50 cc. of acetone and stored in the cold for twenty hours. During this time the *o*-mesylate hydrochloride crystallized. The crystals were collected, washed with cold 50% acetone-chloroform and dried in a vacuum desiccator over solid potassium hydroxide; yield 9.5–10 g. (40–45%), m. p. 126.5–128°. A small sample was recrystallized from acetone affording colorless micro-rhombs, m. p. 130–131°.

Anal. Calcd. for $C_6H_{16}O_3NSCl$: N, 6.44; Cl, 16.20; neut. equiv., 217.5. Found: N, 6.59; Cl, 16.10; neut. equiv., 226.

A sample of the *o*-mesylate hydrochloride was neutralized with aqueous potassium hydroxide at 0° and the oil which separated was extracted with ether–petroleum ether and dried over solid potassium hydroxide. The filtered solution was concentrated to dryness and the residue was converted to a picrate in ethyl acetate–ether solution. Recrystallization from ethyl acetate–ether afforded the picrate of the *o*-mesylate base as fine yellow needles, m. p. 90–91°.

Anal. Calcd. for $C_{12}H_{18}O_{10}N_4S$: C, 35.12; H, 4.39; N, 13.66; S, 7.81. Found: C, 35.39; H, 4.39; N, 13.67; S, 8.53.

Dimethylamino-2-chloropropane from *o*-Mesylate Hydrochloride.—*o*-Mesylate hydrochloride (II), 3.8 g., was sealed under vacuum in an ampule and heated in xylene vapor for four hours. The ampule was cooled. The contents were dissolved in an equal volume of water and treated with an excess of 50% aqueous potassium hydroxide solution. The oil which separated was extracted with petroleum ether, dried over solid potassium hydroxide and the solvent evaporated. The residue was converted to its picrate in ethyl acetate–ether solution and recrystallized from the same solvent as fine yellow needles, m. p. 101–103°. A mixed melting point with authentic picrate of dimethylamino-2-chloropropane was undepressed; yield 3.8–4.2 g. (70–75%).

Anal. Calcd. for $C_{11}H_{15}O_7N_4Cl$: Cl, 10.13; Found: Cl, 9.74.

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An Application of the Delépine Reaction to β-Bromopropionic Acid

BY N. L. WENDLER

A modification of the Delépine reaction[1] has been applied to β-bromopropionic acid for its conversion to β-alanine. A quaternary betaine-complex was formed between β-bromopropionic acid and hexamethylenetetramine according to a method applied by Schubert[2] to iodoacetic acid. This complex was subsequently decomposed by hydrochloric acid in ethanol to afford β-alanine in good yield and high state of purity.

$$(CH_2)_6N_4 + BrCH_2CH_2COOH \xrightarrow{HCO_3^-}$$

$$[(CH_2)_6N_4]^+\text{—}CH_2CH_2COO^- \xrightarrow{C_2H_5O^+H_2} H_3NCH_2CH_2COOH$$

Experimental

To a solution of 5 g. of β-bromopropionic acid[3] in 15 cc. of water and 10 cc. of ethanol was added 2.74 g. of sodium bicarbonate. After neutralization was complete, a solution of 4.57 g. of hexamethylenetetramine in 10 cc. of water was added and the resulting solution allowed to stand at room temperature for fifteen hours. At the end of this time, 50 cc. of ethanol was added to the point of faint turbidity followed by scratching, whereupon voluminous crystallization of colorless needles of the betaine-complex ensued. The crystals were chilled in ice for one to two hours and filtered, 9 g. A second crop afforded 0.5 g. yielding a total of 9.5 g. of material.

The betaine-complex (9.5 g.) was treated with 120 cc. of ethanol and 15 cc. of concentrated hydrochloric acid and refluxed for fifteen hours. The mixture was concentrated to dryness *in vacuo* at 50° and the residue extracted with several portions of ethanol. The filtered extract was concentrated to dryness and the residue boiled under reflux with 50–75 cc. of water for one-half hour. The cooled aqueous solution was treated portion-wise with an excess of silver oxide with stirring to remove chloride ion and subsequently filtered, and the filtrate saturated with hydrogen sulfide gas. The precipitated silver sulfide was removed by centrifugation followed by filtration. The colorless solution was concentrated *in vacuo* to a volume of a few cc. and diluted with ethanol to the point of crystallization. After chilling and filtering there was afforded 2.5 g. (85%) of β-alanine, m. p. 199–200° dec. A mixed melting point with known material was undepressed.

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(1) Delépine, *Compt. rend.*, **120**, 501 (1895).

(2) Schubert, *J. Biol. Chem.*, **116**, 444 (1936).

(3) "Organic Syntheses," Vol. IV, p. 25.

Explosive Properties of Metal Ammines[1]

BY W. R. TOMLINSON, K. G. OTTOSON AND L. F. AUDRIETH

The literature contains numerous references to the explosive nature of certain coördination compounds, but no generalization has thus far been formulated in which an effort has been made to relate chemical composition of such coördination compounds to explosive character. The experimental evidence which is presented below, together with information gleaned from the literature, demonstrates that metal compounds containing (a) coördinated ammonia and related nitrogen-containing donor molecules, and (b) coördinated and/or ionic groups of an oxidizing nature such as perchlorate, chlorate, nitrate, nitrite (or nitrato- and nitro-groups), will decompose violently under various conditions. As is known to be the case among substances classed as explosives, the sensitivity of various coördination compounds to impact, to friction, and to heat will vary widely; nevertheless, some of these same compounds can be caused to detonate when properly initiated. For this reason, due caution should be exercised in the preparation, handling and storage of compounds falling within the categories defined above.

It is significant that "metal nitrates with molecular ammonia" have been incorporated in explosive compositions containing ammonium nitrate as the principal ingredient.[2] Metallic chlorates and perchlorates containing coördinated hydrazine[3] have been found to be brisant and sensitive explosives. Other coördination compounds reported

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(1) Publication of the material contained in this paper has been approved by the Ordnance Department of the United States Army.

(2) Cook, Davis and Lawson (to E. I. du Pont de Nemours and Co.), British Patent 544,582; *cf. Chem. Abstracts*, **36**, 6804 (1942).

(3) Friederich and Vervoorst, *Z. ges. Schiess.-Sprengstoffw.*, **21**, 49, 65, 84, 103, 123, 143 (1926).

TABLE I

THE EXPLOSIVE PROPERTIES[e] OF SOME METAL AMMINES

Metal ammine[d]	Explosion temperature, °C.[c]	Impact sensitivity 2 kg. wt., cm.	Sand test-gm.			
			Power Sand crushed	Sensitivity to initiator, gm., required to cause complete explosion		
				Mercury fulminate	Lead azide	Tetryl
Hexammine chromium(III) nitrate	265	32	40.7	0.20	..	..
Hexammine cobalt(III) perchlorate	360	18	39.2	.25	..	..
Hexammine cobalt(III) iodate	355	100	14.7	.24	..	..
Hexammine cobalt(III) nitrate	295	50	35.9	.27	..	..
Hexammine cobalt(III) hexanitrocobaltate[a]	...	85	34.0	.20	..	..
Nitratopentammine cobalt(III) nitrate	310	48	35.5	.24	..	..
Chloropentammine cobalt(III) perchlorate	320	21	30.6	.20	..	..
Hexaurea chromium nitrate	265	50	3.0	..	..	..
Thiocyanatopentammine cobalt(III) perchlorate	325	55	20.1	..	..	
Dithiocyanatotetrammine cobalt(III) perchlorate	335	35	13.9	..	..	..
Dichlorodiethylenediamine cobalt(III) perchlorate	300	85	9.9	..	..	..
Dichlorodiethylenediamine cobalt(III) chlorate	320	...	13.7	..	..	..[b]
Trinitrotriammine cobalt(III)	305	44	None	..	..	..
tris-Ethylenediamine cobalt(III) nitrate	...	61	None	..	..	0.4
bis-Diethylenetriamine cobalt(III) perchlorate	325	21	39.4	..	0.07	..
Ammonium hexanitrocobaltate(III)	230	33	19.0	.30	..	..
Tetrammine copper(II) nitrate	330	19	17.2	..	..	0.19
Mercuric fulminate	...	5	21.0	..	..	..
Lead azide	335	10	18.0	..	..	..
TNT (*sym*-trinitrotoluene)	470	95	42.0	.24	..	..

[a] This compound was unstable. [b] Requires tetryl. [c] Exposure to the temperature cited causes very rapid decomposition, or explosion, in 5 seconds. [d] All oxalates, chromates, carbonates, sulfates, and non-oxygenated complexes tested were non-explosive (*e. g.*, hexammine cobalt(III) chromate, oxalate and chloride). No compounds containing explosive groupings (*e. g.*, azide) were tested. [e] For details of tests see Picatinny Arsenal Technical Report No. 1401, 18 March 1944; Bureau of Mines Technical Bulletin No. 346, "Physical Testing of Explosives" at the Bureau of Mines Explosives Experiment Station, Bruceton, Pa.

to be explosive include: hexammine cobalt(III) chlorite,[4] chlorate,[3] and perchlorate,[3,5] aquopentammine cobalt(III) chlorate and perchlorate,[5] trihydrazine cobalt(II) nitrate,[6] hexahydroxylamine cobalt(III) nitrate,[7] the tetrammineauric halides[8] and trinitrotriammine cobalt.[9] In light of the evidence available in literature, it seems quite probable that the explosions reported to have occurred during evaporation of filtrates from cobalt determinations were caused, as suggested by Broughton, Laing and Wentworth,[10] by the formation of complex nitro- or nitro-cobaltates(III).

Samples of a number of cobalt(III) and chromium(III) coördination compounds[11] were subjected to standard tests to determine explosion temperature, impact sensitivity, power and sensitivity to initiation (ease with which explosion can be effected). Results of these tests are compared in Table I with values for TNT, mercuric fulminate and lead azide, representing respectively a relatively insensitive high explosive and two very sensitive initiating agents.

The data show quite clearly that oxygenated coördination compounds, particularly those which are "oxygen balanced," vary quite widely with respect to their sensitivities to heat and impact. They represent an extremely wide range in explosive types. Since most of the compounds are capable of exploding sharply and powerfully, and in some cases with but slight provocation, they are to be considered exceedingly dangerous. Some possess sufficient sensitivity to propagate explosion under water; the use or presence of non-solvent liquids is therefore no guarantee of safety. In the absence of specific information the same considerations may be expected to apply also to other metal ammines containing oxidizing radicals such as those of silver, gold, cadmium, lead and zinc.

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(4) Levi, *Atti Lincei*, (5) **32**, I, 623 (1923).

(5) Salvadori, *Gazz. chim. ital.*, **40**, II, 17 (1910).

(6) Franzen and Meyer, *Z. anorg. Chem.*, **60**, 247, 274 (1908).

(7) Werner and Berl, *Ber.*, **38**, 897 (1905).

(8) Ephraim, "Inorganic Chemistry," 4 Ed., Nordeman Publishing Co., Inc., New York, N. Y., 1943, p. 311.

(9) Clark, Quick and Harkins, THIS JOURNAL, **42**, 2498 (1920).

(10) Broughton, Laing and Wentworth, *Anal. Chem.*, **19**, 72 (1947).

(11) The authors desire to acknowledge their indebtedness to Professor John C. Bailar, Jr., of the University of Illinois, for his help in furnishing many of the coördination compounds which were subjected to actual study or used for the preparation of related derivatives.

Preparation of Radioactive CO$_2$ from BaCO$_3$[1]

BY NORMAN ZWIEBEL,[2] JOHN TURKEVICH AND WARREN W. MILLER

To obtain the C*O$_2$ from BaC*O$_3$ either for introduction into a reaction system for synthesis of a

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(1) Work done at the Brookhaven National Laboratory under the auspices of the Atomic Energy Commission. The work was started by one of us (W. W. M.) while a member of the Laboratory of Nuclear Science, Massachusetts Institute of Technology.

(2) Present address: Pyridium Corporation, Yonkers, New York