JOURNAL OF RESEARCH of the National Bureau of Standards—A. Physics and Chemistry
Vol. 66A, No. 6, November–December 1962

Heat of Formation of Nitronium Perchlorate

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(July 25, 1962)

Calorimetric measurements of the heat of solution of nitronium perchlorate (NO_2ClO_4) and of a mixture of potassium nitrate and potassium perchlorate in aqueous potassium hydroxide have been made. These are combined to give:

$$NO_2ClO_4(c)+4KOH(\text{in } 5300\ H_2O)\rightarrow KClO_4(c)+KNO_3(c)+2KOH(\text{in } 5300\ H_2O)+H_2O(\text{liq})$$
$$\Delta H=-285.80\pm 0.38 \text{ kj/mole}$$
$$=-\ 68.31\pm 0.09 \text{ kcal/mole}$$

from which the standard heat of formation of nitronium perchlorate is calculated as

$$\Delta Hf^{\circ}(25\ ^{\circ}\mathrm{C})\ NO_2ClO_4(c)=37.19\pm 1.0 \text{ kj/mole}$$
$$=\ 8.89\pm 0.25 \text{ kcal/mole},$$

in which the uncertainty represents twice the estimated overall standard deviation of the result.

1. Introduction

This investigation was carried out in the Thermochemistry Section of the National Bureau of Standards as part of a program, currently in progress, on the determination of the thermodynamic properties of the "light element" compounds. Nitronium perchlorate is a white crystalline material stable at temperatures up to 120 °C. It is extremely hygroscopic, reacting rapidly with water to form nitric and perchloric acids. The heat of formation of NO_2ClO_4 can be determined by measuring this heat of decomposition. In this investigation, aqueous solutions of potassium hydroxide were used, as the potassium salts of the acids provided more suitable reference substances.

2. Materials

The potassium nitrate and potassium perchlorate were reagent grade materials, dried at 120 °C and stored in a desiccator over anhydrous magnesium perchlorate. The potassium hydroxide was reagent grade material; the calorimetric solutions were prepared with CO_2-free distilled water, and standardized against potassium acid phthalate. The NO_2ClO_4 was obtained from the Callery Chemical Company as a white crystalline powder; an analysis furnished by them showed:

Nitrogen	6.75– 6.74	theoretical	6.874 milliatoms/g
Chlorine	6.90– 6.82	theoretical	6.874 milliatoms/g
Total acid	13.61–13.71	theoretical	13.75 milliequiv/g
NO^+	0.06– 0.1	theoretical	0.00 milliequiv/g

Analyses for total acid by titrations with standard base, and for NO^+ by oxidation with standard ceric sulfate solution and back titration with standard ferrous ammonium sulfate gave:

Total acid	13.74 ±0.01 milliequiv/g
NO^+	0.06 ±0.01 milliequiv/g

The addition of silver nitrate to the acid solution gave a negative test for chloride ion.

From the ratio of total acid measured to total acid theoretical, the purity of the sample was estimated to be 99.93 mole percent or 99.65 weight percent. Since NO_2ClO_4 is extremely hygroscopic the major impurity is presumed to be water.

3. Units of Energy, Molecular Weights, and Conversion Factors

The joule was taken as the unit of energy. All instruments were calibrated in terms of standards maintained at the National Bureau of Standards. For conversion to the conventional thermochemical calorie, one calorie is taken as 4.1840 joules. All weights are corrected to vacuum.

All atomic weights were taken from the 1957 International Table of Atomic Weights [1].[1] The heat capacities were taken, where possible, from the literature [2]. For NO_2ClO_4, an estimated value of 36 cal/deg mole was used.

4. Apparatus and Procedure

The glass calorimeter, thermometric system, apparatus for measurement of electrical energy, and general calorimetric procedure have been described [3, 4, 5]. The calorimeter contained 454.6

[1] Figures in brackets indicate the literature references at the end of this paper

g of a 0.04126 *N* KOH solution. The sealed glass ampoule contained about 0.005 mole NO_2ClO_4. The calorimeter assembly was placed in a thermostatically controlled water-bath maintained at 25.0 ± 0.002 °C. After the run, the calorimeter solution was titrated with standard acid, using a Beckman *p*H meter, as a check on the mass of sample and completeness of reaction. No calculations were based on the titrated values of NO_2ClO_4, since the weighed mass of sample was more accurate.

The heat of solution of an equimolar mixture of crystalline KNO_3 and $KClO_4$ was measured in the same apparatus. The calorimeter contained 454.6 g of a 0.02077 *N* KOH solution. The sample size was adjusted to give the same final solution as in the NO_2ClO_4 hydrolysis experiment.

Two series of electrical energy calibrations were carried out, one with 454.6 g of 0.04126 *N* KOH solution and a bulb containing 0.005 mole NO_2ClO_4, the second with 454.6 g of 0.02077 *N* KOH solution and a bulb containing 0.005 moles each of KNO_3 and $KClO_4$.

5. Results and Calculations

The results of the calibration experiments on the calorimetric system used for the measurement of the heat of reaction of NO_2ClO_4 are given in table 1. ΔRc corresponds to the corrected temperature rise of the system [6]. The energy equivalent, Es, of the "standard" system was obtained as the ratio of the quantity of electrical energy, Ee, to ΔRc, the corresponding rise in temperature.

TABLE 1. *Electrical calibrations of the* NO_2ClO_4 *system*

Expt.	ΔRc	Ee	Es
	Ohm	*j*	*j/ohm*
1	0.094268	1,990.88	21,119.6
2	.097337	2,053.67	21,100.6
3	.096767	2,042.08	21,106.2
4	.096029	2,026.13	21,100.5
5	.095990	2,025.34	21,105.6
Mean			21,106.9
Standard deviation of the mean			±3.5

The results of the experiments on the hydrolysis and neutralization of NO_2ClO_4 in solution I are given in table 3. Here, Δe is the change in the energy equivalent from the "standard"-system, due to deviations in the mass of the glass bulb and sample from that of the reference bulb and sample. The term q(dil) represents the correction for the dilution of the individual final solutions to a uniform concentration. This was calculated from the data in [2], assuming that only the KOH(aq) contributed any heat effect. The total energy, q, is shown by the equation $q = \Delta Rc(Es + \Delta e) + q(\text{dil})$.

The results of the electrical calibration experiments on the $KNO_3/KClO_4$ system, and heat of solution experiments with the equimolar mixture of KNO_3 and $KClO_4$, are given in tables 2 and 4, respectively.

The term $q(KNO_3)$ in table 4 is the product of the difference between moles of $KClO_4$ and moles of KNO_3 and the heat of solution of KNO_3. It is applied to make the molar quantities of KNO_3 and $KClO_4$ exactly equal.

TABLE 2. *Electrical calibration on* $KNO_3/KClO_4$ *system*

Expt.	ΔRc	Ee	Es
	Ohm	*j*	*j/ohm*
1	0.092806	1962.35	21,144.1
2	.086047	1817.33	21,144.6
3	.095288	2013.70	21,137.2
4	.088441	1875.58	21,142.3
Mean			21,142.1
Standard deviation of the mean			±1.7

For the reaction

$$NO_2ClO_4(c) + [4KOH + 5300\ H_2O](soln) \rightarrow$$
$$[KNO_3 + KClO_4 + 2KOH + 5301\ H_2O](soln)$$
$$\Delta H = -199.02 \pm 0.35\ \text{kj}/145.465\ \text{g sample}$$
$$= -47.57 \pm 0.08\ \text{kcal}/145.465\ \text{g sample} \quad (1)$$

based upon mass of sample.

This value must be corrected for the presence of 0.35 weight percent moisture. If it is present as the hydrolysis products HNO_3 and $HClO_4$, it corresponds to 0.0283 mole of each acid.

TABLE 3. *Results of the experiments on the hydrolysis of* NO_2ClO_4

Expt.	Δe	ΔRc	q(dil)	q	Weighed NO_2ClO_4	Titrated NO_2ClO_4	$\frac{NO_2ClO_4(t)}{NO_2ClO_4(w)}$	$-\Delta H$ (25 °C)
	j	*Ohm*	*j*	*j*	*Mole*	*Mole*	%	*kj/mole*
1[a]	−13.6	0.023575	0.34	488.11	0.0024629	0.00238[b]	96.7	202.24
2	−10.1	.042890	.15	904.99	.0046384	.004646	100.2	199.50
3[a]	−10.2	.041598	.15	877.73	.0044600	.004434	99.4	196.58
4	−9.7	.049401	.00	1042.22	.0052450	.005253	100.2	198.71
5	−7.0	.063000	−.53	1329.78	.0066728	.006603	99.0	199.13
6	−7.7	.059705	−.36	1259.36	.0063211	.006246	98.9	199.23
7	−9.0	.046153	.04	973.73	.0049043	.004901	100.0	196.56
Mean								199.02
Standard deviation of the mean								±0.17

[a] Not included in mean value.
[b] Methyl orange end point.

TABLE 4. *Results of the experiments on the solution of* KNO_3 *and* $KClO_4$

Expt.	Δe	$-\Delta Rc$	KNO_3	$KClO_4$	$qKNO_3$	q	ΔH (25 °C)
	j	*Ohm*	*Mole*	*Mole*	*j*	*j*	*kj/mole*
1	−0.47	0.020238	0.0048958	0.0049238	−1.18	426.98	87.03
2	−1.43	.020453	.0049224	.0049990	−2.06	434.48	87.04
3	−1.64	.020401	.0049127	.0049985	−3.00	434.29	86.88
4	−1.32	.020485	.0048677	.0049943	−0.93	434.00	86.90
5	−1.36	.020450	.0049381	.0049863	−1.69	434.02	87.04
Mean							86.98
Standard deviation of the mean							±0.04

Therefore eq (1) actually corresponds to

$$0.9682\ NO_2ClO_4(c)+0.0283\ HNO_3(liq)+0.0283\ HClO_4(liq)+[4\ KOH+5300\ H_2O](soln)\longrightarrow [0.9965\ KNO_3+0.9965\ KClO_4+2.0070\ KOH+5301\ H_2O](soln)$$
$$\Delta H=-199.02\pm0.35\text{ kj}$$
$$=-47.57\pm0.08\text{ kcal.}$$

For 1 mole of NO_2ClO_4 this becomes

$$NO_2ClO_4(c)+0.0292\ HNO_3(liq)+0.0292\ HClO_4(liq)+1.0328\ [4\ KOH+5300\ H_2O]\longrightarrow [1.0292\ KNO_3+1.0292\ KClO_4+2.0728\ KOH+5475\ H_2O]+1.0584\ H_2O(liq)$$
$$\Delta H=-205.56\pm0.36\text{ kj/mole}$$
$$=-49.13\pm0.09\text{ kcal/mole.} \qquad (1a)$$

From data in the literature [2], eq (1b) may be evaluated:

$$HClO_4(liq)+HNO_3(liq)+[4\ KOH+5300\ H_2O]\longrightarrow [KClO_4+KNO_3+2\ KOH+5300\ H_2O]+2\ H_2O(liq)$$
$$\Delta H=-230.9\text{ kj/mole}$$
$$=-55.2\text{ kcal/mole.} \qquad (1b)$$

Appropriate combination of eqs (1a) and (1b) gives

$$NO_2ClO_4(c)+1.0036\ [4\ KOH+5300\ H_2O]\longrightarrow [KClO_4+KNO_3+2.0144\ KOH+5320\ H_2O]+H_2O(liq)$$
$$\Delta H=-198.82\text{ kj/mole}$$
$$=-47.52\text{ kcal/mole.} \qquad (2)$$

From table 4 we have

$$KNO_3(c)+KClO_4(c)+[2\ KOH+5300H_2O](soln)\longrightarrow [KNO_3+KClO_4+2\ KOH+5300\ H_2O](soln)$$
$$\Delta H=86.98\pm0.07\text{ kj/mole}$$
$$=20.79\pm0.02\text{ kcal/mole.} \qquad (3)$$

Combining eqs (2) and (3) and neglecting small dilution effects, we obtain:

$$NO_2ClO_4(c)+4\ KOH(\text{in }5300\ H_2O)\longrightarrow KClO_4(c)+KNO_3(c)+2\ KOH(\text{in }5300\ H_2O)+H_2O(liq)$$
$$\Delta H=-285.80\text{ kj/mole}$$
$$=-68.31\text{ kcal/mole.} \qquad (4)$$

If we take the following values for the heats of formation of the other substances in the reaction [7]

Substance	$\Delta Hf^\circ_{298.15}$ (kcal/mole)
$KClO_4(c)$	−103.45
$KNO_3(c)$	−118.12
$H_2O(liq)$	−68.314
$KOH(2650\ H_2O)$	−115.23

we compute for $NO_2ClO_4(c)$

$$\Delta Hf^\circ_{298.15}=37.19\pm1.0\text{ kj/mole}$$
$$=8.89\pm0.25\text{ kcal/mole.}$$

The uncertainty interval for the measured heats has been taken as twice the overall standard deviation of the mean based on the sum of the variances from the calibration and reaction experiments and reasonable variances assigned to the auxiliary data and the analysis for total acid.

6. Discussion

Cordes and Fetter [8] measured the heat of reaction of NO_2ClO_4 with water, they report a value for the heat of formation of $NO_2ClO_4(c)$ of 8.0 ±0.4 kcal/mole. Recalculating their data with the more recent auxiliary heats of formation used for this work, their value becomes 8.7 ±0.4 kcal/mole, in excellent agreement with the results obtained here.

7. References

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(Paper 66A6–179)