the central metal atom, it is not possible at this time to draw any quantitative conclusions from the trends observed.

Acknowledgment.—The authors wish to thank Professor M. A. El-Sayed of this Department for valuable discussions concerning the interpretation of spectra presented here, the Ethyl Corporation for a gift of manganese carbonyl, and Miss Heather King, Microanalytical Laboratories (this Department) for her assistance in the analyses of noncondensable gases.

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The Heat of Formation of Crystalline Sodium α-Oxyhyponitrite. The Structure of Aqueous α-Oxyhyponitrite Ion[1]

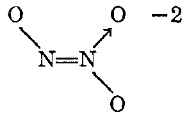
BY HAROLD R. HUNT, JR., JAMES R. COX, JR., AND JAMES D. RAY

Received January 29, 1962

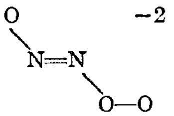
The heat of decomposition of sodium α-oxyhyponitrite (Angeli's salt, α-$Na_2N_2O_3$, sodium N-nitrohydroxylamate) in 0.996 *m* aqueous sulfuric acid to form sodium sulfate solution and nitric oxide gas was found to be -8.42 ± 0.40 kcal./mole. The calculated heat for the reaction: $\alpha\text{-}Na_2N_2O_3(aq) = Na_2N_2O_2(aq) + {}^1/_2\, O_2$, $\Delta H = +20{,}000$ cal., is shown to be compatible with assignment of the structure $Na_2ONN^{O}_{O}$ and not Na_2ONNOO.

Introduction

The two forms of $Na_2N_2O_3$ which have been isolated to date are designated by Addison, Gamlen, and Thompson[2] as sodium α-oxyhyponitrite (Angeli's salt) and sodium β-oxyhyponitrite with the assigned structures


I

Angeli's salt, sodium α-oxyhyponitrite


II

sodium β-oxyhyponitrite

The original structural assignment was based on spectrophotometric evidence and analyses of hydrolysis products. The present study gives thermochemical evidence that the assignment of structure I as the α isomer is correct.

Experimental

Materials.—Sodium α-oxyhyponitrite was prepared by a modification of Angeli's[3] method, eq. 1. The data in Table I show that Angeli's maximum yield of 50% can be greatly surpassed by carrying out the reaction at low temperature with a large mole ratio of hydroxylamine to butyl nitrate. In the best synthetic experiment 0.16 mole of butyl nitrate was added to a solution of 2.0 moles of free hydroxylamine in 1 l. of anhydrous methanol. The solution was kept at 0° during the addition of 0.32 mole of methanolic sodium methoxide in small portions over a 48-hr. period. At the end of this time the solution was heated to boiling for a few minutes to effect conversion of the last approximately 10% of the reagents; yield, 17.88 g. of anhydrous sodium α-oxyhyponitrite, 99.8% of theory, based on butyl nitrate. The material was recrystallized by dissolving 23 g. in 58 ml. of water at 0° and precipitating with 1 l. of anhydrous methanol to recover 19.4 g. Analysis was effected by potentiometric titration at 0° under nitrogen using standard hydrochloric acid. To convert 5.00 mequiv. $Na_2N_2O_3$ to $NaHN_2O_3$ required 4.99 ± 0.02 mequiv. of the hydrochloric acid. Further verifica-

$$C_4HO_9NO_2 + H_2NOH + 2NaOCH_3 = Na_2(ONNO_2) + C_4H_9OH + 2CH_3OH \quad (1)$$

TABLE I

EFFECT OF TEMPERATURE AND MOLE RATIO OF REACTANTS ON YIELD OF SODIUM α-OXYHYPONITRITE FROM BUTYL NITRATE

Mole ratio $NH_2OH/C_4H_9ONO_2$	Temp., °C.	% Yield $Na_2N_2O_4$
3.6	65	63.0
0.74	25	48.5
1.00	25	55.0
1.35	25	61.5
3.15	25	71.3
5.2	25	83.0
10	25	82.0
12	25	83.0
2.75	0	85.0
12.5	0	99.8

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[1] Presented at the 140th National Meeting of the American Chemical Society, Chicago, Illinois, Sept. 3–8, 1961.

[2] C. C. Addison, G. A. Gamlen, and R. Thompson, *J. Chem. Soc.*, 338 (1952).

[3] A. Angeli, *Ahrens Samm. Chem. Tech, Vortrage*, **13**, 2 (1908).

tion of the purity of the salt by analysis of the products of the calorimeter reaction is described below under Measurements and Results. All sodium α-oxyhyponitrite samples were stored under nitrogen or vacuum, since the material was observed to react slowly with atmospheric oxygen.

Apparatus.—The calorimeter used in this study was fashioned from a 700-ml. Pyrex dewar flask to the top of which an epoxy flange was fastened by means of epoxy resin. The top lip of the dewar was roughened with fine emery paper before the resin seal was made. An epoxy closure disk then was fastened to the flange by means of twelve equally spaced bolts and nuts. A Teflon gasket, lightly coated with silicone grease, was used between the flange and the closure disk to make the seal gas tight. A hole in the top disk accommodated a water-jacketed Trubore stirrer, which when lubricated served as an adequate gas seal. The bearing of the stirrer was kept at constant temperature by circulating water directly from the surrounding thermostat through the jacket. Additional holes were made in the top to accommodate the gas inlet and outlet tubes, the Beckmann thermometer, and the spiral heat of water vaporization calibration device. Standard taper joints for mounting the stirrer and calibration device were cemented in place with epoxy resin. The inlet and outlet tubes and Beckmann thermometer were permanently cemented in place. A polyethylene baffle at the gas outlet and a glass check valve on the inlet prevented liquid loss during the reaction.

The sample to be introduced into the calorimeter was contained in a small thin walled ampoule at the bottom of the stirrer. The top of the stirrer was connected through a belt drive to a synchronous motor. The pulley at the top of the stirrer was held above its bearing by a spring, and thus could be pushed down in order to shatter the sample bulb.

Measurements and Results

The calorimeter was used to measure ΔH for the general process

$$\alpha\text{-}Na_2N_2O_3(c) + H_2SO_4(\text{soln.}) \longrightarrow 2NO(g) + Na_2SO_4(\text{soln.}) + H_2O(\text{soln.})$$

For calorimetric purposes a more precise description of solution concentrations and conditions must be specified. The detailed processes studied in the calorimeter were

$$\alpha\text{-}Na_2N_2O_3(c) + 128.4H_2SO_4(\text{soln.}) + 7140H_2O(\text{soln.}) = 2NO(g) + Na_2SO_4(\text{soln.}) + 127.4H_2SO_4(\text{soln.}) + 7141H_2O(\text{soln.});\quad \Delta H = -8423 \pm 400 \text{ cal.}$$

and

$$Na_2SO_4(\text{in soln. of } 127.4H_2SO_4 + 7141H_2O) = Na_2SO_4(c);\quad \Delta H = -3545 \pm 112 \text{ cal.}$$

The calorimetric data for these reactions are listed in Table II.

These data were combined with data of Giauque, Hornung, Kunzler, and Rubin[4] for the heat of dilution of aqueous sulfuric acid

$$7141H_2O(\text{soln.}) + 127.4H_2SO_4(\text{soln.}) = H_2O(l) + 7140H_2O(\text{soln.}) + 127.4H_2SO_4(\text{soln.});\quad \Delta H = 5 \text{ cal.}$$

and

$$127.4H_2SO_4(\text{soln.}) + 7140H_2O(\text{soln.}) + H_2SO_4(l) = 128.4H_2SO_4(\text{soln.}) + 7140H_2O(\text{soln.});\quad \Delta H = -17{,}141 \text{ cal.}$$

to obtain ΔH for the process

$$\alpha\text{-}Na_2N_2O_3(c) + H_2SO_4(l) = 2NO(g) + Na_2SO_4(c) + H_2O(l);\quad \Delta H = -29{,}090 \pm 500 \text{ cal.}$$

From this value and the standard heats of formation of H_2SO_4 (−193,910), NO (+21,600), Na_2SO_4 (−330,900), and H_2O (−68,320),[5] the standard heat of formation of α-$Na_2N_2O_3$ at 25° is −133,000 ± 500 cal./mole (exothermic). Combining this with the measured heat of solution of α-$Na_2N_2O_3$ (−3,610) gives −136,600 ± 500 cal./mole as the heat of formation of α-$Na_2N_2O_3$ as a 0.186 *M* solution in 0.1 *M* aqueous sodium hydroxide.

In a typical calorimetric measurement of the reaction of α-$Na_2N_2O_3$ with H_2SO_4 the following procedure was used.

A 500-ml. sample of H_2SO_4 solution was placed in the calorimeter and a weighed quantity of pure α-$Na_2N_2O_3$ in a sealed nitrogen-filled bulb was fastened to the bottom of the stirrer. In order to prevent secondary oxidation of the NO produced it was necessary to achieve rigorous exclusion of oxygen from the system. The calorimeter was flushed for 15 min. before use and during the run by a slow (80 ml. per min.) stream of prepurified nitrogen which was broken into small bubbles by the action of the stirring paddle. Since the evolution of nitric oxide was frequently rather rapid, a polyethylene baffle system was interposed between the top of the aqueous phase and the gas outlet tube in order to prevent liquid loss.

That this reaction proceeds quantitatively to produce NO was shown by Cambi[6] and confirmed as follows in the present study. Quantities of α-$Na_2N_2O_3$ and H_2SO_4 solution identical with those used in the calorimeter reacted in a vacuum system and the gaseous product was passed through a Dry Ice-cooled trap and then into a 10-cm. infrared gas cell at approximately 0.5

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[4] W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, *J. Am. Chem. Soc.*, **82**, 62 (1960).

[5] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," Circular 500, U. S. Bur. Standards, Govt. Printing Office, Washington, D. C.

[6] L. Cambi, *Ber.*, **69**, 2027 (1936).

TABLE II

SUMMARY OF CALORIMETRIC DATA OBTAINED IN THIS STUDY

Sample	Age and treatment	Weight, g.	Calorimeter temp. change, °C.	Calorimeter C_p, cal./deg.	Heat of reaction, cal./mole	Av. cal./mole and std. dev.
$Na_2N_2O_3$(c)	Freshly pptd.	0.4577	0.0717[a]	567	−10,800	
$Na_2N_2O_3$(c)	Freshly pptd.	.4499	.0699	567	−10,800	
$Na_2N_2O_3$(c)	2-day old	.4555	.0703	567	−10,700	
$Na_2N_2O_3$(c)	1-week old	.4571	.0665	567	−10,100	
$Na_2N_2O_3$(c)	1-week old	.4470	.0624	567	− 9,670	
$Na_2N_2O_3$(c)	2-week old	.4570	.0631	567	− 9,540	
$Na_2N_2O_3$(c)	Freshly pptd., heated at 120° under vacuum	.4372	.0558	567	− 8,830	
$Na_2N_2O_3$(c)		.4406	.0504	567	− 7,920	
$Na_2N_2O_3$(c)		.4401	.0551	567	− 8,640	
$Na_2N_2O_3$(c)		.4401	.0528	567	− 8,300	−8420 ± 400 (last 4 runs) −9530 ± 1070 (all runs)
Na_2SO_4(c)		.4966	− .0217	567	+ 3,520	
Na_2SO_4(c)		.4411	− .0196	567	+ 3,550	
Na_2SO_4(c)		.5508	− .0253[b]	567	+ 3,690	+3,550 ± 112
Na_2SO_4(c)		.5222	− .0222[b]	567	+ 3,420	
$Na_2N_2O_3$(c)		1.1749	.0603[c]	577	− 3,610	

Calorimeter solution was 0.996 molal H_2SO_4 unless otherwise indicated. [a] Temperature changes for the oxyhyponitrite runs are corrected for the heat of vaporization of the H_2O carried out with the NO. [b] Calorimeter solution was 0.992 *m* H_2SO_4. [c] Calorimeter solution was 0.1 *N* NaOH.

atm. pressure. The absorbance at 2349.3 and at 2223.5 cm.$^{-1}$ showed the presence of not more than 0.25% carbon dioxide and 0.2% nitrous oxide, respectively, in the nitric oxide product. A second sample of the NO was collected in a 197-ml. gas buret at 400 mm. pressure and oxidized with alkaline H_2O_2 solution. Less than 0.5 ml. of gas at 1 atm. remained after the reaction, indicating the presence of less than 0.5% N_2.

All measurements were made so that heats of reaction corresponded to the standard temperature, 25°. Calibration was based on the defined thermochemical calorie equal to 4.184 absolute joules. The calibration method based on the heat of water vaporization is described by Ray.[7] In all calibration and heat of reaction runs correction was made for heat loss to the surroundings between the fore and after rating periods as described by White.[8] Table III gives the energy equivalents of the calorimeter containing 500 ml. of 0.996 *m* H_2SO_4 solution or 500 ml. of 0.1 *M* NaOH solution. The value 567 ± 2.65 was used for calculating heats of solution and reaction in sulfuric acid solutions. Four small water sample vaporization heats were measured to establish the calorimetric precision corresponding to temperature changes similar to those observed for oxyhyponitrite decomposition in sulfuric acid solution. The precision of these four determinations was ±1.57%.

TABLE III

CALIBRATION OF CALORIMETER BY HEAT OF WATER VAPORIZATION METHOD[7]

Calorimeter liquid	Wt. water vaporized, g.	Energy equiv., cal./deg.	Av. energy equiv., cal./deg.
H_2SO_4, 0.996 *m*	0.4267	570	
	.9945	566	
	1.0965	565	567 ± 2.65
H_2SO_4, 0.996 *m*	0.0936	558	
	.0884	568	
	.1059	547	
	.1078	567	559 ± 8.8
NaOH, 0.1 *M*	1.0066	577	
	0.0972	575	
	.1051	579	577 ± 1.6

As established above, the large standard deviation of the oxyhyponitrite runs, ±11.2%, cannot be due solely to poor precision associated with the small temperature changes observed. A possible explanation is in variation of the crystal structure or particle size as a function of sample age or treatment. The heat of reaction showed a regular decrease with sample age, and was the smallest for the four samples which had been heated for 1 hr. at 120°. Addison, Gamlen, and Thompson[2] have shown that α-$Na_2N_2O_3$ can be heated at this temperature without decomposition. The average of these

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(7) J. D. Ray, *Rev. Sci. Instr.*, **27**, 863 (1956).

(8) W. B. White, "The Modern Calorimeter," The Chemical Catalog Company, Inc., New York, N. Y., 1928, p. 25.

four runs, -8420 ± 400 cal./mole, has been taken to represent the heat of reaction of α-$Na_2N_2O_3$ in its standard macrocrystalline state.

Discussion

From the measured value of the heat of formation of α-$Na_2N_2O_3$ in 0.1 *m* NaOH solution and the standard heats of formation of sodium ion (−57,279) and $N_2O_2^{-2}$ (−2,590) in dilute aqueous solution given by Rossini, Wagman, Evans, Levine, and Jaffe,[5] ΔH has been calculated for the process

$$\alpha\text{-}Na_2N_2O_3(aq) = Na_2N_2O_2(aq) + {}^1/_2O_2(g); \quad \Delta H = +20{,}000 \text{ cal.}$$

The heat associated with removal of 1/2 O_2 from $NaON^{O}_{O}(aq)$ to form $NaNO_2(aq)$ is calculated from the heat of this reaction for crystalline $NaNO_3$ and $NaNO_2$ [(+24,900)[9]], and the standards heats of solution of $NaNO_3(c)$ (+4,889)[5] and $NaNO_2(c)$ (+3,320)[10]

$$NaON^{O}_{O}(aq) = NaNO_2(aq) + {}^1/_2O_2; \quad \Delta H = +23{,}331 \text{ cal.}$$

Since the heat of rearrangement of NaONOO(aq) to $NaONO_2(aq)$ is −34,000 cal.,[11] it follows that

$$NaONOO(aq) = NaNO_2(aq) + {}^1/_2O_2; \quad \Delta H = -10{,}969 \text{ cal.}$$

By analogy, removal of 1/2 O_2 from an $Na_2ON N^{O}_{O}$ structure would give a ΔH of approximately +23,000, and removal of 1/2 O_2 from Na_2ONNO–O should give ΔH of −11,000. Since the actual value is +20,000, the $Na_2ONN^{O}_{O}$ structure is suggested.

Acknowledgments.—This research was supported in part by a grant from the Research Corporation and in part by a grant (NSF-G15560) from the National Science Foundation.

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[9] J. D. Ray, Abstracts of Papers, 16th Annual Calorimetry Conference, Ottawa, Aug. 14–17, 1961.

[10] C.-H. Wu and L. G. Hepler, *J. Chem. Eng. Data*, in press.

[11] J. D. Ray, "Kinetics and Heat of Isomerization of Peroxynitrite to Nitrate," Abstracts of Papers, Southeastern Regional Meeting, American Chemical Society, Birmingham, Ala., Nov. 3–5, 1960.

Notes

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An X-Ray Diffraction Study of Aqueous Zinc Chloride Solutions[1]

BY R. F. KRUH AND C. L. STANDLEY

Received December 8, 1961

The solubility of zinc chloride in water is so great that the mole ratio of water to zinc chloride can easily be made smaller than 2:1 even at room temperature. At such high concentration it becomes a semantic question as to whether the system is called a solution or a molten salt, and unusual physical properties suggest interesting structural features whose nature might be deduced from diffraction data.

High viscosity, low electrical conductivity, and behavior in extraction experiments all suggest polymerization in concentrated solution. The great increase in viscosity[2] with increasing concentration cannot be accounted for in terms of simple species, and extraction into 2-octanol[3] shows less than one water molecule per zinc ion. One therefore suspects, if he assumes at least four-coördination for zinc, the existence of some polynuclear species in which chlorines are shared. Indeed, four-coördination of zinc by chlorine occurs in crystalline zinc chloride[4] and in solutions containing zinc chloride together with an added chloride,[5–7] but it remains to test the assumption in the system $ZnCl_2$–H_2O and to establish the identity of the ligands.

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[1] The support of the U. S. Atomic Energy Commission is gratefully acknowledged.

[2] L. R. Dawson, H. K. Zimmerman, W. E. Sweeney, and G. P. Dinaga, *J. Am. Chem. Soc.*, **73**, 4326 (1951); L. R. Dawson, A. Tockman, H. K. Zimmerman, and G. R. Leader, *ibid.*, **73**, 4327 (1951).

[3] P. C. Yates, R. Laran, R. E. Williams, and T. E. Moore, *ibid.*, **75**, 2212 (1953).

[4] B. Brehler, *Naturwissenschaften*, **46**, 106, 554 (1959); *Fortschr. Mineral.*, **38**, 198 (1960); H. R. Oswald and H. Jaggi, *Helv. Chim. Acta*, **43**, 72 (1960).

[5] M. Bredig and E. R. van Artsdalen, *J. Chem. Phys.*, **24**, 478 (1956).

[6] B. M. McCarroll and T. F. Young, Technical Report No. 5 ONR Contract N6 ori 02045, January 1, 1959.

[7] M. Delwaulle, *Bull. soc. chim. France*, **22**, 1294 (1955).