data of Hogness[18] and Williams and Miller.[19] The value of the constant in the volume expression was evaluated at 470° as 2290 and 2810 cal./g. atom for the Zn–Cd and Zn–In systems, resp.

It might be argued that the regular solution concept is unrealistic (Lumsdem[20]), but an alternative approach to solution behavior based on a statistical model is so empirical at present that it is impossible to make any predictions of solution behavior from constituent properties. Until the state of statistical theory advances beyond the present empirical state, the concept of regular solutions appears justified.

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(18) T. R. Hogness, THIS JOURNAL, **43**, 1621 (1921).

(19) D. D. Williams and R. R. Miller, *ibid.*, **72**, 3821 (1950).

(20) J. Lumsdem, "Thermodynamics of Alloys," Inst. Metals (London), Monograph and Report Series No. 11, 1950.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND BIOLOGY, FRIENDS UNIVERSITY]

Reaction of Mercury(II) with Halides in Glacial Acetic Acid

BY ORLAND W. KOLLING

RECEIVED JANUARY 28, 1957

The reaction between mercury(II) acetate and potassium halides in glacial acetic acid yields HgX_2 as the predominant species. The stoichiometry of the reaction was determined by potentiometric titrations with the glass and calomel electrodes, in which the glass electrode responds to changing acetate concentration. Potential difference measurements as a function of concentration of solution were made for reactants and products, and demonstrated the order of increasing acidity to be $Hg(OAc)_2 < KCl < KBr < KI$ for these weak acids in glacial acetic acid.

As a result of covalent bonding, mercury(II) chloride, bromide and iodide are soluble in a number of organic solvents, and form non-ionic aqueous solutions. In aqueous solutions containing excess halide, mercury(II) forms tetrahedral complexes of the type $HgX_4^{=}$, through (sp^3) hybridization. Analogous molecular and ionic species might be expected for glacial acetic acid solutions of mercury(II) halides, for it has been demonstrated that mercury(II) acetate reacts with amine hydrohalides, liberating the amine, quantitatively.[1] The present study confirms that the predominant species present in glacial acetic acid solutions of mercury(II) chloride, bromide and iodide is HgX_2, and that such solutions are essentially non-ionic.

The stoichiometry of the reaction between mercury(II) acetate and the potassium halides was established by potentiometric titrations. The covalent nature of the mercury–halide bond in glacial acetic acid solution was shown by potentiometric measurements, using the method of Higuchi, Danguilan and Cooper.[2] Curves representing the potential difference between the glass and calomel electrodes as a function of solution concentration were determined for the reactants and products, as well as for reference salts.

Experimental Details

All chemicals in these experiments were analytical reagent grade and were used without additional purification. Solution concentrations were restricted to the hundredth formal level by the limited solubility of alkali halide salts in glacial acetic acid.

Preparation of Standard Solutions.—Standard solutions of perchloric acid and hydrochloric acid were prepared by adding suitable amounts of the concentrated aqueous acids to glacial acetic acid and adding sufficient acetic anhydride to consume the water present from the concentrated acids. Each acid solution was allowed to stand for one week, then standardized potentiometrically against potassium acid phthalate (primary standard grade, dried two hours at 120°). The glacial acetic acid solution of hydrochloric acid was 0.00343 *F* and the perchloric acid was 0.0414 *F*, with an uncertainty of ±2 p.p.t.

The 0.0100 *F* solutions of potassium chloride, bromide, iodide, acetate and acid phthalate, and mercury(II) acetate and chloride, in glacial acetic acid were prepared from accurately weighed portions of finely ground and dried samples of the salts. All stock solutions and dilutions from these were carefully thermostated at 25.0 ± 0.1°. The somewhat rapid release of triiodide from glacial acetic acid solutions of potassium iodide necessitated immediate measurements on freshly prepared solutions for this salt.

Malachite green indicator solution was 0.001 *F* prepared by dissolving the solid (as the hydrochloride) in glacial acetic acid.

Volumetric Methods.—Indirect titrations of mercury(II) acetate were made by adding to aliquots of the mercury(II) solution known excesses of the potassium halide salt solution, and the equivalent potassium acetate released was titrated with standard perchloric acid. The end-points in these acid-base titrations were determined both potentiometrically with the glass–calomel electrode pair and with malachite green as a visual indicator, using 0.20 ml. of the latter solution per 30-ml. sample solution being titrated.

Direct titrations of 2.00-ml. aliquots of mercury(II) acetate solution with hydrochloric acid and the potassium halide solutions were made in a total solution volume of 15 ml., and the titration curves were determined from potentiometric measurements.

Potential Difference. Dilution Measurements.—The method employed for the determination of the potential difference as a function of concentration was that of Higuchi, Danguilan and Cooper.[2] In all potentiometric measurements a Beckman Model H-2 *p*H meter, equipped with the usual glass and calomel electrodes, was used. The reference solution was 0.100 *F* sodium salicylate in glacial acetic acid, and the reported values are differences in absolute magnitude between the e.m.f. for the sodium salicylate solution and that for the unknown solution. The e.m.f. for the reference solution was checked before and after each unknown solution. The experimental uncertainty in these potential measurements is ±1 millivolt.

Results

Titrations.—To establish the mole ratio in which the halide reacts with mercury(II) acetate, a number of direct and indirect titrations were performed. First, to a fixed amount of mercury(II) acetate, known amounts of potassium halide were added, and in accordance with equation 1 the released

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(1) C. Pifer and E. Wollish, *Anal. Chem.*, **24**, 300 (1952).

(2) T. Higuchi, M. Danguilan and A. Cooper, *J. Phys. Chem.*, **58**, 1167 (1954).

potassium acetate was titrated with perchloric acid.

$$\mathrm{Hg(OAc)_2} + y\mathrm{KX} = \mathrm{HgX}_y + y\mathrm{K(OAc)} \quad (1)$$

The ratio of $\mathrm{Hg(OAc)_2}$:KX was varied in the range 4:1 to 1:10, and for all ratios it was observed that the potassium acetate released was equivalent to the amount of halide consumed. These results, as shown in Fig. 1, indicate the ratio of X:Hg(II) to be 2:1 in the product.

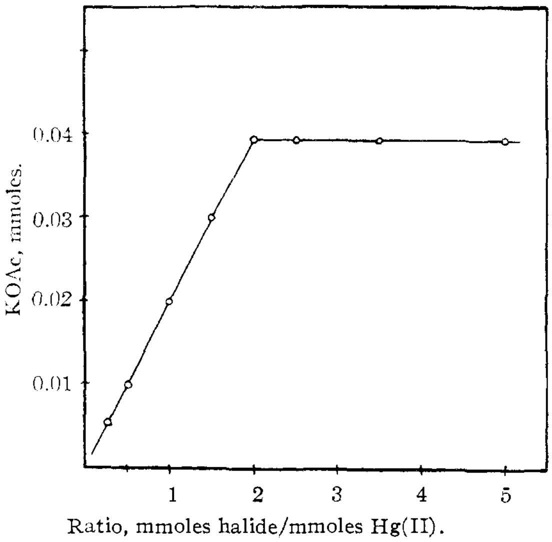

Fig. 1.—The stoichiometry of the reaction between Hg(II) acetate and chloride, bromide and iodide in glacial acetic acid.

Secondly, direct titrations of known amounts of mercury(II) acetate were made, using hydrochloric acid as titrant. The potentiometric titration curve in Fig. 2 may be compared with the comparable curve for the neutralization of hydrochloric acid (a moderately strong acid) with potassium acid phthalate (a moderately strong base). Also, it was observed that mercury(II) acetate could be titrated directly with potassium chloride, bromide and iodide. A typical curve for this direct titration is plotted in Fig. 2. For all direct titrations, the reaction is that given in equation 1, and the product is $\mathrm{HgX_2}$, as was noted above. It is interesting that the curves are not symmetrical in shape, but beyond the break in the curve a nearly constant e.m.f. is obtained (except for the iodide where the magnitude of the e.m.f. becomes greater as triiodide is released from the excess titrant).

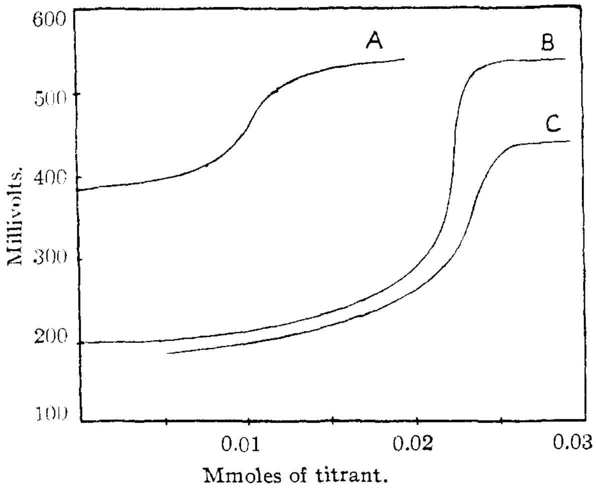

Fig. 2.—Potentiometric titration curves for: (A) potassium acid phthalate with HCl; (B) mercury(II) acetate with HCl; and (C) mercury(II) acetate with KBr.

Potential Difference *vs.* Concentration.—In Fig. 3 the potential difference between the glass–calomel electrode pair is plotted as a function of concentration of solution in glacial acetic acid for potassium acetate, potassium acid phthalate, the potassium halides, mercury(II) acetate and mercury(II) chloride. For all compounds, a linear plot is obtained, and, with the exception of the plot for mercury(II) chloride, the slopes correspond closely to 0.0591/2 volts per tenfold change in concentration. The dilution curves for potassium acetate and potassium acid phthalate are coincident, and that for mercury(II) chloride is indistinguishable from that for the solvent alone.

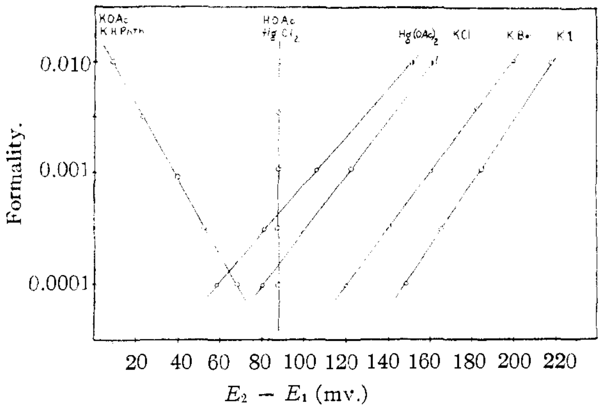

Fig. 3.—Effect of solution concentration on potential difference between the glass–calomel electrode pair in glacial acetic acid. E_1 is the e.m.f. for the reference solution and E_2 is that for the unknown solution.

The dilution curves indicate that the order of decreasing acidity is $\mathrm{I^-} > \mathrm{Br^-} > \mathrm{Cl^-}$ for the potassium salts. This is consistent with the results of Kolthoff and Willman.[3] Mercury(II) acetate is more weakly acidic than the potassium halide salts, sufficiently so that a considerable excess of the former may be present with amines without competing in the quantitative reaction between the bases and perchloric acid. The very weak basicity assigned to mercury(II) acetate by Kolthoff and Willman[3] would suggest that this compound is among the most nearly "neutral salts" in glacial acetic acid. The dilution curve for mercury(II) chloride shows the compound to be a complete non-electrolyte in glacial acetic acid. Potassium acetate and potassium acid phthalate appear to be bases of equal strength.

Discussion and Conclusions

It is apparent that the reaction between mercury(II) acetate and the potassium halides is one between moderately strong electrolytes to produce

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(3) I. M. Kolthoff and A. Willman, THIS JOURNAL, **56**, 1014 (1934).

one non-ionized product and a strong base. In the unsymmetrical titration curves for this reaction it is significant that beyond the break in the curve the e.m.f. increases much less than would be expected from the dilution curves on the potassium halides. This would suggest that the excess titrant undergoes interaction with mercury(II) chloride, probably through ion-pair or ion-multiple formation, or through coördination of halide by mercury(II) to give products of the type K_nHgX_{2+n} (where n = 1, 2, . . .). However, the nature of the product of this interaction cannot be determined by the present experimental approach. It appears certain that the predominant product of the reaction between mercury(II) and halide in glacial acetic acid is molecular HgX_2.

Although it would be expected that the course of the reaction between mercury(II) acetate and a halogen acid could be followed with the glass electrode, it was not anticipated that this indicator electrode would be suitable for the titrations with the potassium halides. Experimentally, it is easily demonstrated that mercury(II) acetate undergoes no detectable neutralization reaction with perchloric acid nor with potassium acid phthalate, when titrated potentiometrically with the glass–calomel electrode pair. Likewise, it is notable that the magnitude of the break in the titration curve for potassium acid phthalate (a strong base) with hydrochloric acid (a moderately strong acid) is significantly smaller than that for the reaction between mercury(II) acetate and the same acid or the potassium halide. It is evident that the mercury(II) acetate–potassium halide reaction cannot be considered as a neutralization reaction involving a direct or indirect proton transfer mechanism. The glass electrode appears to respond as the indicator electrode toward changes in acetate concentration during the titration involving a nearly neutral acetate and the release of a strongly basic acetate. It has been suggested by Higuchi, Feldman and Rehm,[4] that measurements of acidity and basicity in glacial acetic acid with the glass electrode may be expressed in terms of acetate concentrations. Such an interpretation appears to be experimentally valid.

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[4] T. Higuchi, J. Feldman and C. Rehm, *Anal. Chem.*, **28**, 1120 (1956).

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[CONTRIBUTION FROM THE MONSANTO CHEMICAL COMPANY, RESEARCH DEPARTMENT, INORGANIC CHEMICALS DIVISION]

Principles of Phosphorus Chemistry. III. Structure Proofs by Nuclear Magnetic Resonance[1]

BY C. F. CALLIS, J. R. VAN WAZER, J. N. SHOOLERY[2] AND W. A. ANDERSON[2]

RECEIVED NOVEMBER 12, 1956

Structure proofs based on nuclear magnetic resonance measurements are given for some oxyacids of phosphorus and several other phosphorus compounds. Indirect spin–spin coupling shows that essentially all of the primary and secondary phosphite esters, as well as the free acid and its salts, are present in the form in which one hydrogen is attached directly to the phosphorus. Structure proofs are given for the hypophosphate, isohypophosphate and diphosphite molecule-anions, as well as for P_4S_3 and $P_4O_6S_4$. Indirect spin–spin splitting in the tripoly- and tetrapolyphosphate anions shows that the P–O–P linkages are basically covalent; and all of the data indicate that the often postulated P^{+5} ion does not exist in the phosphates and related compounds.

Gutowsky, McCall and Slichter[3] have already shown that indirect spin–spin splitting of nuclear magnetic resonance peaks is a powerful tool for proving structures in the chemistry of phosphorus. Thus, these authors were able to demonstrate that the hydrogen and fluorine atoms are attached directly to the phosphorus by primarily covalent bonds in the following structures: PH_3, PF_3, $(CH_3O)PF_2$, $OPClF_2$, $OPCl_2F$ and the $F_2PO_2^-$, $H_2PO_2^-$, $HPO_3^=$ and PF_6^- ions. In this paper, structure proofs based on both indirect spin–spin splitting and chemical shifts will be presented along with a discussion of bonding in phosphorus compounds. The experimental procedure and the raw data are given in Paper II of this series. Unless otherwise designated, the data are P^{31} spectra. The majority of the measurements were made at 7140 gauss and 12.3 Mc. The chemical shifts relative to 85% orthophosphoric acid are defined as

$$\delta = \frac{H_{\text{sample}} - H_{\text{H3PO4}}}{H_{\text{H3PO4}}} \times 10^6$$

where H is the resonance field strength. The splittings given in cycles per second (c.p.s.) can be converted to parts per million (p.p.m.) of the applied field by dividing by the frequency of the rf probe in Mc., or to field units in gauss by multiplying the p.p.m. value by the field strength (times 10^{-6}) in gauss.

The simplest method of differentiating between chemical shifts and indirect spin–spin splittings is to make measurements at different field strengths. Thus, the separation between resonance peaks attributable to differently situated phosphorus atoms in a molecule or molecule-ion (the chemical shift) is found to be invariant with field strength when measured in p.p m. of the field. In other words, the separation divided by the field strength is a constant. On the other hand, the separation between multiplet peaks due to indirect spin–spin

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[1] Presented in part by C. F. Callis at the Phosphorus Symposium held on April 9, 1956, at the American Chemical Society Meeting in Dallas, Texas. Papers I and II in this series are published in THIS JOURNAL, **78**, 5709, 5715 (1956).

[2] Varian Associates, Palo Alto, California.

[3] H. S. Gutowsky, D. W. McCall and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953); H. S. Gutowsky and D. W. McCall, *ibid.*, **22**, 162 (1954).