This offers a reasonable explanation for the lack of formation of a mixed halide phase of composition $Al_2I_2Cl_4$, corresponding to the $Al_2Br_2Cl_4$ phase found in the bromide–chloride system. The latter appears to have some thermodynamic stability (relative to $AlBr_3$ and $AlCl_3$) but owes most of its inertness toward HCl at 25° to the low reactivity of the bridge halogens.[1]

Experimental Part

The method used to study the exchange equilibrium has been described in an earlier paper.[1] Aluminum iodide (23 g.) (prepared by reaction of resublimed iodine and excess, iron-free aluminum in an evacuated thick-walled glass tube at 300°) was sublimed into the reaction vessel (painted black to minimize photodecomposition of HI), measured volumes of anhydrous HCl added, and the system allowed to equilibrate after each addition for from four to eight days. Only a small amount of hydrogen and iodine was formed during the equilibration. The HCl–HI mixture was purified by fractionation prior to analysis which was effected by measuring the vapor pressure of the liquefied mixture at −45.3°, the melting point of chlorobenzene. The vapor pressures of the pure components at −45.3° were calculated to be 498 mm. (HI)[8] and 4664 mm. (HCl).[9] As the mixtures were nearly pure HI, Raoult's law was used to relate the total vapor pressure to the composition of the mixture.

The composition of the solid at each equilibrium point was determined from the amount of hydrogen halide reacting, and checked at the end of the series of measurements by direct analysis (total halide, Mohr titration; iodine, oxidation of iodide to iodate with hypochlorite solution[1,10]). The AlI_3 was of good quality (>99% AlI_3) and remained white in powder samples of both AlI_3 and the annealed mixtures. The latter were prepared as described for mixtures of $AlBr_3$ and $AlCl_3$.[1]

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[8] J. R. Bates, J. O. Halford and L. C. Anderson, *J. Chem. Phys.*, **3**, 415 (1935).

[9] F. Henning and A. Stock, *Z. Physik*, **4**, 226 (1921).

[10] I. M. Kolthoff and H. Yutzy, *Anal. Chem.*, **9**, 75 (1937).

Department of Chemistry
University of Washington
Seattle 5, Washington

Evidence for the Presence of Hydroxylamine as an Intermediate in the Decomposition of Chloramine by Hydroxide

By Robert E. McCoy

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It has long been known that the reaction of hydroxide with chloramine solutions yields no hydroxylamine but evolves nitrogen in accordance with the equation

$$3NH_2Cl + 3OH^- \longrightarrow NH_3 + N_2 + 3H_2O + 3Cl^-$$

The present author postulated that the initial step in this reaction might indeed be

$$NH_2Cl + OH^- \longrightarrow NH_2OH + Cl^- \quad (1)$$

but that this step is slow compared to the oxidation of hydroxylamine by chloramine

$$NH_2Cl + 2NH_2OH + OH^- \longrightarrow NH_3 + N_2 + 3H_2O + Cl^- \quad (2)$$

Addition of these steps gives the previously reported reaction.

The rate of disappearance of chloramine in alkaline solutions was investigated iodometrically. With OH^- concentrations less than 1 N the decomposition was somewhat too slow to be conveniently studied. A thorough kinetic study was not attempted, since several trials with concentrated OH^- solutions showed only qualitative reproducibility, and the author was interested primarily in testing the tenability of the hypothesis previously stated. In concentrated sodium hydroxide solution the disappearance of chloramine is at first fairly rapid, but soon slows appreciably. For example, a solution initially $6^2/_3$ M in NaOH and 0.0515 M in NH_2Cl lost 32% of its oxidizing power in 5 minutes, but in 41 minutes, only 38%. It was suspected that product inhibition might account, at least in part, for this behavior. This explanation was supported by the observation that the addition of ammonia, one of the reaction products, to chloramine solutions markedly depressed the rate of decomposition by hydroxide.

The oxidation of hydroxylamine by chloramine proved much more rapid than the destruction of chloramine by hydroxide, as required by the postulated reaction route. Evolution of gas (assumed to be nitrogen) was observed on mixing 0.1 M solutions of hydroxylamine and chloramine, and the odor of ammonia could be detected shortly after mixing. Consumption of reactants agreed with the equation

$$NH_2Cl + 2NH_2OH + OH^- \longrightarrow NH_3 + N_2 + 3H_2O + Cl^-$$

Chloramine concentration was determined iodometrically after the complete destruction of hydroxylamine, as indicated by a very sensitive color test.[1] The reaction went to completion in about ten minutes at 0° in approximately neutral solution. The reaction is accelerated by addition of hydroxide and by increase in temperature. In a mixture 30% saturated with NaOH at 0° the reaction was complete within one half minute. In saturated NaOH solution at 50° the reaction was complete before any measurement could be made.

In an attempt to identify hydroxylamine before it could be oxidized, cold chloramine solution was added dropwise to a mixture of concentrated NaOH solution and cyclohexanone, stirred vigorously and maintained at a temperature in the range 50–90°. Cyclohexanone was chosen as the simplest carbonyl compound not attacked by sodium hydroxide or chloramine. The conditions were chosen in an attempt to increase the rate of formation of hydroxylamine and the rate of oxime formation, while keeping the chloramine concentration low to try to minimize the oxidation of hydroxylamine by chloramine. (Unfortunately the high OH^- concentration and higher temperature both favor the oxidation; however, no oxime was obtained at room temperature or low hydroxide concentration.) The precipitate obtained on cooling the reaction mixture contained the sodium salt of cyclohexanone oxime. On neutralization the oxime was obtained in poor over-all yield and somewhat impure condition (m.p. 86° compared to 89° for carefully purified oxime). Positive identification was obtained by X-ray diffraction analysis; similar results were obtained in several trials.

It was shown that chloramine solution attacks cyclohexanone oxime appreciably at 60° even when present as the solid sodium salt. The oxime may

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[1] A. Angeli, *Ber.*, **29**, 1884 (1896).

be much more vulnerable in the reaction mixture prior to precipitation. Moreover, it is to be expected that cyclohexanone would compete poorly with chloramine for hydroxylamine. Quantitative rate data on the formation of cyclohexanone oxime are not available; the author's qualitative observations indicate it is slow. The rate of reaction in neutral solution of hydroxylamine with acetone,[2,3] which is much more soluble than cyclohexanone, is considerably slower than the reaction of hydroxylamine and chloramine. Both reactions are base catalyzed, but it is not certain whether the order of rates is altered in very concentrated sodium hydroxide solution.

The low yield of oxime does not appear to require any path other than equations 1 and 2 for the disappearance of chloramine, and all observations made here are consistent with this as the sole path. Since the completion of this work, the author has learned of a broad program of experimental work by Dr. L. F. Audrieth and co-workers at the University of Illinois which may ultimately show that this picture of the reaction is oversimplified and perhaps incomplete. The evidence obtained here does not exclude other reaction paths, but appears at least to establish that hydroxylamine is present as an intermediate during the reaction.

Preparation and Purity of Chloramine Solutions.—Chloramine solutions were prepared by the method of Coleman and Hauser,[4] using commercial sodium hypochlorite. In some cases the solutions were purified by vacuum distillation, but no gross difference in behavior of initial and purified solutions was observed so long as ammonium and bicarbonate ions were absent. Bicarbonate ion was found to hasten the decomposition of chloramine in a manner not related to *p*H. Ammonium ion appears to slow decomposition of chloramine by hydroxide or bicarbonate.

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[2] S. F. Acree and J. M. Johnson, *Am. Chem. J.*, **38**, 258 (1907).

[3] E. Barrett and A. Lapworth, *J. Chem. Soc.*, **93**, 85 (1908).

[4] G. H. Coleman and C. R. Hauser, THIS JOURNAL, **50**, 1193 (1928).

PHYSICAL RESEARCH LABORATORY
THE DOW CHEMICAL COMPANY
MIDLAND, MICHIGAN

The Mercury-photosensitized Reactions of Tritium with Acetylene and Ethylene

BY LOUIS KAPLAN

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As a part of a study of the feasibility of introducing tritium into organic molecules by reaction with hydrogen atoms produced by mercury photosensitization, experiments were performed on systems containing acetylene and ethylene. Since there appears to have been no previous investigation of the isotopic composition of the products obtained from either of these hydrocarbons by reaction with a mixture of hydrogen isotopes under these conditions, the results of these measurements are reported here.

Experimental

Apparatus.—The reaction vessel consisted of a quartz tube irradiated with two four-watt General Electric "Germicidal" lamps. The reaction mixture was circulated through the irradiated tube by means of a Toepler pump which also served as a mercury saturator. The system, which also included a manometer, had a volume varying from 300 to 600 cc., depending on the position of the mercury in the pump.

Reagents.—Tritiated hydrogen was prepared from tritiated water by reaction with heated zinc. After passage through a trap at −195° it was diluted with electrolytic hydrogen which had been passed through a "Deoxo" catalytic purifier and then through silica gel at −195°. The final tritium content was about 10 microcuries per millimole.

Ethylene and acetylene obtained from the Matheson Chemical Co. were subjected to low-temperature fractional distillation and the center cuts were used in the reactions. The vapor pressures of these fractions remained unchanged by additional distillations.

Procedure.—Hydrogen was used in large excess in order to minimize quenching by the hydrocarbons. The hydrocarbon and tritiated hydrogen were measured into the highly evacuated system, and were mixed by operation of the Toepler pump. The total pressure was in the range of 200 to 400 mm. The mercury vapor lamps were turned on and irradiation was continued, in the experiment with ethylene, until the pressure became constant, in order to avoid the difficulty of separating ethylene from ethane. With acetylene, the reaction was stopped short of completion to permit the determination of the tritium content of the residual acetylene. After irradiation, the hydrocarbons were removed by circulating the reaction mixture through a trap at −195°. (Ethane, ethylene and acetylene were shown to be separated quantitatively in this way from synthetic mixtures with hydrogen; methane is an insignificant product from either reaction and could have little effect on the measured quantity or specific activity of the hydrogen.) The volume of hydrogen was measured manometrically and an aliquot was taken for the determination of its tritium content. The condensed hydrocarbons were transferred to a fractionation train. After each run the entire apparatus was flamed while oxygen was passed through it, in order to prevent the accumulation of polymer on the walls.

Separation of Products.—The mixture of hydrocarbons was subjected to fractionation[1] at low pressure through a train of traps maintained at successively lower temperatures. Each fraction was checked for purity by attempts at further fractionation as well as by measurement of its vapor pressure at several temperatures. Known mixtures of ethane, acetylene and butane were found to be separated quantitatively by this procedure.

Determination of Tritium.—A 10-cc. aliquot of the hydrogen, or the entire sample of hydrocarbon, was introduced into a 250-cc. ionization chamber[2] which was then filled to atmospheric pressure with propane. The ion current at saturation voltage was measured[3] with a vibrating reed electrometer.

Results and Discussion

Reactions[4] between hydrogen and hydrocarbons in the presence of mercury vapor irradiated with the mercury resonance line at 2537 Å. are initiated by the reactions

$$\mathrm{Hg}(6\ ^1S_0) + h\nu \longrightarrow \mathrm{Hg}(6\ ^3P_1) \qquad (1)$$

$$\mathrm{Hg}(6\ ^3P_1) + H_2 \longrightarrow \mathrm{Hg}(6\ ^1S_0) + 2H \text{ (or HgH + H)} \qquad (2)$$

The hydrogen atoms then react with the hydrocarbon to give free radicals which may react further in a variety of ways, including recombination, disproportionation, and attack on other molecules. If HT is present in the hydrogen, tritium atoms

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[1] E. C. Ward, *Ind. Eng. Chem., Anal. Ed.*, **10**, 169 (1938); J. J. Savelli, W. D. Seyfried and B. M. Filbert, *ibid.*, **13**, 868 (1941).

[2] C. J. Borkowski, Atomic Energy Commission document, MDDC-1099, declassified June 12, 1947.

[3] K. E. Wilzbach, A. R. Van Dyken and L. Kaplan, Argonne National Laboratory document, ANL-5143.

[4] Mercury photosensitized reactions of hydrocarbons are reviewed in E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1946.