of sodium in fused sodium bromide, but the present determinations show a solubility of 9 ± 0.5 mole per cent. at that temperature (Table I and Fig. 3). It is difficult to establish with certainty the cause of this discrepancy. The use of glass for the cell and of platinum for the electrodes, both of which are very likely to be heavily attacked by alkali metals, raises serious doubts as to whether the potentials measured were representative of the sodium concentration cell as believed by the investigator or rather of some other not immediately obvious electrode process.

Acknowledgment.—The authors wish to acknowledge discussions with, and assistance of, Mr. H. R. Bronstein of this Laboratory in the development of some of the experimental techniques.

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

The Ammonolysis of the Halides of Carbon(IV)[1]

BY GEORGE W. WATT AND HAROLD T. HAHN

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The rate of formation of guanidine and ammonium iodide from carbon tetraiodide and ammonia increases with temperature from 25 to 150°. Ammonolysis, however, is complete at 100° and the limiting rate in the formation of guanidine is the reaction of an intermediate which may be cyanogen iodide; the reaction is markedly catalyzed by iodide ion. With carbon tetrabromide and ammonia at 125°, ammonolysis is rate limiting; this reaction is catalyzed by ammonium bromide and other ammonia-soluble bromides. Carbon tetrachloride and ammonia do not react at an appreciable rate at temperatures below 300°; at this temperature, however, ammonolysis is rate limiting as in the case of the tetrabromide. Copper and iodine, previously reported as catalysts for this reaction, are relatively ineffective; the ammonolysis is catalyzed by ammonium iodide and conversions in excess of 80% have been observed.

On the basis of the available information relative to the interaction of ammonia and the normal halides of the non-transitional elements of Group IV, it appears that with increase in atomic number there is a decrease in tendency toward solvolytic cleavage and an increase in tendency toward the formation of stable ammonates.[2-10] Although only very limited information is available relative to the halides of carbon(IV), it should be anticipated that just as they are completely hydrolyzed to carbonic acid and hydronium halide,[11] so complete ammonolysis should yield ammonium halide and the nitrogen system analog of carbonic acid, *i.e.*, the ammonocarbonic acid, guanidine.[12] Alternatively, by analogy with partial hydrolysis of carbon tetraiodide to iodoform and hypoiodous acid,[13] comparably extensive ammonolysis should yield iodoform, and iodoamide which is the nitrogen system analog of hypoiodous acid.

It is commonly considered that carbon tetrachloride is unreactive toward ammonia[14] although Stähler[15] has reported that at 140° (*i.e.*, above the critical temperature of ammonia), carbon tetrachloride reacts with ammonia in the presence of copper and iodine to provide a 35–40% yield of guanidine together with lesser quantities of hydrocyanic acid and cyanogen. Apparently the ammonolysis of the other halides of carbon(IV) has not been studied.

The experiments described below are concerned with the interaction of ammonia and the chloride, bromide and iodide of carbon(IV).

Experimental

Materials.—The following materials were prepared and purified by the methods described in the literature to which reference is made: carbon tetrabromide,[16] carbon tetraiodide,[17] cyanogen iodide,[18] cyanuric iodide,[19] silver cyanamide,[20] bismuth(III) iodide,[21] aluminum(III) bromide.[22] X-Ray diffraction data for carbon tetrabromide, carbon tetraiodide and silver cyanamide are given in Table I. All other materials consisted of reagent grade chemicals, or were prepared for use as described previously.[23]

Analytical Methods.—With the exception noted below, all analytical determinations were made using standard procedures.

Guanidine was determined as the picrate in the manner described elsewhere[23] except that the solubility correction factor that must be added to compensate for the appreciable solubility of guanidine picrate was redetermined as a function of temperature. From a stock solution containing 989 mg. of high purity guanidine nitrate dissolved in 100 ml. of water, 10-ml. aliquots (each equivalent to 233 mg. of guanidine picrate) were taken and each was treated with 300 mg. of ammonium iodide, 40 ml. of water and 85 ml. of saturated ammonium picrate solution. Duplicate samples were equilibrated at 25, 30 and 35°, and from the weights of guanidine picrate found, it was computed that the correc-

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

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TABLE I

X-RAY DIFFRACTION DATA FOR CARBON TETRABROMIDE, CARBON TETRAIODIDE AND SILVER CYANAMIDE[a]

Carbon tetrabromide				Carbon tetraiodide[b]				Silver cyanamide	
d, Å.	I/I_1	d, Å.	I/I_1	d, Å.	I/I_1	d, Å.	I/I_1	d, Å.	I/I_1
5.01	0.32	2.94	0.15	5.92	0.1	2.15	0.2	7.20	0.2
4.91	1.00	2.89	.26	5.33	.3	2.12	.1	5.95	.2
4.57	0.09	2.76	.14	5.00	.1	1.93	.2	5.29	.2
4.50	.12	2.68	.34	4.55	.1	1.88	.1	4.98	.2
4.29	.12	2.60	.14	3.90	.2	1.79	.1	4.64	.4
3.96	.15	2.56	.19	3.31	1.0	1.76	.1	3.90	.1
3.50	.15	2.45	.07	2.87	0.1	1.66	.05	3.09	.1
3.47	.20	2.40	.09	2.77	.4	1.60	.1	2.89	.1
3.20	.14	2.38	.10	2.40	.2	1.55	.1	2.77	1.0
3.18	.09	2.26	.07	2.28	.1	1.51	.1	2.40	0.2
3.13	.09	2.02	.11					2.32	.2
3.04	.51	1.98	.16					2.22	.3
3.03	.46	1.95	.25					2.05	.1
2.96	.15	1.56	.08					1.77	.2
								1.68	.1

[a] These data were obtained using a Hayes X-ray spectrometer, Cu, Kα radiation, a Ni filter, a tube voltage of 30 kv., and a filament current of 15 ma. Samples were mounted in capillary tubes prepared as described by Frick, *et al.* [R. Frick, O. Lohrmann and W. Schroeder, *Z. Elektrochem.*, **47**, 374 (1941)]. [b] Since question has been raised concerning the problem of adequate proof of the authenticity of this material,[11] it is significant that by comparison with data available in the A. S. T. M. Index of X-ray Diffraction Patterns and elsewhere, the data listed for carbon tetraiodide do not include diffraction maxima reasonably attributable to any other probable product.

tion factors corresponding to these three temperatures were 44, 49 and 58 mg., respectively. Most of the data reported in this paper involve the correction factor corresponding to a temperature of 30°. The method was also checked for possible interferences due to the presence of iodine; no such interference was observed over the range of iodine–iodide concentrations encountered in the present studies. Guanidine solutions containing copper were analyzed in the usual manner following removal of copper by precipitation with hydrogen sulfide in the presence of 0.3 *M* acid followed by boiling to expel excess hydrogen sulfide.

Procedures.—All reactions in ammonia at or above 25° were carried out under strictly anhydrous conditions in sealed Pyrex tubes that were heated to the desired temperature in a suitable autoclave containing sufficient commercial ammonia to equalize the pressure. Both the equipment and procedures have been described in detail elsewhere.[23]

Results

Carbon Tetraiodide. Preliminary Experiments.—Exposure of pure carbon tetraiodide to ammonia at −38° converted the bright red solid to a yellow solid. When the ammonia was evaporated or displaced by means of a stream of dry nitrogen, orange colored crystals were formed; these were identified as carbon tetraiodide by means of an X-ray diffraction pattern. The iodide absorbs ammonia reversibly at the boiling point of ammonia (−33.5°). When known weights of carbon tetraiodide were treated *in vacuo* with measured quantities of anhydrous ammonia gas at −50°, the up-take of ammonia by the solid was continuous until the mole ratio NH_3/CI_4 was exactly 2.00. Thereafter the character of the solid phase changed abruptly as evidenced by agglomeration indicative of incipient condensation of ammonia. This behavior is clearly indicative of the formation of the 2-ammonate, $CI_4{\cdot}2NH_3$.

At −33.5°, carbon tetraiodide appeared to be only slightly soluble in liquid ammonia; however, the products of the interaction of the iodide and ammonia over the temperature range 25–250° were soluble at −33.5°. After carbon tetraiodide was treated with excess liquid ammonia for 18 hr. at 25°, evaporation of the ammonia followed by addition of water resulted in the precipitation of orange colored crystals of unchanged carbon tetraiodide in quantity considerably less than that introduced initially. The unchanged starting material was identified by analysis (calcd. for CI_4: I, 97.7; found: I, 97.6) and by means of an X-ray diffraction pattern. When 3.0 g. of the tetraiodide was treated with excess liquid ammonia at 75° for 18 hr. and the solvent was thereafter evaporated, addition of water gave a precipitate consisting of *ca.* 25 mg. of tan colored crystals. This product was separated, dried and extracted with diethyl ether. From the ether extract yellow crystals having the odor characteristic of iodoform were isolated, and these crystals gave an X-ray diffraction pattern substantially identical with that for iodoform. Addition of saturated ammonium picrate solution to the original aqueous filtrate yielded insoluble guanidine picrate which was also identified on the basis of its X-ray diffraction pattern.

Unless indicated to the contrary, all of the experiments described below employed 3.0 g. of carbon tetraiodide (either alone or in the presence of other specified reactants) together with sufficient liquid ammonia to provide a total solution volume of 25 ml.

Ammonolysis.—The appearance of both iodide ion and guanidine was determined over the temperature range 25–250°. For reaction times of 18 hr., the yield of guanidine increased progressively from 36% at 25° to 92% at 150°, above which the yield remained essentially constant. At 25°, 87% of the iodine was accounted for as iodide ion; this increased to 100% at and above 100°.

The formation of guanidine and iodide ion in the liquid phase reaction at 125° was studied using the quantities of reactants previously specified. The resulting data are shown in Fig. 1. In separate control experiments, it was found that appreciable decomposition of carbon tetraiodide does not occur when the solid is heated for 12 min. in a sealed tube at 125° *in the absence of ammonia;* most of the carbon tetraiodide was recovered unchanged.

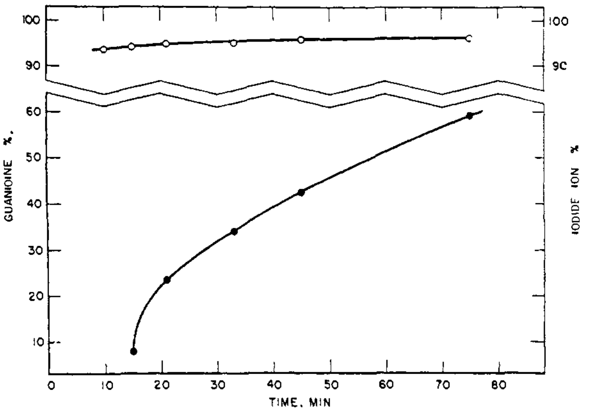

Fig. 1.—Ammonolysis of carbon tetraiodide at 125°: ●, guanidine formed; O, iodine accounted for as iodide ion.

Mechanism of Ammonolysis.—Since in excess of 94% of the carbon tetraiodide reacts before any guanidine is formed (Fig. 1), it is reasonable to assume that the rate-controlling step is the reaction of a single carbon-containing intermediate and that the concentration of all other intermediates is negligible. Thus, a plot of log concentration of this assumed intermediate *vs.* time (Fig. 2, upper curve) shows the reaction to be first order. Supporting evidence was obtained in experiments in which the quantity of carbon tetraiodide was 1.5 rather than 3.0 g., but sufficient ammonium iodide was added to provide the same total iodine concentration as was employed in the runs on a 3.0-g. scale. Thus, the carbon concentration was halved while the iodine and ammonia concentrations were held constant. The experimental data for both series are shown in Fig. 3 and the first-order relationship of concentration of intermediate and time is shown by the lower curve in Fig. 2. Halving the concentration of the carbon-containing intermediate was found to decrease the initial rate from 27×10^{-6} to 13.6×10^{-6} mole/liter/sec., thus confirming the first order dependence.

In view of the data of Fig. 1, experiments having as their objective the isolation of the carbon-containing intermediate(s) were concerned largely with the reaction time interval of 10–14 min. In a typical case, the reactants were heated for 10 min. at 125°, the ammonia was evaporated and the residual solids were extracted with anhydrous diethyl ether. Ammonia was again condensed on the ether-insoluble solid

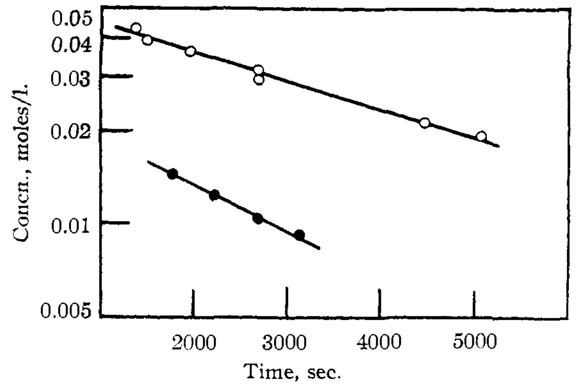

Fig. 2.—Ammonolysis of carbon tetraiodide; first-order rate plots: O, CI_4 intermediate (3-g. scale); ●, CI_4 intermediate (1.5-g. scale), 1.67 g. NH_4I added.

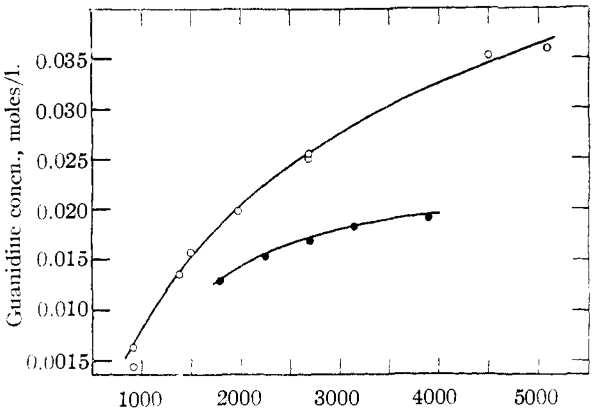

Fig. 3.—Formation of guanidine from carbon tetraiodide at 125°: O, CI_4, 0.00585 mole; ●, CI_4, 0.00289 mole, NH_4I, 0.0116 mole.

(following evacuation) and reaction was continued for 14 hr. at 125° to provide a final guanidine yield of 50%. Ether was evaporated from the extract, whereupon impure iodoform separated. The iodoform was purified by extraction with water; addition of silver nitrate solution to the water extract resulted in precipitation of silver cyanamide. Both iodoform and silver cyanamide were identified by means of X-ray diffraction patterns. The quantities of these two products isolated did not in any case account for more than 2% of the carbon used as carbon tetraiodide.

To determine whether guanidine may be formed from iodoform, 1.03 g. of iodoform and 0.67 g. of iodine in 25 ml. of liquid ammonia was heated for 16 hr. at 125°. After removal of the solvent, the residue was found to yield 0.510 g. of guanidine picrate equivalent to 0.104 g. of guanidine, or a yield of 67%. In order to show that the formation of iodoform from carbon tetraiodide is reversible even at relatively low temperatures, 0.207 g. of iodoform at −70° was treated with 20 ml. of liquid ammonia saturated with respect to iodine at −70°. After evaporation of the ammonia, the residual solid was orange-colored, had the characteristic odor of iodoform, and was insoluble in water. An X-ray diffraction pattern showed that the solid consisted principally of carbon tetraiodide; the increase in weight found (41.5 mg.) corresponds to a 63% conversion.

Since a third-order reaction might be rate-controlling, attention was directed toward the possible involvement of the trimers, melamine and cyanuric iodide. In separate experiments, 1.0-g. samples of melamine and cyanuric iodide in 25 ml. of liquid ammonia were heated for 25 min. at 125°. In both cases, examination of the solid residue that remained upon evaporation of the solvent failed to provide evidence of the presence of guanidine. In related experiments, however, the monomer, cyanogen iodide was shown to react with liquid ammonia to form guanidine.[24] From 0.01 mole of cyanogen iodide and 25 ml. of liquid ammonia after 33 min. at 125°, a guanidine yield of 25% was found; the yield was 36% after 55 min. The yield after 11 min. (8%) was increased to 26% by addition of one mole of ammonium iodide/mole of cyanogen iodide, thus reflecting an additional similarity to the carbon tetraiodide reaction. However, cyanogen iodide sublimes readily, and it could not be detected by heating intermediate products from reactions employing carbon tetraiodide as the starting material.

Catalysis of the ammonolysis of carbon tetraiodide by iodine (or the products of its interaction with ammonia) was shown in early experiments employing carbon tetraiodide contaminated with small but undetermined quantities of elemental iodine. Thus, impure carbon tetraiodide gave a 61% yield of guanidine after 35 min. at 125° while an analogous case employing pure carbon tetraiodide gave only a 36% yield. That this effect is specific to iodide ion was shown as follows. Separate runs employing ammonium iodide and ammonium chloride in a 3:1 mole ratio to carbon tetraiodide were carried out for 12 min. at 125°. The product from the tube containing ammonium iodide gave a 45% yield of guanidine, while that from the tube containing ammonium chloride gave a 9% yield. (With no added salt (Fig. 1), the yield is less than 5%.) As a means of increasing the iodide ion concentration without at the same time increasing the ammonium ion concentration, runs employing the soluble iodide of bismuth(III) were carried out using a reaction time of 15 min. at 125°. In control runs not employing added salt, the guanidine yield was 15%; for NH_4I/CI_4 at 1:1 and 3:1, the yields were 18 and 51%, respectively; for BiI_3/CI_4 at 1:1, the yield was 63%.

In still other experiments bearing upon the mechanism of this reaction but not reported here in detail, (a) the contribution of a free radical mechanism was shown to be either absent or minor, as evidenced by the fact that the guanidine yield was not decreased appreciably by the addition of nitric oxide,[25] and (b) reactions employing silver iodide as one of the initial reactants resulted in appreciable catalysis of the reaction but did not permit isolation of larger quantities of cyanamide at short reaction time intervals.[26]

Carbon Tetrabromide. Preliminary Experiments.—There is no evidence of change when liquid ammonia is condensed upon carbon tetrabromide at temperatures over the range −70 to −33.5°; the bromide is however appreciably more soluble at −33.5° than the tetraiodide. Absence of reaction is further indicated by the fact that the specific conductance of a solution of 1.330 g. of carbon tetrabromide in 150 ml. of anhydrous liquid ammonia increases regularly from 4.87 ohms^{-1} ($\times 10^{-5}$) at −73° to 10.41 at −33°, then decreases regularly to 4.90 at −73°.

When carbon tetrabromide is treated with liquid ammonia at 125° for time intervals of the order of 40 min., and the excess ammonia is evaporated, treatment of the residue with water produces an aqueous solution from which guanidine picrate is precipitated upon addition of ammonium picrate solution. The guanidine picrate was identified by means of its X-ray diffraction pattern. The water-insoluble products consist of a white solid identified as unchanged carbon tetrabromide, m.p., 91°, and a few drops of liquid identified as bromoform, m.p. 8–10°, b.p. 145–150° (*cf.*[27] m.p. 8.3°; b.p. 149.2°).

Ammonolysis.—All experiments in this section employed 3.0 g. of carbon tetrabromide and sufficient anhydrous liquid ammonia to provide a solution volume of 25 ml.

In a manner similar to that described for carbon tetra-

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[24] The formation of guanidine from cyanogen iodide and ammonia in ethanol at 100° has been reported previously [A. Bannow, *Ber.*, **4**, 162 (1871)].

[25] K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 189.

[26] It is of interest to record, incidentally, that when silver nitrate is used similarly guanidine is not found as a reaction product. Since in independent experiments it was found that ammonium nitrate catalyzes guanidine formation to approximately the same extent as ammonium chloride, this cannot be attributed to either silver ion or nitrate ion in the absence of the other. Accordingly, it is suggested that failure to isolate guanidine when silver nitrate is used may be attributed to a silver ion-catalyzed oxidation of guanidine.

[27] J. Timmermans, "Physico-chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York, N. Y., 1950, pp. 225–226.

iodide, bromide ion and guanidine formation was measured for a reaction time of 18 hr. over the temperature range 25–250°. At 25°, the yields of guanidine and bromide ion were, respectively, 0 and 3%; at 75°, 13 and 64%. Over the range 100–250°, the yield of guanidine varied over the range 62–66% while bromine accounted for as bromide ion amounted to 97–100%. In this case also, explosions occurred when attempts were made to carry out the reaction at 300°.

The formation of guanidine and bromide ion at 125° as a function of time is shown in Fig. 4.

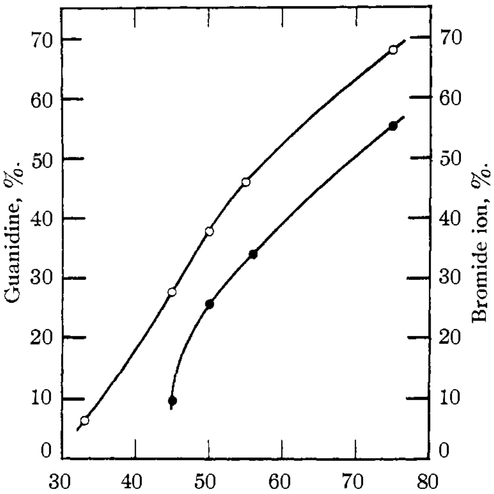

Fig. 4.—Ammonolysis of carbon tetrabromide at 125°: ●, guanidine formed; O, bromine accounted for as bromide ion.

Since addition of 0.01 mole of ammonium bromide to the reaction mixture in a run at 150° for 18 hr. increased the guanidine yield from 62 to 83%, the effect of various bromides was examined in more detail in reactions carried out at 125° in the liquid phase. On the basis of Fig. 4, the reaction time selected for these experiments was 46 min., *i.e.*, that corresponding to the first appearance of guanidine as a reaction product. The resulting data are given in Table II.

TABLE II

CATALYSIS OF THE AMMONOLYSIS OF CARBON TETRABROMIDE BY BROMIDES

Salt	Moles added $(\times 10^{-3})$	Yield, % Guanidine	[a]Br^- from CBr_4
None	. .	<5	15
NaBr	3.6	21	33
KBr	3.6	18	33
$CoBr_2$	1.8	0	5
$BaBr_2$	1.8	<5	. .
$AlBr_3$	1 2	10	19
$BiBr_3$	1.2	5	13

[a] Total Br^- found less that added as salt.

In a similar experiment, addition of equivalent amounts of bromine as elemental bromine and as ammonium bromide showed no significant difference in catalytic effect.

Carbon Tetrachloride.—All experiments described in this section involved the use of 7.90 g. (0.051 mole) of carbon tetrachloride in 25 ml. of liquid ammonia.

Ammonolysis.—For a reaction time of 18 hr. at 100, 150 and 200°, guanidine was not formed by the interaction of carbon tetrachloride and ammonia, and the extent of ammonolysis as indicated by available chloride ion was less than 1%. At 300°, the chloride was 11% ammonolyzed and the yield of guanidine was 10%. The formation of guanidine and chloride ion as a function of time is shown by Fig. 5.

Addition of one mole of ammonium chloride/mole of carbon tetrachloride increased the yield of guanidine from 10 to 24%. The influence of several other catalysts is shown by the data of Table III; these data correspond to a temperature of 150° and a reaction time of 18 hr.

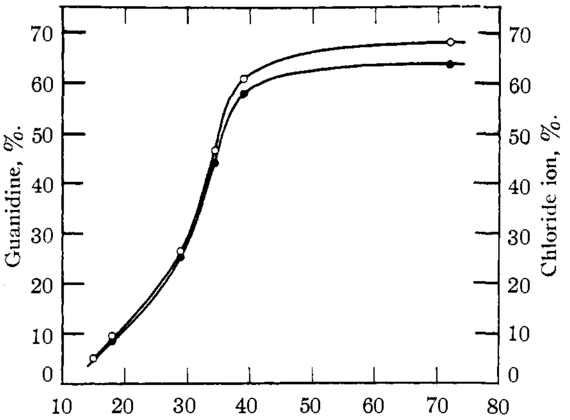

Fig. 5.—Ammonolysis of carbon tetrachloride at 125°: ●, guanidine formed; O, chlorine accounted for as chloride ion.

TABLE III

CATALYSIS OF THE AMMONOLYSIS OF CARBON TETRACHLORIDE AT 150°

Catalyst	Moles added $(\times 10^{-3})$	Guanidine yield, %
None	. .	0
Cu	10.7	2
I_2	5.5	13
	52.0	16
Cu	10.9	
I_2	5.5	8
FeO	5.5	8

The catalytic effect of certain iodides at 300° and a reaction time of 18 hr. is shown in Table IV.

TABLE IV

CATALYSIS OF THE AMMONOLYSIS OF CARBON TETRACHLORIDE BY IODIDES

Salt	Moles salt/ mole CCl_4	Temp., °C.	Guanidine Yield, %
NH_4I	0.1	250	40
	0.6	250	46
	0.5	300	74
	1.0	300	83
	2.0	300	80
KI	1.0	300	84
AgI	1.0	300	32
Cu_2I_2	1.0	300	38
BiI_3	0.1	250	51
CI_4	0.1	250	48

Discussion

At or below the boiling point of liquid ammonia, the interaction of carbon tetraiodide and ammonia is limited to the formation of a 2-ammonate which is unstable at higher temperatures. Even at temperatures as low as 25°, however, reaction as evidenced by the availability of iodide ion is extensive. Use of this criterion for extent of ammonolysis is justified even though it is recognized that iodide ion may arise from a rapid secondary hydrolysis of an iodine-containing intermediate when the product of the reaction under anhydrous conditions is first contacted with water. However, this must necessarily have been preceded by a primary reaction with ammonia. The formation of iodide ion by a rapid direct hydrolysis of carbon tetraiodide (or iodoform) seems precluded by the fact that both are relatively insoluble in and unreactive toward cold water. The extent of formation of iodide ion may therefore be taken as a measure of the minimum extent of conversion of carbon tetraiodide.

With increase in temperature, the yield of guanidine increases and reaches a maximum value at about 150°. As shown by Fig. 1, however, ammonolysis is 94% complete at 125° before any guanidine is formed. Ammonolysis is substantially complete after 18 hr. at 100°. In the early stages of the reaction, carbon tetraiodide must react to provide iodide ion and form a carbon-containing intermediate which is a precursor of guanidine. The reaction has been shown to be first order with respect to the concentration of this intermediate. Although efforts to isolate the intermediate in question were only partially successful, positive identification of cyanamide and iodoform was accomplished. The fact that iodoform was isolated from the products of reaction under strictly anhydrous conditions by extraction with anhydrous ether precludes the possibility that this product was formed in a secondary hydrolysis step. The presence of small quantities of cyanamide (a metaammonocarbonic acid) cannot reasonably be attributed to the deammonation of guanidine (an orthoammonocarbonic acid) since the latter is not even detectable during the time intervals within which the presence of cyanamide could be demonstrated. The presence of iodoform in the early stages of the reaction could result from the reaction

$$CI_4 + NH_4I \rightleftharpoons CHI_3 + I_2 + NH_3$$

as shown by the experiments described above, this reaction is reversible. Alternatively, the iodoform may be converted directly to guanidine, but that this is improbable is indicated by the fact that ammonolysis of iodoform should be expected to yield at least detectable concentrations of HCN. Several attempts to detect cyanide ion led to negative results. Also, it is significant in this connection that efforts to convert bromoform to guanidine by reaction with ammonia were unsuccessful.

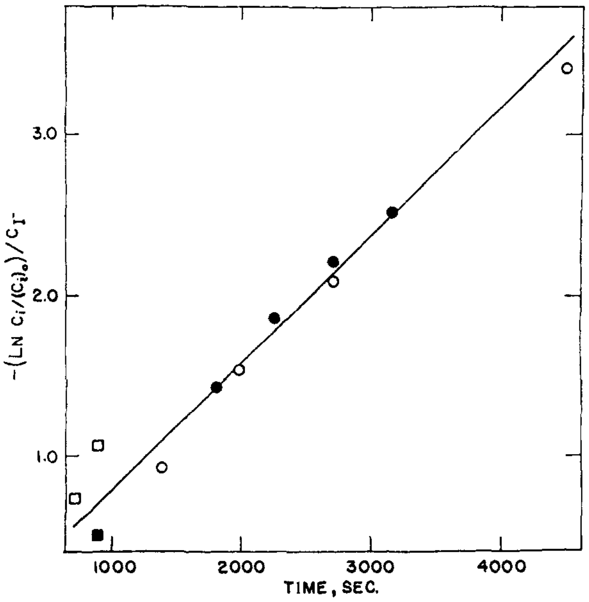

Fig. 6.—Correlation of data relating to the ammonolysis of carbon tetraiodide at 125°: ○, 3.0 g. CI_4; ●, 1.5 g. CI_4 + 1.67 g. NH_4I (1:4 mole ratio); □, CI_4 + NH_4I (1:3 mole ratio); ■, CI_4 + NH_4I (1:1 mole ratio).

Other possible intermediates that merit consideration are either largely ruled out by the experiments described above, or are highly improbable at the elevated temperatures involved in most of the present experiments. A possible exception is cyanogen iodide, the intermediation of which may be represented by

$$CI_4 + 4NH_3 \longrightarrow ICN + 3NH_4I$$
$$ICN + 3NH_3 \longrightarrow NH_2C(=NH)NH_2 + NH_4I$$

Unfortunately, no success attended efforts to demonstrate the presence of cyanogen iodide among the products of reaction at several different time intervals.

If the reaction is assumed to occur entirely in the liquid phase, the volume of which is estimated[28] to be 40 ml. at 125°, the rate data are reasonably well represented (in mole liter sec. units) by

$$\ln \frac{C_I}{(C_I)_0} = -8.0 \times 10^4 (C_{I^-})t \qquad (1)$$

where $(C_I)_0$ is the initial concentration of the carbon-containing intermediate.[29] It was observed that on a mole for mole basis, iodide ion added as ammonium iodide was twice as effective as a catalyst as iodine available (presumably as I^-) from the ammonolytic cleavage of carbon tetraiodide. This is indicated also by the relative slopes of the two curves included in Fig. 2; the slope of the lower curve is greater although the total amount of iodine present was the same in both cases. Accordingly, the iodide ion concentration term in the preceding equation is weighted so as to take this effect into account. Further, a correlation of data relating to runs involving different quantities of carbon tetraiodide both in the presence and absence of added ammonium iodide is shown in Fig. 6, in which

$$-\left[\ln \frac{C_I}{(C_I)_0} \Big/ C_{I^-}\right]$$

is plotted against time. The total iodide ion concentration is taken as equal to one-half of the iodide ion concentration available from the ammonolysis of carbon tetraiodide plus that provided by added ammonium iodide, and it is seen that all of the experimental points fall on or near a straight line of slope = 8.0 × 10^{-4}.

With reference to the interaction of carbon tetrabromide and ammonia, it is evident from the data of Fig. 4 that the limiting rate in the formation of guanidine is the ammonolysis of the bromide and not

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(28) "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 234.

(29) Since the solution volume at the reaction temperature can only be approximated, the concentrations expressed in Figs. 2 and 3 are based upon the total reaction tube volume of 100 ml.

the reaction of an intermediate as in the case of carbon tetraiodide. At 150°, the formation of guanidine apparently reaches equilibrium at a guanidine yield of 83%. If it is assumed that the quantity of carbon tetrabromide that is converted to bromoform (presumably in a manner analogous to that suggested above for iodoform formation) is negligible, and the solution volume is taken to be 40 ml., the data for rate of ammonolysis at 125° are well represented by

$$\ln \frac{C_{\mathrm{CBr_4}}}{(C_{\mathrm{CBr_4}})_0} = -4.4 \times 10^{-4}(C_{\mathrm{Br^-}})t \qquad (2)$$

Values calculated on the basis of equation 2 are in good agreement with the experimental data for ammonolysis up to about 55% conversion; even at 70% conversion, deviation of the calculated from the experimental curve is still not great.

Since Fig. 4 shows that, if a carbon-containing intermediate were involved in this reaction, its steady state concentration would correspond to a maximum of the order of 10% of the total carbon present, hence, the possibility of isolating such an intermediate would be remote. With the single exception of the identification of bromoform as a product of reaction over relatively short time intervals, all other experiments designed to detect intermediates gave either wholly negative results or were inconclusive.

The shape of the initial portion of the curve shown in Fig. 4 suggests that the ammonolysis of carbon tetrabromide is autocatalyzed. This was confirmed by demonstrating a marked increased in initial rate upon addition of ammonium bromide as well as bromides not involving ammonium ion. The relatively greater effectiveness of sodium and potassium bromides (Table II) is probably attributable to their greater solubility in liquid ammonia.

The rate of reaction between carbon tetrachloride and ammonia is appreciable only at temperatures $\geqq 300°$. As in the case of the tetrabromide, the controlling rate is that of ammonolysis (Fig. 5). If concentrations are based upon the entire volume of the reaction tube, it may be shown that the rate data for reactions at 300° may be expressed as

$$\ln \frac{C_{\mathrm{CCl_4}}}{(C_{\mathrm{CCl_4}})_0} = -5.3 \times 10^{-6}(C_{\mathrm{Cl^-}})t \qquad (3)$$

A comparison of observed and calculated rates of ammonolysis shows excellent agreement up to about 60% ammonolysis; thereafter, a marked deviation between the calculated and observed values reflects the experimentally observed approach to equilibrium.

The data included in Table III were obtained in an unsuccessful effort to duplicate the results reported by Stähler to the effect that a 35–40% conversion of carbon tetrachloride to guanidine is obtained from the reaction with ammonia at 140° through the use of copper and iodine as the catalyst. Our results show that copper alone is devoid of catalytic activity while copper and iodine together result in only an 8% yield of guanidine; this is scarcely significant since the same yield was obtained using iron(II) oxide. With iodine in the absence of copper, the yield was 13%, but this is likely attributable to the formation of iodide ion by the interaction of iodine and ammonia. This is reasonable since it was found that iodide ion added in the form of ammonium iodide was more than three times as effective as chloride ion (at the same molar concentration) added as ammonium chloride. As shown in Table IV, the maximum effect of ammonium iodide is realized when this salt and carbon tetrachloride are present in a 1:1 mole ratio.

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An Infrared Study of the Nature of Bone Carbonate[1a]

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Although it has been known for many years that bone mineral and related substances contain carbon dioxide, direct evidence regarding its state in these solids has been lacking. A study of the infrared spectra of pure carbonates and bicarbonates between 11 and 12μ has confirmed the possibility of distinguishing bicarbonate from carbonate. The application of this information to the spectra of apatite, and of bone and other calcified tissues has shown clearly that the carbon dioxide is present as carbonate to the complete exclusion of bicarbonate.

Carbon dioxide is a major constituent of bone mineral, approximately 5% by weight. Its state in the solid has an important bearing on questions concerning the nature of the crystalline lattice and the physiological availability of what could be a tremendous alkali reserve. None of the several theories concerning the nature of the carbon dioxide of bone has been experimentally confirmed or refuted. Rather, there exists an array of suggestions: (a) that the carbon dioxide represents entrapped alkali bicarbonate[2]; (b) that carbon dioxide as carbonate substitutes isomorphically for phosphate ions in the crystal[3]; (c) that much of the carbon dioxide is surface-bound by adsorptive forces[4]; (d) that carbon dioxide is, in part, at least, surface-bound by an ion-exchange process displacing phosphate

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(1) (a) This paper is based on work performed under contract with the United States Atomic Energy Commission at the University of Rochester Atomic Energy Project, Rochester, New York. (b) Department of Chemistry, Emory University, Georgia.

(2) R. Klement, *Klin. Wochschr.*, **16**, 591 (1937).

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