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Isotopic Exchange Reactions in Acetic Acid and Acetic Anhydride[1]

BY ERSEL A. EVANS,[2] J. L. HUSTON[3] AND T. H. NORRIS

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A series of isotopic exchange reactions has been studied in the solvents anhydrous acetic acid and acetic anhydride. Rapid exchange occurs between radiocarbon-labeled sodium acetate and solvent acetic acid. This is explained in terms of direct transfer of protons from acetic acid molecules to acetate ions, rather than by self-ionization of acetic acid. Rapid exchange also occurs between acetic acid and dissolved plumbic acetate and plumbous acetate, as well as between acetic anhydride and dissolved plumbic acetate; these are explained by mechanisms similar to that for sodium acetate in acetic acid and also by formation of complexes. Slow exchange occurs between acetic acid and acetic anhydride showing that the self-ionization of both, to give acetate ions, cannot be fast. Slow exchange occurs between acetic anhydride and dissolved acetyl chloride, which is taken to indicate slow ionization of the latter. Appreciable heterogenous exchange takes place between solid sodium acetate and acetic anhydride, but much less than previously reported. The results of all these experiments are in general interpreted to indicate there has been an over-emphasis on ionic mechanisms, and analogies to the water system, by the proponents of the solvent system of acids and bases. No electronic exchange takes place between plumbic acetate and plumbous acetate, dissolved in pure acetic acid during four hours at 80°. This is contrary to results previously reported by other workers.

The solvent theory formulation of acids and bases envisages for each solvent a self-ionization comparable to that of water, an "acid" being defined as a substance which increases the concentration of the cations of this self-ionization while a "base" increases the concentration of the corresponding anions.[4] This concept has been elaborated by a number of workers and in particular Jander,[5] who has made an experimental study of a number of solvents including sulfur dioxide, acetic anhydride, hydrogen sulfide, etc., his work consisting primarily of studies of conductivities and of metathetical reactions. He has laid great stress on the supposed "water-like" character of these solvents, generally formulating reaction mechanisms in ionic terms; but it has been pointed out[6] that his theories often are based on insufficient experimental evidence and that some of his more crucial experimentation is invalid.

There is in progress in this Laboratory at the present time a program for investigation of nonaqueous ionizing solvents by determining the rates of isotopic exchange of solutes with such solvents as a function of various experimental conditions and it has already been reported[7] that contrary to the ionizations assumed by Jander and others

$$2SO_2 \rightleftarrows SO^{++} + SO_3^{=}$$

$$SOCl_2 \rightleftarrows SO^{++} + 2Cl^-$$

little or no exchange occurs when the acid thionyl chloride, labeled with radiosulfur, is dissolved in liquid sulfur dioxide. On the other hand labeled tetramethylammonium pyrosulfite does undergo rapid exchange when so dissolved. The present paper reports on an extension of this work to the solvents anhydrous acetic acid and acetic anhydride as well as a reinvestigation of early work done by Hevesy and Zechmeister[8] on electron exchange between plumbous acetate and plumbic acetate, both dissolved in acetic acid.

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[2] du Pont Fellow, 1950–1951.

[3] Address inquiries to J. L. Huston.

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[6] L. C. Bateman, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 243 (1944).

[7] (a) R. E. Johnson, T. H. Norris and J. L. Huston, THIS JOURNAL, **73**, 3052 (1951); (b) E. C. M. Grigg and I. Lauder, *Trans. Faraday Soc.*, **46**, 1039 (1950); (c) R. Muxart, *Compt. rend.*, **231**, 1489 (1950).

[8] G. V. Hevesy and L. Zechmeister, *Ber.*, **53B**, 415 (1920); *Z. Elektrochem.*, **26**, 151 (1920).

Experimental

Great care was used to prepare anhydrous reagents and, except in the case of the experiments on acetic acid dissolved in acetic anhydride, to make the runs in such a way that these hygroscopic materials were exposed to the least possible moisture. This was ordinarily accomplished by using high vacuum techniques which frequently were used with all-glass apparatus, and where these procedures were not feasible (in making weighings or transferring salts, for example), a dry-box was used, the air in which had been thoroughly dried by passing through calcium chloride and barium perchlorate columns. "Apiezon N" grease was used wherever stopcocks and ground joints were required.

Radioactivity.—Radioactive carbon was obtained from the Atomic Energy Commission as $BaCO_3$, and radium D from the Canadian Radium and Uranium Corporation (New York) in a solution of high specific activity. Radiocarbon samples were assayed as barium carbonate mounted usually by a standard procedure[9] which was also used to mount samples of lead chromate. This latter is one of the few salts of lead which may be precipitated from an acetate solution and was found to be superior for mounting to the lead dioxide often used by early workers.[8] When lead chromate (labeled with ThB or RaD) was counted, an aluminum filter was used to keep alpha particles of the daughters of these isotopes from reaching the counter tube.

A preparation labeled with ThB will almost certainly be in secular equilibrium with its daughter ThC when counted, but a preparation containing RaD may contain more or less than the secular equilibrium quantity of RaE (by means of whose beta particles it is counted). The equilibrium activity was calculated by counting the same sample several days apart and using the equation

$$\frac{N_{\max} - N_1}{N_{\max} - N_2} = e^{-\Delta t(5.78 \times 10^{-3})}$$

which can be derived from that for the growth curve[10]

$$N = N_{\max}(1 - e^{-\lambda t})$$

As a matter of convenience the expression $e^{\Delta t(5.78 \times 10^{-3})}$, for later use in the calculations, was plotted as a function of Δt.

Combustions.—Barium carbonate samples for radioassay were prepared by wet combustion of sodium acetate which had been obtained by careful vacuum evaporation of aqueous solutions at room temperature so that hydrolysis and loss of acetic acid were prevented, ice-water followed by liquid air being used as coolants to accomplish the evaporation without bumping. During the course of the work an isotope effect in the combustion rate was observed[11] and certain improvements were effected in the combustion procedure, which will be reported in another place, along with a centrifugation technique for mounting barium carbonate samples in small amounts.

Preparation of Materials.—Carboxyl labeled sodium acetate was made in aqueous solution from radioactive acetic acid prepared by a published procedure[12]; the solution was evaporated as described above, a small amount of very dilute acetic acid was added to neutralize any sodium hydroxide which might have been present, and the solution was evaporated again. It was necessary slowly to heat the flask containing the sodium acetate up to 100° *in vacuo* near the end of the dehydration to make the material completely anhydrous. The dehydrated material, over which a vacuum of less than 10^{-5} mm. could be held, was kept in an oven at 110° until used.

Anhydrous acetic acid was prepared from Baker and Adamson 99.5% acid by the procedure of Hess and Haber,[13] using fractional distillation followed by fractional crystallizations. Material was obtained with a melting point of 16.63 ± 0.01° (cor.), as measured by a mercury thermometer calibrated by the Bureau of Standards, and with no tendency to increase on further crystallization. Hess and Haber reported 16.635 ± 0.005°.

The flask containing this pure acetic acid was placed in a dry-box and the acetic acid forced by means of compressed air into dry 25- and 50-ml. flasks having necks with break-off tips for later vacuum line manipulation. The flasks were then sealed with exclusion of moisture. When needed, acetic acid was distilled into small fragile ampoules (each containing about 2 ml.) which were used to make runs as described below.

Acetic anhydride, b.p. 140.0°, was obtained by fractional distillation in a column with thirty plate sections.

Anhydrous plumbous acetate was prepared by the method of Davidson and Chappell[14] with the following modifications. After four recrystallizations of plumbous acetate from dilute acetic acid, approximately one gram of it was dehydrated by the vacuum technique previously described for labeled sodium acetate. Following this, the salt was moistened by a small amount of anhydrous acetic acid which was then distilled off in a vacuum. After desolvation was apparently complete (a very viscous liquid forms first before crystallization takes place) the salt was slowly heated to 100° and kept there two days *in vacuo*, any remaining trace of acetic acid distilling into liquid air; m.p. 202–203°. Davidson and Chappell reported 204°.

Plumbous acetate labeled with radiocarbon was made by distilling a small quantity of acetic acid from one of the 25-ml. ampoules mentioned above, first onto 10 mg. of sodium acetate of high specific activity to label it by exchange, and then onto one gram of lead acetate where it was sealed off and left overnight. The acetic acid was then distilled off and collected in quantities of about 0.15 ml. in small (about 1 ml.) fragile ampoules for later use in the exchange experiments with solvent acetic anhydride. Acetic acid vapor was in contact with stopcock grease for only a few minutes during this procedure. Glass wool was used in the apparatus to filter any particles of sodium acetate or lead acetate which might have been carried along by the acetic acid vapor during the distillation processes.

The sodium acetate left from this procedure had a high surface area and was used for the exchange experiment with acetic anhydride.

Radiolead labeling of plumbous acetate was done both with ThB ($T_{1/2}$ 10.6 hr.) for a few preliminary experiments and with the more convenient RaD ($T_{1/2}$ 22 yr.). The first procedure involved the precipitation of lead sulfide from a thorium nitrate solution and conversion of this, progressively, to lead chloride, basic lead carbonate, and finally plumbous acetate which was dehydrated as described above. The preparation had the correct half-life. Labeling with radium D was accomplished by adding about 0.025 millicurie of high specific activity lead nitrate solution to 23 g. of $Pb(OAc)_2 \cdot 3H_2O$ which was then dissolved in 15 cc. of boiling, dilute acetic acid. Lead acetate was then isolated as described for the inactive material except that it was crystallized only once.

Lead tetraacetate, inactive, was prepared by reaction of red lead with a mixture of acetic anhydride and glacial acetic acid.[15] After filtering and washing, it was freed of acetic acid–acetic anhydride in the same way that plumbous acetate was desolvated and it was then stored in an evacuated flask; m.p. 176–180°, literature 175–180°.[15] It was analyzed by adding water, filtering and weighing the lead dioxide formed, and by titrating the acetic acid. Found: PbO_2, 54.13; $(CH_3CO)_2O$, 45.93. Calcd.: PbO_2, 53.95; $(CH_3CO)_2O$, 46.05.

A portion of this plumbic acetate was labeled in the same manner as the plumbous acetate.

Acetyl chloride, C.P., was transferred to a small flask, half of it distilled off, and the remainder distilled into small fragile ampoules like those used for acetic acid and acetic anhydride.

Procedure for Making Runs.—Exchanges of bases with acetic acid or acetic anhydride solvent were conducted in the apparatus shown in Fig. 1; experiments were done using the labeled bases sodium acetate, plumbic acetate and plumbous acetate with solvent acetic acid, and using the two former bases with solvent acetic anhydride. The apparatus was evacuated and flamed out as thoroughly as possible for a period of at least one hour prior to a run, placed in a dry-box, and a small amount (about 20 mg.) of labeled base

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[9] W. G. Dauben, J. C. Reid and P. E. Yankwich, *Anal. Chem.*, **19**, 828 (1947).

[10] G. Friedlander and J. W. Kennedy, "Introduction to Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1949.

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[12] C. K. Claycomb, T. T. Hutchens and J. T. Van Bruggen, *Nucleonics*, **7**, 38 (1950).

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[14] A. W. Davidson and W. Chappell, THIS JOURNAL, **55**, 4524 (1933).

[15] J. C. Bailar, Jr., *Inorganic Syntheses*, **1**, 47 (1939).

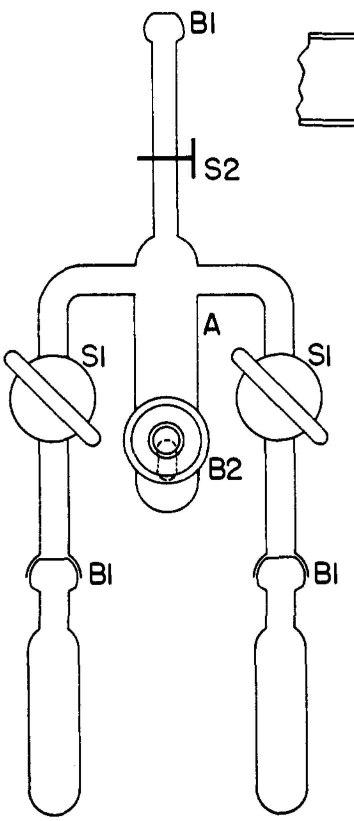

Fig. 1.—Apparatus for exchange reactions of acetic acid and acetic anhydride with acetates: B1, 18/9; B2, 28/15.

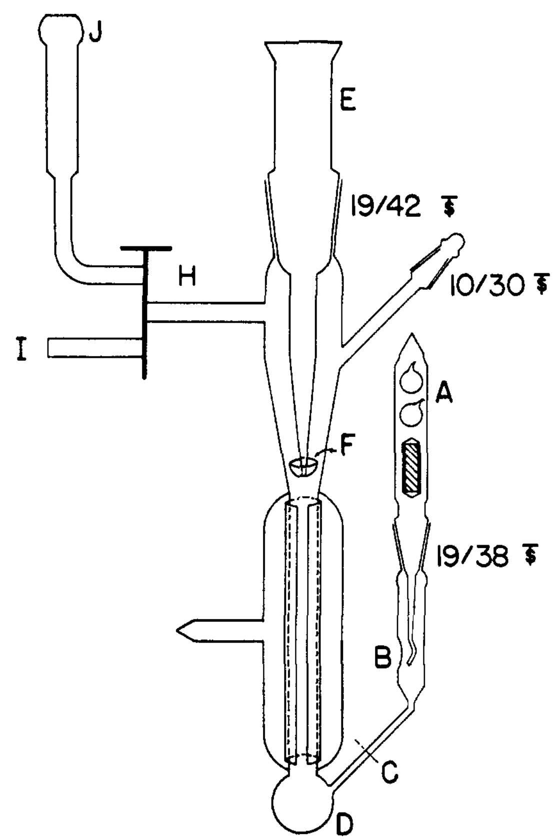

Fig. 2.—Apparatus for exchange reactions of acetyl chloride with solvent acetic anhydride.

placed in the chamber A along with a small ampoule containing about 2 ml. of pure inactive solvent. The apparatus was evacuated and dry carbon dioxide admitted to a pressure of about 20 mm. to prevent spattering when the acetic acid ampoule was broken. The apparatus was closed off by means of stopcock S2 and the ampoule crushed with the glass pestle B. The solution of the base was carefully shaken for a short while, giving complete solution (in all cases except for the sodium acetate–acetic anhydride experiment), and then a small amount of solvent was distilled through one of the stopcocks S1 and into one of the side arms, which was then closed off. When necessary, a second distillate was collected in the other arm. Sodium acetate being insoluble in acetic anhydride, the apparatus was carefully shaken throughout that experiment. D was a Teflon washer, the purpose of which was to prevent the entrance of radioactive solutions or water into the less accessible parts of the pestle arm.

The acetic acid or acetic anhydride distillates were neutralized, the water removed as before described, and barium carbonate samples prepared for radioassay.

Acetyl chloride–acetic anhydride exchange experiments were performed in the apparatus shown in Fig. 2; the micro fractionating column was based largely on one reported by Craig,[16] but with a thin strip of aluminum foil around the central column. A run was started by placing in tube A an ampoule containing acetyl chloride along with an ampoule containing radioactive acetic anhydride and a glass-enclosed breaker; after the tube had been evacuated and sealed off, it was shaken to break the two ampoules and was placed in an ice-bath for the duration of the exchange time interval.

The separation of acetyl chloride from acetic anhydride was effected as follows: the reaction tube A was attached to the fractionating column as shown, and the column was pumped to high vacuum and closed off at H. Then the tip was broken by rotating it against the constriction B, and after bulb B had been cooled in liquid air to condense all of the acetic anhydride and acetyl chloride down into it, a seal was made at the point C. Now the pressure in the column was adjusted, by means of a vacuum system attached at H, to a suitable value. The liquid was stirred magnetically to prevent bumping, and D was surrounded by a room-temperature water-bath.

The distillate condensed on the tip of the collecting cup E (filled with Dry Ice) and was collected in the small (about 0.2 ml.) cup F; samples were removed periodically by admitting dry air to the apparatus and inserting the tip of a long and thin pipet through the 10/30 ground joint. The purity of the acetyl chloride thus obtained was checked by titrating aliquots of hydrolyzed distillate fractions for chloride.[17] The first sample of distillate was 100% acetyl chloride, based on a comparison of its weight with the result of the titration.

Acetic Acid–Acetic Anhydride.—The exchange experiment of acetic anhydride in anhydrous acetic acid solvent was done in an evacuated tube as shown in Fig. 3, one end of which contained a heavy mercury-in-glass breaker and small fragile ampoules each of labeled acetic acid and of acetic anhydride, the latter being present in smaller quantity. The tube was shaken carefully to break the two ampoules, and after thorough mixing of the liquids had occurred, the tube was placed in a 25° constant temperature bath. At the end of the run the solution was fractionally crystallized by shaking the tube while the large end was inserted in a bath at 12°. When crystallization was apparently complete the solution was cooled to 0° in an ice-bath, quickly transferred to a refrigerated centrifuge and acetic anhydride was separated from the frozen acetic acid by centrifugation through the sintered glass disc and into the small tip. The tube was then removed from the centrifuge and the tip snapped off. The tip was transferred to a weighing bottle, weighed, and the centrifugate titrated with sodium hydroxide solution. Then the empty tip and weighing bottle were reweighed.

The methods which have been proposed[18] for the analysis

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(16) L. C. Craig, *Ind. Eng. Chem., Anal. Ed.*, **9**, 441 (1937).

(17) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Second Edition, The Macmillan Co., New York, N. Y., 1943, p. 576.

(18) Reference 5, p. 310.

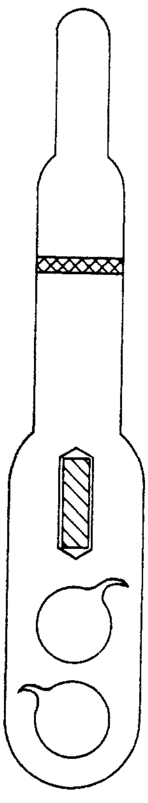

Fig. 3.—Apparatus for exchange reaction of acetic anhydride with solvent acetic acid.

of acetic acid–acetic anhydride mixtures were not suitable for this work where subsequent radioassay is required. The filtrate titrations did not give results consistent with the radioassays—this may have been because of a weighing error due to moisture condensing on the ice-cold glass tip. Since the equivalent weight of the anhydride is not greatly different from that of the acid, a small error of this type in the initial weight would markedly affect the titration results.

The exchange experiment of labeled acetic acid in solvent acetic anhydride involved a separation by water extraction and consequently no attempt was made to exclude traces of moisture as was done in all the other experiments. A small ampoule containing approximately 0.15 ml. of acetic acid was placed in a male standard taper joint which had been pulled down and sealed off at the end so that its shape resembled that of a 15-ml. centrifuge tube. Two milliliters of pure acetic anhydride were then added by means of a calibrated, automatic pipet. The ampoule was quickly crushed with a glass rod, a standard taper cap was placed on the reaction tube and the solution mixed by careful shaking. The tube was then sealed in a sheet of paraffin to keep out water and placed in a bath at 0°.

At the end of the desired exchange time, the tube was opened, the solution was transferred to a 15-ml., graduated centrifuge tube (to avoid trouble with glass particles later in the separation) and 5 ml. of ice-water was added. The tube was then stoppered and shaken vigorously for 20 seconds. It was centrifuged for approximately 15 seconds and the lower anhydride layer separated from the acetic acid–water layer by means of a medicine dropper with an elongated tip.

The two solutions were neutralized with sodium hydroxide solution and the resulting sodium acetate samples converted to barium carbonate and counted.

The last run of this experiment was varied in several respects, in that approximately 0.4 ml. of labeled acetic acid and 5 ml. of acetic anhydride were used and 2 ml. of this solution was removed at the end of two hours and another 2 ml. at the end of five hours. Each of these two samples was then handled as described above, except that the shaking was done by a mechanical shaker and the centrifuging was carried out with the centrifuge tube packed in ice. The radioassays of the resulting samples indicated that more complete separation was accomplished by this method.

Plumbous acetate–plumbic acetate exchange experiments were done in pure acetic acid. In ten runs three different procedures were used to separate divalent and tetravalent lead; they will be illustrated by describing three of the runs. All operations were performed in a dry-box except as otherwise noted.

Run I.—A separation procedure was used based on that used by Zintl and Ranch[19] to separate the divalent and tetravalent lead of Pb_2O_3 without exchange. 0.159 millimole of plumbous acetate and 0.159 millimole of plumbic acetate were weighed into a small volumetric flask and 5 ml. of acetic acid was added by means of an automatic pipet. The flask was shaken to dissolve the salts and after one minute at room temperature it was removed from the dry-box and poured, with vigorous stirring, into 50 ml. of 16 N KOH which had been made free of carbonate by shaking with solid $Ba(OH)_2$, followed by centrifugation. Although the resultant plumbite and plumbate ions are stable in the presence of each other in strong alkali and do not undergo exchange of lead,[19] a transitory, brown precipitate was generally observed in such runs; presumably this was lead dioxide. The color was especially noticeable in a run where the concentrations were higher (the same as run II).

The plumbite–plumbate solution was brought to boiling in a standard taper erlenmeyer flask and 5 millimoles of solid barium hydroxide added. The flask was shaken mechanically for half an hour and the contents then centrifuged. The precipitate (a mixture of barium carbonate, barium hydroxide and barium plumbate) was washed three times by centrifugation with 12 N carbonate-free potassium hydroxide solution, and excess 6 N HNO_3 was then added to form PbO_2. As in all other runs, this was washed and converted to lead chloride with concentrated hydrochloric acid, the solution was diluted, heated, and potassium dichromate was added. If necessary, a few drops of sodium hydroxide solution were added in order to secure precipitation of lead chromate, but this was always precipitated from an acidic solution.

Run II.—0.514 millimole of plumbous acetate and 0.513 millimole of plumbic acetate were weighed into a test-tube provided with a ground joint at the top. A standard taper ground joint thermometer was inserted after 5 ml. of acetic acid had been dosed into the tube, and the tube was rapidly heated to 80° with a cylindrical heating element powered by a Variac. The tube was shaken to dissolve the salts and the temperature of the solution was maintained at 80 ± 5° for ten minutes. The tube was removed from the dry-box and the solution poured into 15 ml. of water which was then boiled and lead dioxide was separated by centrifugation and filtration and converted to lead chromate as described for run I. Lead chromate was precipitated also from the filtrate.

Run III.—1.47 millimoles of plumbous acetate and 1.30 millimoles of plumbic acetate were weighed out and brought into solution as in run II, the solution being maintained at 80 ± 10° for nine minutes. The solution was then cooled to 30° to produce crystallization of plumbic acetate which was collected on a filter and washed once with acetic acid. The crystals were removed from the dry-box and converted to lead dioxide which was processed as in run I. In a similar run acetic acid was used containing 1% water. In this case only, the acetic acid solution was slightly turbid. It may be noted that in this case sufficient water was actually present in the acetic acid solution to hydrolyze completely the plumbic acetate, $Pb(OAc)_4 + 2H_2O \rightarrow PbO_2 + 4HOAc$, but this did not take place.

Results

Bases in Acetic Acid.—Sodium acetate, plumbous acetate (anhydrous) and lead tetraacetate were all found to undergo complete exchange with solvent acetic acid in a few minutes. The following are listed in order: (1) milliequivalents of solute, (2) milliequivalents of solvent, (3) exchange time, (4) specific activity (c./min./mg.) of acetic acid distilled from the solution, and (5) specific activity of the residual solution.

For sodium acetate solute: Run I, (1) 1.3, (2) 150, (3) 5 min., (4) 84.1, (5) 95.3; Run II, (1) 0.12, (2) 12, (3) 3 min., (4) 83.2, (5) 81.4.

For lead diacetate solute: Run I, (1) 0.15, (2) 30, (3) 2.5 min., (4) 9.4; Run I (continued), (3) 12 hr., (4) 9.7, (5) (not determined); Run II, (1) 0.17, (2) 30, (3) 3 min., (4) 10.2; Run II (continued), (3) 2 hr., (4) 10.4, (5) 10.2.

For lead tetraacetate solute: Run I, (1) 0.19, (2) 32, (3) 3 min., (4) 6.7; Run I (continued), (3) 2 hr., (4) 6.7, (5) (not determined); Run II, (1) 0.21, (2) 33, (3) 5 min., (4) 7.2; Run II (continued), (3) 7 min., (4) 7.5, (5) 7.2.

Within experimental error the distillates have the same specific activity as the solution and successively removed distillates experience no increase of their specific activities with time. It is very doubtful that runs could be made more rapidly than these. The difference in the specific activities of distillate and residue in the first sodium acetate run may have been due to incomplete solution of the solute or to spattering of the acetic acid before complete solution had taken place.

Acetic Anhydride–Acetic Acid.—In contrast to this we find a slow rate of exchange between solute acetic anhydride dissolved in solvent acetic acid and, *vice versa*, between solute acetic acid and solvent acetic anhydride. In these types of experiment we must expect incomplete separations and sizeable "blanks" both when acetic acid is extracted from acetic anhydride by water and when acetic anhydride is removed

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(19) E. Zintl and A. Ranch, *Ber.*, **57B**, 1743 (1924).

from acetic acid by freezing; thus the data are not true exchange rates but they suffice to show roughly the rate of exchange. Plots of log (1 − fraction exchange) *vs.* time indicate a half-time of roughly 10 hours[20] for acetic anhydride in solvent acetic acid and of five hours for acetic acid in acetic anhydride.

For acetic anhydride in solvent acetic acid there are listed in order: (1) milliequivalents of acetic acid, (2) milliequivalents of acetic anhydride, (3) time and (4) apparent per cent. exchange: I, (1) 43, (2) 3.7, (3) 25 min., (4) 42; II, (1) 35, (2) 4.1, (3) 3 hr., (4) 49; III, (1) 32, (2) 6.6, (3) 41 hr., (4) 67; IV, (1) 47, (2) 3.7, (3) 111 hr., (4) 99.

For acetic acid in acetic anhydride the order of listing is the same: I, (1) 3.5, (2) 21, (3) 5 min., (4) 25; II, (1) 2.7, (2) 21, (3) 35 min., (4) 30; III, (1) 3.0, (2) 21, (3) 3.75 hr., (4) 31; IV, (1) 2.8, (2) 22, (3) 7.25 hr., (4) 67; V, (1) 2.6, (2) 21, (3) 40 hr., (4) 100; VI, (1) 2.9, (2) 20, (3) 2 hr., (4) 24; VI (continued), (3) 5 hr., (4) 36.[21]

Bases in Acetic Anhydride.—Sodium acetate is not soluble in acetic anhydride[22] (nor is plumbous acetate) and the only experiment possible was a heterogeneous exchange. When 5.9 milliequivalents of labeled sodium acetate was shaken at room temperature for 25 min. with 35 milliequivalents of anhydride a sample of distillate showed that 4.6% exchange had taken place, and this increased to 4.8% at the end of one hour.

Plumbic acetate is soluble and two runs were made. In the first case 0.30 milliequivalent of labeled solute was dissolved in 25 milliequivalents of solvent and a distillate sample which was taken after 5 min. indicated that 82% exchange had taken place, increasing to 100% after 4 hr. This, however, does not mean that the true exchange takes place slowly enough to be measured for a second run using 0.18 milliequivalent of solute and 22 milliequivalents of solvent underwent 95% exchange in 6 min.—virtually complete within experimental error. Probably in the first run some solute had escaped dissolving, at the time the first sample was taken, by washing up on the wall above the liquid. This could easily have happened since lead tetraacetate is more difficultly soluble in acetic anhydride than any of the bases are in acetic acid. At any rate the exchange is quite rapid at room temperature.

Acetyl Chloride in Acetic Anhydride.—This exchange is measurably slow, being of the order of half-time 10 hours at 25°. The following are listed in order: (1) milliequivalents of acetic anhydride (active), (2) milliequivalents of acetyl chloride, (3) time and (4) per cent. exchange. I, (1) 40, (2) 2.0, (3) 10 min., (4) 0; II, (1) 58, (2) 2.5, (3) 4.25 hr., (4) 47; III, (1) 67, (2) 2.1, (3) 36 hr., (4) 83. A kinetic study is projected for this system.

Plumbous acetate and plumbic acetate dissolved in pure anhydrous acetic acid were found to have no appreciable rate of exchange, contrary to the results of early work by Hevesy and Zechmeister.[8] These authors did two experiments. In the first, the two acetates were dissolved in glacial acetic acid, and after ten minutes at 80° the solution was diluted with three times its volume of water and boiled. The radioactivity of the lead dioxide so produced was measured and compared with the radioactivity of the residue left from evaporation of an aliquot of the filtrate. The specific activities were the same, that is 100% exchange had taken place. Our run II (see experimental part) was done in the same way as to time, concentrations, precipitation method, etc., and with the same result. We made other runs for shorter times and at room temperature and again with complete exchange.

Several years after Hevesy and Zechmeister had done this work, Zintl and Ranch[19] showed, by labeling the divalent lead, that the divalent and tetravalent lead atoms of $Pb_2O_3 \cdot 3H_2O$ are not equivalent; in the course of this work they found that when $Pb_2O_3 \cdot 3H_2O$ was dissolved in acid to form lead dioxide complete exchange took place between the two oxidation states of lead, but this could be avoided by dissolving the lead sesquioxide in strong base, to form plumbate and plumbite ions, and separating the two by precipitation of barium plumbate. This suggests, of course, that the "exchange" of Hevesy and Zechmeister may have been due to the separation method used.

However, they had also performed another experiment using a separation method less open to objection. Labeled plumbic acetate and inactive plumbous acetate were dissolved in hot acetic acid, and after a while the solution was cooled to produce a crystallization of plumbic acetate, this was dried and its radioactivity compared with that of the original material; it had been diminished by one-half (equivalent quantities of the two salts were present in the acetic acid solution). Our experiment III was comparable as to separation method and concentrations but after separation by crystallization only 1.0% exchange had taken place and this was probably due to incomplete washing of mother liquor from the crystallized salt. (It could be washed only once because of appreciable solubility in acetic acid.) Other experiments were done at lower concentrations (about 0.6 of the concentrations used in run III) with similar results, one run which was continued for 4 hours at 80 ± 1° resulting in an apparent exchange of only 0.4%.

A few other runs were made using an adaptation of the Zintl and Ranch procedure for separation. Run I resulted in apparent exchange of 1.2% and this small amount of radioactivity probably was due to barium plumbite coprecipitated with barium plumbate. However, when a run was made with a more concentrated solution (the same as run II) a marked brown turbulence was observed for a minute or two, presumably due to lead dioxide, when the acetic acid solution was poured into aqueous alkali. This time the apparent exchange was 10.3%.

It is of interest to note that crystallization of plumbic acetate carried no RaE (bismuth) from acetic acid solution, but RaE was carried completely by the precipitated lead dioxide when the aqueous hydrolysis separation procedure was used.

Discussion

Sodium acetate is a fairly strong base in acetic acid solution and it is not surprising that its acetate ions should undergo rapid exchange with the solvent, but it does not necessarily follow that this exchange takes place entirely or even principally by means of the self-ionization of the solvent

$$2\text{AcOH} \rightleftarrows \text{AcOH}_2^+ + \text{AcO}^-$$

We have seen that acetic anhydride and acetic acid undergo exchange only slowly when dissolved in each other, regardless of which is in excess. If we assume that acetic acid molecules ionize more or less as readily in acetic anhydride as in pure acetic acid, and *vice versa*, it follows that the self-ionizations of both of these solvents (to give acetate ions) cannot be rapid.

It is then worthwhile to inquire whether the exchange may not be effected in another way, by some sort of solute–solvent interaction. It is known that liquid sulfur dioxide undergoes rapid exchange with dissolved sulfite ion[7] and Johnson, Norris and Huston have suggested, on the basis of experiments wherein it was shown that there exists a mobility of oxide ions between sulfur dioxide and dissolved sulfur trioxide, that the former exchange takes place by a direct transfer of oxide ion from sulfite ion (a Lewis base) to sulfur dioxide (a Lewis acid). It is reasonable that this transfer should occur more readily from a sulfite ion than from a

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[20] A straight line can be drawn reasonably between the points, but it could not be expected that the points should actually lie on a straight line, even if the "blank" is the same in every run (which we do not claim), since the techniques used did not permit the reproducing of relative proportions of acetic anhydride and acetic acid from run to run. However, we believe that the "blank" can be standardized for the extraction of acetic acid from solvent acetic anhydride, by using the technique of the last run, and a kinetic study is projected for this system.

[21] Quantities of both substances were estimated volumetrically, acetic anhydride by pipetting when it was the solvent, and otherwise by immersing the containing ampoules in water in a graduate.

[22] Jander reports conductivity studies involving 0.01 *M* NaOAc solutions at room temperature (ref. 5, p. 315) but we find that sufficient solute to make a solution 0.003 *M* will not dissolve after prolonged shaking, either at room temperature or at 50°.

sulfur dioxide molecule (in a reversible self-ionization process), the former being the stronger base.

Similarly, acetate ion is a stronger base than acetic acid and we suggest then that exchange between acetate ion and acetic acid molecule may take place largely by direct interaction between the two, with transfer of a proton. This is not to say that self-ionization does not occur in acetic acid, and it is unfortunate that the exchange proceeds too rapidly to permit a kinetic study aimed at a positive determination of which process is the more important. In this connection it is interesting to note that rapid exchange occurs between liquid ammonia and dissolved ammonium ion.[23] The same considerations apply, since the exchange may occur by self-ionization or by direct transfer of a proton from ammonium ion to an ammonia molecule. Here again it appears that the exchange rate is too rapid to permit a kinetic study.

If we assume, in the absence of positive proof, that the slow rate of exchange between acetic acid and acetic anhydride indicates that any self-ionization of the *latter* compound must be slow, it should be observed that reported values for the conductivity of acetic anhydride[24] are all greater than that of water, but any conclusions which might be drawn from this can be heavily discounted since it does not appear that any of the determinations were made using carefully purified acetic anhydride.

Plumbous acetate is only a weak electrolyte in acetic acid solution[25] and it is amphoteric,[26] showing an increase in solubility when sodium acetate is added and permitting the isolation of acetoplumbites; yet its exchange with the solvent is rapid. The exchange may take place by such ionization as

$$\mathrm{Pb(OAc)_2} \rightleftarrows \mathrm{PbOAc^+} + \mathrm{Ac^-} \text{ or}$$

$$\mathrm{Pb(OAc)_2} + \mathrm{HOAc} \rightleftarrows \mathrm{Pb(OAc)_3^-} + \mathrm{H^+}$$

and in addition, in fact probably to a greater degree, by coördination with one or two acetic acid molecules

$$\mathrm{Pb(OAc)_2} + \mathrm{HOAc} \rightleftarrows \mathrm{Pb(OAc)_3{\cdot}H}$$

Intramolecular transfer of a proton then serves to effect the exchange. The amphoterism and the formation of a solvate[14] support the validity of these last two processes.

Plumbic acetate is a non-electrolyte in acetic acid solution and it also differs from the plumbous salt in that its solubility is decreased by addition of sodium acetate,[25] so it had been hoped that the exchange rate might be slow enough to permit a kinetic study. The rapid exchange observed probably occurs *via* the formation of uncharged complexes with acetic acid by use of coördination numbers greater than four, the processes being similar to the last two postulated for plumbous acetate. Since there is no evidence for acetoplumbates,[27] such complexes are probably of low stability and transitory existence only. To assume that neutral complexes are formed amounts to implying, on account of proton mobility, that ionization also takes place, but to a smaller extent because of requiring charge separation.

Since boron acetate, which also has been described as a covalent compound,[28] would possibly form an acetate complex less readily than the lead because of the small size of the boron atom, it would be interesting to check the exchange rate of this compound with acetic acid.

Unlike thionyl chloride dissolved in sulfur dioxide, acetyl chloride possesses a slow but definite rate of exchange with solvent acetic anhydride. Such behavior is hardly water-like and lends support to previously recorded criticisms that proponents of the solvent system, and in particular Jander, have laid too much stress on ionic mechanisms and analogies to aqueous reactions.[6,7] It is interesting to observe that Usanovich[29] has noted, in performing indicator titrations in acetic anhydride solution, that when a solution of sodium acetate in acetic anhydride is titrated with acetyl chloride the indicator changes color only very slowly. Seemingly, the same phenomenon was observed by Jander,[27] who, while performing titrations conductimetrically, also observed a drifting end-point, but ascribed it to supersaturation of sodium chloride. He observed the same result when other alkali halides were being formed, but not when thallous acetate was titrated.

Usanovich believes on the basis of the kinetics of his reaction that the rate determining step is the ionization of acetyl chloride, which he writes as giving a solvated ion $\mathrm{AcCl} + \mathrm{Ac_2O} \rightleftarrows \mathrm{Ac_3O^+} + \mathrm{Cl^-}$. Some such process must be responsible for our exchange. The result with thallous acetate, then, is presumably to be ascribed to a direct reaction of thallous acetate with un-ionized acetyl chloride molecules.

In connection with the striking difference between the behavior of the acids acetyl chloride and thionyl chloride in their respective solvents and the behavior of acids in water, it is interesting to consider the dinitrogen tetroxide solvent system, which is being studied by Addison[30] and his co-workers. They believe that the self-ionization, $\mathrm{N_2O_4} \rightleftarrows \mathrm{NO^+} + \mathrm{NO_3^-}$, occurs in this liquid (to a very slight degree), and thus nitrosyl chloride is a solvo-

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(23) C. J. Nyman, S. Fung and H. W. Dodgen, THIS JOURNAL, **72,** 1033 (1950).

(24) J. Rameson, *Biochem. Z.*, **207**, 77 (1929); R. Müller, V. Raschka and M. Wittmann, *Monatsh.*, **48**, 661 (1927); "International Critical Tables," Vol. VI, McGraw-Hill Book Co., New York, N. Y., 1926, p. 143.

(25) A. W. Davidson, W. C. Lanning and M. M. Zeller, THIS JOURNAL, **64**, 1523 (1942).

(26) A. Lehrman and E. Leifer, *ibid.*, **60**, 142 (1938).

(27) This illustrates the danger of reasoning by analogy between drastically different solvent systems. Lead dioxide is more acidic than lead monoxide and there are many aquoplumbates.

(28) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, New York, N. Y., 1950.

(29) M. Usanovich and K. Yatsimirskii, *J. Gen. Chem.*, (*U.S.S.R.*), **11,** 957 (1951). ADDED IN PROOF.—At the time our discussion was written we had access only to the abstract of this paper; we have since been able to consult the original. The reaction of acetyl chloride with sodium acetate takes place about fifty times as fast as our exchange reaction, and it thus seems unlikely that the mechanism suggested by Usanovitch and Yatsimirskii for the former process can be valid, but it may still be a valid mechanism for the exchange reaction. It needs to be noted that reaction environments were different, the acetyl chloride solutions used by the Russian workers being more concentrated than those used by us.

(30) C. C. Addison, C. P. Conduit and R. Thompson, *J. Chem. Soc.*, 1303 (1951), *et ante.*

system acid, while nitrates are solvo-system bases. But while it appears that nitrosyl chloride liquid itself is probably ionized to some extent, this ionization is affected no more by dissolving the nitrosyl chloride in dinitrogen tetroxide than by dissolving it in an "inert" solvent such as carbon tetrachloride; *e.g.*, the rate of reaction with metals is about the same in both cases. And no metal was observed to react more rapidly with a NOCl–N_2O_4 solution than with nitrosyl chloride alone. The contrast with the behavior of acids such as HCl in water is both obvious and striking. There is no doubt that formal analogies between different solvent systems can be useful for classification purposes, but they cannot be taken alone to prove that formally similar reactions occur by similar mechanisms in solvents of drastically different properties.

The chief points of interest concerning the exchange observed in the heterogeneous sodium acetate–acetic anhydride exchange is that the rate appears to fall off with time (as the surface area of the sodium acetate diminishes) and that the 4.6% exchange observed is very appreciably less than the 52% reported by Ruben, *et al.*,[31] for a similar experiment and which the authors themselves considered unduly large. The concentrations of the reactants were essentially the same in both cases. As previously mentioned, special efforts were made in the present work to obtain very finely divided sodium acetate, and the exchange mixture was vigorously agitated. It, therefore, appears that the slower rate observed here was not the result of a surface effect or lack of mixing. The acetic anhydride used by Ruben and co-workers may have contained sufficient acetic acid to affect the exchange rate which they observed, since it boiled at 138.5–139.5° (compared to the 140.0° b.p. of pure acetic anhydride).

To give a picture for the mechanism of the rapid exchange between plumbic acetate and solvent acetic anhydride, we may assume a loose coördination of lead to the central oxygen of an acetic anhydride molecule with weakening of the adjacent oxygen–carbon bond and a slight induced ionization

$$Pb(OAc)_4 + Ac_2O \rightleftarrows Ac^+ + Pb(OAc)_5^-$$

In this connection it would be of interest to investigate whether the presence of plumbic acetate might increase the rate of exchange of acetic anhydride and acetyl chloride, though this could hardly occur if the above mechanism for the later exchange is correct. Dissolved plumbic acetate might increase the rate of exchange between acetic acid and acetic anhydride since it undergoes rapid exchange with both.

Unfortunately, the electrolytic properties of the acetic anhydride–plumbic acetate system have not been determined.

It is clear that the two-electron exchange which Hevesy and Zechmeister reported from their experiment when aqueous hydrolysis was used to separate the two oxidation states of lead was only an apparent exchange and was produced by the separation procedure used,[32] but it is not possible to account conclusively for the exchange which they observed when the acetic acid solution was cooled to produce crystallization of plumbic acetate. It will be observed that we made runs closely similar to the ones they made, in time, temperature and concentration of reactants.

Most exchange reactions which have been studied have been carried out in aqueous solutions, and Weiss has recently proposed a theory based upon the water, or oxygen, in such solutions playing an important part in an intermediate oxidation-reduction reaction.[33] It is possible that the glacial acid used by Hevesy and Zechmeister contained some impurity which acted in a similar way to cause exchange, since, apparently, ordinary glacial acid was used. But if this is so the effect was not due to water, for we made a run similar to run III (but with salt concentrations about 0.6 those of run III) with 1% water added to the acetic acid prior to the run. No significant exchange occurred.

It is of interest to note that Sidgwick[28] has pointed to these experiments of Hevesy and Zechmeister as providing the only evidence for the existence of plumbic ion in acetic acid solution. While discounting this evidence we may point out that the rapid exchange of acetate between plumbic acetate and solvent acetic acid would seem to point to the existence of a few plumbic ions, even though in exceedingly small concentration.

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[31] S. Ruben, M. B. Allen and P. Nahinsky, THIS JOURNAL, **64**, 3050 (1942).

[32] This exchange may occur homogeneously during hydrolysis after the acetic acid solution is poured into water, for the precipitation of lead dioxide is not instantaneous and in a run where the concentrations were about $^1/_{10}$ those used in run II (*i.e.*, about 0.002 *M*) several minutes elapsed before precipitation became visible.

[33] J. Weiss, *J. Chem. Phys.*, **19**, 1066 (1951).