Enthalpy of Dissociation of Nitric Acid in Aqueous Sulphuric Acid and its Relation to the Activation Energies of Encounter-controlled Nitrations

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The enthalpy of dissociation of nitric acid to nitronium ion and hydroxide ion is estimated to be +(43 ± 4) kJ mol^{-1} in 68·3 w/w % sulphuric acid and +(19 ± 5) kJ mol^{-1} in 79·2 w/w % sulphuric acid. These values are used to show that the high energies of activation observed in the limiting nitrations of reactive compounds in sulphuric acid are consistent with the interpretation that these reactions are controlled by the rate of encounter of the nitronium ion with the aromatic molecule.

THE results of studies of nitration have provided evidence for the existence of limiting rates of nitration with sufficiently reactive aromatic substrates.[1-3] Limiting rates have been observed for a variety of nitrating conditions,[3] but the effect is most pronounced in sulphuric acid. A comparison of the observed limiting rate constants for nitrations under these last mentioned conditions with those calculated assuming a diffusion controlled process has led to the limiting rate being identified with the rate of encounter of the nitronium ions with the aromatic molecules.[1] Since the reaction is assumed to occur on encounter, there must be a low energy of activation associated with such a process; not larger than *ca.* 8 kJ mol^{-1}. However, experimentally, one would expect to observe a larger ' apparent ' energy of activation, arising from the change in viscosity of the solvent with a change in the temperature.[4] This effect should produce an observed energy of activation for an encounter-controlled nitration of a reactive aromatic substrate of *ca.* 25—30 kJ mol^{-1}.

It has been found, however, that for the nitrations of mesitylene and naphthalene in sulphuric acid (67·1 w/w %) the observed activation energies are in the range 63—75 kJ mol^{-1}.[1] At acidities below *ca.* 90 w/w % sulphuric acid the conversion of nitric acid into nitronium ion is incomplete, indeed, the steep decreases in the rate of nitration of substrates with decreasing acidity is attributed to the diminishing availability of the nitronium ion. The rather high values observed for the activation energies of these encounter-controlled reactions can be understood if it is assumed that the dissociation of nitric acid to nitronium ion under these conditions is a highly endothermic process. It was to test this assumption, and therefore to supply further evidence in support of the idea of encounter-controlled nitrations, that the present work was undertaken.

EXPERIMENTAL

Materials.—Sodium hydroxide (pellets), potassium hydroxide (pellets), and sulphuric acid (*d* 1·84) were of AnalaR grade. Standard solutions of sodium hydroxide and hydrochloric acid were prepared from Volucon ampoules. 2-Amino-2-(hydroxymethyl)propane-1,3-diol (Tris) was supplied as specially purified laboratory reagent and was used without further purification. Pure nitric acid was obtained by the slow vacuum distillation of a solution of equal volumes of fuming nitric acid and concentrated sulphuric acid; it was stored at −10 °C. Solutions of aqueous sulphuric acid were prepared by diluting AnalaR sulphuric acid with the appropriate amounts of distilled water. The composition of each solution was determined either by measurement of the density (for solutions <90 w/w % sulphuric acid) or by titration against a standard solution of sodium hydroxide.

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[1] R. G. Coombes, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1968, 800.

[2] J. G. Hoggett, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1969, 1.

[3] S. R. Hartshorn, R. B. Moodie, K. Schofield, and M. J. Thompson, *J. Chem. Soc.* (*B*), 1971, 2447.

[4] S. R. Hartshorn and J. H. Ridd, *J. Chem. Soc.* (*B*), 1968, 1068.

Calorimeter.—A Dewar vessel (*ca.* 350 cm^3 capacity) was used; this was fitted with a Teflon cover through which passed a fine Nichrome wire heater encased in glass, a glass stirrer, a Beckmann thermometer (1 °C range) and a glass syringe. The last mentioned was a modified 10 cm^3 all-glass syringe, the bottom was sawn off and the end sealed with a Teflon plug. During operation the calorimeter was immersed in a thermostat (25·00 ± 0·005) °C.

Method of Operation.—The calorimeter was loaded with 250 cm^3 of solvent (water, sulphuric acid, or 0·1M-hydrochloric acid), stirred (350 min^{-1}), and allowed to reach thermal equilibrium before addition of a known weight of the sample (nitric acid, sodium hydroxide, or Tris) from the syringe. The temperature change was determined from a plot of the reading of the Beckmann thermometer against time, by extrapolation of the linear cooling curve, which followed the initial rise in temperature, to the time at which the addition was made. Other methods of extrapolation, based on those given by Dickinson,[5] were used in some cases and the results were in essential agreement with those obtained by the method described above.

After addition of the sample, the rise in temperature brought about by a known amount of electrical energy was determined by the same extrapolation procedure. The heating was continued long enough to produce a temperature rise of roughly the same size as that produced by the addition of the sample. The time of heating was measured by a Labgear time period counter (to the nearest 0·01 s), the electrical circuit being arranged so that the calorimeter heater and the timer were connected into the circuit by the same switch. During the heating, the current was determined by measuring the potential difference across a 10 Ω standard resistance. The resistance of the calorimeter heater was known from previous measurement and from these quantities the electrical energy supplied to the calorimeter could be calculated. The above results enabled the molar enthalpy changes to be calculated for the additions of the various samples to the given solvents.

Additions of Nitric Acid and Tris.—The appropriate quantities of these materials were added to the weighed syringe and the exact amount taken was determined by reweighing. No special handling precautions were taken.

Additions of Sodium and Potassium Hydroxides.—These materials were handled in a glove box under an atmosphere of dry nitrogen. The powdered hydroxide, from freshly crushed pellets, was added to the syringe and the weight taken found by difference.

RESULTS

Calibration of the Calorimeter.—In order to check the performance of the calorimeter and the experimental technique, the molar enthalpy change for the neutralisation of Tris in 0·1M-hydrochloric acid was determined. The results in Table 1 lead to a mean value for ΔH_m of $-29·73$ kJ mol^{-1} with a standard deviation of 0·7 kJ mol^{-1}. This figure is in good agreement with the recently measured value of $-(29·744 \pm 0·003)$ kJ mol^{-1}.[6]

The Enthalpy of Solution of Sodium Hydroxide.—For reasons of practical expediency AnalaR sodium hydroxide pellets were used without further purification. Preliminary experiments with pellets indicated that these dissolved too slowly in sulphuric acid solvents to enable accurate temperature measurements to be made. However, powdered sodium hydroxide was found to be suitable and this was used in all subsequent experiments. To estimate the errors involved in this method of handling sodium hydroxide (see Experimental section) its enthalpy of solution in water was determined and the value compared with that obtained from an accurate study.[7] Our results are presented in Table 2, and these compare remarkably well, considering the simple experimental technique employed, with the value of $-44·57$ kJ mol^{-1} obtained by Murch and Giauque.

TABLE 1

The molar enthalpy change for the addition of Tris to hydrochloric acid (0·1M) [a]

m (Tris)/g	$-\Delta H_m$/kJ mol^{-1}
0·8909	29·89
1·3442	29·18
1·6324	29·52
1·3744	29·28
1·2187	30·79

[a] Volume of HCl = 250 cm^3; values of ΔH_m are not corrected to infinite dilution.

After each calorimetric determination, the contents of the calorimeter were made up to 500 cm^3 with distilled water and titrated against standard hydrochloric acid, to determine the weight of sodium hydroxide present. When this was compared with the weight of sodium hydroxide powder taken, it showed that the powder contained *ca.* 96 to 97 w/w % of NaOH. The effect that this small uncertainty in the composition of the sodium hydroxide has upon the enthalpy of solution is shown by the results in Table 2.

TABLE 2

The enthalpy of solution of sodium hydroxide in water [a]

m (NaOH)/g [b]		$-\Delta H_m$/kJ mol^{-1} [b]		$-\Delta H_m\infty$/ kJ mol^{-1} [c]
(I)	(II)	(I)	(II)	
0·1549	0·1500	42·56	43·95	44·40
0·1731	0·1670	40·70	42·19	42·64

[a] Volume of water = 250 cm^3. [b] (I) Using weight of NaOH powder, (II) using weight of NaOH calculated from standardisation. [c] Enthalpy of solution corrected to infinite dilution, using figures in the fourth column and the relation $\Delta H_m\infty = \Delta H_m - \Phi_L$, $\Phi_L = 0·45$ kJ mol^{-1} (extrapolated from data in ref. 8).

Nitric Acid.—The molar enthalpy changes for the addition of nitric acid to various solutions of sulphuric acid are shown in Table 3. All the results indicate that the uncertainties in the mean values of ΔH_m are no larger than the standard deviation quoted above for the calibration experiments.

Sodium Hydroxide.—For the experiments in which sodium (or potassium) hydroxide was added to sulphuric acid, the molar enthalpy changes were calculated on the basis of the weight of solid taken. This imposes an additional uncertainty on the mean values for each set of measurements, because of the small uncertainty in the actual composition of the powdered hydroxide. However, the experiments with sodium hydroxide, mentioned above (Table 2), indicate that these effects should not be too large, so that although

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[5] H. C. Dickinson, *Bull. Natl. Bur. Std.*, 1914, **11**, 189.

[6] J. O. Hill, G. Öjelund, and I. Wadsö, *J. Chem. Thermodynamics*, 1969, **1**, 111.

[7] L. E. Murch and W. F. Giauque, *J. Phys. Chem.*, 1962, **66**, 2052.

[8] V. B. Parker, ' Thermal Properties of Aqueous Uni-univalent Electrolytes,' Nat. Bur. Std., NSRDS-NBS **2**, U.S. Government Printing Office, Washington, D.C., 1965.

Table 3

Molar enthalpy changes for the addition of nitric acid to aqueous sulphuric acid [a]

m (HNO_3)/g	H_2SO_4 (w/w %)	$-\Delta H_m$/kJ mol^{-1}
0·7536	98·1	34·68
0·6469	98·1	34·47
0·4726	92·2	25·36
0·6325	92·2	24·20
1·0230	79·2	6·26
1·6453	79·2	5·93
0·4080	68·3	10·37
1·8562	68·3	10·47

[a] Volume of H_2SO_4 = 250 cm^3; values of ΔH_m are not corrected to infinite dilution.

a larger standard deviation attaches to the results in Table 4 (*ca.* ±2 kJ mol^{-1}) they should still be of sufficient accuracy for our present purposes.

Apart from the enthalpies of solution of sodium hydroxide in water (Table 2) the results have not been corrected to refer to infinite dilution. In all cases the amounts of solutes added have been small enough not seriously to disturb the composition of the solvent. The results in Tables 1, 3, and 4 show that there is no consistent variation in the value of ΔH_m with the amount of sample used.

Table 4

Molar enthalpy changes for the addition of sodium hydroxide to aqueous sulphuric acid :

m (NaOH)/g	H_2SO_4 (w/w %)	$-\Delta H_m$/kJ mol^{-1}
0·1804	98·1	200·04
0·0346	98·1	203·50
0·0808 [b]	98·1	205·52
0·0251	92·2	186·23
0·0383	92·2	189·52
0·0825	79·2	157·18
0·0795	79·2	150·80
0·0848	68·3	130·80
0·0757	68·3	133·97
0·1574 [b]	68·3	131·94

[a] Volume of H_2SO_4 = 250 cm^3; values of ΔH_m are not corrected to infinite dilution. [b] KOH used.

DISCUSSION

The Enthalpy of Dissociation of Nitric Acid to Nitronium Ion.—The enthalpy change which we wish to estimate is for the process:

HNO_3 (in 68·3 w/w % H_2SO_4) =
NO_2^+ (in 68·3 w/w % H_2SO_4) +
OH^- (in 68·3 w/w % H_2SO_4) (1)

In this equation and those below, OH^- (in x w/w % H_2SO_4), the solvated hydroxide ion, is a purely formal description of the equilibrium form of the anionic product of the heterolysis. The complicated proton-transfer equilibria which accompany its formation need not be described, or even known.

Measurements in the calorimeter have been made for the following changes:

HNO_3 + 68·3 w/w % H_2SO_4 =
HNO_3 (in 68·3 w/w % H_2SO_4) (2)

HNO_3 + 98·1 w/w % H_2SO_4 =
NO_2^+ (in 98·1 w/w % H_2SO_4) +
OH^- (in 98·1 w/w % H_2SO_4) (3)

In sulphuric acid with compositions greater than 92 w/w % H_2SO_4 nitric acid is known to be virtually completely dissociated into nitronium ions and in solutions of less than *ca.* 80 w/w % H_2SO_4 the dissociation produces virtually no nitronium ion.

We have also studied the changes:

NaOH(s) + 68·3 w/w % H_2SO_4 =
Na^+ (in 68·3 w/w % H_2SO_4) +
OH^- (in 68·3 w/w % H_2SO_4) (4)

NaOH(s) + 98·1 w/w % H_2SO_4 =
Na^+ (in 98·1 w/w % H_2SO_4) +
OH^- (in 98·1 w/w % H_2SO_4) (5)

In these reactions the hydroxide ion again appears but does not, of course, exist in the final (unknown) state of the solution.

If now we do the following sum with these four equations,

$$\{(4) - (5)\} - \{(2) - (3)\}$$

the following process is obtained:

Na^+ (in 98·1 w/w % H_2SO_4) +
HNO_3 (in 68·3 w/w % H_2SO_4) =
Na^+ (in 68·3 w/w % H_2SO_4) +
NO_2^+ (in 98·1 w/w % H_2SO_4) +
OH^- (in 68·3 w/w % H_2SO_4)

The enthalpy change for this process will be identical to that for equation (1) if it is assumed that the enthalpy change for the following process is zero:

Na^+ (in 68·3 w/w % H_2SO_4) +
NO_2^+ (in 98·1 w/w % H_2SO_4) =
Na^+ (in 98·1 w/w % H_2SO_4) +
NO_2^+ (in 68·3 w/w % H_2SO_4)

in other words that the enthalpy of transfer of the sodium ion from 68·3 w/w % H_2SO_4 to 98·1 w/w % H_2SO_4 is the same as that for transfer of the nitronium ion between the same two media. The nitronium ion, like the sodium ion, is not likely to act as a hydrogen-bond acceptor, so that specific solvation effects should be absent. Some indication that the size of the ion is not an important factor comes from the observation that repeating measurements for the changes represented by equations (4) and (5) with potassium hydroxide instead of sodium hydroxide gives a very similar value (to within 8%) for the difference between the enthalpy changes for these processes. We feel that the assumption will be valid within the overall accuracy of the determination. The final value of the enthalpy change for equation (1) is $\Delta H_m = +(45 \pm 4)$ kJ mol^{-1}.

Since nitric acid is almost completely dissociated in acidities greater than 92 w/w % H_2SO_4, any medium of higher acidity than this may be used in place of 98·1 w/w % H_2SO_4 and the enthalpy change should be unaltered. Use of 92·2 w/w % H_2SO_4 gives for the enthalpy change of equation (1) $\Delta H_m = +(41 \pm 4)$ kJ mol^{-1}. The two values are in satisfactory agreement and the combined value is $\Delta H_m = +(43 \pm 4)$ kJ mol^{-1}. The dissociation of nitric acid to nitronium ion and hydroxide ion is therefore endothermic, in spite of the highly exothermic solvation of the hydroxide ion.

The Activation Energy for the Nitration of Mesitylene in 68·3 w/w % H_2SO_4.—The mechanism of the reaction is believed to be:

$$HNO_3 \underset{}{\overset{K_1}{\rightleftharpoons}} NO_2^+ + OH^-$$
$$NO_2^+ + Ar \xrightarrow{k_1} \text{Products}$$

As stated in the introduction,[1] if the second step is an encounter-controlled process, its apparent activation energy arising largely from the temperature coefficient of the viscosity of the medium, E_{vis}, should be in the range 25—30 kJ mol^{-1}. The enthalpy change for the first step has now been estimated as described above as $+(43 \pm 4)$ kJ mol^{-1}. The observed activation energy [1], $+(72 \pm 4)$ kJ mol^{-1}, is not, therefore, in conflict with the conclusion that the reaction is encounter controlled.

No exact correlation between the kinetic and the calorimetric work may be made, for theoretical as well as for practical reasons. Thus, the observed activation energy, according to the mechanism described above, contains an additional term relating to the unknown, and unmeasurable, temperature dependence of the concentration of the solvated hydroxide ion,

$$k_{obs} = k_1K_1/[OH^-]$$
$$E_{obs} = -R\mathrm{d}(\ln k_{obs})/\mathrm{d}(1/T)$$
$$\therefore E_{obs} = E_{vis} + \Delta H_1 + R\mathrm{d}(\ln [OH^-])/\mathrm{d}(1/T)$$

No ready estimate of the latter quantity presents itself; this work would suggest, however, that it may be quite small. In any event there is no reason to invoke a large value for this quantity in order to explain the large value of E_{obs}.

Also included in Tables 3 and 4 are the results of measurements made in 79·2 w/w % H_2SO_4, from which we may calculate the enthalpy change for the dissociation of nitric acid to nitronium ion in this medium to be $+(19 \pm 5)$ kJ mol^{-1}. This is 24 kJ mol^{-1} less than the value estimated for 68·3 w/w % H_2SO_4 and this reduction in the value of E_{obs} would lead to an increase in the rate of nitration at 25 °C of $1{\cdot}5 \times 10^4$. From the normal acidity dependence of the observed second-order rate constant for nitration $[\mathrm{d}(\log_{10} k_{obs})/\mathrm{d}(\%\ H_2SO_4) \approx 0{\cdot}37]$, the calculated increase in the rate of nitration for the change of medium from 68·3 w/w % to 79·2 w/w % H_2SO_4 is *ca.* 1×10^4. In comparing the above two estimates it should be remembered that the former value was obtained without considering the effects of a change of medium on E_{vis} and $R\mathrm{d}(\ln [OH^-])/\mathrm{d}(1/T)$, but it is expected that such effects would be small. It was also assumed that the variation in the entropy of activation was small compared with the variation in the enthalpy of activation and the available data indicate that this is the case.[9] The calorimetric measurements are, therefore, quite consistent with the view that limiting rates of nitration can be identified with the rate of encounter of the nitronium ion with the aromatic molecule.

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[9] J. G. Hoggett, R. B. Moodie, J. R. Penton, and K. Schofield, 'Nitration and Aromatic Reactivity,' Cambridge University Press, Cambridge, 1971.