a fused silica tube, $^1/_2''$ by $10''$, fitted with a $^{19}/_{38}$ ₮ ground joint. The tube was attached to a vacuum system and evacuated to 10^{-4} mm. The sample was then gradually heated by an electric furnace. Decomposition commenced at about 500° with the evolution of hydrogen and the simultaneous distillation of potassium.

Densities and Refractive Indices of Sodium, Potassium, Rubidium and Cesium Borohydrides.—Powder densities were determined by the method of Schumb and Rittner.[4] Refractive indices were determined by the Becke Line and Half-Shadow techniques. The data are presented in Table I.

TABLE I

DENSITIES AND REFRACTIVE INDICES OF SODIUM, POTASSIUM, RUBIDIUM AND CESIUM BOROHYDRIDES

Compound	Density, g./cc. at R.T.	Refractive index
$NaBH_4$	1.04	1.547
KBH_4	1.11	1.490
$RbBH_4$	1.71	1.487
$CsBH_4$	2.11	1.498

Debye–Scherrer Powder Patterns of Potassium, Rubidium and Cesium Borohydrides.—X-Ray powder patterns were made by filling 1-mm. diameter glass capillaries with the finely powdered borohydrides. The photographs were made in a Debye–Scherrer camera of 114.6 mm. diameter using Cu Kα irradiation and four-hour exposure. "d" spacings were obtained by visual measurement, as were the intensities. These are listed in Table II, and can be considered as tentative values only.

TABLE II

DEBYE–SCHERRER POWDER PATTERNS

KBH_4		$RbBH_4$		$CsBH_4$	
d spacing, Å.	Intensity	d spacing, Å.	Intensity	d spacing, Å.	Intensity
3.84	MS	3.97	MS	4.17	MS
3.33	S	3.60	S	3.65	MS
2.36	MS	2.46	S	2.59	S
2.02	MS	2.11	MS	2.22	S
1.925	W	2.01	MW	2.12	W
1.675	VVW	1.750	VW	1.840	VVW
1.540	VW	1.610	MW	1.695	W
1.500	VW	1.565	MW	1.650	W
1.375	VW	1.435	MW	1.505	W
1.300	VVW	1.350	MW	1.425	VW
1.195	VVW	1.242	VW	1.250	VVW
		1.190	W	1.235	VVW
		1.175	W		

Comparison of Potassium Borohydride with Sodium Borohydride for the Reduction of Organic Compounds.—Methyl ethyl ketone was reduced to *s*-butyl alcohol (yield 85%), chloral hydrate to trichloroethanol (55%), and *m*-nitrobenzaldehyde to *m*-nitrobenzyl alcohol (90%). Yields reported in the corresponding reactions using sodium borohydride as reductant were 87, 61 and 82%.[5]

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[4] W. C. Schumb and E. S. Rittner, THIS JOURNAL, **65**, 1692 (1943).

[5] S. W. Chaikin and W. G. Brown, THIS JOURNAL, **71**, 122 (1949).

Isotopic Exchange Reactions in Triethylamine–Liquid Sulfur Dioxide Solutions

BY ROLFE H. HERBER[1] AND T. H. NORRIS

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In their extensive investigations of the chemistry of liquid sulfur dioxide solutions, Jander and coworkers[2] have described the reaction with the solvent of various amines. Evaporation of a solution of triethylamine (under strictly anhydrous conditions) reportedly leads to the formation of colorless crystals of m.p. 73°, corresponding to a 1:1 addition compound between amine and solvent. On the basis of not altogether convincing evidence, they deduce for this material the formula $[(Et_3N)_2SO]$-SO_3 (I).

Jander's observations and conclusions have been most effectively disputed by Bateman, Hughes and Ingold,[3] who were unable to confirm his results. Under anhydrous conditions they could prepare no colorless crystalline substance, but only an orange-red liquid, corresponding to the 1:1 addition compound, with a melting point well below 0°. However, various saline materials could be obtained from this by absorption of water or oxygen; in particular the absorption of one mole of water yielded crystals with m.p. 74–75° which they identified with Jander's crystalline substance and to which they assigned the formula $(Et_3NH)(HSO_3)$ (II).

More recently, Jander has somewhat modified his position,[4] suggesting that formula I represents but a minor equilibrium form in solution of the 1:1 addition compound, which he concedes to be primarily monomeric. However, he continues to present chemical reactions as going *via* the dimeric thionyl form, and also still reports the addition compound as a white solid with m.p. 80°.[5] No reference is made to the triethylammonium bisulfite of Bateman, *et al.*[3]

In the course of other work on the chemistry of liquid sulfur dioxide solutions,[6] it was considered worthwhile to investigate this system a bit further by means of isotopic exchange reactions.

Experimental Procedure and Results

Reagent preparations, radioactivity techniques and vacuum line manipulations were similar to those already reported.[6a,c] The radiosulfur, S^{35}, was obtained from the U. S. Atomic Energy Commission. Eastman Kodak Co. (white label) triethylamine was dried over freshly cut sodium, frozen into a cold finger with liquid air and subjected to high vacuum pumping; prolonged contact with stopcock grease was avoided.

The Addition Compound and its Exchange with Sulfur Dioxide.—Some preliminary observations were made on the vapor pressure of triethylamine–sulfur dioxide mixtures. To a known small amount of the amine, successive incre-

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[1] Department of Chemistry and Laboratory for Nuclear Science, Massachusetts Institute of Technology, Cambridge, Massachusetts. Taken from the Ph.D. thesis of Rolfe H. Herber, Oregon State College, August, 1952.

[2] K. Wickert and G. Jander, *Ber.*, **70**, 251 (1937).

[3] L. C. Bateman, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 243 (1944).

[4] G. Jander, "Die Chemie in Wasserähnlichen Lösungsmitteln," Springer-Verlag, Berlin, 1949, p. 283, *et seq.*

[5] G. Jander, ref. 4, pp. 225, 226.

[6] (a) J. L. Huston, THIS JOURNAL, **73**, 3049 (1951); (b) R. E. Johnson, T. H. Norris and J. L. Huston, *ibid.*, **73**, 3052 (1951); (c) R. H. Herber, T. H. Norris and J. L. Huston, *ibid.*, **76**, 2015 (1954).

ments of sulfur dioxide were added and the equilibrium pressure was determined. Table I presents the results of one such experiment done at 25°. Although the results are admittedly somewhat rough, it is clear that a minimum in the vapor pressure occurs near a mole ratio corresponding to the 1:1 addition compound.

TABLE I

VAPOR PRESSURES OF SO_2–Et_3N MIXTURES, $T = 25°$

Mole ratio Et_3N/SO_2	Pressure, mm.
3.65	41
2.08	33
1.46	19
1.12	9
0.912	10
.849	11
.663	27

In further observations, it was found that the quantitative mixing of equimolar quantities of triethylamine and sulfur dioxide led always to the formation of a yellow-orange viscous oil, which solidified only at low temperatures, in conformity with the observations of Bateman, *et al.*,[3] and others,[7] and in no case did we observe a crystalline material of the type described by Wickert and Jander.[2] Only in the presence of water (see below) was such a substance formed.

In order to test its rate of exchange with solvent sulfur dioxide, a small amount of S^{35}-labeled addition compound was prepared by distilling together into a reaction tube equimolar quantities of reactants. After permitting reaction to occur, a tenfold excess of inactive sulfur dioxide was distilled in at liquid air temperature. Zero exchange time corresponded to the liquefaction of the mixture, which was accomplished by replacing the liquid air with a Dry Ice–acetone-bath. After about four minutes a volatile fraction was distilled off and radioassayed as barium sulfate; similarly another volatile fraction was taken at about 20 minutes. Finally, after distilling off the remaining excess solvent, the addition compound itself was radioassayed. The specific activities of these three fractions were, respectively, 33.6, 32.7, and 35.0 counts/min./mg. Exchange is thus complete in less than four minutes at −70 to −80°.

The Addition Compound Hydrate and its Exchange with Sulfur Dioxide.—In agreement with the observations of Bateman, *et al.*,[3] we have found the addition compound to form a crystalline hydrate when exposed to moisture. Several grams of this hydrate was prepared by a procedure similar to that used by others with related compounds.[8] Anhydrous sulfur dioxide was passed into a solution of the amine in dry ether. Evaporation of this solution yielded the anhydrous liquid addition compound. However, if a little water was first added, evaporation then yielded a white crystalline mass. Since this method was difficult in application, variable yields being obtained, and difficulty being experienced in drying the highly hygroscopic material, our analytical results were somewhat disappointing. However, the agreement with Bateman, *et al.*,[3] is probably reasonably satisfactory.

Anal. Calcd. for $Et_3NSO_2 \cdot H_2O$: S, 17.5. Found: S, 14.3 (three determinations). M.p. expected 74–75°[3,9]; found 73–75, 71, 67–68°.

In order to determine its exchange rate with liquid sulfur dioxide, a small quantity of labeled hydrate was prepared in the vacuum system. To a portion of the anhydrous addition compound, prepared as before, an equimolar quantity of water was added by means of a micro pipet built into the vacuum line. After completion of reaction, an approximate fourfold excess of sulfur dioxide was distilled in and the same exchange procedure (at Dry Ice–acetone temperature) followed as with the anhydrous addition compound. The specific activities of four-, ten- and twenty-minute volatile fractions and of the addition compound hydrate itself were, respectively, 23.9, 25.2, 25.5 and 24.6 counts/min./mg. Again exchange is complete in less than four minutes at −70 to −80°.

Discussion

Our observations, qualitative and quantitative, on the addition compound and its hydrate appear to agree completely with those of Bateman, *et al.*,[3] and we must conclude that the anhydrous compound is not a crystalline material, melting at 70–80° as reported by Wickert and Jander,[2] and again in Jander's book,[5] but rather that this crystalline substance is the monohydrate.

Our original interest in an exchange with the anhydrous compound was related to Jander's formula (I), the thought being to find whether the cation had sufficient stability to inhibit the exchange of the thionyl sulfur. When it became evident that (I) did not in fact represent the constitution of the material, it seemed of some interest to find whether the monomeric addition compound was of sufficient stability to retard the exchange. Our results, however, indicate a ready dissociability, even at Dry Ice temperature.

The exchange experiments with the hydrate seemed originally to be of greater interest. These were started at a time when our experiments[7b] semed to suggest that the exchange between solvent sulfur dioxide and dissolved sulfites might be measurably slow. In view of the formulation by Bateman, *et al.*,[3] of the hydrate as a bisulfite, it seemed of interest to measure its exchange rate. Again our results show a rapid and complete exchange even at Dry Ice temperature. This observation is in harmony with the earlier results involving tetramethylammonium pyrosulfite.[6b] However, whether the exchange is to be related to a ready mobility of oxide ions in liquid sulfur dioxide, as suggested in the earlier work,[7a,b] or whether it may proceed *via* a reversible dissociation such as

$$2HSO_3^- = H_2O + SO_2 + SO_3^=$$

is not clear at this point. Certainly, though, there is no evidence here for slowness in the sulfite–sulfur dioxide exchange.

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(7) (a) J. R. Bright and J. J. Jasper, THIS JOURNAL, **65**, 1262 (1943); (b) J. A. Moede and C. Curran, *ibid.*, **71**, 852 (1949)

(8) A. Michaelis, *Ann.*, **274**, 173 (1893).

(9) On exposure to dry air, Bateman, *et al.*,[3] report the melting point to drop overnight to 55–60° and subsequently to rise slowly to 117–120°.

Absorption Spectra of Uranium(IV) Fluorides

BY DIETER M. GRUEN AND MARK FRED[1]

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Progress has been made in recent years toward the elucidation of the electronic structures of the heaviest elements, but detailed correlations of theory with magnetic susceptibility and spectroscopic data for example, have not yet been possible.[2]

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(1) Presented at the Fall, 1953, Meeting of the American Chemical Society.

(2) G. T. Seaborg, "The Actinide Elements," McGraw-Hill Book Co., Inc., New York, N. Y., 1954, Chap. 17.