = 1.00$  (at 25 °C)). <sup>d</sup> *R* (ratio) = ( $pK_{BH^+}/n_{bb}^{T_1, T_2}$ ). <sup>e</sup> Experimental data from ref. 21;  $pK_{BH^+}$  at 25 °C from ref. 16. <sup>f</sup> See footnote *f* of Table 5a.

**Table 6b** Intercepts ( $pK_{BH^+}$ )<sup>a</sup> and slopes ( $n_{bb}^{T_1, T_2}$ )<sup>a</sup> for the protonation equilibria of nitroanilines in aqueous perchloric acid (at  $T$  °C)

Nitroanilines <sup>b,c</sup>		15 °C <sup>d</sup>	25 °C <sup>d</sup>	35 °C <sup>d</sup>	45 °C <sup>d</sup>
2) 2-NO <sub>2</sub>	$pK_{BH^+}^T$	-0.247	-0.27	-0.391	-0.435
	$n_{bb}^{T_1, T_2}$	1.00	1.00	1.00	1.00
6) 2,5-Di-Cl-4-NO <sub>2</sub>	$pK_{BH^+}^T$	-1.76	-1.80	-1.83	-1.88
	$n_{bb}^{T_1, T_2}$	1.03	1.10	1.07	1.09
9) 2,4-Di-Cl-6-NO <sub>2</sub>	$pK_{BH^+}^T$	-3.53	-3.50	-3.46	-3.41
	$n_{bb}^{T_1, T_2}$	1.24	1.27	1.26	1.28
10) 2,4-Di-NO <sub>2</sub>	$pK_{BH^+}^T$	-5.36	-5.25	-5.07	-4.98
	$n_{bb}^{T_1, T_2}$	1.39	1.44	1.43	1.43
11) 2,6-Di-NO <sub>2</sub>	$pK_{BH^+}^T$	-6.08	-5.90	-5.73	-5.59
	$n_{bb}^{T_1, T_2}$	1.41	1.45	1.41	1.41

<sup>a</sup> Intercepts ( $pK_{BH^+}$ ) and slopes ( $n_{bb}^{T_1, T_2}$ ) estimated by  $\log [BH^+]/[B][H^+] = \log Q_B$  (at  $T$  °C) vs.  $M_c$  (at  $T$  °C) [see eqn. (19a)];  $M_c$  (at  $T$  °C) referred to 2-nitroaniline (at  $T$  °C) as standard indicator (B\*). <sup>b</sup> Progressive no. of nitroanilines as in Table 4. <sup>c</sup> Experimental data from ref. 21;  $pK_{BH^+}$ ,  $n_{bb}^{T_1, T_2}$ ,  $M_c$  values (at 25 °C) from ref. 16;  $M_c$  (at  $T$  °C) from this work. <sup>d</sup> The slopes of  $n_{bb}^{T_1, T_2}$  vs.  $pK_{BH^+}$  (or *N* values) (at  $T$  °C) are referred to the corresponding  $pK_2^T$  of water (at  $T$  °C), ( $pK_w^T = 14.35$  at 15 °C; 14 at 25 °C; 13.70 at 35 °C; 13.40 at 45 °C).

**Table 7a** Thermodynamic data for the protonation–dehydration equilibria of triphenylmethanols in aqueous sulfuric acid

Triphenylmethanols <sup>a-e</sup>		25 °C <sup>c</sup>	40 °C	60 °C	80 °C	90 °C	$\Delta G^{\circ f}$	$\Delta H^{\circ f}$
1) 4,4'-Di-OCH <sub>3</sub>	$pK_{R^+}$	0.60	0.73	0.96	1.14	1.18	0.82	-2.52
	$n_{bb}^{T_1, T_2}$	1.00	0.97	0.93	0.90	0.87		
	<i>R</i>	0.60	0.75	1.03	1.27	1.35		
2) 4-OCH <sub>3</sub>	$pK_{R^+}$	-1.60	-1.31	-1.06	-0.92	-0.78	-2.18	-5.49
	$n_{bb}^{T_1, T_2}$	1.00	0.91	0.85	0.82	0.79		
	<i>R</i>	-1.60	-1.43	-1.25	-1.12	-0.99		
3) 4-CH <sub>3</sub>	$pK_{R^+}$	-3.70	-3.46	-2.96	-2.67	-2.55	-5.05	-9.15
	$n_{bb}^{T_1, T_2}$	1.00	0.96	0.87	0.82	0.79		
	<i>R</i>	-3.70	-3.60	-3.40	-3.26	-3.23		
4) H	$pK_{R^+}$	-6.05	-5.58	-5.03	-4.30	-4.09	-8.25	-12.81
	$n_{bb}^{T_1, T_2}$	1.00	0.95	0.86	0.75	0.72		
	<i>R</i>	-6.05	-5.87	-5.85	-5.73	-5.68		
5) 4,4',4''-Tri-Cl	$pK_{R^+}$	-7.70	-7.35	-6.69	-6.02	-5.71	-10.50	-15.55
	$n_{bb}^{T_1, T_2}$	1.00	0.98	0.93	0.87	0.83		
	<i>R</i>	-7.70	-7.50	-7.19	-6.92	-6.88		
6) 4-NO <sub>2</sub>	$pK_{R^+}$	-9.10	-8.50	-7.64	-6.90		-12.42	-17.85
	$n_{bb}^{T_1, T_2}$	1.00	0.95	0.88	0.82			
	<i>R</i>	-9.10	-8.95	-8.68	-8.41			
7) 4,4',4''-Tri-NO <sub>2</sub>	$pK_{R^+}$	-13.60	-12.65	-11.70	-10.80		-18.55	-24.71
	$n_{bb}^{T_1, T_2}$	1.00	0.94	0.87	0.81			
	<i>R</i>	-13.60	-13.46	-13.45	-13.33			
8) 4,4',4''-Tri-(NCH <sub>3</sub> ) <sub>3</sub> <sup>+</sup>	$pK_{R^+}$	-15.00	-14.45	-13.45	-12.65	-12.25	-20.46	-23.80
	$n_{bb}^{T_1, T_2}$	1.00	0.97	0.90	0.85	0.83		
	<i>R</i>	-15.00	-14.90	-14.94	-14.88	-14.76		

<sup>a</sup> The protonation–dehydration equilibria of triphenylmethanols ( $ROH + H^+ \rightleftharpoons R^+ + H_2O$ ) are described by the thermodynamic eqn.:  $pK_{R^+} = \log \{ [R^+][H_2O]/[ROH][H^+] \} - \log (f_{ROH}f_{H^+}/f_{R^+}f_{H_2O})$ , or by the empirical eqn.:  $pK_{R^+} = \log \{ [R^+][H_2O]/[ROH][H^+] \} + n_{bb} Mc(i)$  [see also eqn. (9)].

<sup>b</sup> Intercepts ( $pK_{R^+}$ ) and slopes ( $n_{bb}^{T_1, T_2}$ ) estimated by  $\log [R^+]/[ROH] - \log [H^+] + \log [H_2O] = \log V_R$  (at  $T$  °C) vs.  $\log V_R$  (at 25 °C). <sup>c</sup>  $\log V_R$  and  $pK_{R^+}$  (at 25 °C) used as reference values;  $n_{bb}^{T_1, T_2} = 1.00$  (at 25 °C). <sup>d</sup> *R* (ratio) = ( $pK_{R^+}/n_{bb}^{T_1, T_2}$ ). <sup>e</sup> Experimental data from ref. 22;  $pK_{R^+}$  at 25 °C, this work. <sup>f</sup>  $\Delta G^{\circ}$  estimated by  $2.303 RT pK_{R^+}$  (at 25 °C);  $\Delta H^{\circ}$  estimated by plots of  $pK_{R^+}$  vs.  $1/T$  [ $T$  = temperature (K) for  $\Delta G^{\circ}$  and  $\Delta H^{\circ}$  values]; slope of  $\Delta G^{\circ}$  vs.  $\Delta H^{\circ} = 0.87$  (with the exception of methanol no. 8).

**Table 7b** Intercepts ( $pK_R$ )<sup>a</sup> and slopes ( $n_{bb^*T}$ )<sup>a</sup> for the protonation–dehydration equilibria of triphenylmethanols in aqueous sulfuric acid (at  $T$  °C)

Triphenylmethanols <sup>a,b</sup>		25 °C <sup>c,d</sup>	40 °C <sup>d</sup>	60 °C <sup>d</sup>	80 °C <sup>d</sup>	90 °C <sup>d</sup>
1) 4,4'-Di-OCH <sub>3</sub>	$pK_{R^+}$	0.60	0.73	0.96	1.14	1.18
	$n_{bb^*T}$	1.70				
2) 4-OCH <sub>3</sub>	$pK_{R^+}$	-1.60	-1.31	-1.06	-0.92	-0.78
	$n_{bb^*T}$	2.02	1.92	1.90	1.90	1.82
3) 4-CH <sub>3</sub>	$pK_{R^+}$	-3.70	-3.46	-2.96	-2.67	-2.55
	$n_{bb^*T}$	2.20	2.20	2.13	2.12	2.10
4) H	$pK_{R^+}$	-6.05	-5.58	-5.03	-4.30	-4.09
	$n_{bb^*T}$	2.55	2.55	2.43	2.30	2.25
5) 4,4',4''-Tri-Cl	$pK_{R^+}$	-7.70	-7.35	-6.69	-6.02	-5.71
	$n_{bb^*T}$	2.72	2.74	2.70	2.65	2.56
6) 4-NO <sub>2</sub>	$pK_{R^+}$	-9.10	-8.50	-7.64	-6.90	
	$n_{bb^*T}$	2.84	2.80	2.76	2.67	
7) 4,4',4''-Tri-NO <sub>2</sub>	$pK_{R^+}$	-13.60	-12.65	-11.65	-10.80	
	$n_{bb^*T}$	1.97	1.95	1.88	1.85	
8) 4,4',4''-Tri-(NCH <sub>3</sub> ) <sub>3</sub> <sup>+</sup>	$pK_{R^+}$	-15.00	-14.45	-13.45	-12.65	-12.25
	$n_{bb^*T}$	2.21	2.26	2.20	2.19	2.20

<sup>a</sup> Intercepts ( $pK_R$ ) and slopes ( $n_{bb^*T}$ ) estimated by  $\log [R^+]/[ROH] - \log [H^+] + \log [H_2O] = \log V_R$  (at  $T$  °C) vs.  $Mc$  (at  $T$  °C) (see footnote a of Table 7a);  $Mc$  (at  $T$  °C) referred to 2-nitroaniline, with  $n_{bb^*T} = 1$ , as standard indicator (B\*) (at  $T$  °C). <sup>b</sup> Experimental data from ref. 22;  $Mc$  (at 25 °C from ref. 17;  $Mc$  (at  $T$  °C) from this work. <sup>c</sup>  $pK_R$  and  $n_{bb^*T}$  values of triphenylmethanols at 25 °C, using the experimental data of ref. 45 are: (X) = 2,2',2''-tri-Me (-1.28, 1.90); (Y) = 3,3',3''-tri-Me (-5.20, 2.45); (Z) = 4,4',4''-triisopropyl (-5.40, 2.46). <sup>d</sup> See footnote d of Table 5b.

catalysts (i.e. HClO<sub>4</sub>/SiO<sub>2</sub>, CF<sub>3</sub>SO<sub>3</sub>H/SiO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>/SiO<sub>2</sub>) support analogous conclusions.<sup>25,46</sup>

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Paper 8/02521E  
Received 2nd April 1998  
Accepted 9th July 1998