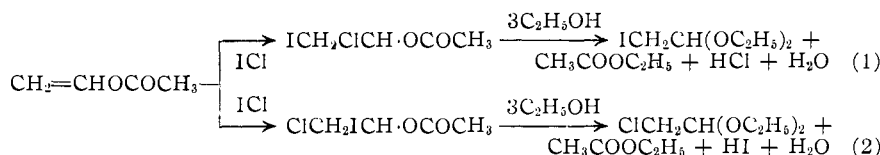# NOTES

A New Synthesis of Iodoacetaldehyde Diethyl Acetal

By Saburo Akiyoshi and Kenzo Okuno
Received June 4, 1952

Iodoacetaldehyde diethyl acetal can be synthesized by the iodination of acetal with iodine and hydroiodic acid,[1,2] or by heating the mixture of bromoacetal and sodium iodide with dry acetone[3] or ethyl alcohol[4] in a sealed tube. The former is time consuming and the yield is very poor, the latter is rather troublesome. On the other hand, Filachione[5] has reported the synthesis of bromoacetals by the bromination of vinyl acetate followed by acetalization with alcohols. Recently Bedoukian[6] has improved this method by brominating vinyl acetate in carbon tetrachloride solution.

Bedoukian's method suggested to us the application of his method to the synthesis of iodoacetal by using iodine instead of bromine, but our attempt was not successful because the addition of iodine to the vinyl double bond was very poor. But if iodine monochloride·was employed as the iodinating agent in carbon tetrachloride solution, the addition took place, yielding iodoacetal as well as chloroacetal as the by-product. The result indicated that the reactions seemed to proceed in two directions

$$CH_2{=}CHOCOCH_3 \left\{ \begin{array}{l} \xrightarrow{ICl} ICH_2CICH{\cdot}OCOCH_3 \xrightarrow{3C_2H_5OH} ICH_2CH(OC_2H_5)_2 + \\ \qquad\qquad\qquad\qquad\qquad CH_3COOC_2H_5 + HCl + H_2O \quad (1) \\ \\ \xrightarrow{ICl} CICH_2ICH{\cdot}OCOCH_3 \xrightarrow{3C_2H_5OH} CICH_2CH(OC_2H_5)_2 + \\ \qquad\qquad\qquad\qquad\qquad CH_3COOC_2H_5 + HI + H_2O \quad (2) \end{array} \right.$$

and the yield of iodoacetal, even under optimum conditions, was below 50% from vinyl acetate.

Then, an attempt was made to use the mixture of iodine monochloride and concentrated hydrochloric acid as the iodinating agent. In this case, the addition is very rapid, yielding α-chloro-β-iodoethyl acetate in almost theoretical quantities. As any chloroacetal was not obtained in this case, the reaction appeared to proceed as in (1). This method is applicable to small or large scale preparations and the yield is 82–85%. Iodoacetal has a pungent odor and a slight decomposition takes place on standing for a long time.

Experimental

Twenty grams of vinyl acetate (b.p. 72–72.5°) was added to 80 ml. of carbon tetrachloride and cooled in an ice–salt-bath. To this solution, a mixture of 30 ml. of hydrochloric acid (39%) and 40 g. of iodine monochloride was added with gentle stirring. The temperature should be kept below 5°, and the stirring should be regulated not to mix the two

layers too vigorously because the main reaction is believed to occur on the intersurface of organic and inorganic phase. After about 20 minutes, when iodine monochloride was no longer decolorized, the iodination was complete. At this point, the lower organic layer was separated rapidly, and was added to the mixture of 150 ml. of ethyl alcohol (99.5–100%) and 15 g. of calcium chloride. The whole was allowed to stand for three days at 10–15°. The temperature of acetalization so seriously influenced the yield, that the yield was halved if it was kept at 25°. Then the light red mixture was poured into 300 ml. of water, and the lower organic layer was separated, and was washed successively with dilute sodium thiosulfate solution, then with water. After drying over calcium chloride, the product was distilled under reduced pressure. Iodoacetaldehyde diethyl acetal (47 g. or 84%) distilled at 53.5–54° (2 mm.), $n^{22}D$ 1.4734, d^{22}_{22} 1.492.

Anal. Calcd. for $C_6H_{13}O_2I$: C, 29.51; H, 5.37. Found: C, 29.42; H, 5.36.

Institute of Applied Chemistry
Kyushu University
Fukuoka, Japan

The High Field Conductance of Mercuric Chloride at 25 and 45°[1]

By Frederick E. Bailey, Jr., and Andrew Patterson, Jr.
Received June 9, 1952

Onsager[2] has suggested that the high field conductance of mercuric chloride should be interesting from two points of view: since it is a weak salt yielding ions other than the very mobile hydrogen ion it should exhibit greater hydrodynamic effects than weak acids, and, in addition, it might be liable to greater chemical relaxation time lags than acids. Such acids as have been investigated[2,3] show no particular deviation from the theory of Onsager for weak electrolytes and no unusual relaxation time effects, while insufficient data are available on bases to allow any distinctions between the behavior of acids and bases to be drawn. We present herewith some high field conductance measurements on mercuric chloride, approximately 9.3×10^{-3} molar, at 25 and 45°, using potassium chloride as reference electrolyte. The experimental results are not sufficiently unambiguous as to permit a clear assessment of Onsager's predictions, but they constitute yet another addition to the list of peculiarities of this unusual salt.[4]

Experimental

Mercuric chloride was purified by recrystallization from conductivity water; the solid was separated from the mother liquor, dried between absorbent paper, and further dried in a desiccator at room temperature over calcium sulfate.

(1) J. Hesse, *Ber.*, **30**, 1442 (1897).
(2) M. S. Losanitsch, *ibid.*, **42**, 4046 (1909).
(3) F. Beyerstedt and S. M. McElvain, This Journal, **58**, 529 (1936).
(4) F. Beyerstedt and S. M. McElvain, *ibid.*, **59**, 2268 (1937).
(5) E. M. Filachione, *ibid.*, **61**, 1705 (1939).
(6) P. Z. Bedoukian, *ibid.*, **66**, 651 (1944).

(1) Contribution No. 1105 from the Department of Chemistry, Yale University.
(2) L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).
(3) F. E. Bailey and A. Patterson, This Journal, **74**, 4756 (1952).
(4) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, New York, N. Y., 1950, p. 324.

The dry, purified salt was weighed and dissolved in a weighed quantity of carbon dioxide-free conductivity water to give a strong stock solution, approximately 0.2 molar in concentration. This stock solution was added from a weight buret to a previously weighed quantity of conductivity water in a conductance cell to attain a desired concentration or resistance, as the case might be. Low field conductance measurements were carried out at 25° using a pulse bridge technique[5] to gain some idea of the variation of equivalent conductance in the concentration range to be employed. Low field conductances of both the potassium and mercuric chloride solutions were measured at 25, 35 and 45° in order to determine the temperature coefficients of conductance. High field measurements were performed using a differential pulse transformer bridge[5] at 25 and 45°. The temperature control was to within 0.015 at 25° and to within 0.02° at the other temperatures. All temperatures were measured relative to a recently calibrated platinum resistance thermometer.

Results

The results of the determination of equivalent conductance versus concentration are given in Fig. 1, together with one point from ICT data[6] at a comparable concentration; equivalent conductance, $1000 \, L/c$, is given as a function of $c^{1/2}$. These values are not in particularly good agreement with the one point from the ICT, a fact which might be explained by two recognized sources of error on our part: the salt may not have been wholly dry; and the resistances used as references in the bridge measurement, although precisely known and entirely satisfactory for relative measurements, had not been calibrated with high accuracy. The original ICT reference was not available for study. However, these data indicate that mercuric chloride in aqueous solution is only slightly ionized, as Sidgwick[4] has pointed out, and that, in comparison with a potassium chloride solution of the same specific conductance and of concentration approximately 10^{-4} molar, the degree of ionization is 1%, or less, depending upon the possibilities of hydrolysis and other reactions.
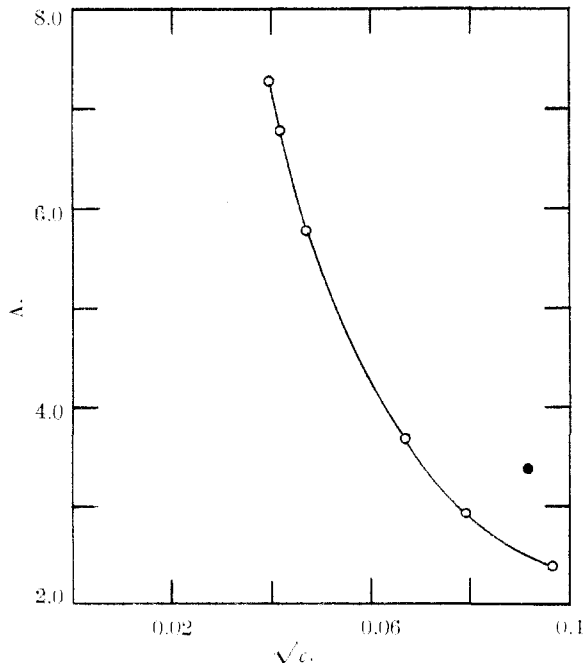

Fig. 1.—Equivalent conductance of mercuric chloride as a function of concentration: O, this paper; ●, ICT data (ref. (6)).

The temperature coefficients of resistance of the mercuric chloride and potassium chloride solutions are compared in Table I.

(5) J. A. Gledhill and A. Patterson, J. Phys. Chem., 56, 999 (1952).
(6) "International Critical Tables," Vol. 6, McGraw-Hill Book Co., Inc., New York, N. Y., p. 232.

TABLE I

TEMPERATURE DEPENDENCE OF RESISTANCE OF MERCURIC CHLORIDE AND POTASSIUM CHLORIDE SOLUTIONS

t, °C.	R, HgCl$_2$, ohms	R, KCl, ohms	
25	956.3 (9.31 × 10^{-3} molar)	898.3 (3.27 × 10^{-4} molar)	
35	671.2	748.1	633.2 (3.85 × 10^{-4} molar)
45	492.5	540.0	

The temperature coefficient measurements were made in conjunction with the high field measurements, and thus it was necessary to add potassium chloride at the higher temperatures in order to bring the resistances of the two cells within the balancing capabilities of the variable resistors provided to compensate for high field resistance changes. This accounts for the two columns of data for potassium chloride. The temperature coefficient of resistance of the mercuric chloride, over this temperature range, is 1.90 ± 0.01 times as great as that of the potassium chloride.

The measurements at high fields were difficult to interpret because of the very considerable change of balance during the period of the 4 microsecond pulses used for observation, a difficulty resulting, presumably, from the decided difference in temperature coefficients noted in the preceding paragraph. Figure 2 is a plot of the fractional high field conductance quotient, $\Delta\lambda/\lambda_0$, versus field strength for the results obtained at 25 and 45°, as estimated from the bridge balances obtained near the end of the 4-microsecond pulse, and at 25° from the beginning of the 4 microsecond pulse as well. At 45°, however, in contrast to the situation at 25°, a perceptible leveling off was observed of the change in resistance balance as a function of applied pulse duration
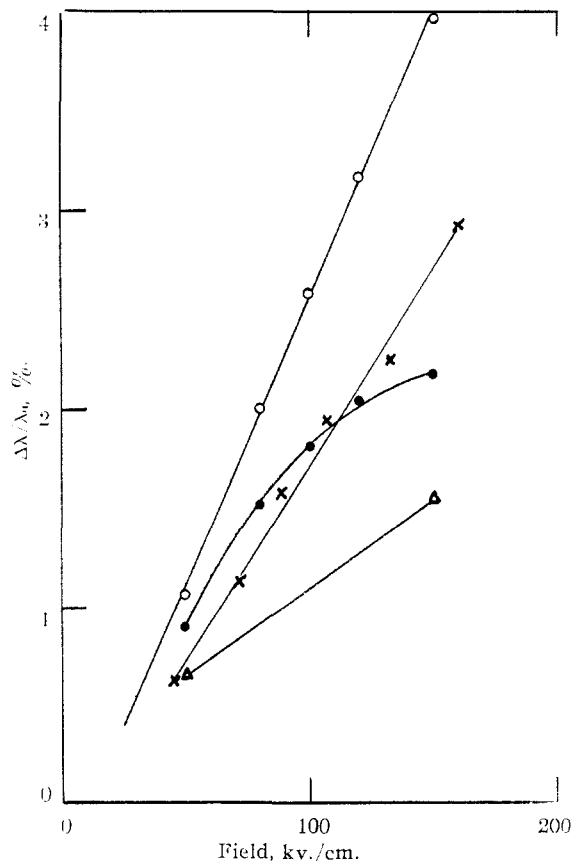

Fig. 2.—High field conductance of aqueous solution of mercuric chloride: O, 25°, end of 4-microsecond pulse; ×, 45°, end of 4-microsecond pulse; ●, 25°, end of 4-microsecond pulse, corrected for results of heating in conductance cell; △, 25°, estimated from beginning of pulse.

toward the end of the 4 microsecond pulse. For this reason the main emphasis has been placed on the results for high field conductance change at the end of the pulse, since the leveling off of the change of resistance suggests that a stable conductance was being attained after a time-of-relaxation phenomenon.

Discussion

It seems proper to assume from the results of the low field conductance measurements above, as well as the data recorded by Sidgwick,[4] that the following equilibrium exists between the entities in solution
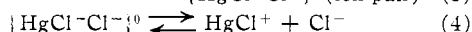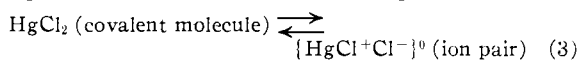
$$HgCl_2 \rightleftarrows HgCl^+ + Cl^- \tag{1}$$
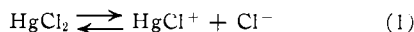
$$K(0) = \frac{[HgCl^+][Cl^-]}{[HgCl_2]} = \frac{c\alpha^2}{1 - \alpha} \tag{2}$$

If we assume that the degree of dissociation is 0.01, then the value of $K(0)$ would be

$$K(0) = (9.3 \times 10^{-3})(0.01)^2/(1 - 0.01) = 10^{-6} \text{ approx.}$$

If the high field conductance increase were due to an influence upon this equilibrium by the high field, then the increase in conductance should be comparable with or greater than that for acetic acid, $K(0) = 1.7 \times 10^{-5}$. For acetic acid at 147 kv./cm. the experimental fractional increase in high field conductance is 7.36%.[3] For a 1–1 valence type electrolyte at a similar field and with a smaller $K(0)$, the high field conductance quotient would be proportionately greater. We may therefore conclude that the above is not the equilibrium principally responsible for the much smaller conductance increase observed with mercuric chloride.

Onsager has assumed the existence of two equilibria in the place of that of equation (1)

$$HgCl_2 \text{ (covalent molecule)} \rightleftarrows$$
$$\{HgCl^+Cl^-\}^0 \text{ (ion pair) } \tag{3}$$
$$\{HgCl^-Cl^-\}^0 \rightleftarrows HgCl^+ + Cl^- \tag{4}$$

and has associated a longer chemical time of relaxation with equation (3) as contrasted with the short Langevin time lag for equation (4). Of these two equilibria, only that of equation (4) is affected by the field, but it is equilibrium (3) which should demonstrate an appreciable relaxation time. From the magnitude of the high field conductance increase actually observed, between 2 and 3%, we may estimate the size of the equilibrium constant for equation (4) to be in the order of 10^{-3}. The magnitude of Wien effect observed is similar to that exhibited by such symmetrical electrolytes as magnesium and zinc sulfates; these electrolytes behave in a manner which may be suitably explained on the basis of an ion-pair equilibrium with the assumption of $K(0)$ values in the order of 10^{-3}.[7]

With a cell resistance of 918 ohms and an applied field of 150 kv./cm., corresponding to the conditions for the highest point on the curve for 25°, the power dissipated during a single pulse is 0.98 joule, equivalent to a temperature rise of 1.16°, if we may assume that at the end of 4 microseconds no significant amount of thermal conduction has taken place from the small solution volume between the electrodes to both the electrodes and the solution nearby. Such a rise in temperature would correspond to a resistance decrease of about 16 ohms more in the mercuric chloride cell than in the reference potassium chloride cell, and would thus

(7) F. E. Bailey and A. Patterson, THIS JOURNAL, **74**, 4428 (1952).

appear indistinguishable from a relative Wien effect of some 1.6%.

We have attempted to estimate the change of resistance due to heating for each of the points on the curve for 25° using the data taken from the end of the 4 microsecond pulses, and have obtained a corrected high field conductance curve which lies in the vicinity of the curve for 45°; see Fig. 2. However, it would be stretching matters entirely too far on such sparse evidence to compare the admittedly similar curves for the "corrected" data for mercuric chloride at 25° with the results for magnesium and zinc sulfates.

The large temperature coefficient of conductance of the mercuric chloride may result from a temperature sensitive equilibrium of the types shown in equations (3) or (4). In the case of magnesium sulfate[7] the ion pair-ion equilibrium was found to be relatively temperature insensitive. Faced with the existence of this large temperature coefficient, however, it is difficult for one to make any more than an educated guess as to the high field conductance change of mercuric chloride. It is thus not presently possible to make any conclusions relevant to time-of-relaxation or hydrodynamic effects to lend support to the postulations of Onsager.[2] Although, as pointed out, the oscilloscope balance patterns at 45° appeared to reach a steady value, nevertheless with longer pulses the heating effects could only be greater and more confusing. If time-of-relaxation effects were present in the range of pulse lengths including 4 microseconds, shorter pulse lengths tending to minimize heating would not reveal the time-of-relaxation effects anticipated with application of high fields. Accordingly, we have not attempted to investigate other pulse lengths.

Since very small quantities of highly ionized electrolytes will entirely overshadow both the low and high field conductance behavior of a weaker electrolyte, some concern must be expressed for the influence of hydrolysis products which are undoubtedly present. Sidgwick[4] states that mercuric chloride is almost wholly covalent, even in water, and so very slightly hydrolyzed. The hydrolysis products may be postulated as HgClOH and HCl; the first compound presumably supplies at least a moderate number of ions to the solution, else the extent of hydrolysis would be greater than it is. The principal strong electrolyte is thus hydrochloric acid, the high field conductance behavior of which is comparatively well known. The authors have found that concentrations of this electrolyte in the order of only 10^{-5} molar will entirely alter the shape of high field conductance plots such as Fig. 2 for weak electrolytes. We may thus conclude from the resulting straight-line plots in Fig. 2, rather than a curve typical of a strong electrolyte, and from the magnitude of the quotients, $\Delta\lambda/\lambda_0$, which have been obtained experimentally, that no significant amounts of a strong electrolyte such as hydrochloric acid are present.