Cleavage of Allylmercuric Iodide by Acid and Iodide Ion[1a,b]

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Abstract: The acid cleavage of allylmercuric iodide has been studied as a function of [I^-]. The kinetic evidence strongly suggests that the substrate complexes weakly with I^-, and that these complexes undergo cleavage in much the same way as the uncomplexed substrate. Consideration of the relative magnitudes of rate constants suggests that the mercury atom is still strongly bound to the rest of the substrate in the transition state, which may resemble that for deoxymercuration. These results further suggest that the positive charge center is at least 7 A removed from the mercury atom in the transition state for cleavage by hydronium ion. In addition, the complexed substrate seems to decompose in a unimolecular rate-determining step, possibly giving the π-allylic system as an intermediate. This is proposed to account for terms in the rate law, independent of the acid concentration and insensitive to the substitution of deuterium for hydrogen in the solvent. An additional cleavage mechanism involves the disproportionation of the substrate to give HgI_2 and diallylmercury, after which the latter reacts with acid. This can quantitatively account for the anomalously high rates observed at low fractional conversions in the presence of 10^{-2}–10^{-3} M I^- and in the absence of HgI_2.

In recent papers[2,3] it was shown that proton transfer to the γ carbon is rate determining for the acid cleavage of allylmercuric iodide. That work was done in the presence of a trace ($\sim 4 \times 10^{-5}$ M) of I^- to trap the HgI^+ as it was formed, but, other than that, it was shown that I^- had no significant effect on the rate or mechanism *at these very low concentrations.*

The present paper describes the effect of much higher I^- concentrations, up to 10^{-1} M. Catalysis is observed, presumably by complexing of I^- with the mercurial, and catalytic coefficients can be evaluated for a number of combinations of acids and iodide ion. From these, certain general conclusions can be drawn about the transition state for the acid cleavage of allylmercuric iodide. In addition, it is shown that allylmercuric iodide is in equilibrium with a small amount of diallylmercury, and that cleavage of the latter provides a significant pathway for the reaction under some conditions.

Results

The gaseous product of the cleavage of allylmercuric iodide by acid, in the presence of up to 0.3 M NaI, is propene, as it was at much lower [I^-]. The propene was identified by its infrared spectrum. As the [I^-] is increased from 10^{-5} toward 10^{-1} M, the ultraviolet spectrum of the water-soluble product changes progressively from that of HgI_2 to that of various mixtures of HgI_2 with HgI_3^- and HgI_4^{2-}. The exact composition of these mixtures varies as a function of the [I^-], but, with substrate concentrations $\sim 5 \times 10^{-6}$ M and [I^-] $> 5 \times 10^{-4}$ M, the latter does not change significantly during the course of an experiment, so that the proportions of the various complexes do not change significantly during the course of any one experiment. The [$HClO_4$] was never less than 10 times the initial substrate concentration and thus did not change significantly in the course of any one experiment.

In a series of semiquantitative control experiments, it was shown that allylmercuric iodide reacts with 10^{-2} M I^- in the absence of added acid at an appreciable rate, giving the complexes of HgI_2. The organic product was not isolated under these conditions. Initial addition of a little I_2 (likely to be present as an impurity in I^- solutions) had no effect on measured rate constants because it was instantly consumed by the substrate, producing the complexes of HgI_2 (observed spectrophotometrically) and (presumably) allyl iodide. Thus I_2 only reduces the amount of substrate available for observation, but does not change its rate of consumption.

At [I^-] $< 5 \times 10^{-4}$ M the course of the reaction was followed by following the *disappearance* of the ultraviolet spectrum of the substrate at 248 mμ, as previously described.[3] At [I^-] $> 3 \times 10^{-3}$ M the *appearance* of the ultraviolet spectrum of HgI_2 and its complexes was monitored at 280 or 320 mμ. The measurements were made in aqueous solutions containing 4% methanol, except where otherwise indicated. Pseudo-first-order rate constants, k_1, were obtained by the graphical application of eq 1 (at 248 mμ) or 2 (at 280 or 320 mμ).[3,4]

$$k_1 = \frac{2.303}{t - t_0} \log \left\{\frac{D_0 - D_\infty}{D_t - D_\infty}\right\} \tag{1}$$

$$k_1 = \frac{2.303}{t - t_0} \log \left\{\frac{D_\infty - D_0}{D_\infty - D_t}\right\} \tag{2}$$

In these equations, D is an optical density and its subscript indicates the time of measurement.

At an [I^-] of 5×10^{-4} M, a [$HClO_4$] of 3×10^{-2} M, and a temperature of 25°, D was monitored both at 248 and 280 mμ; k_1 values of 5.40×10^{-2} sec^{-1} and 5.87×10^{-2} sec^{-1}, respectively, were obtained. The latter is a little high because the [I^-] actually changes by about 10% during the course of this experiment. This has no effect on the substrate band, but causes the

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[1] (a) Presented, in part, at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965; (b) supported, in part, by the National Science Foundation through GP-5088; (c) Sloan Foundation Fellow, 1960–1964; (d) National Science Foundation Undergraduate Participant, summers of 1964 and 1965.

[2] M. M. Kreevoy, P. J. Steinwand, and W. V. Kayser, *J. Am. Chem. Soc.*, **86**, 5013 (1964).

[3] M. M. Kreevoy, P. J. Steinwand, and W. V. Kayser, *ibid.*, **88**, 124 (1966).

[4] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1962, p 29.

change in D at 280 mμ, per unit of reaction, to be a little larger at low conversions than at high, because of the higher extinction coefficients of the complexes. Nevertheless, the similarity of the two values strongly supports the assumption that essentially the same reaction is being monitored regardless of the wavelength used. Equation 1 or 2 is accurately obeyed at low $[I^-]$ ($<10^{-3}$ M) but at higher $[I^-]$ marked deviations are observed unless a quantity of HgI_2 is added, roughly equal to the initial substrate concentration. The reason for this is discussed below, and HgI_2 was added when it was necessary. Values of k_1 obtained in this way at 25° are given in Table I. Several of these values are the average of two determinations, and one, as noted, is the average of four. As in previous work of this sort, the average reproducibility seems to be around ±3–5%.

Table I. Rate as a Function of Acid and Iodide Concentration at 25°

$10^3[H^+]$, M	$10^3[I^-]$, M	10^4k_1, sec^{-1} Found	10^4k_1, sec^{-1} Calcd
1.21	5.92	0.833	0.925
1.25	5.92	1.00	0.945
2.51	5.92	1.52	1.62
4.02	5.92	2.67	2.43
5.03	5.92	3.24	2.97
6.03	5.92	3.33	3.51
8.04	5.92	4.63[a]	4.59
10.1	5.92	6.17	5.69
16.1	5.92	9.18	11.0
0.644	9.86	0.944	1.118
0.805	9.86	1.13	1.26
1.61	9.86	1.78	1.96
2.41	9.86	2.61	2.65
3.22	9.86	3.04	3.35
4.02	9.86	3.75	4.05
3.22	16.7	6.32	6.23
4.02	16.7	7.72	7.58
4.83	16.7	8.98	8.86
5.63	16.7	10.2	10.1
6.44	16.7	11.7	11.4
0.402	19.3	2.6	2.31
0.604	19.2	2.83	2.69
0.805	19.3	3.67	3.08
2.41	19.3	6.78	6.12
3.23	19.3	8.32	7.67
4.02	19.3	9.68	9.17
0.805	25.1	4.15	4.55
1.61	25.1	6.08	6.71
2.41	25.1	8.55	8.84
3.22	25.1	10.7	11.0
4.02	25.1	12.4	13.2

[a] Average of four determinations; the average deviation from the mean, 0.10 × 10^{-4} sec^{-1}.

The results in Table I were fitted to eq 3 by the scheme described in the following paragraphs. The results

$$k_1/S = k_H[H^+] + k_{HI}[H^+][I^-] + k_{HI_2}[H^+][I^-]^2 + k_I[I^-] + k_{I_2}[I^-]^2 \tag{3}$$

were first subdivided into five sections, in each of which the $[I^-]$ is constant while the $[H^+]$ is varied. Within each group k_1 is a linear function of $[H^+]$ within the precision of the measurements. In general, however, these functions have nonzero intercepts. Table II lists the slopes, S_H, and intercepts, I_H, obtained by the method of least squares.[5] The slopes have 50% confidence limits of ~2% of their values. The intercepts have 50% confidence limits of ~0.5 × 10^{-5} sec^{-1}, roughly independent of their magnitude. Both S_H and I_H are seen to be nonlinear functions of $[I^-]$. They can be fitted satisfactorily to the forms shown in eq 4 and 5, in which k_H is the previously determined,[3] iodide-independent, rate constant, 1.41 × 10^{-2} l. mole^{-1} sec^{-1}. The values of the k's were determined by the

Table II. Acid-Dependent (S_H) and Independent (I_H) Portions of the Rate at Various $[I^-]$

$10^3[I^-]$, M	S_H, l. mole^{-1} sec^{-1}	10^5I_H, sec^{-1}
0.05	0.014[a]	0.0[a]
5.92	0.055	2.9
9.8	0.082	4.6
16.7	0.161	12.2
19.3	0.198	19.0
25.1	0.261	20.6

[a] Results taken from ref 3.

$$I_H = k_I[I^-] + k_{I_2}[I^-]^2 \tag{4a}$$

$$I_H/[I^-] = k_I + k_{I_2}[I^-] \tag{4b}$$

$$S_H = k_H + k_{HI}[I^-] + k_{HI_2}[I^-]^2 \tag{5a}$$

$$(S_H - k_H)/[I^-] = k_{HI} + k_{HI_2}[I^-] \tag{5b}$$

application of the method of least squares to the "b" forms of eq 4 and 5.[5] They are shown in Table III, along with their 50% confidence limits and the maximum contribution to an observed rate attributable to each. Table I shows the agreement between observed k_1 values and those calculated from eq 3, using the values of I and S given by eq 4 and 5 with values of the k's given in Table III. The agreement is generally satisfactory, although the discrepancies are somewhat larger than the anticipated experimental imprecision in some cases. The additional discrepancies may be due to small, systematic errors in $[I^-]$ or to electrolyte effects on the k's.

Table III. Parameters of Equations 3, 4, 5, and 7

Parameter, k	Value	Units, sec^{-1}	Max. contribution to k_1, %
H	1.41×10^{-2} [a]	M^{-1}	100
HI	5.6 ± 0.4	M^{-2}	55
HI_2	$(1.8 \pm 0.2) \times 10^{-2}$	M^{-3}	35
I	$(3.2 \pm 1.1) \times 10^{-3}$	M^{-1}	29
I_2	$(2.5 \pm 0.7) \times 10^{-1}$	M^{-2}	40
HFor	$(1.09 \pm 0.05) \times 10^{-4}$ [b]	M^{-1}	80
HForI	4×10^{-2}	M^{-2}	40
$HForI_2$	2	M^{-3}	30

[a] Results taken from ref 3. [b] Unpublished results by M. M. Kreevoy and T. S. Straub.

Measurements of k_1 were also made in formic acid–sodium formate buffer solutions. In these the ratio of acid to conjugate base was always 1.17. Two $[I^-]$ were used, 1.11 × 10^{-2} and 2.22 × 10^{-2} M. These measurements were made at a constant ionic strength, 0.2 M. The results are shown in Table IV. At each

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(5) C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and the Chemical Industry," John Wiley and Sons, Inc., New York, N. Y., 1954, pp 36–40, 231.

Table IV. Rate as a Function of Formic Acid and Iodide Concentration

10^2[HCOOH], M	10^2[I$^-$], M	10^4k_1, sec^{-1} Found	Calcd
2.52	1.11	0.78	0.86
5.04	1.11	1.21	1.06
7.57	1.11	1.18[a]	1.26
10.1	1.11	1.49[a]	1.46
11.9	1.11	1.61	1.60
15.8	1.11	1.92	1.91
20.2	1.11	2.26	2.26
2.52	2.22	1.88	2.00
5.05	2.22	2.53	2.49
7.57	2.22	3.14	2.99
10.1	2.22	3.54	3.48
12.1	2.22	3.72	3.87

[a] Average of four determinations.

[I$^-$], k_1 is given by eq 6 with satisfactory precision. The

$$k_1 = I_{\text{HFor}} + S_{\text{HFor}}[\text{HCOOH}] \qquad (6)$$

parameters of eq 6 were determined by the method of least squares[5] at each [I$^-$] and are given in Table V.

Table V. Parameters of Equation 6

10^2[I$^-$]	10^4S_{HFor}, l. mole^{-1} sec^{-1}	10^5I_{HFor}, sec^{-1} Found	Calcd[a]
0.005	1.1[b]	0.4[b]	0.6
1.11	7.9	6.6	9.8
2.22	19.5	15.1	26.9

[a] $I_{\text{H}} + S_{\text{H}}(\text{H}^+)$. [b] Unpublished results of T. S. Straub.

Table IV shows how well the rate constants calculated from eq 6, k_1^{calcd}, agree with the experimental values. The agreement is generally within the indicated experimental imprecision. The formic acid independent rate, I_{HFor}, should be given by $I_{\text{H}} + S_{\text{H}}[\text{H}^+]$ and Table V contains the values of I_{HFor} calculated in this way, for comparison. The 50% confidence limits on the slopes are about 1% of their values and those on the intercepts range from 0.1 × 10^{-5} to 0.6 × 10^{-5} sec^{-1}. The agreement between calculated and observed I_{HFor} values is moderately satisfactory in view of the fact that the calculations were made with infinite dilution rate constants while the experiments were actually carried out at an ionic strength of 0.2 M. The estimation of [H$^+$], however, took into account both the presence of 4% methanol and the ionic strength.[6]

The number and precision of the S_{HFor} values are not sufficient to unambiguously define their relation to concentration-invariant rate constants, but, if eq 7 is

$$S_{\text{HFor}} = k_{\text{HFor}} + k_{\text{HForI}}[\text{I}^-] + k_{\text{HForI}_2}[\text{I}^-]^2 \qquad (7)$$

assumed by analogy with eq 3, the rate constants k_{HFor}, k_{HForI}, and k_{HForI_2} can be evaluated. They are shown in Table III. To all intents k_{HFor} is S_{HFor} at [I$^-$], 5 × 10^{-5} M, so its 50% confidence limits could be evaluated in the usual way, and are cited in Table III. On the other hand, the values of k_{HForI} and k_{HForI_2} are not completely independent; *i.e.*, one can be raised while the other is lowered without hurting the fit very much. Both of these should be considered uncertain by about 30%.

A limited number of experiments were also carried out with perchloric acid in D_2O at 25°. The ionic strength was not held constant in these experiments, but was never as high as 0.03 M. The reacting solutions contained 1% methanol rather than 4%. The results are shown in Table VI. They form two groups, in each of which the [I$^-$] is constant and the [D$^+$] is varied. For each group there is a satisfactory linear relation between k_1 and [D$^+$]. The slopes, S_{D}, and intercepts, I_{D}, are shown in Table VII. The values of k_1 have been recalculated from these slopes and intercepts, and are compared with the experimental values in Table VI. In general, the agreement with experiment is satisfactory when account is taken of the additional source of imprecision, the possible isotopic contamination of the D_2O. The 50% confidence limits on each S_{D} are about 5% of its value, and those for I_{D} are about 25% of its value.

Table VI. Rate as a Function of [DClO$_4$] and [I$^-$] in D_2O at 52°

10^3[D$^+$], M	10^3[I$^-$], M	10^4k_1, sec^{-1} Found	Calcd
15.3	7.62	3.76	3.89
23.0	7.62	5.50	5.46
30.6	7.62	6.94	7.09
38.3	7.62	8.78	8.74
4.60	22.9	5.26	5.46
6.13	22.9	7.25	6.58
7.66	22.9	7.92	7.70
9.19	22.9	8.23	8.82
10.72	22.9	9.05	9.94
11.49	22.9	12.3	10.5
12.3	22.9	11.3	11.2
13.8	22.9	12.0	12.2

Table VII. Isotope Effects in the Presence and Absence of I$^-$

10^3 [I$^-$], M	0.05	7.62	22.9
10^2 S_{D}, l. mole^{-1} sec^{-1}	...	2.1	7.3
10^5I_{D}, sec^{-1}	...	5	21
$S_{\text{H}}/S_{\text{D}}$	3.1[a]	3.2	3.2
$I_{\text{H}}/I_{\text{D}}$	...	0.8	1.0

[a] Value taken from ref 3, measured at 35°.

Table VII also compares S_{D} and I_{D} with the comparable quantities for H_2O, estimated at comparable [I$^-$] by means of eq 4 and 5 with the rate constants given in Table III. It is clear that $k_{\text{H}}/k_{\text{D}}$, $k_{\text{HI}}/k_{\text{DI}}$, and $k_{\text{HI}_2}/k_{\text{DI}_2}$ must all have nearly identical values—around 3.2 at 25°—since the isotope effect on the acid-catalyzed part of the reaction shows no variation with [I$^-$]. The ratios of intercepts cannot be interpreted as confidently, because of their sizeable uncertainties, but it would appear that there is no isotope effect on the acid-independent portion of the rate.

At [I$^-$] >10^{-3} M plots of log ($D_\infty - D_t$) *vs.* t showed small but reproducible deviations from linearity at low fractional conversions in the absence of added HgI_2. These deviations became progressively more pronounced as [I$^-$] was increased. Two plots illustrating the deviant behavior are shown in Figure 1. The curvature was not suppressed by decreasing the initial

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(6) (a) J. Julliard, *Bull. Soc. Chim. France*, 3069, (1964); (b) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Butterworth and Co. (Publishers) Ltd., London, 1959, p 492.

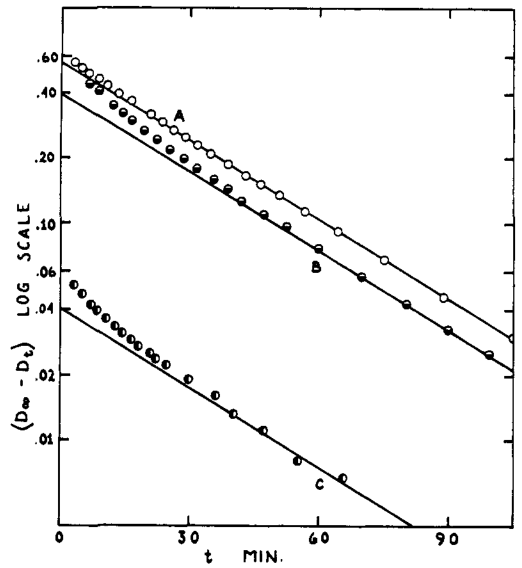

Figure 1. Plots of log $(D_\infty - D_t)$ *vs. t* at various substrate concentrations, and with added HgI_2: Curve A, ○, had initial substrate concentration 5.6×10^{-5} *M*, and an initial $[HgI_2]$ of 6.0×10^{-5} *M;* curve B, ◒, had initial substrate concentration of 5.6×10^{-5} *M* and no added HgI_2; curve C, ◐, had an initial substrate concentration of 7.3×10^{-6} *M*, and no added HgI_2. All three had initial $[HClO_4]$, 4.02×10^{-3} *M*, and initial [NaI], 5.94×10^{-3} *M*. The three lines are drawn with identical slopes, all obtained from curve A.

substrate concentration, eliminating a higher order reaction as a cause. It did not become more pronounced with the aging of the allylmercuric iodide, nor was it reduced by using allylmercuric chloride, prepared *via* a Grignard reaction, as substrate. The latter, in fact, gave an identical curve, which would be expected since the halide ions are presumed to be rapidly exchangeable, and I^- was present in over 100-fold excess and has a greater affinity for mercury than Cl^-. These observations minimize the possibility that the curvature was due to impurities carried along with the substrate. At $[I^-] \leq 10^{-2}$ *M* the curvature was effectively suppressed by adding, initially, to the reaction mixture a concentration of HgI_2 about equal to the initial substrate concentration. This is also shown in Figure 1. When the curvature was so suppressed, the resultant line had a slope identical with that obtained at *high* fractional conversion in the absence of added HgI_2.

These observations are all consistent with the rate law shown in eq 8, which was obtained from a mechanism given in the Discussion section. The parameter, α, is a known function of $[I^-]$ and the complexing constants of HgI_2 with I^-, K_{HgI_3}, and K_{HgI_4};[7] it is shown in eq 9. Equation 8 can be integrated in closed form but the result is cumbersome, so a Pace electronic analog computer and standard computational methods[8] were used to evaluate $(D_t - D_0)$ as a function of *t* directly from the differential equation at a number of values of the new parameter, k_2'. Previously, k_1 was evaluated from a similar reaction in which HgI_2 had been added to supress the curvature; D_∞ and D_0 were obtained from the experimental data. (Special method of obtaining D_0 is described in the Experimental Section.) The "best" value of k_2' was assigned by inspection. A typical example of the curve-fitting process is shown in Figure 2. The resultant values of k_2' are shown in Table VIII. These were all obtained at 35°, rather than at the 25° temperature used for the rest of this work, in the presence of 4% of methanol.

$$\frac{dD}{dt} = k_1(D_\infty - D_t) + \alpha k_2' \frac{(D_\infty - D_t)^2}{D_t - D_0} \qquad (8)$$

$$\alpha = 1 + K_{HgI_3}[I^-] + K_{HgI_3}K_{HgI_4}[I^-]^2 \qquad (9)$$

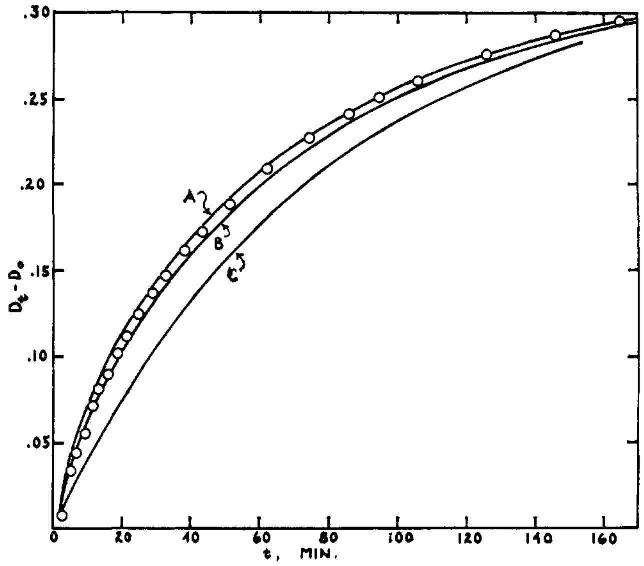

Figure 2. $D_\infty - D_t$ as a function of *t*. The circles are experimental points. The solid curves were produced by the computer. For curve A, k_2' was 1.9×10^{-4} sec^{-1}; for curve B, k_2' was 1.2×10^{-4} sec^{-1}; for curve C, k_2' was identically zero. The best value for k_2' was chosen as 1.6×10^{-4} sec^{-1}.

Table VIII. Values of k_2' as a Function of $[H^+]$ and $[I^-]$ at 35°

$10^3[H^+]$, *M*	$10^3[I^-]$, *M*	$10^4k_2'$, sec^{-1}
2.02	5.94	0.6
4.03	0.72	0.8
4.03	1.08	0.9
4.03	1.44	1.4
4.03	2.16	1.3
4.03	3.06	1.5
4.03	5.94	1.2[a]
4.03	9.36	1.0
4.03	11.9	0.9
8.04	5.94	1.9

[a] This is the average of nine determinations. The average deviation from the mean is 0.1×10^{-4} sec^{-1}. The initial substrate concentration varied from 7.3×10^{-6} to 5.6×10^{-5} *M*.

The resultant k_2' values are clearly not of high precision. Figures 1 and 2 show that they are derived from rather small deviations from first-order behavior, and the roughly 10% average deviation from the mean on repetitive determinations is all that could be expected. Within this uncertainty, it seems that k_2' is directly proportional to the acid concentration and independent of the iodide concentration. It is also invariant under an almost 10-fold variation in initial substrate concentration, as indicated in the footnote to Table VIII.

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(7) J. Bjerrum, G. Schwarzenbach, and L. G. Sillen, "Stability Constants, Part II; Inorganic Ligands," The Chemical Society, London, 1958, p 121.

(8) A. E. Rogers and T. W. Connolly, "Analogue Computation in Engineering Design," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

Discussion

The deviations from first-order behavior in the presence of higher [I^-] and in the absence of added HgI_2 are most readily explained by the following mechanism. (In these and subsequent equations, R is allyl.) This is superimposed on the reaction shown

$$2RHgI \overset{K_S}{\rightleftharpoons} R_2Hg + HgI_2 \tag{10}$$

$$HgI_2 + I^- \xrightarrow{K_{HgI_3}} HgI_3^- \tag{11}$$

$$HgI_3^- + I^- \overset{K_{HgI_4}}{\rightleftharpoons} HgI_4^{2-} \tag{12}$$

$$R_2Hg + I^- + H^+ \xrightarrow{k_2} RHgI + RH \tag{13}$$

in eq 14, which leads to the pseudo-first-order rate laws shown in eq 1 and 2. Equations 13 and 14 readily

$$RHgI + H^+ + I^- \xrightarrow{k_1} RH + HgI_2 \tag{14}$$

lead to the rate law shown in eq 15 if the approximation is made *that no significant fraction of starting material is ever converted to R_2Hg.* This approximation is formalized in eq 16. The quantity, α, is given by eq 9.

$$\alpha d[HgI_2]/dt = k_1[RHgI] + k_2[R_2Hg] \tag{15}$$

$$[RHgI] = \alpha([HgI_2]_\infty - [HgI_2]) \tag{16}$$

When this is multiplied by [HgI_2] it gives the total inorganic Hg(II) concentration. Further substitution of eq 16 and the various mass action expressions into eq 15 leads to eq 17. Substitution of the appropriate

$$\frac{d[HgI_2]}{dt} = k_1([HgI_2]_\infty - [HgI_2]) + \alpha k_2 K_S \frac{([HgI_2]_\infty - [HgI_2])^2}{[HgI_2]} \tag{17}$$

optical density changes for concentrations then leads to eq 8, in which k_2' is, clearly, k_2K_S.

As already shown, eq 8 gives a satisfactory quantitative representation of the data. It is also qualitatively apparent that it has the proper characteristics. It reduces to the differential form of eq 2 at high fractional conversion, because the second term goes to zero as the numerator becomes small and the denominator becomes large. It predicts that the fractional change in optical density, per unit time, should be independent of the initial substrate concentration, in accord with experiment.

Since k_2 is the rate constant for a reaction quite reasonably supposed to be acid catalyzed it is reasonable that k_2' should be linearly dependent on the acid concentration. The lack of I^- catalysis is reasonable in view of the generally small complexing constants of dialkylmercurials with halide ions. Only the perfluorodialkylmercurials are known to form complexes with halide ions.[9] It is assumed in eq 17 that K_S is small, and this is reasonable,[10] but it is interesting that it has a significant effect on reactivity. While the foregoing does not unequivocally prove that the mechanism shown in eq 10–13 is responsible for the observations, in the absence of an attractive alternative it creates a strong presumption in its favor. It seems to be the first time such a mechanism has been documented for the acidolysis of an organometallic. The reactions shown in eq 10–12 are, however, analogous to those required for the ammonia symmetrization reaction, studied by Nesmeyanov, Reutov, Jensen, and their co-workers.[11]

The acceleration of the reaction shown in eq 14 by higher concentrations of iodide ion is to be expected. It probably arises through the complexing shown in eq 18 and 19. The complexed species then undergo the reaction in the usual way.[2,3] The mechanism of the

$$RHgI + I^- \overset{K_{RHgI_2}}{\rightleftharpoons} RHgI_2^- \tag{18}$$

$$RHgI_2^- + I^- \overset{K_{RHgI_3}}{\rightleftharpoons} RHgI_3^{2-} \tag{19}$$

parent reaction requires general acid catalysis, and it has been observed.[2,3] In the same way the general acid catalyzed cleavage of $RHgI_2^-$ and $RHgI_3^{2-}$ gives rise to k_{HForI} and k_{HForI_2}, respectively. The invariance of S_H/S_D under changes in the iodide concentration further supports this view.

It would be attractive to attribute k_I and k_{I_2} to the general acid catalysis of the reactions of $RHgI_2^-$ and $RHgI_3^{2-}$ by *water*. However, considering the ratio of acid dissociation constants for formic acid and water (almost 10^{12} if the activity of water in the liquid is taken as its concentration, 55 *M*) the ratios, $55k_{HForI}/k_I$ and $55k_{HForI_2}/k_{I_2}$, seem small. They are both between 10^2 and 10^3, while a Brønsted α of 0.6–0.7, which seems appropriate for the parent reaction,[3,12] would lead to values around 10^8. The values of I_H/I_D, close to unity, also seem inconsistent with a rate-determining proton transfer. Instead we are inclined to suspect that truly unimolecular decompositions of $RHgI_2^-$ and $RHgI_3^{2-}$ give rise to these terms. Such unimolecular decompositions could well yield the corresponding π-allylic compounds[13] as intermediates. In view of the fact that organic products have not yet been isolated in the absence of acid it is also possible that some other, nonacid-catalyzed reaction, such as an oxidation, could be responsible for these terms.

The ratio of rate constants, k_{HI}/k_H, has the significance of the iodide ion complexing constant of the proton-catalyzed cleavage transition state.[14] Similarly, the ratio k_{HI_2}/k_{HI} has the significance of the second complexing constant. These ratios have the values, 4×10^2 M^{-1} and 3×10 M^{-1}, respectively. They are, thus, similar to, but smaller than, K_{HgI_3}, 5×10^3 M^{-1}, and K_{HgI_4}, 10^2 M^{-1}.[7] The first is notably smaller than K_{HgI_2}, 10^{11} M^{-1}, the formation constant for HgI_2 from HgI^+ and I^-. This excludes the possibility that the HgI^+ fragment is substantially liberated *before* the proton is transferred. The ratios, k_{HI}/k_H and k_{HI_2}/k_{HI}, are similar to the analogous ratios for deoxymercuration (3×10^3 and 3×10 M^{-1}, respectively).[14] This supports the view that the rate-determining step in the present reaction leads to the same intermediate as that for deoxymercuration, the olefin–mercuric iodide π complex.[14,15]

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The ratios of rate constants, $k_{\mathrm{HForI}}/k_{\mathrm{HFor}}$ and $k_{\mathrm{HForI_2}}/k_{\mathrm{HForI}}$, have the values 4×10^2 and $5 \times 10\ M^{-1}$, respectively. These, of course, have the significance of the iodide ion complexing constants of the formic acid catalyzed cleavage transition states. They are remarkably similar to the corresponding ratios for proton-catalyzed cleavage. One might have expected at least an electrostatic exaltation of the formation constants in the latter case. The fact that it is not observed suggests that the positive charge center and the mercury atom are quite widely separated in the transition state. A simple electrostatic calculation,[16] taking 78.5 as the appropriate dielectric constant,[17] gives 7 A as the distance at which the electrostatic potential energy between two electronic charges falls below RT, 600 cal mole^{-1}, near room temperature. Such a calculation can more easily underestimate than overestimate that distance because the effective dielectric constant can hardly be greater than, but may be less than that of pure water.[16] It is possible, of course, that this line of reasoning is entirely invalid because of differences in charge distribution between the formic acid catalyzed transition state and that for hydronium ion catalysis. A distance of 7–10 A between the charge centers, if it can be accepted, is easily accommodated if a short chain of water molecules intervenes between the H_3O^+ unit and the substrate in the transition state.[3] It is hard to reconcile so large a distance with a transition state in which the H_3O^+ unit and the substrate are contiguous.

Experimental Section

The materials, solutions, and general techniques used in this investigation were essentially identical with those previously described.[3,14,18] The only new technique required is that for getting the zero-time optical density in experiments with high [I$^-$] and no added HgI_2. This is required in eq 8, and is not reliably given by plots such as those shown in Figure 1 because of the strong curvature near zero time. This problem was solved by extrapolating the line based on the points at high fractional conversion back to zero time. The logarithms of the differences between that line and the experimental points were a linear function of time, which could be extrapolated to zero time without difficulty. This zero-time difference was then added to the value obtained from the high conversion extrapolation to get $(D_\infty - D_0)$, from which D_0 itself is readily obtained.

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Radical Abstraction of Iodine from Aryl Iodides[1]

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Abstract: The main product from decomposition of bis(p-chlorobenzoyl) peroxide in a benzene solution of iodobenzene is p-chloroiodobenzene. Likewise, iodobenzene is the major product from thermolysis of benzoyl peroxide in a benzene solution of m-chloroiodobenzene. The formation of these and lesser products is best accounted for by direct iodine atom abstraction from aryl iodides by aryl radicals. The fact that no p-bromochlorobenzene is formed from decomposition of bis(p-chlorobenzoyl) peroxide in the presence of bromobenzene shows that p-chlorophenyl radicals failed to abstract bromine under the conditions employed.

Although radical abstraction of halogen atoms from alkyl halides of appropriate constitution is well recognized,[4a,b] the corresponding reaction of aryl halides does not appear to have been described.

We have found that radicals readily abstract iodine from aryl iodides. This reaction was recognized by observing p-chloroiodobenzene as a prominent product from the decomposition of bis(p-chlorobenzoyl) peroxide in a benzene solution containing iodobenzene. Other products detected, all in smaller yields than p-chloroiodobenzene, included 4-chlorobiphenyl, biphenyl, and chlorobenzene.

The formation of these products is readily accounted for by the set of reactions shown in Scheme I. All the reactions proposed in this scheme have ample precedent in the modern literature, except for iodine atom transfer (reaction 2). The phenyl radical produced in reaction 2 appears as a reactant in reaction 4. The hydrogen donor in reaction 5 probably is, at least in part, the cyclohexadienyl radical shown as an intermediate in reaction 3 or the corresponding intermediate implied in reaction 4.

Decomposition of bis(p-chlorobenzoyl) peroxide in neat iodobenzene also afforded p-chloroiodobenzene as the principal product. No chlorobiphenyl was detected in this case, as might have been anticipated, but two isomeric 4-chloro-x'-iodobiphenyls and two isomeric iodobiphenyls were formed. The chloroiodobiphenyls obviously represent p-chlorophenylation of the iodobenzene, and the iodobiphenyls, phenylation by phenyl radicals generated as by-products of iodine atom transfer (reaction 2).

An independent demonstration of iodine abstraction involved decomposition of benzoyl peroxide in a benzene solution of m-chloroiodobenzene. The major product was iodobenzene, whose formation is attrib-

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