[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MEMORIAL UNIVERSITY COLLEGE, ST. JOHN'S, NEWFOUNDLAND]

Interhalogen Compounds: Dissociation of Halide Complexes, Dissociation, Hydrolysis, Distribution Ratios in Acid Solution

BY J. HORACE FAULL, JR.

Many equilibrium studies have been made on systems containing free halogens and halide ions to determine the stability of such complex ions as I_2Cl^-,[1] I_2Br^-, I_3^-,[2] Br_2Cl^-, Br_3^-,[3] etc.[4] Early workers[5,6] with iodine monobromide and iodine monochloride attributed the solubility of these compounds in halide solutions to the formation of complexes. Until now no successful attempt has been made to determine dissociation constants of these complexes, although Cremer and Duncan[7] in a series of papers, and others, have isolated and studied a number of solid salts, their behavior in solution and the dissociation pressures of ICl and IBr. Yost, Anderson and Skoog,[8] in a paper published after the present research was well under way, gave a provisional dissociation constant for IBr_2^-.

The need for exact determinations of dissociation constants of IBr^-, $IBrCl^-$ and ICl_2^- has arisen from equilibrium and electrometric titration studies by Forbes[9] and Faull[10] in which they report the constants for such equilibria as $2IBr_2^- \rightleftharpoons I_2Br^- + Br_3^-$ but are unable through lack of data to report such as $2IBr \rightleftharpoons I_2 + Br_2$ in aqueous solvents. Also the work of Yost[8] and others on the free energy of formation of interhalogens in gas and solution phases can be extended, particularly by the aid of distribution ratios. Previous investigations have failed as a result of the extreme hydrolysis of IBr and ICl. The unique feature of the present research is the solution of this difficulty.

Hydrolysis constants of I_2,[11] Br_2 and Cl_2 are known. Several investigators report on the extreme hydrolysis of iodine monobromide and iodine monochloride.[6,7,12,13,14] Sullivan's extensive studies[10] and work by Skrabal[14] established the accepted hydrolysis equations which have been convincingly confirmed by the experiments of Cremer and Duncan.[13] Under the conditions of the latter authors hydrolysis almost removed ICl and IBr from their solutions, a condition studiously avoided herein.

The present research, then, undertook to determine the distribution ratios of ICl and IBr between water and carbon tetrachloride and also (with varying degrees of certainty) equilibrium constants at 25° for

$$IBr + Br^- \rightleftharpoons IBr_2^- \tag{1}$$
$$IBr + Cl^- \rightleftharpoons IBrCl^- \tag{2}$$
$$ICl + Cl^- \rightleftharpoons ICl_2^- \tag{3}$$
$$5IBr + 3H_2O \rightleftharpoons H^+IO_3^- + 5H^+Br^- + 2I_2 \tag{4}$$
$$IBr + H_2O \rightleftharpoons HOI + H^+Br^- \tag{5}$$
$$5HOI \rightleftharpoons H^+IO_3^- + 2I_2 + 2H_2O \tag{6}$$
$$5ICl + 3H_2O \rightleftharpoons H^+IO_3^- + 5H^+Cl^- + 2I_2 \tag{7}$$
$$ICl + H_2O \rightleftharpoons HOI + H^+Cl^- \tag{8}$$
$$I_2 + Br_2 \rightleftharpoons 2IBr \text{ (aq. soln.)} \tag{9}$$
$$I_2 + Cl_2 \rightleftharpoons 2ICl \text{ (aq. soln.)} \tag{10}$$

Materials

All chemicals were highest quality reagent chemicals (A. R. of the British Drug Houses), and as a rule further purified. Hydrochloric and hydrobromic acids were redistilled. Iodine was resublimed twice, once over potassium iodide; bromine was purified by an elaborate method.[9] Chlorine was prepared from potassium permanganate and passed through Emmerling towers of water and concd. sulfuric acid. Carbon tetrachloride was saturated with chlorine, refluxed for an hour, treated with sodium thiosulfate, washed, filtered to dry and redistilled; used material containing halogens only as impurity was recovered.

Iodine bromide was usually prepared in the equilibrium bottles by adding equal quantities of analyzed equal concentration iodine and bromine solutions in carbon tetrachloride, special apparatus being used to avoid loss of bromine.

Iodine monochloride was prepared in solution by bubbling pure dry chlorine into carbon tetrachloride and iodine until yellow ICl_3 separated. Thereafter pure dry air was aspirated through the mixture until potentiometric measurements showed excess of neither chlorine nor iodine.

Experimental

Four series of distribution experiments between carbon tetrachloride and aqueous solvent were performed: two with iodine monobromide and two with iodine monochloride. The carbon tetrachloride served a double pur-

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(1) Rây and Sarkar, *J. Chem. Soc.*, **121**, 1449 (1922).

(2) Jones and Kaplan, THIS JOURNAL, **50**, 1848 (1928).

(3) Linhart, *ibid.*, **40**, 159 (1918).

(4) Kiss and Urmanczy, *Z. anorg. Chem.*, **202**, 172 (1931).

(5) Schutzenberger, *Compt. rend.*, **84**, 389 (1877).

(6) Bornemann, *Ann.*, **189**, 183 (1878).

(7) Cremer and Duncan, *J. Chem. Soc.*, 181 (1933).

(8) Yost, Anderson and Skoog, THIS JOURNAL, **55**, 552 (1933).

(9) Forbes and Faull, *ibid.*, **55**, 1820 (1933).

(10) Faull and Forbes, *ibid.*, **55**, 1809 (1933).

(11) W. C. Bray, *ibid.*, **32**, 932 (1910); G. Jones and Hartman, *ibid.*, **37**, 241 (1915).

(12) Sullivan, *Z. physik. Chem.*, **28**, 542 (1899).

(13) Cremer and Duncan, *J. Chem. Soc.*, 2031 (1932).

(14) Skrabal and Buchta, *Chem.-Ztg.*, **33**, 1184, 1193 (1909).

pose: (a) to dissolve some IBr so its concentration in the water layer could be calculated (b) to serve a similar purpose for I_2, thereby enabling the extent of hydrolysis to be calculated by application of equation (4) or (7).

The preparation of the carbon tetrachloride layer has just been described; its volume was usually 40 cc. The aqueous phase, likewise 40 cc., was prepared determinately from distilled water and analyzed stock solutions of the several acids. The series shown in Table I determined the distribution ratio of iodine bromide between water and carbon tetrachloride; so here the water layer either contained no acid or else sulfuric acid to repress hydrolysis. The series in Tables II and III were designed to determine the complex constants, the aqueous layer containing various amounts of hydrobromic and hydrochloric acids, respectively Similarly with iodine monochloride in Table IV perchloric acid was used in the aqueous layer, and in the series shown in Table V hydrochloric acid was used and also perchloric to prevent hydrolysis.

TABLE I

$K_d = (IBr)_c/(IBr)$

Run	N H_2SO_4	T_w	E_w	T_c	E_c
21a	1.002	0.0375	0.00384	0.1163	0.0096
21b	1.002	.03765	.00381	.1167	.0102
23a	0.2096	.0457	.00726	.0966	.0180
23b	.2096	.0459	.00704	.0962	.0189

Run	(I_2)	$(IBr)_c$	$(Br_2)_c$	$(^*Br^-)$	$(^*IBr)$	(IBr)	K_d
21a	0.0048	0.0533	0.0007	0.0042	0.0164	0.0129	4.13
21b	.0051	.0532	.0007	.0037	.0160	.0129	4.10
23a	.0090	.0393	.0002	.00875	.0175	.0106	3.71
23b	.0094	.0386	.0003	.00850	.0177	.0106	3.61

Summary of 16 results like 4 above

Run	7	11 abc	12 abc	23 ab	13 abc	22 ab	21	20
N, H_2SO_4	0.00	0.010	0.10	0.21	0.52	0.52	1.0	4.8
ca. $(^*Br^-)$	.050	.006	.003	.009	.0015	.006	.004	.00005
ca. $(^*IBr)$	.10	.007	.005	.018	.005	.017	.016	.010
K_d	2.9*	2.6*	3.5	3.6	3.8	4.0	4.1	7.8*

Mean (excluding*) $K_d = 3.9$

TABLE II

$K_1 = (IBr)(Br^-)/(IBr_2^-)^2$

Run	6	14	18	28b	30
N, H_2SO_4	0.00	0.1048	0.00	0.00	0.00
$(IBr)_c$	.00076	.0265	.0207	.00127	.0055
$(^*Br^-)_i$	.0090	.00837	.00	1.090	.218
(IO_3^-)	.000057	.00089	.00226		
$(^*Br^-)$	.0090	.01317	.0113	1.090	.218
$(^*IBr)$	.00087	.0158	.0128	0.1026	.0796
(IBr)	.00195	.0068	.0054	.00034	.00141
(IBr_2^-)	.00067	.0099	.0074	.102	.078
(Br^-)	.0083	.0042	.0039	.99	.140
K_1	.0024	.0032	.0028	.0033	.0025

Average of 21 results $K_1 = 0.0027$

TABLE III

$K_2 = (IBr)(Cl^-)/(IBrCl^-)$

Run	$(^*Cl^-)$	$(^*IBr)$	(IBr)	$(IBrCl^-)$	(Cl^-)	K_2
9	0.1008	0.124	0.00230	0.0098	0.091	0.021
10	.5042	.0355	.00155	.0033	.0471	.022
25a	3.89	.104	.00069	.103	3.78	.026
b	3.89	.102	.00072	.102	3.78	.027
c	3.89	.097	.00077	.096	3.78	.030
26a	0.971	.0956	.00231	.093	0.88	.022
b	.971	.0967	.00232	.094	.88	.022
c	.971	.0840	.00211	.082	.89	.023
27	.1952	.0678	.00912	.058	.138	.022

Average (excluding 25) $K_2 = 0.022$

TABLE IV

$K_d' = (ICl)_c/(ICl)$

Run	$(HClO_4)$	$(ICl)_c$	$(^*Cl^-)$	$(^*ICl)$	(ICl)	K_d'
40	2.24	0.0124	0.084	0.110	0.038	0.38
44	2.24	.0114	.1377'	.156	.038	.29
49a	2.2	.0272	.206	.269	.077	.35
Average of 7 runs $K_d' = 0.34$						
39	5.5	.1014	.0291	.0847	.0622	1.6
39a	5.5	.0332	.0244	.0492	.0290	1.1

TABLE V

$K_3 = (ICl)(Cl^-)/(ICl_2^-)$

Run	$(HClO_4)$	$(Cl^-)_i$	$(^*Cl^-)$	$(^*ICl)$	K_3
36	2.11	0.233	0.449	0.387	0.0050
42	1.12	.233	.244	.187	.0068
43	2.22	.233	.233	.179	.0075
46	1.12	.000	.166	.148	.0062

Average of 8 runs $K_3 = 0.0060$

TABLE VI

$K = (H^+)^6 (Br^-)^5 (I_2)^2 (IO_3^-)/(IBr)^5 = ca.\ 10^{-21}$

K	10^{-19}	10^{-20}	10^{-21}	10^{-22}	10^{-23}	10^{-24}	10^{-25}
No. runs	2	2	6	1	3	0	2

Result mean of 16 runs

All runs were carried out in 200 cc. g. s. bottles which were frequently shaken by hand and brought to equilibrium in a 25 ± 0.02° thermostat. Equilibrium between the two layers was reached quickly (see experiment with iodine and hydrobromic acid following) but hydrolysis was so rapid at first, especially with iodine monochloride, that it was a day before measurements could be made with assurance; usually at least a week was allowed, though hydrolysis was still going on.

Both aqueous and carbon tetrachloride layers were analyzed for total halogen using excess potassium iodide and titrating with 0.1, 0.01 or 0.001 N sodium thiosulfate solutions which were standardized or prepared frequently. The titers in normality are designated T_w or T_c, respectively. It should be mentioned that the 2-cc. sampling pipet used was standardized for both water and carbon tetrachloride, the delivered volumes being respectively 1.998 and 2.017 cc.

Further, both layers were analyzed potentiometrically, the carbon tetrachloride layer for iodine in excess of IBr or ICl, and the aqueous layer for "excess bromine." The iodine was produced according to equations (4) or (7) and was absorbed almost entirely by the carbon tetrachloride, thereby creating an excess there and leaving a deficiency in the water layer herein spoken of as "excess bromine." These quantities, designated, respectively, E_c and E_w, were determined by adding standard bromine or iodine to a measured sample to convert the excess halogen to iodine bromide. The "iodine bromide end-point" as an electrometric end-point in analysis was first thoroughly investigated by Forbes and Faull[9] but used by others.[8,15] Our technique was as follows. The sample was

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(15) Gorbatscheff and Kassatkina, *Z. anorg. Chem.*, **191**, 105 (1930).

added to an open beaker containing about 50 cc. of 4 N hydrochloric acid and 50 cc. of 4 N hydrobromic acid. The mixture was stirred mechanically and the potential measured by a good potentiometer against a calomel electrode. Reagent was then added quickly at first but 0.1 or 0.05 cc. at a time at the end-point, which was very sharp, permitting the desired 1% accuracy in the titer. Several precautions were necessary. In analyzing excess iodine in the carbon tetrachloride layer, solutions of bromine in hydrobromic acid were used and these were analyzed after each determination, though at the usual laboratory temperature of 15° or lower this was not always necessary. In analyzing the water layer, the iodine or potassium iodide standard solutions were prepared frequently to avoid deterioration by oxidation. In the case of the water layer, so much free bromine was liberated (see equation (18)) that it was necessary to add almost the correct amount of reagent before adding the sample.

Iodine chloride samples were analyzed exactly as for iodine bromide, the former being converted to the latter on being added to hydrobromic acid.

It should be pointed out that in the case of ICl, the carbon tetrachloride layer was replaced once before analysis to remove most of the iodine.

The following measurements of the distribution of iodine between carbon tetrachloride and 0.0869 N hydrobromic acid show how well equilibrium was established aside from hydrolysis. Titrations were made on three successive days.

	1	2	3
Water layer	0.002120	0.002107	0.002116
Carbon tetrachloride layer	.00829	.00827	.....

Figures give normality of iodine. Using the distribution ratio 83.5 for iodine[16] it was possible to calculate $(I_2)(Br^-)/(I_2Br^-) = 0.0765$ in good agreement with others.

Calculation

The abbreviated Tables I to V show the figures and calculations of distribution ratios and complex constants. The experimental quantities T_w, T_c, E_w, E_c have been defined. The acid added initially provided at once $(^*Br^-)_i$, $(^*Cl^-)_i$, and $(H^+)_i$. From these from the below described method it is possible to calculate $(IBr)_c$, $(I_2)_c$, the respective molal concentrations in carbon tetrachloride, and the following in the water layer: (I_2), $(^*I_2)$, (IO_3^-), $(^*Br^-)$, $(^*IBr)$. Starred quantities indicate inclusion of complexes; *e. g.*, $(^*IBr) = (IBr) + (IBr_2^-) +$. The mathematical relations are

$$(IBr)_c = {}^1/_2[T_c - E_c] \qquad (11)$$

$$(I_2)_c = {}^1/_2E_c \qquad (12)$$

$$(I_2) = (I_2)_c/83 \qquad (13)$$

$$(^*I_2) = (I_2) + (I_2Br^-) = (I_2) + (I_2)(Br^-)/0.077 \qquad (14)$$

$$(IO_3^-) = {}^1/_4[E_w - 2(^*I_2)] \qquad (15)$$

$$(^*Br^-) = (Br^-)_i + 5(IO_3^-) \qquad (16)$$

$$(^*IBr) = {}^1/_2[T_w - 6(IO_3^-) - 2(^*I_2)] \qquad (17)$$

Equation 15 results from the stoichiometrical relations in

$$5HBr + HIO_3 \rightleftharpoons IBr + 2Br_2 + 3H_2O \qquad (18)$$

This equation describes the reaction producing "excess bromine" measured as E_w. The $5(IO_3^-)$ term in equation (16) arises from relations in equation (4). Equation (17) becomes apparent when one considers the nature of T_w in one of our solutions.

The values of $K_d = (IBr)_c/(IBr)$ and $K_1 = (IBr)(Br^-)/(IBr_2^-)$ were obtained as a result of successive approximations using the average value of K_d first found from Table I to find K_1 in Table II and then correcting K_d and so on until no further change follows. The difference between first and final approximations was 25% or more. K_d' and K_3 were determined jointly in the same manner (see Tables IV and V). K_2 was found simply after K_d and K_1 had been determined (see Table III). Hydrolysis constants were calculated from data now available in Tables I to V and are shown in Table VI, to be discussed later.

Results

The constants reported are $K_d = (IBr)_c/(IBr) = 3.9 \pm 0.1$.

$K_d' = (ICl)_c/(ICl) = 0.34 \pm 0.02$;

$K_1 = (IBr)(Br^-)/(IBr_2^-) = 0.0027 \pm 0.0002$

$K_2 = (IBr)(Cl^-)/(IBrCl^-) = 0.023 \pm 0.0002$;

$K_3 = (ICl)(Cl^-)/(ICl_2^-) = 0.0060 \pm 0.0005$

The reported distribution ratios are mean values in the experimental range of lowest possible acidity (0.3 N sulfuric acid with K_d and 2 N perchloric acid with K_d'). Variations in accord with the salting-out effect are observed but no extrapolation is attempted to pure water. Determinations of K_1 were not carried above 1 N because of the difficulties involved. In the case of K_2 the results in 4 N hydrochloric acid were likewise difficult due to the great solubility of iodine bromide therein, so the unsteady results were eliminated from the average. K_3 could be determined in weak hydrochloric acid less than 0.4 N and large ICl concentrations only, for similar reasons. In general, hydrolysis made the results with ICl much more uncertain than those for IBr. No correction was made for dissociation of IBr in the carbon tetrachloride, as this exceeded 1% in but a few cases.

Within the limits of error, K_1, K_2, K_3 show no variation with concentration of halogen or acid—

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(16) Pearce and Eversole, *J. Phys. Chem.*, **28**, 245 (1924).

quite as to be expected from the behavior of similar complex constants of the pure halogens. K_1 agrees well with the preliminary value of Yost, 0.003.[8]

Dissociation of IBr and ICl in Aqueous Solution

Forbes and Faull found $(Br_3^-)\ (I_2Br^-)/(Br_2I^-)^2 = 1.81 \times 10^{-8}$ in 1 *N* hydrobromic acid and 2.92×10^{-8} in 4 *N* hydrobromic acid.[10] Accepting the dissociation constants of Br_3^- as 0.062[3] and for I_2Br^- as 0.077[17] and for IBr_2^- as 0.0027, direct substitution gives $(I_2)(Br_2)/(IBr)^2 = 1.18 \times 10^{-5}$ in 1 *N* hydrobromic acid and 1.90×10^{-5} in 4 *N* hydrobromic acid. The difference is hard to explain but may be due to unexpected change of complex constants with acid concentration or to disproportionate change in activity of I_2, Br_2 and IBr.

In a similar way from values of $(Cl_3^-)\ (I_2Cl^-)/(ICl_2^-)^2 = 2 \times 10^{-15}$ in 2 *N*, 2.8×10^{-15} in 4 *N* and 5.6×10^{-15} in 6 *N* hydrochloric acid[9] and the dissociation constant of Cl_3^- as 4.8,[18] I_2Cl^- as 0.62[1] and ICl_2^- as 0.0060, it is possible to calculate $(I_2)\ (Cl_2)/(ICl)^2 = 1.62 \times 10^{-10}$ in 2 *N*, 2.27×10^{-10} in 4 *N* and 3.9×10^{-10} in 6 *N* hydrochloric acid.

Dissociation of IBr and ICl in other Solvents.—If the distribution ratios of the halogens and interhalogen compounds are known between any two solvents and also the dissociation or free energy in one solvent is known, the dissociation or free energy can be calculated at once for the other. Use has already been made of the dissociation of iodine bromide in carbon tetrachloride and has likewise been found by Yost by an entirely different method[8] than that suggested here. Using the previously mentioned distribution ratios and the value of 28 for bromine[19] it is possible to calculate from data in 1 *N* hydrobromic acid $(I_2)\ (Br_2)/(IBr)^2 = 1.80 \times 10^{-3}$. This value is higher than it would be if data were available in pure water, though it is not easy to account for an error larger than 10%. This is not in agreement with the excellent work of Yost, who found iodine bromide 9.5% dissociated (giving a constant of 2.75×10^{-3}) and apparently the errors inherent in the present method minimize the discrepancy.

Hydrolysis

The very large hydrolysis of iodine bromide and iodine monochloride has been repeatedly referred to especially for iodine chloride. Although hydrolysis was proceeding very slowly at the end of a week or more, it is probable that true equilibrium was only approximated. The tentative constants of equations (4) and (7) are: $(H^+)^6\ (Br^-)^5\ (I_2)^2\ (IO_3^-)/(IBr)^5 = ca.\ 10^{-21}$ and $(H^+)^6\ (Cl^-)^5\ (I_2)^2\ (IO_3^-)/(ICl)^5 = ca.\ 10^{-7}$. These figures are means of a number of experiments made under widely varying conditions of concentrations and time, the necessary data for calculation being contained in suitable runs of Tables I to V. While the results cluster about the means there were a few erratic results departing even several powers of ten, not a very surprising occurrence.

It is of interest now to calculate a value for the primary hydrolysis as represented in equations (5) and (8). The desired hydrolysis constant of IBr can be found from a consideration of the following equations, all of whose equilibrium constants are known

$$2I^- + Br_2 \rightleftharpoons 2Br^- + I_2 \qquad (9)$$

$$2IBr \rightleftharpoons Br_2 + I_2$$

$$\underline{2I_2 + 2H_2O \rightleftharpoons 2HOI + 2H^+I^-} \qquad (11)$$

$$IBr + H_2O \rightleftharpoons HOI + H^+Br^- \qquad (5)$$

Forbes and Faull found the replacement constant of iodine in bromide solutions 2.0×10^{-16}, and Bray found the hydrolysis constant of iodine 6×10^{-13}; the dissociation of IBr has just been reported. Hence it is possible to calculate the equilibrium for equation (5): $(HOI)(Br^-)(H^+)/(IBr) = ca.\ 1.5 \times 10^{-7}$. Similarly using the additional value for the replacement constant of iodine in hydrochloric acid found by Faull and Forbes[10] as 10^{-27}, it is possible to calculate $(HOI)\ (Cl^-)\ (H^+)/(ICl) = ca.\ 10^{-4}$.

At equilibrium calculations show that in all cases reported above for IBr, the concentration of HOI is about 1% of the HIO_3, a negligible amount. The proportion is about the same in the case of ICl.

For completeness, it can be mentioned that the equilibrium for equation (6) can be calculated from data for ICl and also for IBr, and in both cases is about 10^{13}.

Finally, the present investigation reveals some new facts about the relation between the properties of interhalogen compounds and the pure halogens. It has long been the custom to refer to the manner in which the properties of the interhalogens fall intermediate between those of the free halogens from which they are formed. The present findings are exceptions to the rule:

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(17) Jakowkin, *Z. physik. Chem.*, **20**, 19 (1896).

(18) Sherrill and Izard, THIS JOURNAL, **53**, 1667 (1931).

(19) "Int. Crit. Tables," Vol. 3, p. 419.

(a) the complexes are invariably very stable, being exceeded in stability by I_3^- only; (b) the solubility in water as compared with that in carbon tetrachloride is but a fraction of that of any pure halogen, with the possible exception of chlorine. (c) the hydrolysis constants are much larger throughout.

Summary

A method has been devised for determining the equilibrium constants of complexes of interhalogen compounds, the distribution ratios of interhalogen compounds between water and carbon tetrachloride, and the hydrolysis constants of interhalogens.

The equilibria for the complexes studied are: $(IBr)(Br^-)/(IBr_2^-) = 0.0027$; $(IBr)(Cl^-)/(IBrCl^-) = 0.023$; $(ICl)(Cl^-)/(ICl_2^-) = 0.0060$.

The distribution ratios of IBr and ICl between carbon tetrachloride and water are: $(IBr)_c/(IBr) = 3.9$; $(ICl)_c/(ICl) = 0.34$.

By the aid of previously collected data it has been possible to calculate a value for the dissociation of iodine chloride and iodine bromide in aqueous solution: $(I_2)(Br_2)/(IBr)^2 = 1.2 \times 10^{-5}$ and $(I_2)(Br_2)/(IBr)^2 = 1.6 \times 10^{-10}$.

Hydrolysis of interhalogen compounds is commented upon and preliminary values given for equilibria constants of the generally recognized equations.

Attention is drawn to the divergence of these results from the rule that the properties of interhalogen compounds are intermediate between those of the halogens from which they are formed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Kinetics of the Thermal Reaction of Gaseous Alkyl Iodides with Hydrogen Iodide

BY RICHARD A. OGG, JR.[1]

There appears to have been very little study of the reactions of organic iodides with hydrogen iodide, although such a reaction is an important step in a process widely used in organic syntheses, namely, the reduction of alcohols to hydrocarbons through the agency of red phosphorus and hydriodic acid. Kekulé[2] observed that iodobenzene on heating in a sealed tube with hydriodic acid yielded benzene and iodine. Butlerow[3] heated methyl and ethyl iodides with hydriodic acid and obtained methane and ethane, respectively. Apparently no study has been made of the reactions in the gas phase. That the presumably reversible reaction of an alkyl or aryl iodide with hydrogen iodide proceeds practically to completion with the formation of iodine and hydrocarbon is indicated by the well-known fact that iodination of saturated hydrocarbons can be accomplished only in the presence of oxidizing agents (iodic and nitric acids, persulfates, etc.) which destroy the hydrogen iodide formed.

It appeared to the author that reactions of alkyl iodides with hydrogen iodide in the vapor phase offered an interesting problem for kinetic study, especially because of their apparent simplicity (bimolecular metatheses involving only univalent atoms and radicals) and the opportunity for observing the effects of increasing radical size on the reaction rate. The present investigation was therefore undertaken with the object of establishing the suitability of such reactions for kinetic study, and of then measuring the rates quantitatively.

Qualitative Study of Alkyl Iodides and Hydrogen Iodide.—The first experiments were made by heating in an air-bath sealed bulbs containing measured quantities of purified hydrogen iodide and alkyl iodide vapor, and judging the extent of the reaction by the depth of iodine color produced. At pressures of the reactants around 50–100 mm., the reactions of methyl, ethyl and *n*-propyl iodides with hydrogen iodide were observed to proceed with convenient rapidity in the temperature range 250–300°. Blank tests with the pure alkyl iodides showed them to be comparatively stable at these temperatures, even *n*-propyl iodide decomposing at a negligible rate. From the work of Bodenstein[4] it is known that the decomposition of hydrogen iodide is exceedingly slow at these temperatures. It therefore appeared that there would be no appreciable side reactions. No trace of tarring was observed.

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(1) National Research Fellow in Chemistry.

(2) Kekulé, *Ann.*, **137**, 163 (1866).

(3) Butlerow, *ibid.*, **144**, 36 (1867).

(4) Bodenstein, *Z. physik. Chem.*, **13**, 56 (1894); **22**, 1 (1897); **29**, 295 (1898).