alcohol concentration follow a general empirical equation, $S = K_1C + K_2AC$, where

S = concentration of suppressor needed (M.S.P. value)
A = concentration of ethanol in volume percentage
C = concentration of reducible ionic species in molarity (must be dilute solutions, below about 5×10^{-3} M)
K_1 and K_2 = constants characteristic of particular suppressor

A small value of K_1 indicates that the suppressor functions at low concentrations. The magnitude of K_2 is indicative of the susceptibility to change of the M.S.P. values by increasing alcohol concentration. These values are given in Table II for the colloidal suppressors investigated here. Similar determinations for other useful colloidal agents should prove helpful in choosing proper maxima suppressor concentrations, understanding their function, and ensuring their proper use in polarography.

TABLE II

MAXIMA SUPPRESSION CONSTANTS OF COLLOIDAL AGENTS IN ALCOHOL-WATER SOLUTIONS

Colloidal agent	K_1	K_2
Methyl cellulose[a]	0.19	0.0054
Gelatin[a]	1.3	.19
Lauryltrimethylammonium bromide[b]	0.023[c]	.0013[c]

[a] Based on concn. in percentage in empirical equation. [b] Based on concn. in molarity in empirical equation. [c] Value satisfactory up to about 30% alcohol.

PORTLAND, OREGON RECEIVED JUNE 29, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

The Reaction of Dilute Iodine and Ammonia Solutions

BY R. K. MCALPINE

The decolorization of an iodine solution by ammonia at relatively low *p*H cannot be accounted for in terms of hydrolysis to form HIO or the production of $N_2H_3I_3$. The reaction involved is readily reversible as shown by the ease with which the color decreases with increasing amounts of NH_3 and increases on the addition of KI or NH_4Cl. Assuming that NH_2I is formed the net reaction would be $2NH_3 + I_2 \rightleftarrows NH_2I + NH_4^+ + I^-$. A series of 24 decolorization experiments involving varying amounts of 3 different NH_4Cl-NH_4OH solutions and five $0.01N$ KI_3 solutions with differing amounts of KI were carried out. The data gave values for the equilibrium constant of this reaction ranging from 1.2 to 2.6, the average being 1.8. The precipitation of $N_2H_3I_3$ and the dissolving of this compound in excess of ammonia solution may be represented by the equations $NH_2I + 2I_2 + 3NH_3 = N_2H_3I_3 + 2NH_4^+ + 2I^-$ and $N_2H_3I_3 + NH_3 = 3NH_2I$.

At present, chemists generally regard this reaction as involving, first, the hydrolysis of the iodine in the somewhat alkaline solution to form HIO, and, second, the reaction of NH_3 with the HIO to form nitrogen iodide, $N_2H_3I_3$; followed later by slow conversion in part to iodate and iodide, and in part by decomposition. This idea of the primary reaction was expressed clearly by Seliwanov[1] confirmed by Chattaway,[2] and retained by Partington.[3]

There have been occasional suggestions that NH_2I and NHI_2 might be intermediates in the formation of nitrogen iodide. Thus Cremer and Duncan[4] wrote equations for the action of HIO on NH_3, giving NH_2I and NI_3 as successive products, and Roederer,[5] having obtained some evidence for the formation of NH_2I in the reaction of dry NH_3 on I_2 dissolved in CCl_4, noted the possibility that even in aqueous solutions NH_2I may be formed and then rearranged to give the nitrogen iodide. However, these suggestions appear to be simple speculations without experimental support.

It is now possible to report direct experimental studies which make it appear very probable that the initial reaction between iodine and ammonia does involve the formation of iodamine, NH_2I. These experiments are concerned mainly with the loss in color which occurs when standard amounts of iodine solutions are added to buffered solutions containing varying amounts of NH_4Cl and of NH_4OH. This loss of color cannot be accounted for in terms of simple hydrolysis of the iodine in the somewhat alkaline solution to form HIO, nor can it be due to the formation of nitrogen iodide in solution. Two simple experiments are sufficient to justify this statement. First: when 50 ml. of 0.01 N KI_3 solution is added to 200 ml. of 0.2 M Na_2HPO_4 no recognizable decolorization takes place, yet with 25 ml. of 5 N NH_4OH present and sufficient NH_4Cl to give the same *p*H as before, over 90% of the color is lost. Second: when 50 ml. of the 0.01 N KI_3 solution is added to 200 ml. of water containing only 1 ml. of 5 N NH_4OH a moderate black precipitate forms within a few minutes, proving that nitrogen iodide is sufficiently insoluble to precipitate if it were being formed as a main product in this reaction.

From the consideration of such experiments it was concluded that the soluble, colorless form of iodine is probably iodamine, NH_2I. The only alternative explanation would be to assume that ammonium hypoiodite is being formed as a very slightly ionized compound such that the hydrolysis of the iodine and the dissociation of the HIO, which normally take place very slightly under the conditions given, are actually being carried nearly to completion by the removal of the hypoiodite ion as the ammonium salt. Such an assumption is too highly improbable to warrant serious consideration.

As additional support for the belief that NH_2I is formed as the primary product in the reaction of dilute iodine and ammonia solutions the attempt was made to use the decolorization experiments as a basis for calculating an equilibrium constant for

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[1] Th. Seliwanov, *Ber.*, **27**, 1012 (1894).

[2] F. D. Chattaway and K. J. P. Orton, *Am. Chem. J.*, **24**, 342 (1900).

[3] J. R. Partington, "Textbook of Inorganic Chemistry," 6th ed., The Macmillan Co., New York, N. Y., p. 527.

[4] H. W. Cremer and D. R. Duncan, *J. Chem. Soc.*, 2750 (1930).

[5] E. Roederer, *Z. anorg. allgem. Chem.*, **226**, 144 (1936).

the reversible reaction involved. The labile nature of this reaction is easily demonstrated by noting the extreme promptness with which the color adjustment is made, either in the original mixing of the reagents or on the addition of KI, NH_4Cl, or more of the NH_4Cl–NH_4OH mixture to a solution already set up. On the basis of these facts the following equation was used to represent the reversible reaction: $I_2 + 2NH_3 = NH_2I + NH_4^+ + I^-$. Twenty-four decolorization experiments were then carried out using standard amounts of iodine but with variations in the concentrations of OH^-, NH_4OH and I^-. By comparison of the solutions with a set of standards the per cent. of decolorization was obtained.

In preliminary experiments a spectrophotometer was used to measure the extent of decolorization of the iodine solutions, but the labile nature of the system and the probable temperature coefficients of the reactions made the results erratic. This was then abandoned in favor of simple visual comparison of the unknowns with a set of standards of the same volume and in similar flasks.

Assuming that the loss in color could be taken as a direct measure of the concentration of NH_2I, the final concentrations of I_2, NH_4^+, NH_3 and I^- were calculated from the experimental data by use of the appropriate equilibrium constants. These values were then inserted in the expression for the constant of the proposed reaction.

$$K = \frac{[NH_2I] \times [NH_4^+] \times [I^-]}{[I_2] \times [NH_3]^2}$$

The data and results are summarized in Table I.

TABLE I

DECOLORIZATION OF IODINE SOLUTIONS BY NH_3

A. Using NH_4Cl–NH_4OH mixture no. 1

Ml. of mixture	25	50	75	50	75	100
KI_3 soln.	1	1	1	2	2	2
% decolorized	56	72	80	56	64	72
K	1.4	1.6	1.8	2.2	2.4	2.6

B. Using NH_4Cl–NH_4OH mixture no. 2

Ml. of mixture	20	30	40	25	50	75	40	60	80
KI_3	1	1	1	2	2	2	3	3	3
% decolorized	76	82	86	60	75	86	56	69	76
K	1.3	1.2	1.3	1.5	1.6	2.2	1.7	2.0	2.1

C. Using NH_4Cl–NH_4OH mixture no. 3

Ml. of mixture	20	30	40	25	50	75	40	60	80
KI_3 soln.	3	3	3	4	4	4	5	5	5
% decolorized	55	66	74	46	69	80	55	69	76
K	1.4	1.6	1.7	1.3	1.8	2.2	1.9	2.3	2.5

Two other reactions were also considered, $I_2 + NH_3 + OH^- = NH_2I + H_2O$, and $NH_3 + HIO = NH_2I + H_2O$. The calculations gave equally consistent values for the corresponding constants, as would be expected if the various reactions in this complex system are readily reversible.

In the values of K reported in the table it may be noted that each successive group of 3 consists of three experiments involving the use of increasing amounts of the given NH_4Cl-NH_4OH mixture and that there is a recognizable increase in K throughout each series. Similarly, from a comparison of those experiments in which the same NH_4Cl–NH_4OH mixture is tried with different iodine solutions, it can be seen that an increase in the concentration of KI produces an increase in the value of K. On the other hand an increase in the concentration of OH^- causes an apparent decrease in the value of K. These trends appear to be somewhat more than accidental. However, a general summary of the data shows a maximum shift of K from 1.2 to 2.6 with an average value of 1.8 in a series of twenty-four experiments in which NH_4^+ ranged from 0.064 to 0.32 M, NH_3 from 0.04 to 0.384 M, I^- from 0.0053 to 0.0245 M, I_2 from 1.31×10^{-5} to 9.7×10^{-5} M, and the decolorization from 46 to 86%. This consistency is sufficient to lend strong support to the belief that NH_2I is actually present in these solutions.

If one adds NH_2I to the picture, the several equilibria required to represent an ammoniacal solution to which some KI_3 has been added will now include the following

$$\begin{array}{ll}
I_3 \rightleftharpoons I_2 + I^- & K = 1.4 \times 10^{-3} \\
I_2 + H_2O \rightleftharpoons HIO + I^- + H^+ & K = 3 \times 10^{-13} \\
HIO \rightleftharpoons H^+ + IO^- & K = 3 \times 10^{-11} \\
NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- & K = 1.8 \times 10^{-5} \\
H_2O \rightleftharpoons H^+ + OH^- & K_w = 1 \times 10^{-14} \\
I_2 + 2NH_3 \rightleftharpoons NH_2I + NH_4^+ + I^- & K = 1.8\ (?)
\end{array}$$

In a solution containing a considerable amount of KI and moderate amounts of NH_3 at a pH less than 10, the reducible iodine will be largely in the form of I_3^-. With a lower concentration of KI and larger amounts of NH_3 it will be present chiefly as NH_2I. Or in a system with small amounts of KI and NH_3, but strongly alkaline, it may be largely IO^-. However, the ready reversibility of all these equilibria means that any reaction which uses up any one of these forms of iodine will promptly shift all the others to that one.

Following the initial establishment of equilibrium among the different forms of iodine in such a solution, two further reactions may take place; one, the disproportionation of the HIO to form iodate and iodide—an irreversible reaction in the alkaline solution—and, two, the precipitation of nitrogen iodide by a reversible reaction, although, after formation, the nitrogen iodide may undergo irreversible decomposition. Some exploratory experiments carried out during the course of these studies lead to several definite conclusions concerning these secondary reactions.

(1) The rate of change of the iodine to iodate–iodide is decreased by the presence of NH_3, due to conversion of the I_2 or HIO largely to NH_2I. Thus such a solution showed only a fifth as much change in 71 hours as an equivalent solution buffered with Na_2HPO_4.

(2) In the precipitation of $N_2H_3I_3$ there must be significant amounts of I_2 or HIO still present to react with the NH_2I formed. This conclusion follows from an experiment in which 50-ml. portions of 0.01 N KI_3 solution were added to 200 ml. of 0.025, 0.125, and 0.25 M NH_3 solutions. The first gave a definite black precipitate, the second was cloudy, and the third remained clear, yet the third contained the highest concentration of NH_2I. The equation for the precipitation is of the type

$$NH_2I + 2I_2 + 3NH_3 = N_2H_3I_3 + 2NH_4^+ + 2I^-$$

(3) The dissolving of $N_2H_3I_3$ in ammonia does

not involve a mere reversal of the process by which precipitation occurs. Instead the I_2 or HIO formed by solubility in water is converted to NH_2I by the NH_3, the net reaction being

$$N_2H_3I_3 + NH_3 = 3NH_2I$$

(4) In the slow decomposition of $N_2H_3I_3$ a loss in total oxidizing power occurs, corresponding to the conversion of part of the nitrogen to N_2. In the experiment mentioned in (2) the three solutions were permitted to stand overnight and then analyzed. The first (with most precipitate) had lost 39% in total oxidizing power, the second 2%, and the third only 0.5%. From this it would appear that $N_2H_3I_3$ does not exist to more than a minor extent as a molecular compound in solution, but only as a precipitate.

(5) If $N_2H_3I_3$ is precipitated from a solution containing sufficiently low concentration of NH_3 it may undergo spontaneous decomposition into N_2 and I_2 in a series of mild explosions over a period of several minutes. This effect was observed repeatedly when 50 ml. of 0.01 *N* KI_3 (low in KI) solution was added to 200 ml. of 0.01 *N* NH_3. Judging solely from the visible effects one would guess that the reaction is of the Meldrum[6] type with the concentration of NH_3 in the aqueous solution too low to stabilize the $N_2H_3I_3$.

Preparation of NH_4Cl–NH_4OH mixtures: Stock solutions of 4.00 *N* NH_4Cl and NH_4OH were prepared and 100 ml. of the NH_4Cl solution used with 50, 100 or 150 ml. of the NH_4OH solution and diluted to 500 ml. to give mixtures 1, 2 and 3.

Preparation of 0.01 *N* KI_3 solutions: A stock solution was prepared containing 400 g. of KI in 1 liter. Then 25.4 g. of I_2 was dissolved in 200 ml. of this solution and diluted to 2 liters to give a 0.1 *N* KI_3 solution. To 100 ml. portions of this reagent were added 0, 10, 20, 30 and 40 ml. of the stock KI solution and then diluted to 1 liter to give 0.01 *N* KI_3 solutions numbers 1, 2, 3, 4 and 5, with the concentrations of KI accurately adjusted to the ratio 1:2:3:4:5.

Preparation of color standards: Thirteen 500-ml. glass stoppered erlenmeyer flasks were set up with 50 ml. of 0.2 *M* KH_2PO_4, 50 ml. of 0.2 *M* Na_2HPO_4 and 25 ml. of KI solution (2 g. of KI). To these, in order, were added 50, 40, 30, 25, 20, 17, 14, 12, 10, 8, 6, 4, and 2 ml. of 0.01 *N* KI_3 solution and sufficient water to give a total volume of 250 ml. Course of an experiment.

The measured amount of the NH_4Cl–NH_4OH mixture was placed in a 500-ml. glass-stoppered erlenmeyer flask, plus sufficient water to give a volume of 200 ml., then 50.0 ml. of the selected KI_3 solution added. After thorough mixing the color of the solution was checked against the color standards and the per cent. loss of color noted.

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[6] F. R. Meldrum, *Trans. Faraday Soc.*, **34**, 947 (1938); *Proc. Roy. Soc.* (*London*), **A174**, 410 (1940). At low temp and press, dry $N_2H_3I_3$ decomposes as follows

$$N_2H_3I_3 = NH_3 + NI_3$$
$$2NI_3 = N_2 + 3I_2$$

ANN ARBOR, MICHIGAN

RECEIVED APRIL 21, 1951

[FROM THE DEPARTMENT OF CHEMISTRY OF SAINT LOUIS UNIVERSITY]

Reactions between Dry Inorganic Salts. VII. An X-Ray Study of the Reciprocal System RbCl + KBr ⇄ RbBr + KCl[1a,b]

BY LYMAN J. WOOD AND L. J. BREITHAUPT, JR.

A detailed X-ray diffraction study of the reciprocal system RbCl + KBr ⇄ RbBr + KCl has been made. This system appears to be unique among reciprocal systems. The unit cell edge of rubidium chloride is very nearly the same as that of potassium bromide and the average unit cell edge of rubidium bromide and potassium chloride is almost the same as that of either rubidium chloride or potassium bromide. The sums of the heats of formation of the two reciprocal salt pairs are very nearly equal. The average melting points are very nearly equal. The molecular weight of rubidium chloride is 120.94 and that of potassium bromide 119.01. The X-ray diffraction results indicate that when any mixture of these salts is melted one solid solution is formed which contains all of the cations and anions in the original mixture.

Some time ago it was reported[2] that the reciprocal system

$$RbCl + KBr \rightleftharpoons RbBr + KCl$$

is one of only three of the 60 reciprocal systems of the common alkali halides that do not go to completion in the direction of the pair of balanced mass[3] upon heating. This system is perhaps unique among reciprocal systems. The unit cell edge of rubidium chloride is very nearly the same as that of potassium bromide and the average unit cell edge of rubidium bromide and potassium chloride is almost the same as that of rubidium chloride or potassium bromide. Furthermore the sum of the heats of formation of the rubidium chloride–potassium bromide pair is 199.00 kcal. which is very nearly equal to 200.36 kcal., which is the sum of the heats of formation for the rubidium bromide–potassium chloride pair. The melting point of rubidium chloride is 720° and that of potassium bromide is 731°. The average of the two melting points (725.5°) differs by only a little from the average melting point of rubidium bromide and potassium chloride which is 729.5°. The molecular weight of rubidium chloride is 120.94 and that of potassium bromide is 119.01. In the preliminary investigation two mixtures of this reciprocal system were examined and the tentative conclusion was reached that a single solid solution was formed that contained all of the rubidium, potassium, bromide and chloride in the mixture. An extensive investigation has now been made and the results obtained are described below under experimental results.

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[1] (a) Read at the XIIth International Congress of Pure and Applied Chemistry. (b) For the table of data from which Figures 2, 3 and 4 of this article were drawn order Document 3367 from American Documentation Institute, 1719 N Street, N.W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

[2] E. B. Thomas with Lyman J. Wood, THIS JOURNAL, **57**, 822 (1935).

[3] The salt pair having the heavier cation united with the heavier anion and the lighter cation united with the lighter anion has been designated as the pair of Balanced Mass by Link and Wood [Harold L. Link with Lyman J. Wood, *ibid.*, **62**, 766 (1940)] while the other pair has been called the reactive or reciprocal pair.