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Preparation, Characterization and Physical and Chemical Properties of Tetramethylammonium Ozonide[1]

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The new compound, tetramethylammonium ozonide, has been prepared and characterized. Electron paramagnetic resonance measurements showed that the compound is a free radical with one unpaired electron. Its visible spectrum is very similar to those of the alkali metal ozonides which have wave length maximums near 450 mμ. The solubility of tetramethylammonium ozonide at −63° is 1.3 ± 0.1 g. per 100 g. of liquid ammonia. The heat of formation of the pure material was found to be 49.5 ± 4.2 kcal. per mole.

The ozonides of cesium,[3,4] rubidium,[4] potassium[3,5,6] and sodium[3,5,7] have been known for some time. These ozonides are prepared by the reaction of the respective hydroxide with gaseous ozone. Since its chemical and physical properties resemble those of the alkali metal hydroxides, tetramethylammonium hydroxide was also treated with gaseous ozone, and it was found that tetramethylammonium ozonide can be formed in this manner. When Traube and Kuhbier[8] used this procedure, they obtained a red solid. However, this solid was not fully characterized, and it was tentatively identified as $(CH_3NOH)_2O_2$.

Results and Discussions

It has been established[9] that the ozonides can be identified by their visible spectra. Tetramethylammonium ozonide was identified in this manner, and its spectrum is shown in Fig. 1 along with the spectra of a number of other ozonides. The absorption peaks of these spectra are given in Table I, where it can be seen that all of the ozonides have essentially the same spectra with a λ_{max} near 450 mμ and a fine structure of about five additional peaks.

TABLE I

SPECTRA OF OZONIDES IN LIQUID AMMONIA

Compound	Wave length, mμ					
$(CH_3)_4NO_3$		489	468	451_{max}	437	422
NaO_3	502	484	467	449_{max}	434	421
KO_3	503	485	466	449_{max}	433	418
RbO_3	502	484	468	450_{max}	436	
CsO_3	500	483	467	449_{max}	437	

Three solvents found to dissolve the alkali metal ozonides are liquid ammonia, methyl amine and dimethylformamide. However, only liquid ammonia and dimethylformamide were found to dissolve the tetramethylammonium ozonide. The spectra of the five ozonides listed in Table I were also run with dimethylformamide as the solvent. The results are very similar, the only difference being that the λ_{max} is shifted to approximately 460 mμ. It was found that ammonia is a much better solvent for the ozonides than is dimethylformamide. Another disadvantage of using dimethylformamide is that it slowly reacts with the ozonides.

Since the ozonide ion contains an unpaired electron, the ozonides were expected to be paramagnetic, a property useful for further characterization purposes. Its electron paramagnetic spectrum shows that tetramethylammonium ozonide is a free radical having a g value of 2.012 and a width between inflection points of 55 oersteds. Thus, these data help to substantiate the structure of this new compound. The details of the electron paramagnetic work will be published elsewhere.

In the preparation of the heavier alkali metal ozonides, the respective hydroxide is treated with gaseous ozone, and the product is isolated by extraction with liquid ammonia. Essentially this procedure was followed in the preparation of tetramethylammonium ozonide. However, it was found that the starting material, tetramethylammonium hydroxide, must be dry if a pure product is to be obtained. When this procedure was used, it was not uncommon for the reaction to proceed smoothly for 5–10 minutes; but then a dark red spot would appear and the sample would ignite. Thus, it is necessary to carry out the ozonization slowly and with constant agitation of the reaction mixture.

The solubility of tetramethylammonium ozonide in ammonia at −63° was found to be 1.3 ± 0.1 g. per 100 g. of ammonia. For comparison, the solubility of potassium ozonide in ammonia was also determined. Conventional means could not be used to determine the solubility of potassium ozonide because the intense color of the solution obscured the presence or absence of a solid phase. The solubility was found from observations of the vapor pressure of potassium ozonide solutions. When the solution is saturated, a constant vapor pressure is observed. The results of the experiment are given in Table II. As can be seen, the vapor pressure becomes constant at about 12%, and therefore it is assumed that this is the value for the solubility of potassium ozonide in ammonia at − 63°. As a check on this method of determining solubilities, the solubilities of

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[2] Richardson Company, 2728 West Lake Street, Melrose Park, Illinois.

[3] T. P. Whaley and J. Kleinberg, THIS JOURNAL, **73**, 79 (1951).

[4] G. P. Nikolskii, Z. A. Bagdassaryan and I. A. Kazarnovskii, *Doklady Akad. Nauk S.S.S.R.*, **77**, 69 (1951).

[5] Wurtz, "Dictionnaire de Chimie pure et appliquee," Vol. II, 1868, p. 721.

[6] I. A. Kazarnovskii, G. P. Nikolskii and T. A. Abletsova, *Doklady Akad. Nauk S.S.S.R.*, **64**, 69 (1949).

[7] A. D. McLachlan, M. C. R. Symons and M. G. Townsend, *J. Chem. Soc.*, 952 (1959).

[8] W. Traube and F. Kuhbier, *Ber.*, **62B**, 809 (1929).

[9] I. J. Solomon and A. J. Kacmarek, *J. Phys. Chem.*, **64**, 168 (1960).

lithium chloride and potassium nitrate in ammonia were determined. In each case the values found agreed within 2% of those found by conventional means.

TABLE II

VAPOR PRESSURES OF LIQUID AMMONIA SOLUTIONS OF POTASSIUM OZONIDE AT −63°

Conc., g. KO_3/100 g. NH_3	Vapor pressure, mm.[a]
6.0	123.8
9.1	122.9
12.0	122.4
15.0	122.3
26.0	122.3
39.0	122.3

[a] Vapor pressure of pure NH_3 at −63° is 125.8 mm.

The heat of formation of tetramethylammonium ozonide was determined by means of the reaction shown in eq. 1, since a similar method had previously been used for the determination of the heat

$$(CH_3)_4NO_3 + HCl_{aq} \xrightarrow{\Delta H_R} (CH_3)_4NCl + 1/2\,H_2O + 5/4\,O_2 \quad (1)$$

of formation of potassium ozonide.[4] Although a difficulty existed in that the heat of formation of tetramethylammonium chloride was not known, the required value was estimated in the following manner.

Smith and Calvert[10] studied the vapor pressure of the system shown in eq. 2, for which the heat of reaction at 233° (v.p. = 1 atm.) can be calculated.

$$(CH_3)_4NCl \rightleftarrows CH_3Cl + (CH_3)_3N \quad (2)$$

However, this value must be converted to 25° to be of use. It is a simple matter to set up a cycle to determine the heat of formation of tetramethylammonium chloride at 25°, but not all of the needed data were known. The only value found for ΔH_f^0 of trimethylamine was − 26 kjoules.[11] The C_P of trimethylamine has not been directly measured but has been estimated by the group contribution method.[12] The C_P for tetramethylammonium chloride is not known and was estimated as 0.2 cal./g. deg. since the compound is a solid. The C_P and ΔH_f^0 for methyl chloride are 16.8 cal./mole deg.[13] and − 19.6 kcal./mole,[14] respectively. With these values, the ΔH_f^0 of tetramethylammonium chloride was calculated to be −76.2 kcal./mole. Since the heat of dilution of hydrochloric acid is small in the range of concentrations employed,[15] it was neglected. The heat of solution of tetramethylammonium chloride was not known, so it was determined experimentally and was shown to be negligible.

Based on observations of the heat of reaction 1 in three independent experiments and the assumptions listed above, the heat of formation of tetramethylammonium ozonide was found to be 49.5 ± 4.2 kcal./mole.

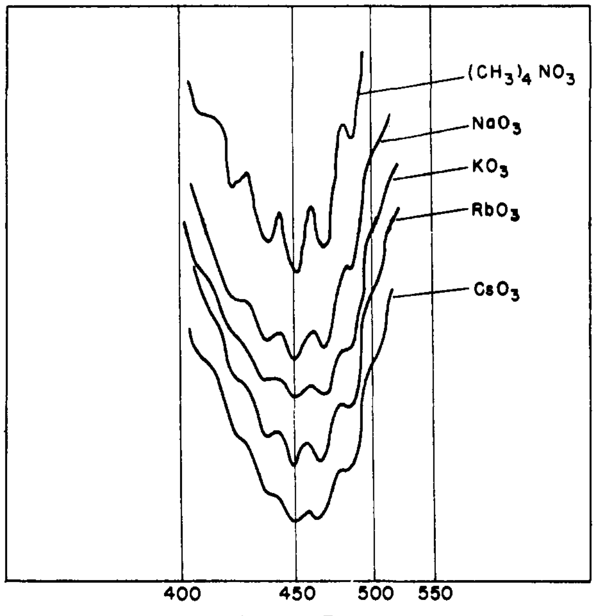

Fig. 1.—Visible spectra of ozonide compounds.

A qualitative study of the rate of decomposition of pure tetramethylammonium ozonide showed that the sample was completely decomposed after 48 hr. at 25°. The stability of the ozonide decreases as the purity of the sample increases. The decomposition products were oxygen, trimethylamine, water, tetramethylammonium hydroxide, tetramethylammonium formate and tetramethylammonium carbonate. A small fraction which consisted of less than 1% of the total decomposition products was not identified.

Experimental

Preparation of Tetramethylammonium Ozonide.—In the preparation of tetramethylammonium ozonide, tetramethylammonium hydroxide was treated with dilute gaseous ozone at 25°. So that solid tetramethylammonium hydroxide could be obtained, the water was evaporated from a 10% commercial solution (Eastman Organic Chemicals), and the solid residue was dried over phosphorus pentoxide. The dilute gaseous ozone used consisted of a mixture of 3–5 % ozone in oxygen prepared in a commercial Welsbach ozonizer.

Since water, which is a by-product in the formation of tetramethylammonium ozonide, is known to decompose ozonides, a problem existed in the isolation of the product. This difficulty was overcome in two ways. In the first method, both the product and the water were extracted with liquid ammonia, and then the ammonia was evaporated. The water that had been extracted reacted with the product, which resulted in some conversion of the ozonide to the hydroxide. The product was then re-extracted, leaving behind the insoluble hydroxide. In the second method advantage is taken of the fact that tetramethylammonium ozonide is insoluble in methyl amine. The water is removed by a pre-extraction with methyl amine, and then the ozonide is separated from the unreacted hydroxide by extraction with liquid ammonia.

Preparation of Alkali Metal Ozonides.—Sodium ozonide[9] was prepared by the ozonization of sodium hydroxide at −60°. The other alkali metal ozonides were prepared from reactions of the respective hydroxides with dilute gaseous ozone at 25° followed by extraction of the product with liquid ammonia.

[10] A. Smith and R. P. Calvert, THIS JOURNAL, 36, 1363 (1914).

[11] International Critical Tables, Vol. V, 1928, p. 182.

[12] O. A. Hougen and K. M. Watson, "Chemical Process Principles," John Wiley and Sons, Inc., New York, N. Y., 1947, p. 759.

[13] R. D. Vold, THIS JOURNAL, 57, 1192 (1935).

[14] N. B. S. Bulletin No. 599, p. 104.

[15] *Ibid.*, p. 22–24