In Table III is shown the distribution of radiocarbon activity among various formal oxidation states. Where the individual ion charges in a simple ionic crystal are not very different we would expect the energetic carbon recoils to come to rest in terminal hot-spots which exhibited a more or less symmetrical distribution of oxidizing and reducing characters. Provided that the solvent has a similar character (*e.g.*, it is not capable only of causing reduction, as would be the case with liquid ammonia), we would expect a similar symmetrical distribution of radiocarbon among various final oxidation states. This result is actually observed not only for beryllium nitride, but for ammonium sulfate target[3] where both reducing and oxidizing species are available in the lattice.

TABLE III

PERCENTAGE OF TOTAL RADIOCARBON ACTIVITY IN VARIOUS OXIDATION STATES, Be_3N_2 TARGET

	%
+4	43.9
+2	14.9
0	2.4
−2	15.4
−4	25.8

Effect of Pile Radiations.—In the foregoing discussion we have presumed that there is no sensible integrated effect of the pile flux of γ– and X-rays. In the absence of more detailed information concerning the specific origins of the several product species, one can only estimate the possible importance of radiation-induced reactions. Following the calculation method employed in a previous publication,[3] we find that the chance for direct influence of radiation on the state of radiocarbon at the end of the irradiation is of the order of 0.02. This is an approximate lower limit for the occurrence of a radiation effect. Any estimate of a reasonable upper limit will depend upon a decision concerning the size of the volume about the entrapped hot-atom in the crystal within which the occurrence of a radiation-induced process will affect the state of the hot-atom.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

Reactions of Carbon(IV) Iodide with Ammonia and Hydrazine[1]

BY GEORGE W. WATT, WILLIAM R. MCBRIDE AND DONALD M. SOWARDS

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Carbon(IV) iodide is stable toward solvolysis by liquid ammonia at or near its boiling point, but is reversibly ammoniated to form only $CI_4\cdot 2NH_3$; the first-order rate constant for this ammoniation at −35.0° and 420 mm. is 1.28×10^{-4} sec.$^{-1}$ and the dissociation pressure of the 2-ammoniate at −35.0° is 95 mm. On the basis of potentiometric titration data, the initial reaction between carbon(IV) iodide and potassium amide in liquid ammonia at −37° is interpreted as involving a base-catalyzed ammonolysis to form iodoform and iodoamide. The primary reaction between carbon(IV) iodide and hydrazine in liquid ammonia yields iodoform and elemental nitrogen.

Earlier studies in these laboratories have shown that the halides of carbon(IV) undergo solvolytic cleavage when treated with anhydrous liquid ammonia at elevated temperatures[2] but suggest that these halides are ammoniated but not ammonolyzed at or near the boiling point of liquid ammonia. The existence of a 2-ammoniate of carbon(IV) iodide was reported, and this has since been confirmed by means of pressure–composition isotherms and the 2-ammoniate has been characterized. Also, the reaction between carbon(IV) iodide and potassium amide in liquid ammonia has been studied by means of potentiometric titrations with a view to detecting the formation of the tetramide of carbon(IV). The interaction of carbon(IV) iodide and hydrazine in liquid ammonia also has been investigated.

Experimental

Materials.—The following materials were prepared and purified by the methods to which reference is made: carbon(IV) iodide,[3] anhydrous hydrazine[4] and potassium amide.[5]

Methods.—Methods used for the detection or determination of guanidine[6] and hydrazine[7] are described elsewhere. For the analysis of solutions containing both hydrazine and iodide ion, the total concentration of these two constituents was determined by iodate titrations[7] and hydrazine was determined separately as benzalazine by adding a slight excess of benzaldehyde to solutions made slightly acidic with acetic acid.

All reactions involving either gaseous or liquid ammonia were carried out under strictly anhydrous conditions. The quartz helix balance and the procedures employed in the establishment of pressure–composition isotherms are described elsewhere.[8] The equipment and methods used in carrying out potentiometric titrations in liquid ammonia also have been described previously.[5]

Results.—The pressure–composition isotherm for the system carbon(IV) iodide–ammonia is

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[1] This work was supported in part by the U. S. Navy Bureau of Ordnance, Contract N123s-67363, Task Order 2.

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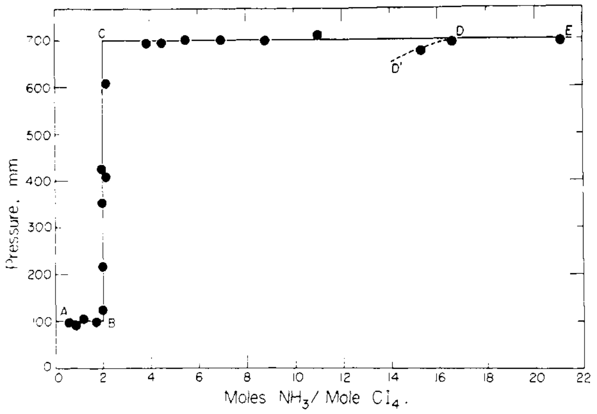

Fig. 1.—Pressure–composition isotherm for the system CI_4–NH_3 at −35°.

shown in Fig. 1 and the phases coexistent at equilibrium are listed in Table I. A plot of log concentration (% unreacted) *vs.* time for the initial ammoniation of a sample of carbon(IV) iodide of unknown surface area at −35.0° leads to a first-order rate constant of 1.28×10^{-4} sec.$^{-1}$. The characteristic lemon-yellow color of the 2-ammoniate in contrast to the red color of carbon(IV) iodide provides visual evidence of both the occurrence and completion of ammoniation.

TABLE I

COMPOSITION OF PHASES IN EQUILIBRIUM

Curve	Phases
AB	CI_4(s), $CI_4 \cdot 2NH_3$(s), NH_3(g)
BC	$CI_4 \cdot 2NH_3$(s), NH_3(g)
CD	$CI_4 \cdot 2NH_3$(s), satd. soln., NH_3(g)
DD'	Supersatd. soln., NH_3(g)
DE	Dil. soln., NH_3(g)

Data for a typical potentiometric titration of carbon(IV) iodide with potassium amide in liquid ammonia at −37° are given in Fig. 2. Essentially identical results were obtained using a mercury-saturated mercury(II) chloride reference electrode[9] *vs.* a platinum electrode and a "difference-indicator" electrode[5] *vs.* a platinum electrode. In a typical titration, incremental addition of 93.5 m*M* potassium amide solution to the light yellow solution of 0.445 mmole of carbon(IV) iodide and 0.2 g. of potassium iodide (as a supporting electrolyte) in 30 ml. of liquid ammonia at −37° produced a transitory wine-red solution until about 4.5 equivalents of potassium amide had been added; the final solution was pale yellow to nearly colorless. After evaporation of the solvent, the residue was only slightly basic, thus indicating complete consumption of the added potassium amide. Qualitative tests[6] for guanidine were negative. Owing to the small quantities of reaction products available from such titrations, efforts to separate and characterize reaction products were unsuccessful.

Addition of solid carbon(IV) iodide to excess anhydrous hydrazine results in a reaction so exothermal that the residual hydrazine is usually ignited. If the iodide is suspended in carbon(IV) chloride and treated with hydrazine, the reaction is controllable although still apparently heterogeneous. In anhydrous liquid ammonia, however, the reaction is homogeneous and proceeds rapidly and smoothly. In a typical experiment, 2.862 g. of CI_4 (5.52 mmoles) in 15 ml. of liquid ammonia at −40° was treated with 0.2099 g. (6.55 mmoles) of 99.2% N_2H_4. From the ensuing reaction, 74.6 cc. of nitrogen gas (3.33 mmoles) was collected; residual hydrazine amounted to 0.1030 g. (3.22 mmoles) and the iodide analysis (by difference from the iodate titration) gave 6.76 mmoles. The iodoform produced in the reaction weighed 1.909 g. (4.83 mmoles), m.p. 119–120° cor. In independent experiments it was found that iodoform reacts relatively slowly with anhydrous hydrazine to evolve nitrogen gas in an exothermal and apparently solvolytic reaction.

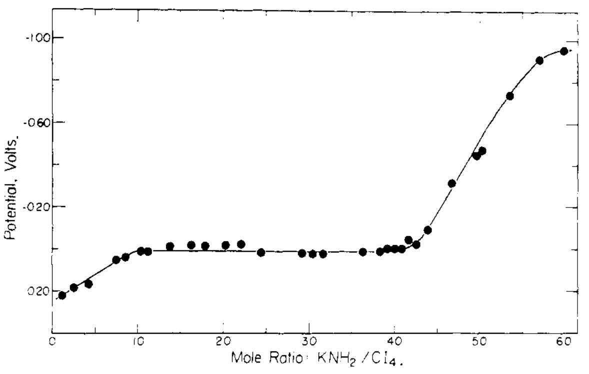

Fig. 2.—Potentiometric titration of CI_4 with KNH_2 in liquid ammonia at −37°.

Discussion

The data of Fig. 1 show conclusively that $CI_4 \cdot 2NH_3$, with a dissociation pressure of 95 mm., is the only ammoniate formed by carbon(IV) iodide at −35.0°. That ammonolysis does not occur under these conditions is shown by the fact that the ammoniation is completely reversible. Because the ammonia pressure of the invariant system comprising the 2-ammoniate in equilibrium with its saturated solution corresponds closely to the condensation pressure of ammonia at this temperature, it is possible only to estimate that the composition of the saturated solution is 16.3 moles NH_3/mole CI_4, or 188 g. CI_4/100 g. NH_3. The first-order rate, 1.28×10^{-4} sec.$^{-1}$, for the ammoniation at 420 mm. and −35.0° is comparable to data previously obtained for the ammoniation of ammonium chloride and fluoride,[8] thiourea and urea.[10]

Although study of the interaction of carbon(IV) iodide and potassium amide in liquid ammonia provided no evidence for the formation of carbon(IV) amide, the results given in Fig. 2 indicate that one of the four iodine atoms is more reactive than the other three, which are apparently equivalent in reactivity. Guanidine is the most probable deammoniation product of carbon(IV) amide, but its absence as a reaction product is substantiated by analytical determinations, the lack of basicity of the gross reaction product following elimination of the solvent, and the failure of formation of the ammo-

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nia-insoluble dipotassium salt of guanidine during the course of the potentiometric titrations. Furthermore, it is significant that neither carbon(IV) iodide nor iodoform was present at the end of the titration; this is shown by the fact that the gross product was water-soluble. Accordingly, one may postulate either a metathesis resulting in the formation of H_2NCI_3 and KI or a base-catalyzed ammonolysis yielding HCI_3 and NH_2I. The latter product would undoubtedly react with potassium amide to form hydrazine, which has been shown to react with carbon(IV) iodide as

$$2CI_4 + N_2H_4 + 2NH_3 \longrightarrow N_2 + 2NH_4I + 2HCI_3 \quad (1)$$

Iodoform so produced should be expected to be consumed in a reaction analogous to that reported[11] for chloroform.

$$CHCl_3 + 4KNH_2 \longrightarrow KCN + 3KCl + 3NH_3 \quad (2)$$

This would account for the consumption of four equivalents of potassium amide in addition to the one equivalent required for the formation of iodoamide, and the assumption of the base-catalyzed ammonolysis followed by the indicated secondary reactions is therefore consistent with the results of the potentiometric titrations. Apparently the only alternative is to consider that carbon(IV) amide is formed and undergoes ultimate deammoniation to form cyanamide. However, this product should form an ammonia-insoluble dipotassium salt,[11] and no such product was obtained.

As shown by equation 1, carbon(IV) iodide acts as an oxidizing agent toward hydrazine in liquid ammonia in a manner apparently strictly analogous to that previously reported for the reactions between hydrazine and carbon(IV) chloride[12] and bromide.[13] Moreover, all of the hydrazine lost from the system appears quantitatively as elemental nitrogen, and it is suggested that this reaction might be employed for the analytical estimation of hydrazine in liquid ammonia solutions. The occurrence of the secondary reaction

$$HCI_3 + N_2H_4 + 2NH_3 \longrightarrow N_2 + CH_3I + 2NH_4I \quad (3)$$

is indicated by the fact that the iodate titrations gave a titer value about 2% greater than expected solely on the basis of equation 1, and the loss of carbon-containing substances amounting to about 10%. The over-all consumption of hydrazine is sufficient to account for the utilization in reaction (3) of about 10% of the iodoform resulting from reaction (1). Finally, the methyl iodide formed in (3) would probably react with the solvent to form a mixture of the corresponding primary, secondary, and tertiary amines.[14]

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AUSTIN, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NEW BRUNSWICK]

The Kinetics of Mutarotation of D-Glucose with Consideration of an Intermediate Free-aldehyde Form

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The rate constants of the mutarotation equilibrium $\alpha \underset{k_1'}{\overset{k_1}{\rightleftarrows}} \gamma \underset{k_2}{\overset{k_2'}{\rightleftarrows}} \beta$ as applied to D-glucose have been measured by a polarographic method in phosphate buffer solutions (*p*H about 6.9) for different buffer concentrations and ionic strengths, but constant buffer ratio. The rate constants are shown to be a linear function of the buffer concentration and independent of the ionic strength within experimental error. The concentration of intermediate free aldehyde (γ) has been determined from the rate constants and was found to be (0.0026 ± 0.0002%) of the total glucose concentration (0.655 mole/l.). Its value showed a small trend of decreasing with increasing buffer concentration. Possible reasons for this trend have been discussed.

Under the tacit assumption that diffusion is the only process determining the limiting current in the reduction of a number of aldose sugars at the dropping mercury electrode (d.m.e.), Cantor and Peniston[2] were led to calculate the free aldehyde concentration of these sugars from the Ilkovic equation. However, it was pointed out by Wiesner[3] that the polarographic waves observed behave quite differently from waves controlled by diffusion. Their limiting currents show an unusually great dependence on temperature and *p*H and in certain instances (*e.g.*, for glucose, galactose and xylose) they are practically independent of the head of mercury. These phenomena have been interpreted through the concept of kinetic waves.[3] The cyclic hemiacetal form of the aldose—itself non-reducible—produces a reducible form, presumably the free aldehyde, in a very fast chemical reaction at the electrode surface. If the concentration of the non-reducible substance at the electrode surface in the potential range of the limiting current is practically the same as that in the bulk of the solution, the current is said to be completely rate controlled.

Complete rate control requires that i_k, the kinetic limiting current, be very small as compared to i_{hd}, the hypothetical diffusion current (*i.e.*, the current in case the non-reducible component were reducible as well), or, consequently, that i_k be independent of the head of mercury.[4] Using the latter criterion Wiesner also found that D-glucose gives a completely rate-controlled wave.

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