Notes

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Ammonium Perbromate

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Received May 16, 1969

Perbromic acid and alkali metal perbromates have recently been isolated and characterized.[1,2] The perbromates are chemically similar to the perchlorates, although somewhat less stable. An interesting difference is that the order of stability of the alkali metal salts is $MBrO_3 > MBrO_4$, while the reverse is true of the chlorine compounds, $MClO_3 < MClO_4$.

Ammonium chlorate (NH_4ClO_3) also is less stable than its perchlorate.[3] However, since the mechanism of decomposition is much more complex in this case, it is not possible to predict the stability of ammonium perbromate (NH_4BrO_4) from that of the bromate, which explodes on heating.[4] It was of considerable interest to us, therefore, to determine whether ammonium perbromate is sufficiently stable to isolate and to compare its physical and chemical properties with those of the perchlorate, especially its stability and mode of decomposition.

Experimental Section

Synthesis.—A sample of 3 *M* perbromic acid was generously supplied by E. Appelman, Argonne National Laboratory. Its synthesis and analysis have been described.[2] This solution was chilled and carefully neutralized with excess concentrated aqueous ammonia. The solution was evaporated at room temperature, and the solid was dried over P_2O_5 in a vacuum desiccator. Before use, the product was recrystallized from water. NH_4BrO_4 is neither shock nor friction sensitive.

Analysis.—The salt was analyzed for NH_4^+ by the hypobromite method[5] and for BrO_4^- by the method described by Appelman.[2] *Anal.* Calcd for NH_4BrO_4: NH_4^+, 11.5; BrO_4^-, 88.5. Found: NH_4^+, 11.1; BrO_4^-, 85.2.

Titration of a separate sample in 0.01 *M* acid and 0.1 *M* acid with molybdate gave values for the hypobromite and bromate contents of 1.0 and 0.6%, respectively. These are upper limits only, of course, because of the slow reduction of perbromate under these conditions. No precipitate was observed when 1 *M* $AgNO_3$ was added to a solution of NH_4BrO_4. The bromide content is believed to be less than 0.1%.

Infrared Spectrum.—The infrared spectrum of ammonium perbromate was examined by means of a Perkin-Elmer Model 621 grating infrared spectrophotometer. The sample was mulled with Nujol and supported between KBr disks. Strong bands were observed at 870 and 405 cm^{-1}, with a tiny, sharp peak at 795 cm^{-1} (on the edge of the former broad band). Appelman[2] reported ν_1, 798 cm^{-1}; ν_3, 883 cm^{-1}; ν_4, 410 cm^{-1}. No bands attributable to BrO_3^- were observed near 800 or 420 cm^{-1}.

Solubility.—The solubilities of NH_4BrO_4 in water and in several organic solvents were determined by weighing 1-ml aliquots of the saturated solutions.

Decomposition.—Preliminary decomposition experiments were performed with very small samples in melting point capillaries. Thermograms were obtained using a Fisher differential thermalyzer, Model 260, with a heating rate of 5°/min. Each 25-mg sample was diluted with 75 mg of Al_2O_3.

X-Ray Diffraction.—Powder patterns were obtained by the Geiger counter-goniometer method, using a Philips Norelco instrument. Copper Kα radiation (nickel filter) was employed. Samples were ground to <325 mesh and sifted into $^1/_{16}$ in. deep rectangular aluminum cells. The spectrum was scanned from $2\theta = 50$ to 5° at 1°/min.

Results

Ammonium perbromate is stable at room temperature and has solubilities similar to the perchlorate (Table I). Heats of solution in water calculated from the data in Table I are 4.4 kcal/mol for NH_4BrO_4 and 3.9 kcal/mol for NH_4ClO_4.

TABLE I

SOLUBILITY OF NH_4BrO_4 AND NH_4ClO_4

Solvent	Temp, °C	Solubility[a] NH_4BrO_4	Solubility[a] NH_4ClO_4[b]
Water	0.0	9.5	10.74
Water	15.0	13.9	...
Water	25.0	17.8	20.02
Water	45.0	26.3	28.02
Methanol	25.0	8.22	6.862
Ethanol	25.0	2.94	1.907
Acetone	25.0	3.22	2.26
Acetonitrile	25.0	1.36	...

[a] Solubility in H_2O in grams per 100 g of solution. Solubility in organic solvents in grams per 100 g of solvent. [b] Data for NH_4ClO_4 from J. C. Schumacher, "Perchlorates," Reinhold Publishing Corp., New York, N. Y., 1960.

NH_4BrO_4 is much less hygroscopic than NH_4ClO_4, although in humid atmospheres the perbromate does tend to "cake" slightly. Thus at 95% humidity, a 500-mg sample of NH_4BrO_4 gained 20 mg (4%) in the first 4 days, after which its weight remained approximately constant. A similar NH_4ClO_4 sample, however, gained a total of 115 mg (23%) in 4 weeks and was visibly wet.

NH_4BrO_4 begins to decompose around 170–180°, smoothly in most cases, although explosions sometimes occur. In one case, observed visually, dense brown fumes (Br_2) appeared at 176°, and the clear crystals became opaque. The decomposition seemed to subside until the sample gradually disappeared at 295° without melting or subliming.

NH_4BrO_4 exhibited two exotherms, a sharp one at 186° and a broad one beginning at 209°, with a small inflection at 228°. On one occasion, a 75-mg sample exploded upon reaching the 186° exotherm. For comparison, thermograms of NH_4ClO_4 were obtained under identical conditions. NH_4ClO_4 exhibited an endotherm at 239° (orthorhombic–cubic transition)

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(1) E. H. Appelman, *J. Am. Chem. Soc.*, **90**, 1900 (1968).

(2) E. H. Appelman, *Inorg. Chem.*, **8**, 223 (1969).

(3) F. Fairbrother, *J. Am. Chem. Soc.*, **44**, 2419 (1922).

(4) P. J. M. Radford in "Bromine and Its Compounds," Z. E. Jolles, Ed., Academic Press, New York, N. Y., 1966, p 165.

(5) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1948, Chapter XL.

and two exotherms, a small one at 344° and a large one at 356°.

Although a substantial temperature difference exists between the two NH_4BrO_4 exotherms and no activity was observed in the sample after the first step in the decomposition, slow decomposition continues at the lower temperature when the sample is heated in a sealed tube, probably due to catalysis by the decomposition products. Thus a 70.4-mg sample, heated overnight at 170°, decomposed only partly but decomposed completely when heated at 260°. Another sample (1.80 mmol) decomposed completely in 3 days at 170°, leaving no solid residue. The major products were N_2 (0.58 mmol), O_2 (1.09 mmol), Br_2 (0.9 mmol), and H_2O (not measured), with small amounts of N_2O (0.1 mmol) and NO_2 (estimated 0.2 mmol). Thus the decomposition of NH_4BrO_4 more closely resembles that of NH_4BrO_3 (N_2, Br_2, O_2, H_2O) than that of NH_4ClO_4 (little N_2, nitrogen oxides major products).

However, firm conclusions about the stability or modes of decomposition of these salts must await the synthesis and purification of larger samples of both NH_4BrO_4 and NH_4BrO_3.

The powder diffraction spacings, presented in Table II, are correlated on the basis of an orthorhombic unit cell, with $a = 9.20$ Å, $b = 6.04$ Å, and $c = 7.63$ Å; the density, based on four molecules in the unit cell, is 2.54 g/cm^3 (by flotation, 2.5 g/cm^3). $KBrO_4$ is also orthorhombic,[6] as are NH_4ClO_4 and several metal perchlorates.

TABLE II
X-RAY POWDER DATA FOR NH_4BrO_4

d, Å			
Obsd	Calcd	Intens	*hkl*
5.85	5.87	50	101
5.24	...	4	...[a]
4.77	4.74	100	011
4.60	4.60	41	200
4.21	4.21	8	111
3.94	3.92	72	201
3.810	3.815	55	002
3.660	3.659	90	210
3.517	3.524	25	102
3.302	3.298	70	211
3.038	3.044	82	112
2.938	2.936	32	202
2.685	2.686	32	121
2.642	2.641	43	212
2.450	2.451	9	103
2.398	2.397	6	221
2.295	2.300	24	400
	2.293		122
2.209	2.222	37	401
	2.202		312
2.159	...	7	...[a]
2.106	2.105	5	222
2.088	2.088	3	213
1.905	1.905	28	004
	1.903		123
1.877	1.873	15	412
1.865	1.862	12	313

[a] Denotes impurity.

Acknowledgment.—Financial support for this research was provided by the Office of Naval Research, under Contract No. N00014-68-C-0279 with Dr. Richard L. Hanson as Scientific Officer. The authors wish to express their gratitude to Dr. Evan Appelman, Argonne National Laboratory, for providing them with a sample of perbromic acid, prepared in his laboratory, and for making available his data on perbromates in advance of publication.

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[6] S. Siegel, B. Tani, and E. Appelman, to be published.

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Icosahedral Carboranes. XIV. Preparation of Boron-Substituted Carboranes by Boron-Insertion Reaction[1,2]

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Received May 23, 1969

The syntheses of derivatives of *o*-carborane which bear aliphatic,[3-6] aromatic,[4] amino,[7] diethylamino,[6] hydroxy,[8] and ethoxy[6] substituents on the boron atom have been reported. A mixture of 8- and 9-ethyl-*o*-carboranes[3] was obtained from the reaction of 1- and 2-ethyldecaborane(14) with acetylene. The novel boron insertion reaction of Hawthorne, *et al.*,[4] afforded 3-ethyl-,[4] 3-phenyl-,[4] 3-diethylamino-,[6] and 3-ethoxy-*o*-carboranes.[6] The 3-aminocarborane[7] was produced by reduction of *o*- or *m*-carborane with sodium metal in liquid ammonia, followed by oxidation of the intermediate with potassium permanganate. This compound underwent Sandmeyer reaction to yield 3-halo-*o*-carborane.[9] The 9-hydroxy-*o*-carborane[8] was prepared from *o*-carborane by nitration with nitric acid and subsequent hydrolysis of the intermediate.

This paper describes an application of the Hawthorne

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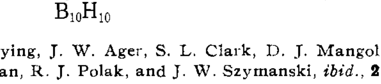
[1] Preceding communication: J. F. Sieckhaus, N. S. Semenuk, T. A. Knowles, and H. Schroeder, *Inorg. Chem.*, **8**, 2452 (1969).

[2] Nomenclature of the *closo* boron–carbon hydrides was discussed by R. Adams, *ibid.*, **2**, 1087 (1963), and appropriate rules approved by the Council of the American Chemical Society are presented in *ibid.*, **7**, 1945 (1968). The terms *o*-, *m*-, and *p*-carborane are used to designate 1,2-, 1,7-, and 1,12-dicarbo-*closo*-dodecaborane. In accord with current practice, the following symbols are employed for representation of these isomers



[3] T. L. Heying, J. W. Ager, S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *ibid.*, **2**, 1089 (1963).

[4] M. F. Hawthorne and P. A. Wegner, *J. Am. Chem. Soc.*, **87**, 4392 (1965); **90**, 896 (1968).

[5] B. M. Mikhailov and T. V. Potapova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1629 (1967); *Chem. Abstr.*, **68**, 39680 (1968).

[6] T. V. Potapova and B. M. Mikhailov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2367 (1967); *Chem. Abstr.*, **68**, 49671 (1968).

[7] L. I. Zakharkin and V. N. Kalinin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2585 (1967).

[8] L. I. Zakharkin, V. N. Kalinin, and L. S. Podvisotskaya, *ibid.*, 1713 (1965); *Chem. Abstr.*, **63**, 18135 (1965).

[9] (a) L. I. Zakharkin, V. N. Kalinin, B. A. Kvasov, and E. I. Fedin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2415 (1968); (b) L. I. Zakharkin and V. N. Kalinin, *ibid.*, 685 (1968).