Solution Calorimetry of Nitrosonium Salts

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The standard enthalpies of formation of crystalline $[NO][ClO_4]$, $[NO][HSO_4]$, and $[NO]_2[S_2O_7]$ have been determined as 59.0, −680.3, and −1 041.0 kJ mol^{-1} respectively, based on enthalpies of reaction with aqueous base. The discrepancies between these and some previously published values are discussed in terms of the competing neutralisation and disproportionation reactions of nitrous acid in aqueous medium.

ALTHOUGH many nitrosonium salts are well known, thermodynamic data are sparse and discrepant. In particular, (i) there are serious discrepancies between independent measurements of the standard enthalpy of formation of nitrosonium hydrogensulphate, $[NO][HSO_4]$ [1,2] and (ii) there are errors of calculation and interpretation in an investigation of $[NO][ClO_4]$.[3] The majority of measurements have involved degradative solution calorimetry in aqueous base. Under such conditions it is clear that nitrous acid is formed, at least transiently, *via* $NO^+ + OH^- \longrightarrow HNO_2$, but its subsequent reaction is dependent on experimental conditions,[4] *e.g.* pH. In some previous calorimetric work the consequences of this, and of reaction of oxygen with the liberated NO, have been largely ignored. Although simple neutralisation predominates in very strongly basic media the contribution from disproportionation is nevertheless significant. In this paper we report detailed enthalpy measurements and post-calorimetric analyses, under oxygen-free conditions, on three salts, $[NO][HSO_4]$, $[NO][ClO_4]$, and $[NO]_2[S_2O_7]$, using 0.1 mol dm^{-3} Na[OH]. Appropriate values of standard enthalpies of reaction and formation are calculated and compared with reported values.

EXPERIMENTAL

Preparations.—The salt $[NO][ClO_4]$ was prepared by a laboratory scale modification of a patented industrial process.[5] Perchloric acid (70%, 8.5 cm^3) was added dropwise to a stirred solution of fuming nitric acid (15 cm^3) and N_2O_4 (30 cm^3) cooled in an ice-salt bath. The precipitated $[NO][ClO_4]$ was filtered off and dried *in vacuo* at ambient temperature over anhydrous magnesium perchlorate (Found: Cl, 27.3; NO, 23.15. Calc. for $ClNO_5$: Cl, 27.4; NO, 23.15%). The salt $[NO][HSO_4]$ was prepared according to the method of Richards and Woolf [2] which is essentially a modification of a reported method [6] (Found: NO, 23.65; S, 25.35. Calc. for HNO_5S: NO, 23.6; S, 25.2%). The salt $[NO]_2[S_2O_7]$ was prepared from SO_2 and N_2O_4 in a sealed tube according to Jones *et al.*[7] (Found: NO, 25.35; S, 27.15. Calc. for $N_2O_9S_2$: NO, 25.4; S, 27.2%).

Calorimetry.—Enthalpies of reaction in 100 cm^3 of 0.1 mol dm^{-3} aqueous sodium hydroxide solution were measured at 298.2 K under oxygen-free nitrogen using a solution reaction calorimeter constructed in these laboratories and fully described elsewhere.[8] The aluminium lid of the calorimeter was coated on the underside with a film of Teflon to avoid chemical attack by oxides of nitrogen. The performance of the calorimeter was checked repeatedly by measuring the enthalpy of neutralisation of tris[(hydroxymethyl)amino]methane in an excess of 0.1 mol dm^{-3} HCl.

Post-calorimetric Nitrogen Analysis.—Following measurement of the enthalpy of reaction, NO was displaced from the calorimeter and calorimetric fluid using a current of oxygen-free nitrogen gas. Nitrite was determined directly in an aliquot by titration with $K[MnO_4]$.[9] Total nitrate and nitrite in an aliquot of solution were determined using Devarda's method.[9] The small-scale decomposition did not permit direct measurement of the volume of NO gas. This was calculated from the total nitrate and nitrite assay and the nitrogen content of the sample decomposed. The experimental value for the NO : NO_3 mol ratio, which is at variance with the theoretical value of 2 : 1, reflects the low precision of the nitrate analysis. However the derived ratio is well within the limits of experimental error of the titrimetric procedure.[10]

RESULTS AND DISCUSSION

Hydrolysis of Nitrous Acid.—The basic hydrolysis of a nitrosonium salt, [NO]X, may be considered in terms of competing neutralisation and disproportionation reactions. Consider that a mol fraction x of the transient HNO_2 is neutralised [equations (1)—(4)]. Hence in the absence of adventitious oxygen the overall degradation of nitrosonium salt [NO]X in aqueous base is represented by equation (5). Thus, measurement of the standard enthalpy of reaction, $\Delta H_R^{\ominus}$, and analytical determination of the coefficient x, defines the system thermodynamically.

$$3[NO]X + 3OH^- \longrightarrow 3HNO_2 + 3X^- \quad (1)$$

$$3xHNO_2 + 3xOH^- \longrightarrow 3xH_2O + 3xNO_2^- \quad (2)$$

$$3(1-x)HNO_2 \longrightarrow (1-x)HNO_3 + (1-x)H_2O + 2(1-x)NO \quad (3)$$

$$(1-x)HNO_3 + (1-x)OH^- \longrightarrow (1-x)NO_3^- + (1-x)H_2O \quad (4)$$

$$3[NO]X(c) + 2(2+x)OH^-(aq) \longrightarrow [3X^- + 3xNO_2^- + (1-x)NO_3^-](aq) + 2(1-x)NO(g) + (x+2)H_2O \quad (5)$$

An obvious simplification results if values for $\Delta H_R^{\ominus}$ are measured under identical conditions for a series of compounds, such that the value of x remains constant. Thus, the measured differences in the respective enthalpies of reaction of two compounds [NO]X and [NO]Y may be expressed as $\Delta H_f^{\ominus}[NO]Y(c) - \Delta H_f^{\ominus}[NO]X(c) + \Delta H_f^{\ominus}X^-(aq) - \Delta H_f^{\ominus}Y^-(aq)$. Hence if the value

TABLE 1

Enthalpies of reaction of [NO]X (X = ClO_4 or HSO_4) and $[NO]_2[S_2O_7]$ with 0.1 mol dm^{-3} Na[OH] at 298.2 K

$[NO][ClO_4]$/g	n *	$-\Delta H_R^\ominus$/ kJ mol^{-1}	$[NO][HSO_4]$/ g	n *	$-\Delta H_R^\ominus$/ kJ mol^{-1}	$[NO]_2[S_2O_7]$/ g	n *	$-\Delta H_R^\ominus$/ kJ mol^{-1}
0.1717	4 173	110.79	0.1130	6 224	209.68	0.1044	6 259	441.29
0.1358	5 276	110.83	0.0949	7 411	209.26	0.0948	6 893	439.28
0.1240	5 777	109.20	0.1208	5 822	207.01	0.1040	6 283	444.78
0.1311	5 464	108.53	0.1030	6 829	207.47	0.0848	7 706	437.84
0.0869	8 248	108.99	0.1404	5 010	210.23	0.1227	5 326	449.32
0.1494	4 796	109.79	0.0927	7 587	211.39	0.1366	4 784	440.79
0.1575	4 548	109.58	0.0988	7 119	210.35			
0.1540	4 651	109.62						
Mean $\Delta H_R^\ominus = -109.58 \pm 0.75$ kJ mol^{-1}			Mean $\Delta H_R^\ominus = -209.33 \pm 1.46$ kJ mol^{-1}			Mean $\Delta H_R^\ominus = -442.21 \pm 4.39$ kJ mol^{-1}		

* Mol ratio (n : 1) of water to nitrosonium ion.

TABLE 2

NO_2^- level in solution after decomposition of NO^+ salts

$[NO][HSO_4]$/ mmol	NO_2^-/ mmol	x	$[NO]_2[S_2O_7]$/ mmol	NO_2^-/ mmol	x	$[NO][ClO_4]$/ mmol	NO_2^-/ mmol	x
0.959	0.819	0.854	0.440	0.626	0.712	1.437	1.084	0.755
1.346	1.138	0.846	0.520	0.747	0.719	1.014	0.775	0.764
1.967	1.631	0.829	0.578	0.818	0.707	1.371	1.050	0.766
1.472	1.177	0.800				2.100	1.559	0.742
						1.715	1.290	0.752
		$\langle x \rangle = 0.84$			$\langle x \rangle = 0.71$			$\langle x \rangle = 0.76$

of the standard enthalpy of formation of any one salt is established, values for others may be calculated. Unfortunately, the nitrite analyses listed in Table 2 show that significantly different, but reproducible, values of x are derived from degradations of the different salts under identical conditions. Thus, separate equations [(6)—(8)] are given for each compound, following detailed potassium manganate(VII) titrations; experimental details are given elsewhere.[10] Values of $\Delta H_f^\ominus$ for each

$[NO][ClO_4]$

$$\Delta H_R^\ominus = -22.01 - 37.7x - \Delta H_f^\ominus[NO][ClO_4](c) \quad (6)$$

$[NO][HSO_4]$

$$\Delta H_R^\ominus = -858.1 - 37.7x - \Delta H_f^\ominus[NO][HSO_4](c) \quad (7)$$

$[NO]_2[S_2O_7]$

$$\Delta H_R^\ominus = -1\,429.7 - 75.3x - \Delta H_f^\ominus[NO]_2[S_2O_7](c) \quad (8)$$

compound, calculated using experimental data from Tables 1, 2, and 3 and ancillary data from Table 4, are compared with reported values in Table 5.

Comparison with Reported Values.—(*i*) $[NO][ClO_4]$. Cruse *et al.*[3] have reported a calorimetric study, using basic hydrolysis and supplemented by careful post-calorimetric analyses; Richards and Woolf[2] have noted and corrected an error of calculation. A careful study of the analytical data, however, shows clearly that the degradative reaction was not reproducible, and that separate values of $\Delta H_f^\ominus[NO][ClO_4](c)$ were calculated from each calorimetric run: the overall reaction, on which the recalculation was made, *viz.* $9NO^+ + 16OH^- \longrightarrow 6NO_2^- + NO_3^- + 2NO + 8H_2O$, does not in fact represent the decomposition. Recalculation, using equation (5) and updated ancillary data, yields a value for $\Delta H_f^\ominus[NO][ClO_4](c) = 65.15$ kJ mol^{-1}, in modest agreement with that reported here, *viz.* 59.0 kJ mol^{-1}.

TABLE 3

NO : NO_3^- mol ratio following the decomposition of NO^+ salts by aqueous base

	X = ClO_4	X = ClO_4	X = HSO_4
[NO]X/g	0.2719	0.2220	0.2500
[NO]X/mmol	2.100	1.715	1.967
$NO_3^- + NO_2^-$/mmol	1.760	1.440	1.760
NO_2^-/mmol	1.559	1.290	1.631
NO_3^-/mmol	0.201	0.150	0.129
NO/mmol	0.340	0.275	0.207
$-\Delta H_R^\ominus$/kJ mol^{-1}	109.41	108.74	208.99
NO : NO_3^- mol ratio	1.70 : 1	1.83 : 1	1.60 : 1

TABLE 4

Ancillary thermochemical data

Compound	$-\Delta H_f^\ominus$/kJ mol^{-1}	Ref.
NO(g)	-90.21 ± 0.21	12
NO_2^-(aq)	104.60 ± 4.18	12
NO_3^-(aq)	207.19 ± 0.46	12
SO_4^{2-}(aq)	909.27 ± 0.00	12
ClO_4^-(aq)	129.33 ± 0.43	*a*
Cl^-(aq)	167.08 ± 0.00	*a*
OCl^-(aq)	109.72 ± 4.18	*b*
HNO_2 (aq)	119.24 ± 4.18	12
H_2SO_4(l)	811.28 ± 0.10	*c*
OH^-(aq)	230.02 ± 0.00	12
H_2O(l)	285.83 ± 0.00	12

[a] J. D. Cox, 'Halogen Compounds,' CATCH Tables, University of Sussex, 1972. [b] J. E. McDonald, J. P. King, and J. W. Cobble, *J. Phys. Chem.*, 1960, **64**, 1345. [c] F. M. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, *Nat. Bur. Stand.* (*U.S.*) *Circ.*, U.S. Govt. Printing Office, Washington D.C., 1952, no. 500.

TABLE 5

Thermochemical data for nitrosonium salts

Compound	$-\Delta H_f^\ominus$/kJ mol^{-1}	Ref.
$[NO][ClO_4]$ (c)	−59.0	This work
	−65.2	3 corrected
	165.7	3
$[NO][HSO_4]$ (c)	680.3	This work
	687.8	1
	764.4	2
$[NO]_2[S_2O_7]$ (c)	1 041.0	This work
	1 058.6	12
	1 191.6	11
	1 152.3	2

(*ii*) [NO][HSO$_4$]. Two independent values are available.[1,2] That of Kunin,[1] based on measurements of the enthalpy of dissolution of [NO][HSO$_4$] in aqueous sulphuric acid of varying concentrations, is in excellent agreement with that reported here (−687.8 *cf.* −680.3 kJ mol^{-1}), derived from basic hydrolysis studies and calculations involving (5) and (7). The very different value of Richards and Woolf,[2] $\Delta H_f^{\ominus}$[NO][HSO$_4$](c) = −764.4 kJ mol^{-1}, depends on measurements involving oxidative hydrolysis with alkaline hypochlorite, according to: $NO^+ + 2OH^- + OCl^- \longrightarrow NO_3^- + Cl^- + H_2O$. This assumes that NO_3^- is formed entirely by oxidation of NO_2^-, and that no disproportionation occurs. Exploratory experiments in this laboratory showed that after reaction of [NO][HSO$_4$] with OCl^- in an oxygen-free environment, NO was displaced from the calorimeter vessel. Clearly reaction of NO^+ with base will proceed as in (1) to (4). If complete oxidation of NO_2^- to NO_3^- occurs then the overall reaction may be represented by: $3[NO][HSO_4] + (7 + 2x)OH^- + 3xOCl^- \longrightarrow 3SO_4^{2-} + 3xCl^- + (5 + x)H_2O + 2(1 - x)NO + (1 + 2x)NO_3^-$ and the reaction enthalpy given by $\Delta H_R^{\ominus} = -897.7 - 197.9x - \Delta H_f^{\ominus}$[NO][HSO$_4$](c). The magnitude of $\Delta H_R^{\ominus}$ is seriously affected by variations in x. Assuming, as a first approximation, that the extent of disproportionation is the same as in the absence of OCl^- and putting $x = 0.84$ and $\Delta H_R^{\ominus} = -318.9$ kJ mol^{-1} [10] then $\Delta H_f^{\ominus}$ [NO][HSO$_4$](c) = ≈ −703 kJ mol^{-1} *i.e.* a change of *ca.* 60 kJ mol^{-1} from the reported value.

(*iii*) [NO]$_2$[S$_2$O$_7$]. Three independent studies have been reported: in 1928 Briner *et al.*[11] and also Vaughan,[12,13] using aqueous base and, more recently, Richards and Woolf[2] using alkaline hypochlorite oxidation. The enthalpy of reaction reported by Vaughan, −447.7 kJ mol^{-1}, is in very good agreement with that from the present study, −441.8 kJ mol^{-1}. Recalculation using recent ancillary data, leads to a value of $\Delta H_f^{\ominus}$[NO]$_2$[S$_2$O$_7$] = −1 058.6 kJ mol^{-1} in excellent, although possibly fortuitous, agreement with the value of −1 041.0 kJ mol^{-1} reported here. Since no consideration was taken of disproportionation it is unlikely that oxygen-free calorimetric conditions were employed.

Values reported by Richards and Woolf for $\Delta H_f^{\ominus}$[NO][HSO$_4$](c) and $\Delta H_f^{\ominus}$[NO]$_2$[S$_2$O$_7$](c) were justified by the consistency of two derived values of $\Delta H_f^{\ominus}$[NO][SO$_3$F](c),[2] calculated from separate measurements of enthalpies of solution of [NO][HSO$_4$](c) and [NO]$_2$[S$_2$O$_7$](c), respectively, in fluorosulphonic acid. These derivations require a value for the enthalpy of solution of $H_2S_2O_7$, in fluorosulphonic acid, and it is apparently assumed that this is equal to the sum of the enthalpies of solution of H_2SO_4(l) and of SO_3(l) in fluorosulphonic acid. This is not supported by an analysis of the available data, which suggests a difference of *ca.* 25 kJ.

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