The mixture was chilled 10 min. in an ice bath and the product (1.1 g., m.p. 205–208°), was collected as a bright yellow solid. An analytical sample, m.p. 213–214°, was recrystallized from ethanol; infrared spectrum (KBr): 3.00–3.08 (doublet), 6.05 μ.

Anal. Calcd. for $C_{17}H_{15}N_2O_6Cl.H_2O$: C, 53.63; H, 4.50; N, 7.30. Found: C, 53.41; H, 4.51; N, 7.34.

Borohydride Reduction of Dihydroisoquinoline Reissert Perchlorate Salt.—A suspension of sodium borohydride (0.5 g. in 30 ml. of ethanol) was treated with 0.95 g. of dihydroisoquinoline Reissert perchlorate. The color at first was orange, but this quickly faded on heating. A white solid that remained undissolved after heating 10 min. was dissolved by addition of water. Further dilution with water brought the boiling solution to the point of turbidity, and a small quantity of alcohol was added to give a clear solution. On chilling in an ice–water bath a colorless granular solid was deposited (0.8 g.), m.p. 146–148°; this was raised to 147–149° by recrystallization. This compound was identified as 2-benzyl-1,2,3,4-tetrahydroisoquinaldamide (**5**) by mixture melting point and infrared spectrum.

Hydrolysis of Dihydroisoquinoline Reissert Compound.—To 0.5 g. of dihydro Reissert compound **10** was added 11 ml. of concentrated hydrochloric acid, and the mixture was allowed to reflux 8 hr. The cooled mixture deposited a feathery colorless solid (0.18 g., 78%), m.p. 118–120°. This product proved to be benzoic acid.

A similar result was obtained when the perchlorate salt **11** was heated with aqueous hydrochloric acid (1:1 by volume) and 2,4-dinitrophenylhydrazine. No benzaldehyde derivative was obtained, but benzoic acid was recovered from the reaction mixture.

Deoxymercuration in the Presence of Both Acid and Iodide Ion[1]

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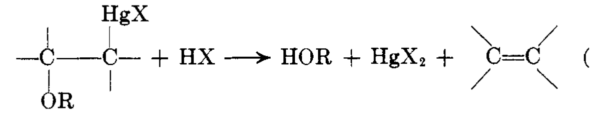
The deoxymercuration rate of 2-methoxyethylmercuric iodide in solutions containing both hydronium ion and iodide ion contains contributions from terms of the first and second order in iodide as well as a term of the zeroth order in iodide. The rate is of the first order in hydronium ion throughout. A previous report that 2-isopropoxyethylmercuric chloride is inert to perchloric acid (ref. 3) is in error. Substantial differences are found between deoxymercuration rates of 2-methoxyethylmercuric iodide and the corresponding hydroxy compound at all iodide concentrations. This precludes a fast reversible formation of the olefin–mercuric iodide complex and it is suggested that the formation of this complex, in fact, is rate determining.

The hydrohalic acid-induced deoxymercuration reaction, shown in equation 1, has been reported to be first order in hydrochloric acid[2] and also second order in hydrochloric acid.[3] Both of these reports pertain to alcohol rich alcohol–water mixtures in which kinetic salt effects may be quite large,[4] and in which incomplete ion-pair dissociation may be a factor.[5] In neither study was the halide ion concentration varied independently of the acid concentration. The present paper reports a study of the deoxymercuration reaction induced by combinations of acid and sodium iodide in water as a solvent (containing 2% methanol). The principal substrate was 2-methoxyethylmercuric iodide, but certain points were established by using 2-hydroxyethylmercuric iodide and 2-isopropoxyethylmercuric chloride.



$$-\underset{\mathrm{OR}}{\overset{|}{\underset{|}{C}}}-\overset{\mathrm{HgX}}{\overset{|}{\underset{|}{C}}}- + \mathrm{HX} \longrightarrow \mathrm{HOR} + \mathrm{HgX_2} + \mathrm{>C{=}C<} \quad (1)$$

Results

Rates were measured spectrophotometrically using previously described techniques.[6a] The build-up of absorption at 3200 Å. due to mercuric iodide and its iodide ion complexes was followed. This absorption is primarily due to HgI_4^{-2} and HgI_3^-, which are in equilibrium with HgI_2 in the presence of excess iodide ion. Since the I^- concentration did not change appreciably in the course of any one experiment, the fraction of HgI_2 converted to each absorbing species was fixed and the change in optical density was proportional to the fraction of the reaction which had taken place. Thus the usual form of the integrated first-order rate law (equation 2) could be used.[6b] Plots of $\log \{(D_\infty - D_0)/(D_\infty - D_t)\}$ *vs.* t were precisely linear. (The optical density is D with the subscript indicating the time, t, at which it was measured. The pseudo first-order rate constant is k_1.) The slopes of such plots, obtained graphically, were used to get values of k_1. Substrate concentrations were in the range 10^{-4}–10^{-6} M. All reactions were pseudo first order. The iodide concentration exceeded the substrate concentration by at least a factor of 12 in all experiments and in most by far more than that. The acid concentration was either in excess over the substrate by at least a factor of 100 or else it was held constant by buffering.

$$k_1 = \frac{2.303}{(t - t_0)} \log \frac{(D_\infty - D_0)}{(D_\infty - D_t)} \qquad (2)$$

All measurements were made at least in duplicate and generally did not differ by more than 5%. In case of discrepancies of 10% or more, the measurement was repeated until the difficulty could be eliminated. This suggests a reliability of about ±5% for cited values of k_1.

All of the rate constants reported in this paper were measured at 25.0 ± 0.1°. All measurements were made in water containing 2% by volume of methanol because the substrates were handled as stock solutions in that solvent.

(1) This work was supported by the Air Force Office of Scientific Research through Contract No. AF 49(638)711. Reproduction in whole or in part is permitted for any purpose of the U. S. Government.

(2) O. W. Berg, W. P. Lay, A. Rodgman, and G. F. Wright, *Can. J. Chem.*, **36**, 358 (1958).

(3) K. Ichikawa, H. Ouchi, and S. Araki, *J. Am. Chem. Soc.*, **82**, 3880 (1960).

(4) S. D. Ross, M. Finkelstein, and R. C. Peterson, *ibid.*, **83**, 5335 (1960).

(5) C. A. Kraus, *J. Chem. Educ.*, **35**, 324 (1951).

(6) (a) M. M. Kreevoy, *J. Am. Chem. Soc.*, **81**, 1099 (1959); (b) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 28.

Rate as a Function of Acid Concentration.—Rates were measured as a function of hydronium ion concentration at two (constant) sodium iodide concentrations, 4.07×10^{-3} and 0.1536 *M*. The latter is close to the highest iodide ion concentration used in this work. With 4.07×10^{-3} *M* iodide ion, hydronium ion concentration was varied with perchloric acid. Four determinations were made over the range of acid concentration, 8×10^{-4} to 3×10^{-3} *M* giving values of k_1 very nearly proportional to the acid concentration. A pseudo second-order rate constant, k_2', is given by $k_1/[\mathrm{H}^+]$ and has the value $0.510 \pm .008$ l. mole^{-1} sec.$^{-1}$. This value becomes $0.590 \pm .014$ $[k_2'^0]$ when each rate constant is corrected for the ionic strength effects described subsequently.

At the higher iodide ion concentration acetic acid–sodium acetate buffers were used to provide the hydronium ion, and $k_2'^0$ was again invariant under changes in its concentration. (In acetic acid–sodium acetate buffers $k_2'^0$ is defined as $k_1[\mathrm{OCOCH_3}^-]/K[\mathrm{HOCOCH_3}]$, where K is the thermodynamic dissociation constant of acetic acid and quantities in brackets are concentrations. It is shown, subsequently, that this is equivalent to the similar quantity defined for strong acid.) Four measurements over the range, 5×10^{-6} to 6×10^{-5} *M* hydronium ion gave a $k_2'^0$ of $1.10 \pm .04 \times 10^2$ l. mole^{-1} sec.$^{-1}$. Sodium acetate concentration was held constant in these experiments and the hydronium ion concentration was varied by varying the acetic acid concentration so that there was no change in the ionic strength within the series. The acetic acid concentration was $< 1.7 \times 10^{-2}$ *M*. It is shown below that there is no significant catalysis by molecular acetic acid under these conditions.

Experiments designed to test for catalysis by molecular acetic acid were carried out both at low (8×10^{-4} *M*) and at high (0.170 *M*) iodide concentration. The ionic strength was not held constant in these experiments but it is shown, subsequently, that $k_2'^0$ is independent of ionic strength to a first approximation when it is determined in acetic acid–sodium acetate buffers. At the low iodide concentration a $k_2'^0$ of 0.140 was obtained in an experiment carried out with 0.325 *M* acetic acid. The value of $k_2'^0$ predicted from similar experiments with perchloric acid is 0.136. If it is concluded from this that the molecular acetic acid contributes < 5% of the total rate under these conditions then the molecular acetic acid rate coefficient, $k_2'^{\mathrm{HOAC}}$, must be smaller than $k_2'^{\mathrm{H}}$, the hydronium ion rate coefficient, by at least a factor of 10^4.

At the higher iodide concentration rates were measured in dilute acetic acid–sodium acetate buffers (both constituents around 5×10^{-3} *M*) as well as more concentrated buffers (both constituents around 0.1 *M*) of about the same buffer ratio. A $k_2'^0$ of 1.34×10^2 was obtained with the dilute buffer and 1.25×10^2 with the more concentrated buffer. If it is concluded from this that the molecular acetic acid contributes < 5% of the total rate in the more concentrated buffers, then the corresponding rate coefficient, $k_2'^{\mathrm{HOAc}}$, must be smaller than $k_2'^{\mathrm{H}}$ by a factor of at least 10^5.

These results, coupled with similar findings in the absence iodide ion,[6,7] established that $k_2'^0$ is independent of hydronium ion concentration over the whole range of iodide concentrations. They strongly suggest the absence of general acid catalysis.

Rate as a Function of Electrolyte Concentration.—At 3.80×10^{-3} *M* perchloric acid and 2.33×10^{-3} *M* sodium iodide, k_1 was studied as a function of electrolyte concentration with added sodium perchlorate, sodium nitrate, and potassium nitrate. The results are shown in Table I.

Table I

Effect of Added Electrolyte on k_1 in 3.8×10^{-3} *M* Perchloric Acid and 2.3×10^{-3} *M* Sodium Iodide

Salt	$10^2 \times$ total electrolyte, *M*[a]	$10^3 k_1$, sec.$^{-1}$	$10^3 k_1{}^0$, sec.$^{-1\,b}$	$10^3 k_1{}^0$, sec.$^{-1\,c}$
None	0.61	1.26	1.48	1.47
$\mathrm{KNO_3}$	1.61	1.18	1.47	1.45
$\mathrm{KNO_3}$	3.11	1.07	1.46	1.43
$\mathrm{KNO_3}$	4.61	0.94	1.35	1.30
$\mathrm{KNO_3}$	5.61	0.97	1.43	1.37
$\mathrm{KNO_3}$	8.11	0.95	1.48	1.38
$\mathrm{KNO_3}$	10.61	0.93	1.51	1.38
$\mathrm{NaClO_4}$	1.46	1.23	1.55	1.53
$\mathrm{NaClO_4}$	3.21	1.05	1.44	1.40
$\mathrm{NaClO_4}$	5.69	0.96	1.41	1.35
$\mathrm{NaClO_4}$	10.76	0.95	1.58	1.45
$\mathrm{NaClO_4}$	20.91	0.94	1.68	1.42
$\mathrm{NaNO_3}$	2.61	1.09	1.46	1.43

[a] Since only 1:1 electrolytes are involved this is exactly half the ional strength. [b] Calculated from equations 3 and 4. [c] Calculated from equations 3 and 5.

If two ions of opposite charge are combined to make a formally neutral transition state, equation 3 gives the Brønsted law[8] for $k_1{}^0$, the rate constant in infinitely dilute electrolyte.

$$k_1{}^4 = k_1/f_t{}^2 \tag{3}$$

Changes in electrolyte concentration should not change $k_1{}^0$, although k_1 may vary considerably. The mean ion activity coefficient, $f_\pm$, can be calculated from the Debye–Hückel theory (equation 4)[9] for dilute solutions (ional strength, Γ, $< \sim 0.2$). For more concentrated solutions the extended Debye–Hückel theory[10] (equation 5) may be successful. In both equations 4 and 5 the notation

$$\log f_\pm = -\frac{S_f\sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} \tag{4}$$

is that of Harned and Owen.[9,10]

$$\log f_\pm = -\frac{S_f\sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} - \frac{B\Gamma}{2} + \frac{D'\Gamma^2}{4} \tag{5}$$

Equation 3 has been applied to the present data, using both equations 4 and 5 for $f_\pm$, and the results are shown in Table I. The theoretical value was used for S_f.[11] Empirically obtained values appropriate to hydrogen iodide were used for B, D', and $\mathring{a}$,[12] the mean ionic diameter. (The latter is required to evaluate A.) Since these parameters were determined for solutions containing only hydrogen iodide they constitute a source of serious uncertainty in $f_\pm$, particularly at higher ional strengths. Nevertheless the deviations

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(7) M. M. Kreevoy and F. R. Kowitt, *J. Am. Chem. Soc.*, **82**, 739 (1960).

(8) J. N. Brønsted, *Z. Physik. Chem.* (Leipzig), **102**, 169 (1922).

(9) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, pp. 64–66, 508–512.

(10) Ref 9, pp. 66–68.

(11) Ref. 9, p. 165.

(12) Ref. 9, p. 510.

from constancy in the k_1^0 values calculated from equations 3 and 5 do not exceed the experimental uncertainty. If equations 3 and 4 are used instead, systematic deviations outside of the experimental uncertainty are observed with ional strengths of 0.2 and higher. Changes of about 25% in k_1 can be observed on going from the lowest to the highest ional strength.

In acetic acid–sodium acetate buffers the hydronium ion concentration is given by $K[\text{HOAc}]/[\text{OAc}^-]f_\pm{}^{2\text{HOAc}}$. In such a buffer k_2' would be given by $k_1[\text{OAc}^-]f_\pm{}^{2\text{HOAc}}/K[\text{HOAc}]$. To get the infinite dilution value, k_1^0 would be used, giving $k_1[\text{OAc}^-]$-$f_\pm{}^{2\text{HOAc}}/K[\text{HOAc}]f_\pm{}^2$ for $k_2'^0$. However, equation 4 also gives $f_\pm{}^{\text{HOAc}}$ in moderately dilute solutions if 5.6 Å. is used for $\mathring{a}$.[13] This is not too different from the value of $\mathring{a}$ (5.0 Å.) that permits equation 4 to successfully predict $f_\pm$ up to 0.1 M electrolyte. Thus the two activity coefficient terms cancel to a good approximation in dilute buffers, and $k_2'^0$ is simply given by $k_1[\text{OAc}^-]/K(\text{HOAc}]$.

If the hydronium ion is provided by a strong acid $k_2'/f_\pm{}^2$ gives k_2'.[4] Equation 5 (or 4 within its range of applicability) can be used to get $f_\pm$. This has been done in obtaining the values of $k_2'^0$ which were measured in perchloric acid solutions.

Rate as a Function of Iodide Concentration.—Values of $k_2'^0$ were obtained at sodium iodide concentrations ranging up to 0.17 M. They are shown in Table II. Table II also shows the acid system, perchloric or acetic acid–sodium acetate, and the quantity $[\text{H}]^+f_\pm{}^2$ so that the measured values of k_1 can be regenerated from it. In all of these experiments the ratio of molecular acetic acid concentration to hydronium ion concentration was low enough to preclude significant catalysis by acetic acid.

TABLE II

THE INFLUENCE OF $[\text{I}^-]$ ON $k_2'^0$

Acid	$[\text{H}^+]f_\pm{}^2$, M	$[\text{I}^-]$, M	$k_2'^0$ obsd., l. mole^{-1} sec.$^{-1}$	$k_2'^0$ calcd., l. mole^{-1} sec.$^{-1}$
$HClO_4$	2.47×10^{-3} [a]	None	0.0380[b]	0.038
HOAc	5.62×10^{-4}	8.00×10^{-4}	0.140	0.136
$HClO_4$	2.21×10^{-3}	1.02×10^{-3}	0.159	0.162
$HClO_4$	2.18×10^{-3}	2.03×10^{-3}	0.291	0.292
$HClO_4$	7.95×10^{-3}	2.33×10^{-3}	0.361	0.321
$HClO_4$	2.16×10^{-3}	3.05×10^{-3}	0.432	0.436
$HClO_4$	c	4.07×10^{-3}	0.590	0.586
HOAc	5.79×10^{-5}	6.99×10^{-3}	1.082	1.05
HOAc	5.79×10^{-5}	1.40×10^{-2}	2.71	2.48
HOAc	5.79×10^{-5}	2.80×10^{-2}	7.17	6.50
HOAc	5.79×10^{-5}	4.19×10^{-2}	12.64	12.0
HOAc	5.79×10^{-5}	5.59×10^{-2}	20.7	19.1
HOAc	5.79×10^{-5}	7.86×10^{-2}	35.3	34.0
HOAc	5.79×10^{-5}	1.05×10^{-1}	58.8	56.4
HOAc	c	1.57×10^{-1}	110	117
HOAc	2.54×10^{-5}	1.70×10^{-1}	134	136
HOAc	2.18×10^{-5}	1.70×10^{-1}	125	136

[a] In the absence of iodide ion the ional strength correction is inappropriate; this is simply the acid concentration. [b] Calculated as described in ref. 6 and 7. This value can be compared with 0.0340 previously reported (ref. 7). The latter is probably more accurate but the former is used for consistency in the present paper. [c] The average of four acid concentrations was used for this point, as described in the section on the variation of the rate with acid concentration.

Casual inspection shows that no constant order with respect to iodide ion will reproduce all of the data in Table II since $k_2'^0$ is nearly proportional to the iodide concentration at low iodide concentration but nearly proportional to its square at high iodide concentration. Further there is a reaction in the absence of iodide. If it is assumed that $k_2'^0$ is governed by equation 6 with the indicated constants it is possible to fit most of the $k_2'^0$ values within their experimental reliabilities. The value of k_2 is that obtained in the absence of iodide ion. Values of k_3 and k_4 were obtained by an iterative process, in which a k_3 value was first obtained by ignoring the square term at low iodide concentration; this value was then used in equation 6 with the high iodide values of $k_2'^0$ to get a value of k_4. The latter was then used in equation 6 to obtain an improved value of k_3. This process was repeated twice more, at which point the values obtained for k_3 and k_4 were no longer changing.

$$k_2'^0 = k_2 + k_3[\text{I}^-] + k_4[\text{I}^-]^2 \qquad (6)$$

$$k_2 = 3.80 \times 10^{-2}\ \text{l. mole}^{-1}\ \text{sec.}^{-1}$$

$$k_3 = 1.19 \times 10^{2}\ \text{l.}^2\ \text{mole}^{-2}\ \text{sec.}^{-1}$$

$$k_4 = 4 \times 10^{3}\ \text{mole}^{-3}\ \text{sec.}^{-1}$$

The $k_2'^0$ values at low iodide concentration, on which k_3 is primarily based, are quite firmly established. All of the known variables which might influence them (ionic strength effects, complexing) have either been eliminated or corrected for. Since they are very well correlated by equation 6, k_3 can probably be considered as reliable as the values of $k_2'^0 \sim \pm 5\%$.

On the other hand a number of difficulties impair the accuracy of $k_2'^0$ values at high iodide concentrations and thereby render k_4 numerically unreliable. Experiments with methylmercuric iodide[14] suggest that a significant fraction of the substrate may be complexed with iodide ion at the higher iodide concentrations, causing $k_2'^0$ to fall below the values that are required to obtain correct values of k_4 from equation 6. Equations 3 and 4 have been experimentally tested only at lower iodide concentrations and equation 4 has been shown to fail at higher electrolyte concentrations, so that the cancellation of the hydrogen iodide and acetic acid activity coefficients may well be imperfect. Neither of these effects, however, call the *reality* of k_4 into question. At high iodide concentrations $k_2'^0$ is five times as large as would be predicted by the combined k_2 and k_3 terms in equation 6. The cancellation of the electrolyte effects is unlikely to be in error by as much as 20%, since the predicted effects themselves are not much larger than this. Complexing would act to *reduce* the apparent values of $k_2'^0$ at high iodide concentrations, and thereby reduce the estimated k_4.

2-Hydroxyethylmercuric Iodide.—Rates were measured for 2-hydroxyethylmercuric iodide at 0.0140 M sodium iodide and 0.130 M sodium iodide. In both cases an acetic acid–sodium acetate buffer was used with $K[\text{HOAc}]/[\text{OAc}^-]$, 5.79×10^{-5}. At the former iodide concentration $k_2'^0$ was 12.3 l. mole^{-1} sec.$^{-1}$ while at the latter it was 240 l. mole^{-1} sec.$^{-1}$. The former is about a factor of 4 larger than that for 2-methoxyethylmer-

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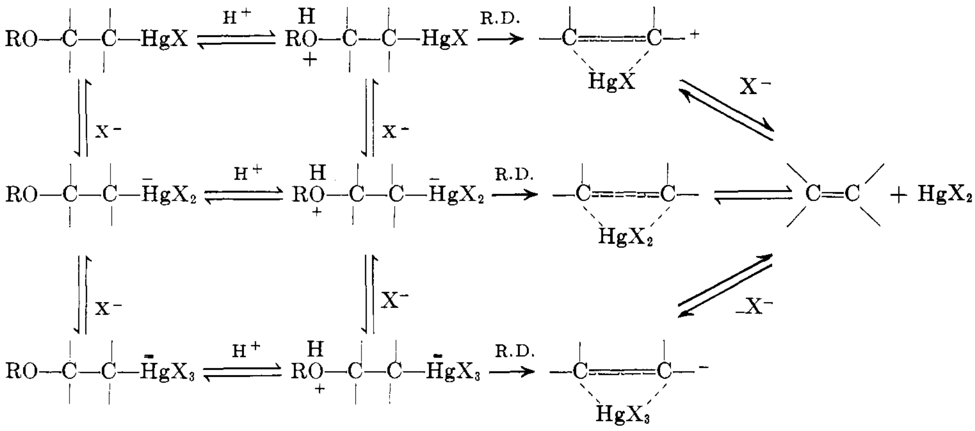
(13) H. S. Harned, *J. Phys. Chem.*, **43**, 275 (1939).

(14) M. Visot, unpublished results.

CHART I



curic iodide under comparable conditions and the latter is larger by a factor of about 3.

2-Isopropoxyethylmercuric Chloride.—Rates were measured for the deoxymercuration of 2-isopropoxyethylmercuric chloride by perchloric acid in a mixture containing 79.7% by volume ethanol. The reactions were followed by following the build-up of the mercuric chloride absorption at 2400 Å. Pseudo first-order rate constants were evaluated by means of equation 7. Equation 7 differs from equation 2 by a factor of two in the denominator on the right hand side. This enters because, in the absence of added halide ion, the mercuric halide product is formed by removing a halide ion from a molecule of unreacted starting material, inactivating it.[6a] Because the reactions appeared to be markedly autocatalytic[6a] (none of the other reactions described in this paper are autocatalytic) the initial slopes of plots

$$k_1 = \frac{2.303}{2(t - t_0)} \log \frac{(D_\infty - D_0)}{(D_\infty - D_t)} \qquad (7)$$

of log $(D_\infty - D_t)$ against t were used. The second-order rate constants, k_2, obtained by dividing k_1 by the perchloric acid concentration, were strongly dependent on the perchloric acid concentration, as has previously been observed for reactions of this type[15] in largely alcoholic solutions. As before[15] a plot of log k_2 against the perchloric acid concentration is linear. It has a slope of 0.90, which may be compared with slopes of 0.73 and 1.25 previously reported[15] in 76.8 and 84.0% ethanol, respectively. It has an intercept of −3.478, corresponding to a k_2 of 3.3×10^{-4} in infinitely dilute acid.

Discussion

It is clear from the foregoing that catalysis by none, one, or two halide ions is possible. If a narrow range of iodide concentrations is studied any order between zero and two may be obtained. The iodide ion presumably functions by complexing the mercury atom, which can certainly accommodate at least four ligands in its coordination shell.[16] This is presumably true of the other halide ions as well, although the term of the second order in halide ion will be harder to observe due to the weaker complexing power of chloride and bromide with mercury.

The report by Ichikawa and co-workers[3] that hydrochloric acid induced deoxymercuration rates are given by a rate law of the form $k[H^+][Cl^-][S]$ is oversimplified. Their reported observation[3] that 2-isopropoxyethylmercuric chloride does not react with perchloric acid is in error, as shown above. With increasing dilution their observed rates did not fall so fast as required by a square dependence on the hydrochloric acid concentration.[3] This can now be explained on the basis of equation 8. Using 2-isopropoxyethyl-

$$\text{rate} = k_2[H^+][S] + k_3[H^+][Cl^-][S] \qquad (8)$$

mercuric chloride as an example, k_2 was evaluated in 79.7% ethanol from equation 9. This is based on the

$$\log k_2 = 0.90[H^+] - 3.478 \qquad (9)$$

assumption that k_2 will be the same in hydrochloric and perchloric acids. Equation 8 could then be used to obtain k_3. Table III shows the values obtained, along with those originally given by Ichikawa and co-workers.[3] The former are clearly much more nearly constant. However, even equation 8 is still oversimplified by the omission of a term in $[Cl^-]$,[2] as explained above. In the deoxymercuration of 2-acetoxyethylmercuric chloride it is likely that a solvolytic term, of the zeroth order in hydrochloric acid is also present in the rate law.[17]

TABLE III

CALCULATED VALUES OF k_3 FOR HCl DEOXYMERCURATION OF 2-ISOPROPOXYETHYLMERCURIC CHLORIDE IN 80% ETHANOL

[HCl], M	$10^2 \times k_3{}^a$ l.^{2} mole^{-2} sec.$^{-1}$	$10^2 \times k_3{}^b$ l.^{2} mole^{-2} sec.$^{-1}$
0.0128	8.5	5.8
.0257	6.5	5.1
.0500	5.9	5.8
.0975	5.6	5.5
.1614	5.7	5.6

[a] Taken from ref. 3. [b] Calculated from equation 8.

A general scheme for deoxymercuration in the presence of halide ion is shown in Chart I. The mercuric halide formed will, of course, assume its equilibrium state of complexation with the halide ion present. The orientation and dynamics of the carbon atoms, the oxygen, and the mercury in the transition state is probably very similar to that previously established for the case of deoxymercuration catalyzed only by acid.[7] The

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(15) M. M. Kreevoy, J. W. Gilje, and R. A. Kretchmer, *J. Am. Chem. Soc.*, **83**, 4205 (1961).

(16) J. Bjerrum, G. Schwarzenbach, and L. G. Sillen, "Stability Constants," The Chemical Society, London, 1958, p. 121.

(17) M. M. Kreevoy and G. B. Bodem, *J. Org. Chem.*, **27**, 4539 (1962).

modification suggested by Ichikawa,[3] in which the decomposition of the olefin-mercuric halide complex is rate determining, is definitely excluded by the repeated observations[3] that 2-alkoxyethylmercuric halides and 2-hydroxyethylmercuric halides give rise to unique rates. If the formation of the olefin–mercuric halide complex were fast and reversible a common rate would be observed (or at least a marked tendency of the rates to drift toward a common value as the reaction proceeds). If the formation of the olefin-mercuric halide complex is essentially irreversible, as suggested by Ichikawa, it is, by definition,[18] rate determining.

The observation that 2-acetoxyethylmercuric chloride is converted to 2-ethoxyethylmercuric chloride in ethanolic perchloric acid is mentioned by Ichikawa as evidence for the reversible formation of olefin–mercuric chloride π-complex. However, the facile solvolysis of 2-acetoxyethylmercuric iodide[17] makes it seem likely that this conversion simply proceeds *via* deoxymercuration to ethylene and mercuric chloride followed by readdition to the ethylene.

If the reaction scheme shown previously is correct, then the ratio k_3/k_2 is given by equation 10. It is

$$k_3/k_2 = [*_3]/[*_2][I^-] \qquad (10)$$

$*_n \equiv$ Transition state giving rise to k_n

identical in form and analogous in substance with the formation constant for a complex of a metallic ion with iodide ion. In this case, however, the central ion is the transition state containing only one iodine atom. In the same way k_4/k_3 is the formation constant for the transition state containing three iodine atoms from that containing only two. The former ratio, k_3/k_2, has a value, 3.2×10^3 l. mole^{-1}, and the later ratio, k_4/k_3, a value, 34 l. mole^{-1}. It is interesting to compare these with the various complexing constants of the mercuric ion. If the mercury were very weakly bound to the carbon skeleton in the transition state, so that the iodomercuric group resembled HgI^+ when only one iodine atom was present, the formation constants for the complexed transition states would be expected to resemble K_2 and K_3. On the other hand, if the mercury is firmly bound k_3/k_2 and k_4/k_3 might resemble K_3 and K_4, respectively. The values of K_2, K_3, and

$$K_2 = [HgI_2]/[HgI^+][I] \qquad (11)$$

$$K_3 = [HgI_3^-]/[HgI_2][I^-] \qquad (12)$$

$$K_4 = [HgI_4^-]/[HgI_3^-][I^-] \qquad (13)$$

K_4 are 10^{11}, 5×10^3, and 10^2,[16] supporting the hypothesis that the mercury is still firmly bound. This is consistent with the deoxymercuration transition state structure previously proposed,[7] in which the mercury is not being split away from the carbon skeleton in the rate-determining step.

Experimental

The preparation of solvents and acids have been previously described,[19] as has the kinetic method[6] and the preparation of 2-methoxyethylmercuric iodide.[20] The general method of Hofmann and Sand[21] was used to prepare 2-hydroxyethylmercuric iodide, m.p. 145° dec., lit.[21] 147°. The method of Ichikawa and coworkers[3] was used to prepare 2-isopropoxyethylmercuric chloride, m.p. 84.5–86°, lit.[3] 85–86°. Inorganic solutions were made up by weight from the best quality reagents commercially available.

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Reactions of Aromatic Carboxylates. I. Evidence for the Intermediacy of Benzyne in the Pyrolyses of *o*-Halobenzoates[1]

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The formation of benzyne in the pyrolysis of *o*-halobenzoates has been demonstrated by trapping experiments with tetracyclone to form 1,2,3,4-tetraphenylnaphthalene. The intermediacy of benzyne in the formation of xanthone in alkali metal *o*-halobenzoate reactions has been shown by the isolation of two dichloroxanthone isomers in the pyrolysis of potassium 2,4-dichlorobenzoate. 3,4-Benzocoumarin has been found as the major product of the pyrolysis of potassium *o*-iodobenzoate and has been detected in other *o*-halobenzoate systems. The major reaction path can often be polymerization by intermolecular aromatic SN2 reaction and benzyne-type reactions can be suppressed by temperature control.

The dismaying violence and the unpredictable products of *o*-halobenzoate pyrolyses have done little to encourage their study until recent years when *o*-halobenzoates have been regarded as potential sources of benzyne.[2] The rationale behind these views[3–6] is that benzyne should be formed from *o*-halobenzoates by a decarboxylation and elimination of halide ion since benzyne is generated in an aromatic system by an initial carbanion formation with a subsequent elimination of a suitable *ortho* group. Attempts to form benzyne from carboxylates with an *ortho* diazonium group[7] and an *ortho* phenyliodonium group[8] have been successful. This paper is a presentation of results which demonstrate the presence of benzyne in the pyrolyses

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[1] Presented in part at the 141th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

[2] The following works are excellent reviews on benzyne: (a) R. Huisgen, "Organometallic Chemistry," H. Zeiss, Ed., Reinhhold Publishing Co., New York, N. Y., 1960, pp. 36–87; (b) J. F. Bunnett, *J. Chem. Educ.*, **38**, 278 (1961); (c) H. Heaney, *Chem. Rev.*, **62**, 81 (1962).

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