ml. of ether. The aqueous phase was acidified with 5% hydrochloric acid and the blue suspension which resulted was extracted with ether. The separated ether layer was washed twice with water and dried over sodium sulfate. The solvent was removed and the residue was chromatographed on silicic acid. Ether removed a blue band which gave 0.155 g. (77.7%) of 1-azulylmethylmalonic acid as blue needles, m.p. 134–135° dec. An ethanol solution showed λ_{max} in mμ (D_{max}) in the ultraviolet at 238 (0.59), 278 (1.88), 284 (1.72), 343 (0.18), and 357 (0.10). Absorption in the visible was observed at 592 (1.20), 643 (1.08), and 710 (0.35).

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.85; H, 4.92. Found: C, 68.54; H, 5.16.

3-(1-Azulyl)propanoic Acid (XV).—A mixture of potassium acid sulfate (50 mg., 0.365 mmole) and 1-azulylmethylmalonic acid (0.131 g., 0.537 mmole) was heated in a vacuum sublimation apparatus at 150° and 0.5 mm. The evolution of carbon dioxide began immediately and the product was collected on the cold finger (an appreciable amount of material slowly turned brown and remained unsublimed). The sublimate was dissolved in a small volume of benzene and chromatographed on silicic acid. Methylene chloride eluted a blue band which gave 56 mg. (52%) of 3-(1-azulyl)-propanoic acid as blue needles, m.p. 89–90°. A methylene chloride solution showed λ_{max} in mμ (D_{max}) in the ultraviolet at 238 (0.40), 279 (1.25), 284 (1.22), and 344 (0.12). Absorption in the visible was observed at 600 mμ. The infrared spectrum was recorded.

Anal. Calcd. for $C_{13}H_{12}O_2$: C, 78.00; H, 6.00. Found: C, 77.83; H, 6.32.

1-Methylazulene (XVI). Method A.—A mixture of 15 ml. of absolute ethanol, 1-azulylmethyltrimethylammonium iodide (0.2 g., 0.61 mmole), and an excess of sodium borohydride was heated under reflux for 45 min. and then diluted with 100 ml. of water. The whole was extracted with ether and the separated organic layer was washed with water and dried over sodium sulfate. The solvent was removed on a rotary evaporator and the residue was chromatographed on acid-washed alumina. *n*-Pentane eluted a blue band which gave 56 mg. (64.5%) of 1-methylazulene as a blue oil. The ultraviolet, visible, and infrared spectra of the product were identical with those of an authentic sample.[6]

Method B.—To a suspension of 0.15 g. (0.46 mmole) of 1-azulylmethyltrimethylammonium iodide in 20 ml. of dry benzene was added an excess of a 52% oil dispersion of sodium hydride and the mixture was heated under reflux for 2.5 hr. The solution was then washed thoroughly with water and dried over sodium sulfate. The solvent was removed and the residue was chromatographed over acid-washed alumina as described in method A. There was obtained 60 mg. (92.2%) of 1-methylazulene as a blue oil identical in all respects to the product in Method A.

The Solvolysis of 2-Iodomercuriethyl Esters[1]

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Received June 25, 1962

A solvolytic deoxymercuration has been discovered—that of 2-iodomercuriethyl esters. Solvolysis rate constants for the benzoate in mixtures of water with 30% or more of dioxane, ethanol, or acetic acid are linearly related to the Grunwald–Winstein Y's (ref. 8–10). For the acetate, solvolysis rate constants are linearly related to the Grunwald-Winstein Y's in all mixtures of ethanol and dioxane with water, but no linear relation exists over any substantial range of acetic acid–water mixtures. With both compounds a separate slope (m) is obtained for each organic diluent. These results are interpreted in terms of the mechanism of the deoxymercuration reaction and the structure of the transition state.

Some time ago, Sand[2] reported that 2-iodomercuriethyl benzoate (I) is decomposed only slowly by boiling hydrochloric acid. The implications of this report hardly seem credible since halide ion and hydronium ion are now known to catalyze the deoxymercuration reaction, both alone and in combination, quite vigorously around room temperature.[3–6] A re-examination of I was, consequently, undertaken. Compound I, and other 2-iodoethylmercuric esters, react readily in neutral or acid solutions in water or partially aqueous solvents. This paper reports on the neutral solvolysis reactions of I and 2-iodomercuriethyl acetate, II.

Reactions were carried out in dilute, homogeneous solution in water and in mixtures of water with ethanol, acetic acid, and dioxane. The course of the reactions was followed spectrophotometrically by observing the buildup of the mercuric iodide peak around 2800 Å. Compound I has a half-life of around three minutes in dilute aqueous solution at 25°.

Results

Each mole of I solvolyzed yielded one-half mole of mercuric iodide, identified by its ultraviolet spectrum.[5] The solvolysis was also carried out in glacial acetic acid on a larger scale, using a substantially higher concentration of I and a somewhat higher temperature. One-half mole of ethylene, identified by its very characteristic infrared spectrum, was produced per mole of starting material. Ethylene was also identified as a product when II was allowed to solvolyse in water, 20% dioxane, and 20% ethanol. This leads to the overall stoichiometry shown in equation 1.

$$2RCOOCH_2CH_2HgI \longrightarrow RCOO^- + CH_2{=}CH_2 + HgI_2 + RCOOCH_2CH_2Hg^+ \quad (1)$$

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[1] This research was supported by the Air Force Office of Scientific Research through Grant No. AF49(638)711. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] J. Sand, *Ber.*, **34**, 1390 (1901).

[3] J. Chatt, *Chem. Rev.*, **48**, 7 (1951).

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

[5] M. M. Kreevoy, *J. Am. Chem. Soc.*, **81**, 1099 (1959).

[6] K. Ichikawa, H. Ouchi, and S. Araki, *ibid.*, **82**, 3880 (1960).

By analogy with acid-induced deoxymercuration[5] it was assumed that a second mole of substrate reacts with the mercuric monoiodide produced in the first step to give the mercuric iodide and a mole of $RCOOCH_2CH_2Hg^+$. Presumably the latter associates with the carboxylate ion in the solvents of lower dielectric constant.

Rate constants were evaluated graphically by means of equation 2, in which D is the optical density at 2800 Å. and other symbols have their usual significance. (Equation 2 is the usual integrated form of the first order rate law except for the two in the denominator which enters because of the second mole of substrate consumed in producing the mercuric iodide.) Substrate concentrations between 10^{-5} and 10^{-4} M were used. Beer's law was shown to hold for mercuric iodide in water, 95% ethanol, and glacial acetic acid in this concentration range. Plots of log $(D_\infty - D_t)$ against

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

t were linear up to 70% reaction, then sometimes showed slight downward curvatures.[5] Obedience to a first order rate law was verified by doubling the concentration of I under otherwise identical conditions in a solvent contining 29.3% ethanol, 4.0% dioxane, and 66.7% water. A value of 2.40 × 10^{-4} sec.$^{-1}$ was obtained at the lower concentration and 2.49 × 10^{-4} sec.$^{-1}$ at the higher. Within the experimental uncertainty these are identical.

Rate constants were obtained at 25.0° in water and mixtures of water with ethanol, acetic acid, and dioxane. They are shown in Table I. The rate constant for I in 34.6% ethanol was measured five times and was reproducible with a precision of ± 1%. In general the precision of the rate constants is not thought to be this good; ± 3% is probably more realistic in view of past experience with the method.[5] A number of other tabulated values are averages of several measured values.

To demonstrate the solvolytic character of the reaction, the rate for I in 32% ethanol was also measured in a solution containing 0.067 M acetic acid and 0.033 M sodium acetate. This buffer would increase by several powers of ten the lyonium ion concentration of the solvent and correspondingly decrease the lyate ion concentration, so that, if the reaction had been due to the former, it would have been substantially accelerated, while it would have been suppressed if it had been due to the latter. In fact, k_1 was 2.99 × 10^{-4} l. mole^{-1} sec.$^{-1}$, almost indistinguishable from k_1 in the absence of buffer. An acid catalyzed reaction of II is detectable in ~ 0.01 M. aqueous perchloric acid.

No results are available yet on the effect of acids or salts on the rates of reactions in media of very low dielectric constant—*i.e.*, almost anhydrous acetic acid. However, the concentrations of substrate used were so low as almost to preclude major effects from the ionic reaction products. This is supported by the invariance of k_1 during a given experiment.

TABLE I

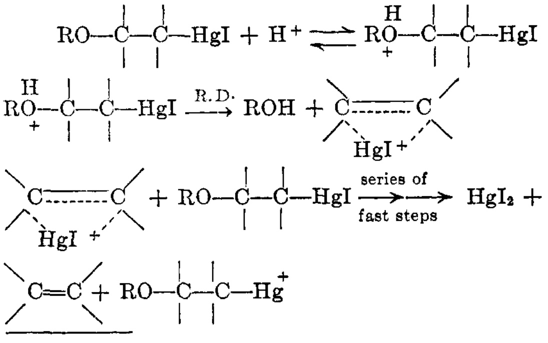
SOLVOLYSIS RATE CONSTANTS AT 25°

Compound	organic solvent[a]	Vol. % organic	L. mole^{-1} sec.$^{-1}$
I	D	0.2	2.0×10^{-3}
I	D	26.5	2.95×10^{-4}
I	D	30.0	2.39×10^{-4}
I	D	34.6	1.74×10^{-4}
I	D	51.0	3.94×10^{-5}
I	D	67.3	7.37×10^{-6}
I	E	27.4	4.75×10^{-4}
I	E	34.6	2.22×10^{-4}
I	E	33.2	2.71×10^{-4}
I	E	32.0	3.29×10^{-4}
I	E	33.3[b]	2.45×10^{-4}
I	E	66.2	4.62×10^{-5}
I	E	77.0	2.39×10^{-5}
I	E	99.9	3.30×10^{-6}
I	A	30.0	3.58×10^{-4}
I	A	34.6	2.86×10^{-4}
I	A	51.0	1.10×10^{-4}
I	A	18.2 M H_2O	7.33×10^{-5}
I	A	9.1 M H_2O	4.13×10^{-5}
I	A	0.06 M H_2O	5.76×10^{-6}
II	D	1.0	6.17×10^{-4}
II	D	2.0	5.78×10^{-4}
II	D	14.8	3.53×10^{-4}
II	D	21.6	2.11×10^{-4}
II	D	30.0	1.22×10^{-4}
II	D	34.6	8.40×10^{-5}
II	D	45.5	3.49×10^{-5}
II	D	51.0	2.25×10^{-5}
II	D	67.3	4.13×10^{-6}
II	A	18.3	3.84×10^{-4}
II	A	30.0	2.79×10^{-4}
II	A	34.6	2.74×10^{-4}
II	A	51.0	1.83×10^{-4}
II	A	15.6 M H_2O	1.44×10^{-4}
II	A	9.1 M H_2O	1.05×10^{-4}
II	A	4.9 M H_2O	6.18×10^{-5}
II	A	0.06 M H_2O	7.37×10^{-6}
II	E	2.0	5.86×10^{-4}
II	E	18.3	4.11×10^{-4}
II	E	34.6	1.75×10^{-4}
II	E	51.0	6.27×10^{-5}
II	E	67.3	2.72×10^{-5}
II	E	99.8	1.86×10^{-6}

[a] E is ethanol, A is acetic acid, and D is dioxane. [b] Including 4% dioxane.

Discussion

Acid-induced deoxymercuration has been shown to have the mechanism given in equations 3–5.[7]



(3)

(4)

(5)

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

The facility of the acid-induced deoxymercuration[5,7] suggests that a solvolytic reaction of similar mechanism (but lacking the protonation step) will occur if the alkoxide group in the starting material is replaced with a somewhat better leaving group. To test the hypothesis that the present reaction *is* that of solvolysis, the dependence of rate on solvent composition was examined.

Grunwald, Winstein, and co-workers have shown[8–10] that solvolysis rates are frequently correlated by equation 6 if the cation being formed does not have strong, covalent interactions with the solvent. (The notation is that of Winstein, Grunwald, *et al.*[8–10])

$$\log k = \log k_0 + m\,Y \qquad (6)$$

The possibility of strong covalent interaction between the π-complex, which is the product of the postulated rate-determining step, and the oxygen of the solvent is remote because of its structure and because no such bonds are found in the ultimate products. Plots of log k_1 against Y are shown in Fig. 1 and Fig. 2. The predicted linear relations are obtained for II in mixtures of ethanol (m = 0.47) and dioxane (m = 0.67) with water although the slope is quite different in the two kinds of solvent mixtures. For I in these same two solvent pairs, linear relations are obtained for solvent mixtures containing 30% or more of the organic component (with m = 0.67 for dioxane–water mixtures and 0.42 for ethanol–water mixtures). In acetic acid–water mixtures I behaves much as it does in other solvents, giving an m of 0.31. In all the highly aqueous solvent mixtures I gives increasingly positive slopes. On the other hand, II does not obey equation 6 in acetic acid–water mixtures at all, giving a continuously curved plot.

Dispersion into separate lines for the different organic components has been observed before.[8,11,12] It seems to be related to the structure and stability of the cation as well as the structure of the leaving group. The curvature obtained with I in highly aqueous media may be due to a rapid diminution of its activity coefficient as organic diluents are added to its aqueous solution. It has a low solubility in pure water (~ 10^{-5} M) which rises sharply as organic diluent is added. Anomalies were also observed in highly aqueous mixed solvents when the activity postulated[10] was applied to acid catalyzed deoxymercuration data.[13] The complete failure of equation 5 for II (but not for I) in acetic acid–water mixtures is puzzling. It may be, at least partially, due to ion pair recombination.[14] In general, it can be said that the agreement with the predictions of equation 5 is comparable to that which has been previously obtained in systems differing widely in structure from *tert*-butyl chloride[8,11,12] and supports the hypothesis that the reaction is a solvolytic deoxymercuration.

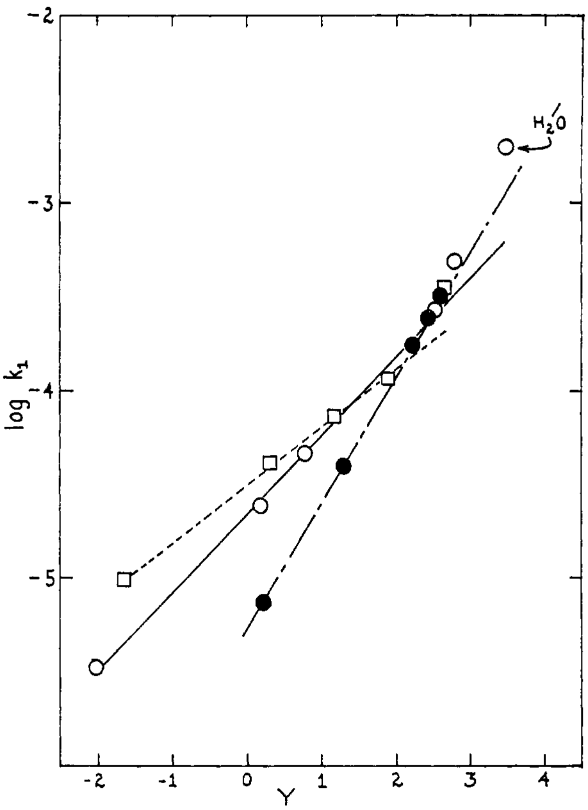

Fig. 1.—A plot of log k_1 *vs.* Y for I. Points in ethanol–water mixtures are ○, points in dioxane–water mixtures are ●, points in acetic acid–water mixtures are □. Three ethanol–water points and one acetic acid–water point in the vicinity of Y, 2.5; log k_1, −3.5; have been omitted for clarity.

The rather low values of m support the suggestion[15,16] that the deoxymercuration transition state is intermediate between the product and starting state of the rate determining step, rather than closely resembling the product (carbonium ion) as seems to be true in many conventional solvolyses.[17]

The existence of a facile, solvolytic deoxymercuration strengthens the argument that metal promoted β-eliminations pass through an organometallic intermediate, and that deoxymercuration can be used as a model for the second step of such reactions.[7]

Ichikawa and co-workers[6] have used the conversion 2-chloromercuriethyl acetate to 2-ethoxyethyl

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(8) S. Winstein, A. H. Fainberg, and E. Grunwald, *J. Am. Chem. Soc.*, **79**, 4146 (1957).

(9) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

(10) E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948); other work done by these authors is referred to in ref. 8 and 9.

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(12) C. G. Swain, T. E. C. Knee, and A. MacLachlan, *ibid.*, **82**, 6101 (1960).

(13) M. M. Kreevoy, J. W. Gilje, and R. A. Kretchmer, *ibid.*, **83**, 4205 (1961).

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(16) L. L. Schaleger, M. A. Turner, T. C. Chamberlin, and M. M. Kreevoy, *J. Org. Chem.*, **27**, 3421 (1962).

(17) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956).

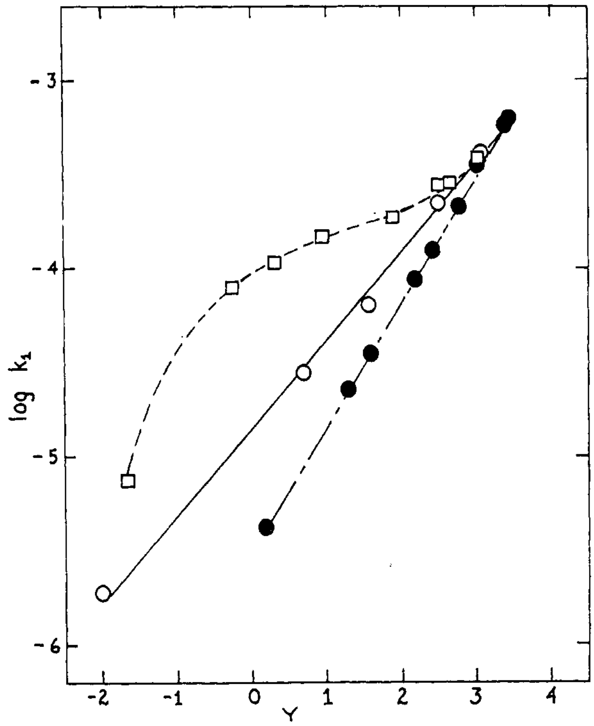

Fig. 2.—A plot of log k_1 *vs.* Y for II. Points in ethanol–water are O, points in dioxane–water are ●, points in acetic acid–water are □. An ethanol–water point around Y, 3.5; log k_1, 3.2; has been omitted for clarity.

mercuric chloride on standing in aqueous alcohol as evidence for an olefin–mercuric chloride π-complex *preceding* the rate determining step in deoxymercuration. The facile solvolysis of a closely related compound, demonstrated in the present paper, suggests that this result was actually obtained by solvolytic deoxymercuration followed by re-addition. This is consistent with the evidence, previously advanced, that the *formation* of the olefin–mercuric halide π-complex is rate-determining in deoxymercuration.

The origin of Sand's original report[2] on the unreactive nature of I is not clear. Solubility difficulties have been suggested,[13] and the similarities in physical properties between I and its solvolysis product, benzoic acid, may also have been involved

Experimental

Product Determination.—The solubility of ethylene in glacial acetic acid was measured by admitting the gas to a standard manifold of known volume to which a flask of acetic acid was attached. (The manifold and the acetic acid had been previously degassed.) No appreciable absorption of the ethylene took place without stirring. After measuring the initial vapor pressure the acetic acid was stirred magnetically until no further gas was absorbed. (About 15 min. was required.) The solubility was determined from the pressure drop and the equilibrium pressure of ethylene from the final pressure in the system. Five such determinations gave a solubility of $1.21 \pm 0.02 \times 10^{-4}$ moles l.$^{-1}$ mm.$^{-1}$.

In the product analysis 0.73 g. (1.53×10^{-3} moles) of I and 50.0 ml. of acetic acid were degassed and then heated to 70° for about 1 hr. with magnetic stirring. The solid went into solution during the heating process. Kinetic experiments at this temperature suggested a reaction half-life of about 5 min. The solution was then cooled to 25° and the vapor pressure over it was found to be 74 mm. (of which 16 mm. is the vapor pressure of acetic acid.)[19] This gave 0.46×10^{-3} moles of gas in the vapor phase and the solubility of the gas in acetic acid gave 0.35×10^{-3} moles in solution for a total of 0.81×10^{-3} moles of product. This is in excellent agreement with the 0.76×10^{-3} moles predicted by equation 1. The product gas was then permitted to expand through a −80° cold trap into an infrared gas cell and its infrared spectrum was found to be identical with the well known and characteristic vapor phase spectrum of ethylene.

Kinetic Measurements.—The techniques for spectrophotometric determination of deoxymercuration rates have been previously described.[5] All reactions except that in the least aqueous dioxane–water mixture were followed to at least 50% of completion and most were followed to 80–90% of completion. In all cases followed that far log $\{(D_\infty - D_0)/D_\infty - Dt)\}$ was a linear function of t for at least 70% of the reactions. In some (but not all) cases a downward curvature was observed as the reaction approached completion. This curvature may be due to a slight catalysis by the reaction products.[5]

Solvents.—Dioxane was purified by the method (a) described by Fieser.[20] Its exact water content is not critical since at least 33% water was added in all kinetic experiments with this solvent. Anhydrous ethanol and glacial acetic acid were analyzed for water by determining the intensity of the 1.9-μ water combination band[21] after 10:1 dilution with carbon tetrachloride. Both were found to have ~ 0.1% water.

Substrates were handled as a stock solution in the organic component of the solution or in dioxane. To make up a reaction mixture, appropriate portions of water and organic solvent were mixed and 2% by volume of the stock solution was added except where otherwise noted. The percentage of the organic component listed in Table I is the total organic solvent (including the dioxane if such a stock solution was used, divided by the total of all the liquids added times 100%. The small fraction of dioxane was thus assumed to be interchangeable with the ethanol or acetic acid in mixtures containing those solvents. The use of these dioxane stock solutions did not alter the measured rates appreciably when comparison was possible.

2-Iodomercuriethyl Benzoate.—Compound I was prepared essentially by the method of Sand.[2] It was purified by washing its chloroform solution three times with 10% sodium iodide and three times with 5% sodium bicarbonate and recrystallized from a chloroform–petroleum ether mixture. The yield after purification was 16% and the m.p. 115–118°.

It was necessary to carry out the original reaction at 0°. If this precaution was not observed or if the product was crystallized from ethanolic sodium iodide, extensive deoxymercuration takes place and the ultimate product is largely benzoic acid.

2-Iodomercuriethyl Acetate.—Compound II was prepared by the method of Ichikawa, Ouchi, and Araki[6] and had m.p. 83–85° (d).

Anal. Calcd. for $C_4H_9O_2HgI$: C, 11.58; H, 1.70. Found: C, 11.72; H, 1.61.

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[18] F. C. Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., Inc., New York, N. Y., 1921, p. 110.

[19] E. W. Washburn, "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1928, Vol. III, p. 217; confirmed by direct measurement.

[20] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed., D. C. Heath and Co., Boston, Mass., 1955, p. 284.

[21] R. F. Goddu in C. N. Reilly, "Advances in Analytical Chemistry and Instrumentation," Interscience Publishers, Inc., New York, N. Y., 1960, p. 347.