Figures 4 and 5 show the results obtained from the measurements on chloroform and monofluorodichloromethane with dimethyl ether of tetraethylene glycol [$CH_3O(CH_2CH_2O)_4CH_3$]. The maxima again do not differ in height by more than the experimental error, and the fact that they come at approximately 0.75 mole fraction of halogenated hydrocarbon indicates that combination occurs between three molecules of halogenated hydrocarbon and one ether molecule. Since the ether contains five oxygen atoms, only alternate ones are available for combination. This result is in accord with the suggestion (b) above and implies that steric hindrance is the most important factor.

The degree of association existing in these mixtures may be estimated roughly by using the value for the strength of the C–H ← O bond found by McLeod and Wilson.[3] From the curves of Figs. 2 and 3 it is calculated that approximately 2300 cal. of heat are liberated when one mole either of chloroform or of monofluorodichloromethane is mixed with one mole of dimethyl ether of ethylene glycol; assuming that all the heat evolved is due to reaction, this corresponds to 38% association. From the maxima of the curves of Figs. 4 and 5, one calculates that 5400 cal. are liberated when three moles of halogenated hydrocarbon are mixed with one mole of the ether. If combination between halogenated hydrocarbon molecules and alternate oxygens of the ether occurs to the same extent, 30% association is indicated.

Conclusion

The large heat of mixing of the CHX_3 type of halogenated hydrocarbon with the polyethylene glycol ethers is explained as due to complex formation. This association is caused by the tendency of the hydrogen of the halogenated hydrocarbon to form a C–H ← O bond with the oxygen of the ether. The locations of the maxima of the heat of mixing curves indicate that, due to steric hindrance, only the alternate oxygen atoms of the polyethylene glycol ether molecules are available for bonding. Complex formation occurs to the extent of from 30–40%.

BLOOMINGTON, ILLINOIS RECEIVED MARCH 18, 1938

[COMMUNICATION NO. 655 FROM THE KODAK RESEARCH LABORATORIES]

Acidity Measurements with the Hydrogen Electrode in Mixtures of Acetic Acid and Acetic Anhydride

BY J. RUSSELL AND A. E. CAMERON

The introduction of the chloranil electrode by Hall and Conant[1] made possible the study of acid and base behavior in glacial acetic acid solutions.[2] The hydrogen electrode has been used in glacial acetic acid by Isgarischew and Pletenew[3] and for the determination of activity coefficients of sulfuric acid in anhydrous acetic acid by Hutchison and Chandlee.[4] The present writers have used the hydrogen electrode for the titration of gelatin and amino acids in glacial acetic acid solutions.[5]

The acetylation of hydroxy compounds, such as cellulose, by acetic anhydride in glacial acetic acid solution is catalyzed by addition of strong acids, such as sulfuric and perchloric acids. Conant and Bramann[6] have investigated the effect of hydrogen-ion activity upon the rate of acetylation of β-naphthol by acetic anhydride and found the rate to vary nearly a millionfold and to depend upon the acidity or basicity of the medium. In their measurements, they apparently assumed that the addition of the acetic anhydride to the buffer of known *p*H(HAc) had no effect upon the hydrogen-ion activity. The chloranil electrode could not be employed in the presence of acetic anhydride because of acetylation of the indicator substances. The hydrogen electrode, however, appeared to offer a means of measuring the hydrogen-ion activity in the presence of anhydride and the measurements described here are the outcome.

Experimental

The customary platinum black electrode catalysts did not prove satisfactory for these measurements. Investiga-

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(1) N. F. Hall and J. B. Conant, THIS JOURNAL, **49**, 3047 (1927).

(2) J. B. Conant and N. F. Hall, *ibid.*, **49**, 3062 (1927); N. F. Hall and T. H. Werner, *ibid.*, **50**, 2367 (1928); J. B. Conant and T. H. Werner, *ibid.*, **52**, 4436 (1930); N. F. Hall, *ibid.*, **52**, 5115 (1930).

(3) N. Isgarischew and S. A. Pletenew, *Z. Elektrochem.*, **36**, 457 (1930).

(4) A. W. Hutchison and G. C. Chandlee, THIS JOURNAL, **53**, 2881 (1931).

(5) J. Russell and A. E. Cameron, *ibid.*, **58**, 774 (1936).

(6) J. B. Conant and G. M. Bramann, *ibid.*, **50**, 2305–2311 (1928).

tion of various other possibilities showed that palladium black catalysts were far superior to anything else. Platinum foil electrodes of 2 sq. cm. area were plated with gold from a gold cyanide bath and coated with palladium black from a 2% solution of palladium chloride in molar hydrochloric acid saturated with lead chloride. A high current density was necessary or smooth plates were obtained. It was found essential to prepare all solutions from water redistilled from alkaline permanganate and to wash the electrodes thoroughly in this water after plating. The laboratory distilled water contained traces of an organic material which caused poisoning of the catalysts in the presence of acetic anhydride.

A satisfactory brand of tank hydrogen was freed of oxygen by passage over platinum black supported upon sulfur-free asbestos in a heated silica tube, dried over fused calcium chloride, and saturated with acetic acid before passing into the titration vessel, through a porous bubble head. A positive pressure of hydrogen was maintained in the vessel.

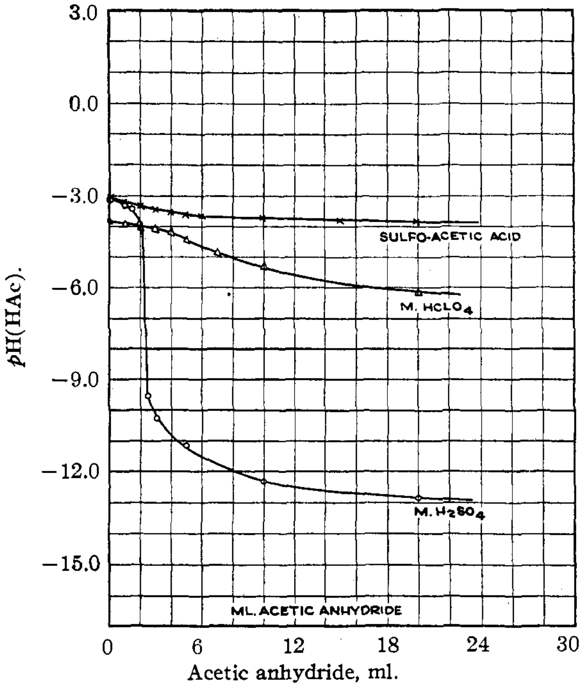

Fig. 1.—Molar solution of sulfo-acetic acid, perchloric and sulfuric acids in glacial acetic acid solution titrated with acetic anhydride.

The chloranil electrode in molar sulfuric acid solution in glacial acetic acid was used as a half-cell. The connection was made through a ground-glass plug to a bridge of saturated solution of lithium chloride in glacial acetic acid which connected with the solution under investigation through another ground-glass plug. Because of the high electrical resistance of the cell, the potential readings were taken using a ballistic galvanometer and one microfarad condenser as null-point indicator with a student type potentiometer. Charging times of ten to twenty seconds sufficed for balancing to a precision of 0.5 mv.

The titration vessel was shaken by an eccentric mounted on the shaft of a controllable speed motor at such a rate that a swirling motion was imparted to the contents. Electrodes, salt bridge and buret tips entered the necks of the titration vessel through well-paraffined cork stoppers. The buret stopcocks were lubricated with a pasty mixture of vaseline and paraffin which withstood the solvent effect of acetic acid.

Acetic acid was refluxed for eight hours with chromic acid in an all-glass apparatus according to the directions of Eichelberger and La Mer[7] and was then distilled off. No effort was made to dehydrate this acid. *Care should be exercised in the chromic acid treatment,* because the initial heating often produces a violent reaction with oxidizable material present. All inorganic chemicals were of reagent quality. The organic chemicals were obtained from the Synthetic Chemical Division of the Eastman Kodak Company. The sulfonic acids used were tested with barium ion to be sure that no free sulfuric acid was present.

The molar sulfuric acid solution was prepared by adding a weighed amount of analyzed concentrated sulfuric acid to glacial acetic acid and making up to volume after addition of enough acetic anhydride to react with the water present in the sulfuric acid. Standard sodium acetate solutions were prepared by dissolving dry sodium carbonate in glacial acetic acid. Potassium acid phthalate may also be employed for the standardization of acid solutions and has the advantage of a greater equivalent weight.

Electrode behavior was found to be satisfactory. Three electrodes in the same solutions agreed within 1–3 mv., even in extremely acid solutions, in the presence of 30% acetic anhydride. Equilibrium was attained in from five to ten minutes. A drastic change in medium from anhydride to a solution having an excess of water required from a few minutes to several hours for the electrodes to accommodate themselves but recovery was complete. The reverse change was characterized by rapid attainment of electrode equilibrium.

The chloranil electrode in a solution of zero pH(HAc) on the scale selected by Conant and Hall shows a voltage of 0.566 measured against a saturated aqueous calomel electrode through a saturated solution of lithium chloride in glacial acetic acid as a bridge. The molar sulfuric acid used in the half-cell was found to have a pH(HAc) of −3.23 when so measured. The chloranil electrode in glacial acetic acid was found by Heston and Hall[8] to have a potential of 0.680 v. against the hydrogen electrode in the same medium. This value was verified by the present writers. The values of pH(HAc) in the following data are calculated from the relationship that 0.680 v. = −3.23 pH(HAc), using the equation $p\text{H(HAc)} = (E - 0.871)/0.059$.

The procedure followed in making these measurements consisted in pipetting 50 ml. of acid solution, standardized by titration of sodium acetate solution, into the vessel and titrating with acetic anhydride (99–100% pure). Titrations were carried out at room temperature, approximately 25°. The concentrations of acids given in Table I have been corrected for change in volume resulting from the addition of the acetic anhydride.

Figure 1 shows the titration curves for sulfo-acetic acid, perchloric acid, and sulfuric acid. The sulfo-acetic acid

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(7) W. C. Eichelberger and V. K. La Mer, THIS JOURNAL, **55**, 3633 (1933).

(8) B. O. Heston and N. F. Hall, *ibid.*, **55**, 4729 (1933).

was prepared by allowing sulfuric acid to stand in contact with excess acetic anhydride in glacial acetic acid solution for a month. At the end of that time, no test was given for sulfate ion when barium ion was added. The excess anhydride was destroyed by the addition of a slight excess of water.

The curves indicate that the acidity of sulfo-acetic acid is practically independent of the presence of acetic anhydride, while the acidity of perchloric acid is apparently somewhat increased. Sulfuric acid shows a startling increase in acidity as soon as the solution is anhydrous. The anhydride titrations were repeated for several dilutions of the stock solutions and for several concentrations of those sulfonic acids which were found sufficiently soluble. The results of these investigations are given in the following table where the values of *p*H(HAc) are listed for the stated concentration of acid in the presence of approximately 30% acetic anhydride.

TABLE I

ACIDITIES IN 28–32% ACETIC ANHYDRIDE

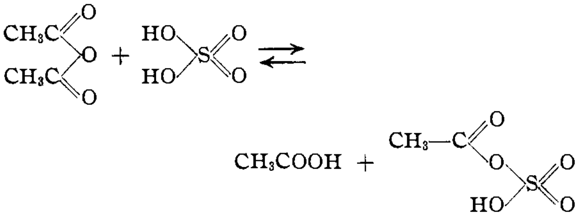
Compound	Concn., *M*	*p*H(HAc)
Sulfuric acid	0.715	−12.86
	.071	−11.45
	.036	−10.96
	.007	− 9.53
	.004	− 7.97
	.0007	− 3.43
Perchloric acid	0.83	− 6.16
	.083	− 5.61
	.008	− 4.32
	.0008	− 3.29
Sulfo-acetic acid	0.715	− 3.83
	.100	− 3.65
	.010	− 2.51
2,5-Dichlorobenzene sulfonic acid	0.0733	− 4.79
	.0073	− 3.24
	.0007	− 2.41
2-Chlorotoluene-5-sulfonic acid	0.2380	− 9.80
	.0238	− 8.86
	.0024	− 6.61
2-Nitrobromobenzene-4-sulfonic acid	0.0750	− 7.30
	.0075	− 4.20
	.0007	− 2.83
4-Nitrochlorobenzene-2-sulfonic acid	0.0407	− 4.25
	.0041	− 3.55
	.0004	− 1.48
m-Nitrobenzene sulfonic acid	0.0670	− 4.27[a]
	.0067	− 3.66
	.0006	− 1.44

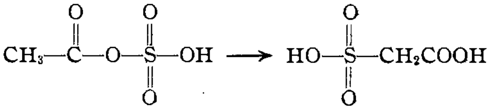
[a] After 18 hours this became −7.64.

Discussion

Of the acids recorded here only sulfo-acetic and 4-nitrochlorobenzene-2-sulfonic failed to show some sign of increased acidity owing to the presence of anhydride. The increase in the acidity of sulfuric acid was the most marked. The increased acidity occurred with propionic and butyric anhydrides and could be produced by the addition of fuming sulfuric acid. The action was reversible and addition of water caused a reversal of the titration curve. The ultra-acidic compound was found to be monobasic when titrated with sodium acetate solution. Sulfuric acid is dibasic in acetic acid solution, although titration with sodium acetate is not complete because of salt precipitation which occurs. It may be titrated as dibasic with aniline, diethyl-*o*-toluidine or guanidine.

It was concluded that the ultra-acidic compound was a mixed anhydride of sulfuric and acetic acids produced as outlined in the following equation. Upon standing, this compound undergoes rearrangement as indicated to form sulfoacetic acid, which is also monobasic but which does not show the ultra-acidic behavior.





$$CH_3-\overset{\overset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH \longrightarrow HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-CH_2COOH$$

In this connection, it may be mentioned that the sulfuric acid solutions showed a slow decrease in *p*H(HAc) upon standing in the presence of acetic anhydride, indicating that the rearrangement of the mixed anhydride was proceeding with the formation of sulfo-acetic acid.

Some indication of compound formation was noted in the case of perchloric acid. The addition of water returned the *p*H(HAc) to the expected value, but resulted in the formation of a yellow solution which became orange and then dark brown and foamed when gas was passed through it. This change did not occur unless water was added in excess of that required to decompose the acetic anhydride present. The titration of perchloric acid with sodium acetate in the presence of acetic anhydride showed that there were two breaks in the curve very near together, which appears to indicate the presence of two forms of the acid.

It appears from these measurements that any work upon acetylation reactions, such as that of Conant and Bramann mentioned above, must take into account the effect of the presence of acetic anhydride upon the acidity of the solution. Since it has been shown that it is possible to use the hydrogen electrode in the presence of anhydride, it should be possible to correlate the velocity of acetylations with the hydrogen-ion activity of the solution with considerable success.

Summary

1. A technique is described for making measurements with the hydrogen electrode in acetic acid–acetic anhydride solutions.
2. Sulfuric acid, perchloric acid, and certain sulfonic acids show increased acidities in the presence of acetic anhydride which cannot be accounted for by dehydration of the solution.
3. In the case of sulfuric acid, the effect is concluded to be due to the formation of a mixed anhydride of sulfuric and acetic acid which rearranges on standing into sulfo-acetic acid which does not exhibit ultra-acidic behavior.
4. This effect of acetic anhydride upon the acidity of such solutions must be considered when investigations of the effect of hydrogen-ion activity upon rate of acetylation reactions are being made.

ROCHESTER, N. Y. RECEIVED FEBRUARY 17, 1938

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 645]

The Internuclear Distance in the Fluorine Molecule

BY L. O. BROCKWAY

The structure of the fluorine molecule in the ground state is still unknown in spite of the great interest which attaches to fluorine as a member of the halogen family. In the only spectroscopic investigation reported in the literature[1] several emission bands were observed for a transition $^1S \rightarrow {}^1P$. The internuclear distances for the initial and final states of this transition are 1.48 and 1.28 Å., but these results afford no information about the ground state. The electron diffraction investigation which has now been made on fluorine vapor is the subject of this report.

The gas was prepared by Professor D. M. Yost and Dr. C. S. Garner by means of the electrolysis of potassium bifluoride in a fluorine generator constructed largely of monel metal. The product was passed over potassium fluoride to remove hydrogen fluoride and condensed to a liquid. After a first fraction had been evaporated and rejected, a sample was collected in a Pyrex flask for the electron diffraction investigation. The flow of gas during the exposures was controlled by an all-metal valve sealed to the flask by a metal-to-glass joint.

Five rings were observed on the photographs, but the first three were dark and smudgy while the fourth and fifth were well resolved. In spite of the very short exposures (of the order of one-half second) the removal of the fluorine introduced into the apparatus was not rapid enough to prevent the gas from spreading through the camera during the exposure. The scattering of electrons by fluorine molecules at various points along the electron beam then gave rise to a heavy background in the photographs. The momentary rise in pressure also caused high voltage discharges through gas in the electron-accelerating tube, and the resulting unsteadiness in the operation of the tube contributed somewhat to a lack of sharpness in the diffraction pattern.

Four samples of fluorine prepared at different times were used. In order to eliminate the possibility of contamination by silicon tetrafluoride the last sample was handled in brass and copper vessels and kept from contact with glass at all stages. The diffraction photographs from this sample have the same appearance and give the same measured ring diameters as the photographs from the earlier samples, and there is no evidence of contamination of the fluorine.

The diffraction pattern of a diatomic molecule is represented by the simple $(\sin ls)/ls$ function. The visually measured diameters of the five maxima and the two outer minima given as s_0 values $(= 4\pi (\sin \theta/2)/\lambda)$ are compared with the corresponding maxima and minima of the $(\sin ls)/ls$ function in Table I. The first of the internuclear distances in the last column is 12% smaller than the average of the remaining values. This difference is rather large. It suggests the possibility that the pattern is that of a mixture of

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[1] Gale and Monk, *Astrophys. J.*, **69**, 77 (1929).