

bility of BF_4^- has been estimated previously as about 3×10^{-24} cm.³.¹⁶ However, taking the refractive index, n_D , of KBF_4 as 1.32 ± 0.01 ¹⁷ and using the method of Tessman, *et al.*,¹⁴ a polarizability for BF_4^- of $(4.85 \pm 0.15) \times 10^{-24}$ cm.³ can be obtained. The "main frequency" energy ϵ_- for BF_4^- is not available. However, it seems probable that it will lie somewhere near those of the halide ions.¹³ An average value of $(15 \pm 5) \times 10^{-12}$ ergs/mole is assumed for ϵ_- for BF_4^- . Using these data, the van der Waals energies for KBF_4 and NH_4BF_4 resulting from the dipole-dipole interactions are 6 and 7 kcal./mole, respectively. The energy contributions resulting from the dipole-quadrupole interactions¹³ are taken as $0.2 C/r_0$.⁶ The total van der Waals energy terms for KBF_4 and NH_4BF_4 are about 8 and 9 kcal./mole, respectively.

The total lattice energies for KBF_4 and NH_4BF_4 (obtained by adding the contributions from the Born equation and the van der Waals energies) are 152 (at 300°) and 145 (at 260°) kcal./mole. The total uncertainties in the lattice energies resulting from the use of the Born equation, the approximate calculation of the van der Waals energy, and the approximation involved in the addition of the component energy terms are probably ± 5 to 10 kcal./mole. Previously, a very approximate lattice energy calculation gave a lattice energy for KBF_4 of 148 kcal./mole.¹⁶

The lattice energy of KBF_4 can be combined with the heat of formation of $\text{KBF}_4(\text{s})$ and that of $\text{K}^+(\text{g})$ in the reaction $\text{KBF}_4(\text{s}) \rightarrow \text{K}^+(\text{g}) + \text{BF}_4^-(\text{g})$ to obtain the heat of formation of the gaseous fluoborate ion. The heats of the dissociation reactions $\text{MBF}_4 \rightarrow \text{MF} + \text{BF}_3$ have been determined for the alkali metal fluoborates.¹⁶ In the case of KBF_4 the dissociation reaction has been studied from below the m.p. of KBF_4 (530°) to 930°. The heat of dissociation is calculated to be 29 kcal./mole from the slope of the line in the plot of $\log p$ versus $1/T$.¹⁶ Since no break occurs in the line at the m.p. of KBF_4 , the heat of the reaction $\text{KBF}_4(\text{s}) \rightarrow \text{KF}(\text{s}) + \text{BF}_3(\text{g})$ at 510° also is about 29 kcal./mole. The $\Delta H_f^\circ(\text{KF}, \text{s})$ at 510° is -128 kcal./mole,¹⁸ while $\Delta H_f^\circ(\text{BF}_3, \text{g})$ at 510° is -261 kcal./mole.^{8,19} Consequently, the heat of formation of $\text{KBF}_4(\text{s})$ at 510° is -418 kcal./mole and at 25° is about -424 kcal./mole (assuming $H^\circ - H_0^\circ$ for KBF_4 is about the same as those of the alkali metal halides¹⁸). The heat of formation of $\text{BF}_4^-(\text{g})$ at 25° can be calculated to be -395 ± 10 kcal./mole from the reaction $\text{KBF}_4 \rightarrow \text{K}^+(\text{g}) + \text{BF}_4^-(\text{g})$, since the heat of the reaction is the lattice energy of 152 kcal./mole (the change in lattice energy with temperature is negligible), $\Delta H_f^\circ(\text{KBF}_4, \text{s})$ is -424 kcal./mole and $\Delta H_f^\circ(\text{K}^+, \text{g})$ is 123 kcal./mole.²⁰

The heat of reaction (1) at 25° is -62 ± 10

(16) J. H. de Boer and J. A. M. Van Liempt, *Rec. trav. chim.*, **46**, 124 (1927).

(17) J. H. de Boer, *Verlag. Akad. Wetenschap*, **36**, 161 (1927).

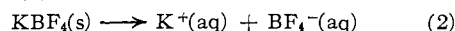
(18) L. L. Quill, Editor, "The Chemistry and Metallurgy of Miscellaneous Materials," Paper 6, "The Thermodynamic Properties of the Halides," by L. Brewer, L. A. Bromley, P. W. Gilles and N. F. Lofgren, McGraw-Hill Book Co., Inc., New York, N. Y., 1950.

(19) D. D. Wagman, T. R. Munson, W. H. Evans and E. J. Prosen, NBS Report 3456, August 30, 1954.

(20) F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," NBS Circular 500, 1952.

kcal./mole. This value is based on a $\Delta H_f^\circ(\text{BF}_3, \text{g})$ at 25° of -268 kcal./mole¹⁹ and a $\Delta H_f^\circ(\text{F}^-, \text{g})$ at 25° of -65 kcal./mole.²⁰ Combining the heat of reaction (1), with its entropy gives a free energy of -53 ± 10 kcal./mole. The corresponding equilibrium constant at 25°, K_{eq} , has the value 10^{39} . Thus the reaction is spontaneous in the direction indicated above, and the equilibrium is very far over toward the formation of $\text{BF}_4^-(\text{g})$.

The heat of solution of KBF_4 in water is about 22 kcal./mole using approximate solubility data.¹⁶ The $\Delta H_f^\circ(\text{BF}_4^-, \text{aq})$ is -342 ± 10 kcal./mole, using $\Delta H_f^\circ(\text{KBF}_4, \text{s})$ of -424 kcal./mole, $\Delta H_{\text{soln.}}$ of 22 kcal./mole and $\Delta H_f^\circ(\text{K}^+, \text{aq})$ of -60.0 kcal./mole²⁰ in reaction (2)



The heat of hydration of BF_4^- also can be calculated from the heats of formation of $\text{BF}_4^-(\text{g})$ of -395 kcal./mole and $\text{BF}_4^-(\text{aq})$ of -342 kcal./mole as about -54 kcal./mole ($\Delta H_f^\circ(\text{H}^+, \text{aq}) = +107$ kcal./mole).²¹

(21) H. O. Pritchard, *Chem. Revs.*, **52**, 529 (1953).

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The Boron Trifluoride-Nitrogen Tetroxide Complex. Its Composition and Chemical Behavior

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RECEIVED AUGUST 22, 1955

When boron trifluoride and the equilibrium mixture of nitrogen dioxide and nitrogen tetroxide are brought together in the vapor phase, the liquid phase, or in solution, heat is evolved and a stable, white, solid complex immediately separates. Mention is made of such a complex by Kuhlmann,² although he gives no data on its method of preparation, composition, analyses or properties. Batey and Sisler³ mention a white, crystalline solid formed in the reaction of BF_3 with NO_2Cl containing N_2O_4 as an impurity, which they formulate as $\text{N}_2\text{O}_4 \cdot 2\text{BF}_3$. These authors also supply no other data on this complex.

Composition of the Complex.—Since we had expected for theoretical reasons that boron trifluoride and nitrogen tetroxide would form a complex of the type $\text{BF}_3 \cdot \text{N}_2\text{O}_4$ it was first decided to study the combining ratios of the two substances. This was done both gravimetrically and volumetrically. The results in both cases confirmed the expected composition.

Physical Properties of the Complex.—The white solid obtained by any of the various methods of mixing the component compounds is essentially insoluble in all solvents with which it does not react. Even nitromethane, nitrobenzene and liquid N_2O_4 do not dissolve it appreciably. It is also insoluble in aliphatic hydrocarbons and chlorinated hydrocarbons. It reacts with oxygenated solvents such as water, carboxylic acids, esters, ketones and

(1) Taken in part from the M.S. Thesis of C. M. Vogt, Purdue University, August, 1954.

(2) F. Kuhlmann, *Ann. chim. phys.*, [3] **2**, 116 (1941).

(3) H. H. Batey and H. H. Sisler, *THIS JOURNAL*, **74**, 3408 (1952)

ethers and with basic nitrogen derivatives such as amines and pyridine.

The above behavior makes it impractical to crystallize the complex which is normally obtained as an amorphous solid with a waxy consistency and no visual evidence of crystallinity. Solvents and other liquid impurities such as excess N_2O_4 may be removed by pressing on a porous plate. This must be done fairly rapidly since the complex sublimes with dissociation into its component parts at room temperature and reacts rapidly with atmospheric moisture. In a sealed melting point tube no melting is evident at temperatures of 300° and dissociation into NO_2 so darkens the tube that observation of the contents becomes difficult or impossible at these or higher temperatures. In closed containers and in the absences of substances with which it can react the $BF_3-N_2O_4$ complex appears to be perfectly stable for months.

Chemical Behavior of the Complex.—In view of the ease of dissociation of the $BF_3-N_2O_4$ complex it is not surprising that it reacts with substances which normally react with either BF_3 or N_2O_4 alone. Thus with water, hydrofluoric acid, boric acid, fluoboric acid, nitrous acid and nitric acid are rapidly generated. With cyclohexene the same products are isolated, although in poorer yields, as are obtained from cyclohexene and N_2O_4 alone.⁴ With methyl acrylate the complex gives methyl 3-nitroacrylate and methyl 3-nitro-2-hydroxypropionate in low yields. These compounds and others are reported by Shechter and Conrad⁵ to result from the reaction of methyl acrylate with N_2O_4 alone.

There would appear to be little advantage in using $BF_3-N_2O_4$ in place of N_2O_4 for reactions in which N_2O_4 is to be added to unsaturated molecules. Not only are the yields of expected products poorer in those cases where comparisons can reasonably be made, but also the reactions are more difficult to control and are not successful when addition of N_2O_4 itself is not successful.

The $BF_3-N_2O_4$ complex reacts substitutively with benzene at ice-bath temperatures to produce detectable amounts of nitrobenzene almost immediately. At -9° a 12% yield is obtained in 3 to 4 hours and at 0° a 40% yield is obtained in one week. Small amounts of *m*-dinitrobenzene are formed at the same time. The complex reacts with naphthalene at 0° in 36 hours to give a 65% yield of dinitronaphthalenes containing principally the 1,5- and 1,8-isomers. Nitrobenzene gives a 7% yield of *m*-dinitrobenzene in one week at room temperatures.

The complex is an unusual nitrating agent in that it contains no water, no hydrogen atoms and no hydroxyl groups. Furthermore it is insoluble in the reaction medium and in the products of nitration. These attributes can be turned to advantage to certain cases, a subject which is being studied in further detail in this Laboratory. For the present it may be noted that the complex leads to a different ratio of products in the nitration of naphthalene than is obtained with nitric acid. Hodgson and Whitehurst⁶ report a ratio of 1,5-:1,8-dinitronaphthalenes of about 1:2 using mixed acids at $0-35^\circ$,

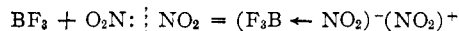
(4) H. Baldoek, N. Levy and C. W. Scaife, *J. Chem. Soc.*, 52 (1948).

(5) H. Shechter and F. Conrad, *THIS JOURNAL*, **75**, 5610 (1953).

(6) H. H. Hodgson and J. S. Whitehurst, *J. Chem. Soc.*, 202 (1945).

while we find the reversed ratio of about 2:1 of the same isomers using the complex at 0° . With readily oxidized compounds such as aniline and resorcinol the complex is hypergolic (*sic*) and produces instantaneous combustion.

The Structure of the Complex.—The high melting point and the insolubility in non-polar solvents indicate the complex to be a polar molecule. The rapid nitrating action on aromatic compounds indicates the presence in it of nitronium ions. For these reasons we wish to propose the following mode of formation and structure of the complex.



Nitrogen tetroxide can dissociate homolytically into $\cdot NO_2$ radicals or heterolytically into $(NO_2)^+$ and $(:NO_2)^-$ ions. The first process is evidently favored by heat. The second process would be promoted by any reagent capable of combining readily with either the $(NO_2)^+$ or the $(NO_2)^-$ ions. Since BF_3 is one of the most powerful acceptor molecules known, and hence combines strongly with anions, it is not surprising that it reacts with N_2O_4 to form the salt-like molecule pictured for the complex.

Experimental

Preparation of $BF_3-N_2O_4$ Complex.—A three-necked 1000-ml. flask fitted with an all-glass stirrer, reflux condenser and gas inlet tube is immersed in a pail of crushed ice and salt. Dry nitromethane or nitroethane, 350 ml., is introduced and stirring is started. Previously collected, dry liquid, $NO_2-N_2O_4$, 100 g. (110 ml.), is added, and when the temperature has fallen below 0° , a rapid stream of BF_3 is started through the gas inlet tube, which should dip below the surface of the liquid in the flask. When excess BF_3 is present as indicated by white fumes at the top of the condenser, the stream of BF_3 is interrupted. The flask now contains a quantitative yield of a slurry of the complex in nitro alkane. It may be stored as such or filtered off on a sintered glass funnel, rapidly pressed free of adhering liquid on a porous plate in a dry atmosphere, and sealed in glass tubes.

Gravimetrically 100 g. of $NO_2-N_2O_4$ was found to combine with 97.2, 104.4 and 96.8 g. of BF_3 in three separate experiments. Volumetrically, 50 ml. of $NO_2-N_2O_4$ (corrected for the degree of dissociation according to the equations and data of Verhoek and Daniels⁷) combined with 50.0 ± 0.5 ml. of BF_3 in six separate experiments in an all-glass apparatus.

Reaction of Complex with Benzene.—The complex, 72 g. (0.450 mole), was added slowly with stirring to 35.2 g. (0.44 mole) of benzene cooled in a flask to partial crystallization in an ice-bath. The mixture was allowed to warm up to room temperature and let stand for a week. It was then poured into ice-water to destroy unreacted complex. The water layer had a blue color. Urea was added to decompose any nitrous acid present, and the non-aqueous layer was separated, dried and distilled. The fraction, b.p. $210-212^\circ$, was 21.4 g. (39.5% yield) and was nitrobenzene. The undistilled residue was recrystallized from methanol to give 1.18 g. (1.6% yield) of *m*-dinitrobenzene, m.p. 90° .

Reaction of the Complex with Nitrobenzene.—A similar experiment but using 30 g. (0.178 mole) of nitrobenzene and 40 g. (0.25 mole) of complex gave after one week a 7% yield of *m*-dinitrobenzene, m.p. 90° .

Reaction of the Complex with Cyclohexene.—Cyclohexene, 30.0 g. (0.36 mole) in 158 g. of CCl_4 was added to a slurry of 160 g. (1.0 mole) of the complex in 1175 g. of CCl_4 at 0° over a period of two hours. Oxygen was bubbled through the reaction mixture continuously. The product was allowed to warm to room temperature within six hours. It was then decomposed with ice and water and urea, the CCl_4 layer separated, dried and distilled under vacuum. A large number of products appeared to be present. All of these were not identified, but 2-nitrocyclohexanol and 1,2-dinitrocyclo-

(7) F. H. Verhoek and F. Daniels, *THIS JOURNAL*, **53**, 1250 (1931).

hexane were isolated in small amounts and identified by comparison with authentic samples prepared by the method of Baldock, Levy and Scaife⁴ from cyclohexene and nitrogen tetroxide.

Reaction of the Complex with Methyl Acrylate.—Methyl acrylate, 58.6 g. (0.68 mole) in 93 g. of CCl₄ was added slowly to 160 g. (1.0 mole) of complex in 322 g. of CCl₄ during 1.5 hours at 0° while oxygen gas was bubbled into the mixture. The product was allowed to warm up to room temperature and to stand overnight. It was decomposed with ice and water and 101 g. of urea. The lower layer was separated, washed with water till neutral, dried and fractionally distilled. There were obtained 1.38 g. (1.5% theory) of methyl 3-nitroacrylate, b.p. 36–40° (1 mm.), freezing point 33°; and 3.91 g. (3.8% theory) of methyl 3-nitro-2-hydroxypropionate, b.p. 86–89° (1 mm.), glassy at –70°. Other unidentified products including a polymer were also present.

Reaction of the Complex with Naphthalene.—A slurry of 80 g. (0.50 mole) of the complex in 200 ml. of nitroethane was cooled to ice temperature. A solution of naphthalene, 30 g. (0.234 mole), in 200 ml. of nitroethane also cooled to 0° was added dropwise to the flask with rapid stirring. The mixture developed a light yellow-green color during the final stages of the addition. Stirring was continued at ice temperatures for 5 hr., then the mixture was allowed to stand 24 hours at ice temperatures. Finally the reaction mixture was heated gently for 3 hours, cooled and poured into a mixture of ice and water to destroy the complex. Again the water layer became blue in color. The non-aqueous layer was separated, dried and the nitroethane solvent removed by distillation. The residue solidified on cooling and weighed 36.5 g. (65% theory calcd. as dinitro-naphthalenes).

Anal. Calcd. for C₁₀H₈N₂O₄: N, 12.81. Found: N, 13.00.

Following the separation procedure of Hodgson and Turner⁸ the product was partially reduced with sodium sulfide and sulfur to a mixture of 1,8-dinitronaphthalene, 13.2 g., m.p. 171°, and 5-nitro-1-naphthylamine, soluble in acid, 19.8 g., m.p. 119°. From this it may be calculated that the ratio of dinitronaphthalenes formed was 1,8-/1,5- = 36.5/63.5.

Acknowledgment.—We are indebted to the Office of Naval Research for the financial support of part of this work.

(8) H. H. Hodgson and H. S. Turner, *J. Chem. Soc.*, 318 (1943).

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Quinoline Derivatives of Iodine(I)

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RECEIVED AUGUST 15, 1955

The positive character of the halogens is well established,¹ and the cationic nature of iodine is almost to be expected from its metallic-like appearance and its position in the periodic classification.

Carlsohn² and his students pioneered in the field of coordination compounds of unipositive iodine. These investigators were able to stabilize a number of salts of the hypothetical base, IOH, by coordination with organic tertiary amines. The general method of preparation is illustrated by the following equation, the calculated amounts of material being brought together in some non-aqueous medium, usually chloroform.

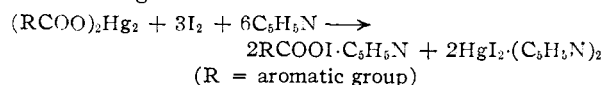


The mercurous salt can also be used as a starting material for obtaining unipositive iodine complexes.

(1) J. Kleinberg, *J. Chem. Ed.*, **23**, 559 (1946).

(2) H. Carlsohn, "Über eine neue Klasse von Verbindungen des einwertigen Iods," Verlag Hirzel, Leipzig, 1932.

In this case, benzene appears to be the best medium for effecting reaction.



A series of unipositive iodine derivatives of carboxylic acids, with pyridine, α - and β -picoline as coordinating agents, has been reported.^{3,4} This paper reports the preparation of some compounds of iodine(I) coordinated with quinoline.

Experimental

Materials.—The iodine used was J. T. Baker C.P. grade. It was stored in a desiccator over phosphoric anhydride. Eastman Kodak Co. white label quinoline was placed over potassium hydroxide pellets for two weeks and then distilled twice through a 30" fractionating column, the middle cut boiling at 234° at 732.1 mm. being collected. The acids were Eastman Kodak Co. white label products and were recrystallized prior to use. All solvents were dried and distilled before use.

Procedure.—The silver salts were prepared by dissolving a known weight of acid in 95% ethanol, with slight heating if necessary, and then adding aqueous sodium carbonate until the solution tested just basic to litmus. Dilute nitric acid was then added until the solution tested just acid to litmus, and any organic acid precipitating at this point was removed. A solution of silver nitrate containing a quantity of silver equivalent to the amount of organic acid used was added, and a heavy white precipitate of the silver salt of the acid formed. The white solid was allowed to settle, removed by filtration, washed well with 95% ethanol, and dried at 70° for 24 hours before use.

The method of preparation of the derivatives of iodine(I) is similar for all acids and that for *p*-bromobenzoic acid will be given in detail. Exactly 9.6 g. of silver *p*-bromobenzoate was suspended in 100 ml. of dry chloroform. While the suspension was shaken continuously, iodine and quinoline were added alternately in small portions until 8 g. of the former and 4 g. of the latter had been introduced. A reaction began immediately, and silver iodide precipitated. After 25 minutes of continuous shaking, 50 ml. of chloroform was added to dilute the reaction mixture. The heavy precipitate of silver iodide was removed by filtration, and 500 ml. of low boiling petroleum ether was added to the filtrate. A large quantity of crystals formed at once. After 30 minutes, the crystalline product was collected on a filter and washed with petroleum ether and dry diethyl ether and then dried *in vacuo* over sulfuric acid for 24 hours. The yield was 9.7 g., 68% of theoretical, based on the amount of silver salt employed. The sparkling light yellow crystals decomposed at 139–143°, uncor.

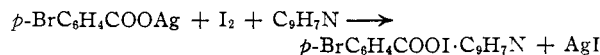


TABLE I

Salt ^a	Yield, %	Decomp. range, °C. ^b	% Iodine	
			Calcd.	Found
Benzoate	73.4	141–150	33.7	33.6, 33.5
<i>p</i> -Bromobenzoate	68.0	139–143	27.8	27.8, 27.8
<i>m</i> -Chlorobenzoate	60.8	121–124	30.8	30.7, 30.6
<i>p</i> -Chlorobenzoate	76.8	136–141	30.8	30.3, 30.5
<i>o</i> -Chlorobenzoate	38.4	129–133	30.8	30.8, 30.6
<i>o</i> -Iodobenzoate	43.1	110–113	25.3	25.4, 25.2
<i>m</i> -Iodobenzoate	75.3	125–133	25.3	25.0, 25.3
<i>o</i> -Nitrobenzoate	71.1	122–127	30.1	30.1, 30.2
<i>m</i> -Nitrobenzoate	23.8	160–181 ^c	30.1	29.8, 29.7

^a All salts were pale yellow or golden. ^b Uncorrected. ^c This compound began to turn pink at 160° and was completely decomposed at 181°.

(3) R. A. Zingaro, J. E. Goodrich, J. Kleinberg and C. A. VanderWerf, *THIS JOURNAL*, **71**, 575 (1949).

(4) R. A. Zingaro, C. A. VanderWerf and J. Kleinberg, *ibid.*, **72**, 5341 (1950).