pressure, in contradiction to all expectations. This effect is probably spurious; the other substances do not show it.

While the isotherms of all three fluids are closely similar, the isosteres of silicon tetrafluoride deviate systematically from nearly straight lines, and almost seem to belong to portions of different sets, as though some permanent change had affected the adsorbent between the work at lower and at higher temperatures. Unfortunately this was not noticed until the apparatus had been demolished and control experiments made impossible.

Summary

Adsorption equilibrium between charcoal and three gases is investigated with particular attention to the region near the critical point. The results are of the general nature anticipated. In the case of carbon dioxide, a successful application of the Polanyi theory has been made.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

Hydrazoic Acid[1]

BY EDWARD C. FRANKLIN

Some of the methods for the preparation of hydrazoic acid and a majority of its reactions lead fairly definitely to the conclusion that it is an ammono nitric acid. Other methods of preparation and a few of its reactions are best explained on the assumption that it is a cyclic nitrous acid acid hydrazide, while certain minor considerations lend support to the view that it is a cyclic ammono hyponitrous acid.

The tautomeric properties of hydrazoic acid are discussed in another place.[2] Here an account is given of experimental work which supports the view, first expressed by Turrentine,[3] that hydrazoic acid may be regarded an ammono nitric acid.

Ammonolysis of Potassium Aquonitrate to Potassium Ammononitrate.—On the assumption that hydrazoic acid is an ammono nitric acid it was surmised that it might be possible to obtain the acid by the ammonolysis of aquo nitric acid say in accordance with the one or the other of the equations, $HONO_2 + 2NH_3 = HN{=}N{\equiv}N + 3H_2O$ or $KONO_2 + 2NH_3 = KN{=}N{\equiv}N + 3H_2O$. As a matter of fact no such reactions take place when either ammonium nitrate or potassium nitrate is heated in liquid ammonia solution. However, it was found that hydrazoic acid in the form of its potassium salt, together with potassium hydroxide, is formed when a liquid ammonia solution containing potassium aquonitrate and potassium amide is heated for a time at temperatures around 80–90°. It was later found that higher temperatures up to 130 to 140° give better yields in a shorter time. At still higher temperatures, 200° or higher, liberal quantities of nitrogen are set free and the yield of potassium azide is lower. Representing the reaction involved by the equation $KONO_2 + 3KNH_2 = KN{=}N{\equiv}N + 3KOH + NH_3$, and assuming that the nitric acid nitrogen present in potassium aquonitrate persists as such in potassium azide, it will be clear that potassium aquonitrate undergoes ammonolysis to form a potassium ammononitrate.

A liquid ammonia solution containing potassium nitrate and potassium amide was heated in a sealed glass tube at a temperature of 90° for three hours. After cooling, a crystalline precipitate, which was later identified as potassium hydroxide, was observed to have settled to the bottom of the tube. After opening the tip of the tube and allowing the liquid ammonia to evaporate away, the solid residue left behind was dissolved in water and the solution thus obtained was rendered slightly acid by means of dilute nitric acid. Addition of ferric chloride to a portion of this solution gave the brown coloration described by Curtius as a test for hydrazoic acid. On adding silver nitrate to the remainder of the solution, a white precipitate was formed which was filtered off, washed, and after dividing into small portions, dried in an exsiccator over sulfuric acid. The dried solid, when touched with a hot glass rod or when struck with a hammer, exploded with the powerful detonation characteristic of silver azide.

Following the above described procedure and using potassium amide in excess, Harker obtained yields of potassium azide as high as 75% of the amount calculated on the basis of the above equation. By using sodium nitrate and sodium amide

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[1] The laboratory work upon which this report is based was done by the author, Faw Yap Chuck, Thesis, Stanford University, 1925, J. B. Harker, Thesis, Stanford University, 1927, and E. S. Goodyear, Thesis, Stanford University, 1928.

[2] "The Nitrogen System of Compounds," American Chemical Society Monograph, 1934.

[3] Turrentine, THIS JOURNAL, **34**, 385 (1912).

he obtained yields of sodium azide up to 16%, while an 80% yield of lead azide was achieved by heating lead nitrate with an excess of potassium amide in liquid ammonia solution. It is interesting to add that attempts to ammonolyze potassium nitrate by heating liquid ammonia solutions of this salt together with potassium amide in a closed steel tube were unsuccessful. Iron was found to inhibit the formation of potassium azide. Chuck identified potassium azide as a product of the action of fused potassium amide on potassium nitrate in an atmosphere of ammonia.

Browne and Wilcoxon[4] obtained good yields of sodium azide by the action of fused sodium amide on sodium nitrate.

The reaction represented by the above equation read from right to left has not been accomplished. That is to say, potassium azide has not been converted into potassium nitrate by the action of water alone or of water acidulated with sulfuric acid or made alkaline by the presence of potassium hydroxide.

Action of Hydrazoic Acid on Metals.—Curtius and Rissom[5] report that zinc, iron, cadmium and manganese dissolve in aqueous hydrazoic acid with the evolution of hydrogen, Curtius and Darapsky[6] that metallic arsenic dissolves readily in hydrazoic acid solution with vigorous evolution of gas and that zinc dissolves to form zinc azide, hydrogen and ammonia. As will be shown below, the gas formed when these metals dissolve in aqueous hydrazoic acid is nitrogen and not hydrogen. Browne and Houlehan,[7] found that ammonium azide in liquid ammonia solution acts on lithium, sodium, calcium and magnesium to form the respective metallic azides with the evolution of hydrogen. Turrentine and Moore,[8] observed that hydrazoic acid in water solution acts on copper to form cupric azide, ammonia and nitrogen, while Cooke[9] identified hydrazine among the products of the action of reducing agents on hydrazoic acid.

Working in this Laboratory Chuck, Harker and Goodyear have found that aqueous hydrazoic acid acts on zinc, iron, manganese, nickel and copper without the evolution of hydrogen to form the respective metallic azides, nitrogen and ammonia together with small amounts of hydrazine, and that metallic magnesium dissolves with the formation of magnesium azide, nitrogen, hydrogen, ammonia and hydrazine. The amounts of nitrogen, ammonia and hydrazine, and in the case of magnesium the amount of hydrogen, varied within rather wide limits. It does not seem worth while to record the experimental data here.

The action of aqueous hydrazoic acid on zinc, iron, manganese nickel and copper resembles in a very striking way the action of ordinary nitric acid on the same metals. When for example metallic zinc dissolves in aquo nitric acid, zinc nitrate and, depending upon conditions, various reduction products of nitric are formed. Nitric acid oxidizes the zinc while simultaneously the zinc reduces the nitric acid. Similarly as may be represented by the equations, $Zn + 2HN{=}N{\equiv}N = Zn(N{=}N{\equiv}N)_2 + 2H$ and $HN{=}N{\equiv}N + 2H = HN{=}N{-}NH_2 \xrightarrow{-NH_3} N_2$, hydrazoic acid nitridizes (augments) metallic zinc to the dipositive state while at the same time the ammono nitric acid is reduced, let us say, to ammono nitrous acid.[10] This unknown compound immediately loses ammonia to form a hypothetical nitrous anammonide which of course appears as elementary nitrogen.

It is obviously not necessary to assume that hydrogen ions are first reduced by the zinc and that the nascent hydrogen thus formed in turn reduces the ammono nitric acid. Much more reasonably it may be supposed that the zinc reduces the nitric acid nitrogen directly as represented, in principle, by the equation, $Zn + HN{=}N{\equiv}N = Zn^{++} + HN{=}N{-}N^{--}$. Two electrons passing from the zinc atom to the nitric acid nitrogen atom brings about the augmentation of the zero valent zinc atom to the zinc ion and the concomitant reduction of nitric acid nitrogen to nitrous acid nitrogen. In any event, and independently of what the mechanism of the reactions involved may be, it is clear that the action of hydrazoic acid on zinc closely resembles that of aquo nitric acid on the same metal.

Action on Halogen Acids.—A mixture of hydrazoic acid and hydrochloric acid in water solution shows the properties of aqua regia to the extent at least that such a solution dissolves gold and platinum.[11]

(4) Browne and Wilcoxon, THIS JOURNAL, **48**, 682 (1926).

(5) Curtius and Rissom, *J. prakt. Chem.*, [2] **58**, 291 (1898).

(6) Curtius and Darapsky, *ibid.*, [2] **61**, 419 (1900).

(7) Browne and Houlehan, THIS JOURNAL, **33**, 1750 (1911).

(8) Turrentine and Moore, *ibid.*, **34**, 382 (1912).

(9) Cooke, *Proc. Chem. Soc.*, **19**, 213 (1903).

(10) It is assumed that the middle nitrogen atom in the formula $HN{=}N{\equiv}N$ represents nitric acid nitrogen, the middle one in $HN{=}N{-}NH_2$, nitrous acid nitrogen and that the remaining nitrogen atoms in both of the formulas represent ammonia nitrogen.

(11) Curtius and Rissom [*J. prakt. Chem.*, [2] **58**, 682 (1898)] retract an earlier statement to the effect that the noble metals are attacked by concentrated aqueous hydrazoic acid [Curtius, *Ber.*, **23**, 3027 (1890)].

A water solution containing sodium azide and hydrochloric acid, together with a few centigrams of metallic gold, was sealed in a glass tube and heated in a water-bath at 100°. After a few minutes it was obvious from the yellow color of the liquid that gold was going into solution. After an hour the gold had disappeared and the solution had taken on the strong yellow color of a solution of auric chloride. Addition of stannous chloride to a small portion of the solution, diluted for the purpose of the test, gave the purple of Cassius reaction. Furthermore, metallic gold was recovered from the remaining solution by the reducing action of ferrous sulfate.

A few centigrams of platinum black were similarly heated in a sealed tube with an aqueous solution of sodium azide and hydrochloric acid. The platinum was attacked and after a time a precipitate of ammonium chloroplatinate made its appearance, the ammonia necessary for the formation of this salt resulting from the reduction of the hydrazoic acid. Neither gold nor platinum is attacked when heated with liquid ammonia solutions of ammonium azide and ammonium chloride at temperatures as high as 200°.

When a water solution containing hydrazoic acid and hydrochloric acid is boiled chlorine is slowly evolved,[12] when hydrobromic acid is used instead of hydrochloric acid bromine is set free,[13] while quantitative yields of nitrogen and ammonium are achieved in a short time by boiling a water solution of hydrazoic acid with an excess ot hydriodic acid.[14]

Action on Certain Inorganic Compounds.—Harker observed that ferrous azide, formed by dissolving metallic iron in aqueous hydrazoic acid, is augmented to the ferric salt when the solution is warmed with excess of hydrazoic acid.

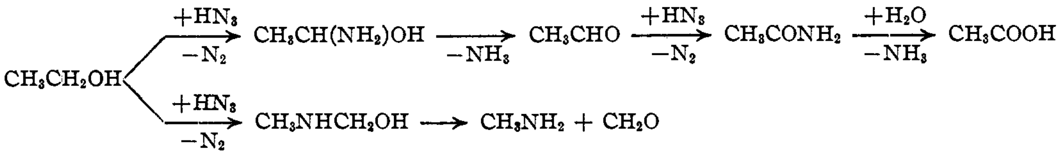
Hydrogen sulfide is nitridized to sulfur by the action of hydrazoic acid and of many organic azides.[15] Chuck found that sulfur is augmented to sulfuric acid by the action of hot aqueous hydrazoic acid and that in liquid ammonia solution at elevated temperatures it is augmented by the action of ammonium azide to sulfur compounds of undetermined composition.

Chuck dissolved stannous chloride in molten sodium amide in an atmosphere of ammonia. It was found on treating the cold melt with water and acidifying the hydrolytic products with hydrochloric acid that the tin was present as stannous tin. In a second experiment sodium azide was gradually added to the yellow melt, formed by dissolving stannous chloride in fused sodium amide, until the color had disappeared. The cold cake was treated with water and then dissolved in dilute hydrochloric acid. The tin in the solution thus formed was found to be in the stannic state. It follows from these observations that a sodium ammonostannite, formed by dissolving stannous chloride in an excess of sodium fused sodium amide is nitridized to a sodium ammonostannate by the action of sodium ammononitrate. The reactions involved may be represented by the equations $SnCl_2 + 3NaNH_2 = SnNNa + 2NaCl + 2NH_3$ and $SnNNa + NaNNN = Sn(NNa)_2 + N_2$.[16]

An account of the nitridizing action of sodium azide on sodium cyanide to form disodium cyanamide is recorded and discussed elsewhere.[17]

Action on Alcohols, Aldehydes and Ketones.—Just as nitric acid energetically oxidizes the alcohols, aldehydes and ketones so one might expect to find these compounds ready to undergo nitridation, or in general terms augmentation, under the action of hydrazoic acid. Only a limited number of reactions of this kind have been studied.

Chuck found that acetaldehyde, acetic acid, methylamine and ammonia are formed when a water solution containing ethyl alcohol, sodium azide and sulfuric acid is heated. A reasonable explanation of Chuck's results is summarized by means of the scheme



in accordance with which ethyl alcohol is augmented partly to aldehyde ammonia and partly to the formaldehyde-acetal, CH_3NHCH_2OH. The former compound, in the presence of sulfuric acid, yields acetaldehyde which in turn is augmented to acetamide. This aquo ammono acetic acid is then hydrolyzed to aquo acetic acid and ammonia. The latter compound, in acid solu-

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[12] Browne and Hoel, THIS JOURNAL, **44**, 2116 (1922).

[13] Observations made in this Laboratory.

[14] Hofmann, Hock and Kirmreuther, *Ann.*, **380**, 140 (1911).

[15] Hart, THIS JOURNAL, **50**, 1924 (1928).

[16] It is noted that a potassium ammonostannite [Bergstrom, *J. Phys. Chem.*, **32**, 438 (1929)] and a potassium ammonostannate [Fitzgerald, THIS JOURNAL, **29**, 1693 (1907)] have been prepared. Raschig ["Schwefel- und Stickstoffstudien," Berlin, p. 213] reports the reducing action of stannous chloride on hydrazoic acid.

[17] Franklin, *J. Phys. Chem.*, **27**, 172 (1923).

tion, breaks down to form formaldehyde and methylamine. Chuck was unable to identify formaldehyde or formic acid among the reaction products. He did not look for carbon dioxide.

Benzyl alcohol heated in a similar manner with sodium azide and dilute sulfuric acid was found to yield benzaldehyde, benzoic acid and aniline in liberal quantities. Considerable amounts of a tarry oil, the nature of which remains unknown, were formed at the same time.

A liquid ammonia solution containing methylamine and an excess of ammonium azide was heated in a closed tube at 200° for twelve hours. Nitrogen and guanidine were found among the products of the nitridizing action of ammono nitric acid on this ammono alcohol. The yields, which were abundant, were not determined quantitatively.

Guanidine was obtained by similarly heating liquid ammonia solutions of hexamethylenetetramine with ammonium azide and with sodium azide. A dimer of methylene nitride, which is as near the nitrogen analog of formaldehyde as the trivalency of nitrogen permits, is nitridized to an ammono carbonic acid.

When heated in liquid ammonia solution with ammonium azide benzylamine is nitridized to a product, either benzamidine or phenyl cyanide, which on hydrolysis yields aquo benzoic acid.

Among the products formed by heating hydrobenzamide with ammonium azide in liquid ammonia solution benzonitrile and lophine were identified. Benzonitrile, which is the anammonide of benzoic acid, is formed by the nitridizing action of ammono nitric acid on the benzaldehyde-acetal. Lophine has long been known as a product of the oxidation of hydrobenzamide.

The action of hydrazoic acid on certain aldehydes and ketones as reported by Schmidt[18] involves the nitridizing action of ammono nitric acid.

Summary

An account is given of experimental work which supports the assumption that hydrazoic acid is an ammono nitric acid.

[18] Schmidt, *Ber.*, **57**, 704 (1924); *Chem. Abst.*, **19**, 3248 (1925).

STANFORD UNIV., CALIF. RECEIVED OCTOBER 18, 1933

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Kinetics of the Decomposition of the Trichloroacetates in Various Solvents[1]

BY FRANK H. VERHOEK

The decomposition of trichloroacetic acid is reported in the literature to follow the equation

$$CCl_3COOH \longrightarrow CHCl_3 + CO_2 \qquad (1)$$

A marked change in the rate of decomposition with change in concentration indicated that the reaction was not a simple unimolecular decomposition of the acid molecule. The decomposition of salts of the acid had not been studied quantitatively. Extension to several solvents seemed to offer interesting possibilities for studying the effect of solvent on reaction rate. For these reasons the present investigation was undertaken.

Trichloroacetic acid decomposes in water, and in aniline and related solvents[2a,b] where the trichloroacetate of the amine is formed. On the other hand, trichloroacetic acid does not decompose in relatively non-basic solvents; there is no decomposition in benzene, carbon bisulfide, carbon tetrachloride, ethyl ether, acetone, nitrobenzene, ethyl benzoate,[3] in toluene and chloroform.[4] In methyl[4] and ethyl[4,5] alcohols, the only reaction is that of ester formation.

Procedure

Qualitative work in connection with the present investigation showed that the presence of the ion is always necessary for decomposition. A large number of salts of trichloroacetic acid—with aniline, piperidine, pyridine, triethanolamine, ammonia, sodium, barium, copper—were prepared and their behavior studied in various solvents, chiefly at 70°. It was found that the free acid and all the salts decompose in water at practically the same rate, and that the salts decompose, also, in isoamyl alcohol, ethyl acetate, aniline, ethyl alco-

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[1] Further details concerning this work may be obtained from a thesis prepared under the direction of Farrington Daniels and submitted by the author to the University of Wisconsin in 1933 in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] (a) Silberstein, *Ber.*, **17**, 2664, (1884); (b) Goldschmidt and Brauer, *ibid.*, **39**, 109 (1906).

[3] Timofeew, *Chem. Zentr.*, II, 1651 (1925).

[4] Pearce and Nelson, *Proc. Iowa Acad. Sci.*, **36**, 251 (1929).

[5] Lichty, *Am. Chem. J.*, **18**, 597 (1896).