described previously and has been variously termed "thermal aging"[8] and "recrystallization."[18] Because, as described above, the rate of step III is independent of ionic strength the term "thermal aging" seems preferable. Certainly the process does not involve a solution and redeposition of ions. While it is possible that certain ions may be able to "diffuse" throughout the lattice of certain crystals, in the present instance where the lattice is quite dense and where the diffusing ion, phosphate, is large and multicharged, it seems more probable that ion-migration is mediated throughout the presence of unoccupied lattice positions or "faults" in the crystals. This view is supported by the fact that high-temperature ashing markedly reduces the recrystallization or thermal equilibration of fresh bone.[18] Such heat treatment would be expected to render the crystals more perfect with fewer "faults" and vacant positions as attested by improved X-ray diffraction patterns.[9] The participation of "holes" which move as the result of thermal vibration of adjacent ions is also consistent with the ever-decreasing rate of reaction, Fig. 9, as the diffusing ion penetrates deeper layers of the crystals. With aged crystals, the reaction rate falls so rapidly that one must conclude that only a few "molecular layers" can take part in equilibria covering an observational period of a few weeks.

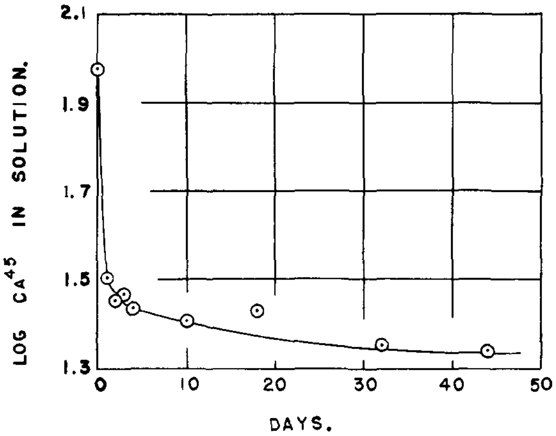

Fig. 9.—A long-term calcium exchange showing a continued but progressively slowed removal of Ca^{45} from solution by the solid phase. In this experiment eight identical flasks containing apatite and Ca^{45} were rotated at a constant temperature of 37°, and sampled serially for radioactivity assay and Ca concentration of the liquid.

Despite the complexity and variability of the hydroxy apatite lattice, its extremely small crystal size makes it an excellent material for the study of solid:solution interactions.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Electrokinetics of Hydrogen Evolution. IV. Isotopic Separation at Mercury Cathodes[1,2]

BY MARTIN ROME[3] AND C. F. HISKEY[4]

RECEIVED MARCH 16, 1954

Techniques have been developed and a cell designed for the determination of the electrolytic separation factor at a mercury cathode by means of a mass spectrometer. The separation factor has been determined over a range of temperatures from 0 to 96.5° and of current densities from 10^{-4} to 3×10^{-2} amp./cm.^{2}. Impurity effects of stopcock grease have been evaluated. The dual theory of Horiuti and Okamoto for the mechanism of electrode separation is applied for the case of a mercury cathode.

Recent studies of hydrogen and deuterium overvoltages[5,6] at a mercury cathode have stimulated interest in the related problem of the electrolytic separation factor of these isotopes. This factor is expressed as a ratio of the rates of electrolytic evolution of the two isotopes, *viz.*

$$S = \frac{dH/H}{dD/D} = \frac{(C^H/C^D)_g}{(C^H/C^D)_s} = \frac{i^H/i^D}{(C^H/C^D)_s} \qquad (1)$$

In this definition C^H and C^D are the concentrations of hydrogen and deuterium, and the subscripts g and s refer to the gas and solution phases, respectively. Values of the separation factor have been reported by Topley and Eyring,[7] Eucken and Bratzler,[8] Walton and Wolfenden,[9] and Horiuti and Okamoto[10] for mercury cathodes. A resumé of these reported separation factors is given in Table I and

TABLE I

RESUMÉ OF REPORTED SEPARATION FACTORS FOR MERCURY

Author	*i*, amp./cm.^{2}	*T*, °C.	% D_2O	Electrolyte	*S*	Reported error
Topley and Eyring	7×10^{-1}	20	8	H_2SO_4 0.5 *N*	2.8	0.15
			9	H_2SO_4 .5 *N*	2.9	
			10	H_2SO_4 0.75 *N*	2.7	
			15	H_2SO_4 1 *N*	2.8	
Walton and Wolfenden	5×10^{-4}	15	30	HCl 0.5 *N*	3.3	.2
	to	55	to	and	3.5	.1
	10^{-2}	95	50	KCl 0.5 *N*	3.3_5	.1
Eucken and Bratzler	5×10^{-2}		15	H_2SO_4 1.5 *N*	4.3	.1
	2×10^{-1}				4.8	.1
Horiuti and Okamoto			6	H_2SO_4 0.1 *N*	3.1	

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(1) The experimental data reported herein are part of the thesis submitted by Martin Rome to the faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Presented, in part, before the Division of Physical and Inorganic Chemistry at the 122nd meeting of the American Chemical Society at Atlantic City, N. J., on September 18, 1952.

(3) Westinghouse Electric Corp., Elmira, N. Y.

(4) International Biochemical Corp., Brooklyn, N. Y.

(5) B. Post and C. F. Hiskey, THIS JOURNAL, **72**, 4203 (1950).

(6) B. Post and C. F. Hiskey, *ibid.*, **73**, 161 (1951).

(7) B. Topley and H. Eyring, *J. Chem. Phys.*, **2**, 217 (1934).

(8) A. Eucken and K. Bratzler, *Z. physik. Chem.*, **A174**, 273 (1935).

(9) H. F. Walton and J. H. Wolfenden, *Trans. Faraday Soc.*, **34**, 436 (1938).

(10) J. Horiuti and G. Okamoto, *Sci. Papers Inst. of Phys. Chem. Res.*, (*Tokyo*), **28**, 231 (1936).

shows considerable variations as well as some apparent discrepancies.

Most of these data were taken prior to the development of satisfactory techniques for overvoltage measurement[11] so that many precautions which are commonplace in electrode studies of today were not practiced at that time. It seemed advisable, therefore, to re-investigate the fractionation problem for the purpose of obtaining reliable data over a range of current densities and temperatures.

Experimental

(a) **The Electrolytic Cell.**—The all-Pyrex electrolytic cell is shown in Fig. 1 and is similar in principle to overvoltage cells previously described. Because of the need for high purity in the mercury and in the electrolyte, provisions were made in the cell design for *in situ* distillations. Stillpot compartments for the mercury cathode material (A) and the electrolyte (F) were electrically heated by nichrome wire wrapped around the outside of the glass. The vacuum for distillation was drawn through a trap (C), stopcock (B), and an all-glass vacuum line (D). The mercury in the reservoir (E) is available to the cathode chamber (I), where the hydrogen gas is evolved through the ungreased mercury well vacuum stopcock (J). A platinum seal (K) using no glass other than Pyrex, makes electrical contact with the mercury cathode in the lower portion of chamber (I).

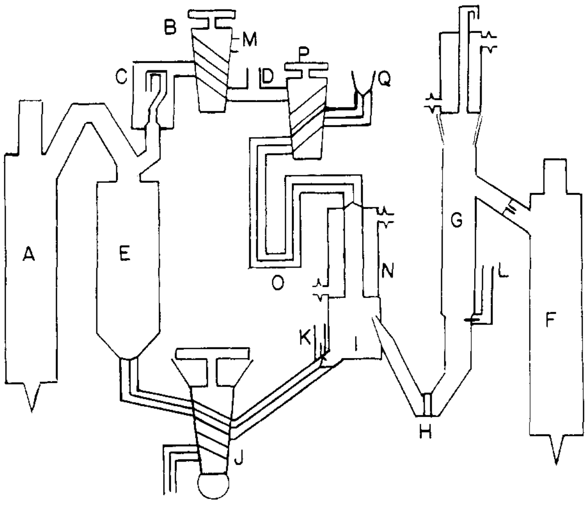

Fig. 1.—Electrolysis cell.

The electrolyte was distilled into the anode chamber (G) directly. Electrical contact at the anode was made by a second platinum seal (L). A glass frit (H) at the bottom of the U bend served to prevent back diffusion of liberated gases; in addition, a long vertical path length was interposed between the electrode and the frit. The entrance seal into the cathode chamber from the anode has a small aperture and is directed upward to prevent the diffusion of hydrogen into the anode chamber.

Evolved gas was collected above the surface of the electrolyte in the region of the cathode chamber jacketed by a condenser (N). During runs above room temperature tap water was circulated through the condenser to prevent condensation of vaporized electrolyte in the two-foot length of one-mm. i.d. capillary section (O). The capillary provided a long and devious path for the creep of grease from the takeoff stopcock (P). The lower bend in the capillary tubing was maintained at Dry Ice temperature and served as a trap. A sample bulb consisting of a 10-cc. bulb, a stopcock, and the inner member of a 7/25 joint, was affixed to the outer member of a 7/25 tapered joint (Q). The bulb was evacuated through the takeoff stopcock and the vacuum line. Cathodic gas bled into the bulb was then ready for analysis.

(b) **Details of an Experiment.**—Following the removal of stopcock grease with carbon tetrachloride, the tops of the stillpots are cut open and the cell filled with a mixture of 40% HNO_3–60% H_2SO_4. The acid mixture is circulated through the cell and maintained between 60° and boiling for 6–8 hours. After a long rinse with tapwater the cell is thoroughly flushed with distilled water. The entire cell is then carefully flamed with a hand torch.

The mercury is purified by vigorous agitation with a solution of dilute nitric acid and mercurous nitrate for 24 to 48 hours. After washing with distilled water, the mercury is vacuum distilled three times. The stopcock (J) is closed and the left side of the cell evacuated. The mercury is then transferred directly into the stillpot (A) which is then sealed with a torch. The cell is flushed with helium and then re-evacuated. This cycle is repeated several times until the residual atmosphere is replaced with helium for the mercury distillation.

The heavy water[12] as 99.8% D_2O is distilled in an evacuated three-compartment still from sodium peroxide and potassium permanganate at slightly higher than room temperature into a receiver maintained at Dry Ice temperatures. The stillpot is then sealed off from the rest of the still and the heavy water redistilled into the third section. The electrolyte is then prepared by weight dilution using doubly distilled water.

The prepared electrolyte is placed in the still (F) which is then sealed with a torch. Before and during the distillation of the electrolyte into the anode chamber (G), helium is flushed through the anode and cathode chambers by way of the lower arm of the main stopcock (J). When sufficient electrolyte is distilled to both fill the cathode chamber up to the juncture of the capillary at the condenser section and cover the anode connection, the potential is applied. A mercury cathode is then let in from the reservoir (E) through the main stopcock. Distilled sulfuric acid is admitted into the anode compartment to make up a 0.1 *N* solution as indicated by the cell conductance. The current is supplied by a d.c. generator and is filtered to reduce the a.c. ripple to less than 0.1%. Pre-electrolysis at 10^{-2} to 10^{-1} amp./cm.^{2} is maintained for about 12 hours after which the cathode is discarded through the lower arm of the stopcock (J) and a fresh mercury surface admitted. After the current density is adjusted to the desired value and the temperature set by immersing the entire cell in a thermostated bath, the generation of gas samples is begun. The initial samples after each change of current or temperature are discarded. Approximately 3 cc.-atmospheres of gas is collected for each sample. The time requirements for a sample range from 3 minutes for the highest current density at a surface area of approximately 5 cm.^{2} to 1.5 hours at 10^{-4} amp./cm.^{2} for the largest cathode surface (50 cm.^{2}) used.

(c) **Analysis of Samples.**—The gas samples are analyzed for their isotopic ratio by means of a mass spectrometer. A Nier type[13] 60 degree tube is used with fixed slits and collector plates for mass 2 and mass 3. Separated amplifiers are provided for each slit and the output balanced by a null method to give the ratio of the currents directly.

The mass 2 current is due to H_2^+ whereas mass 3 current is composed of H_3^+ and HD^+. Bleakney[14] found that H_2^+ and HD^+ are direct functions of the gas pressure, whereas H_3^+ varies as the square of the pressure. The isotope ratio of HD^+/H_2^+ could therefore be found by plotting the ratio of (mass 3)/(mass 2) as a function of either pressure behind the leak or mass 2 current, and extrapolating to zero pressure, *i.e.*, H_2^+ current. In practice, however, the isotope ratio is found by direct comparison of mass ratios of standard gas samples at fixed H_2^+ currents. These standard gas samples are prepared by the total decomposition of diluted heavy water by reaction with Mg turnings at 475°. The isotope concentrations of the water samples were chosen so as to be very nearly like those of the evolved gases from the electrolytic cell. The region of the curve of mass ratio *vs.* H_2^+ current chosen for comparison of the unknown to the standard samples has a small and constant slope to minimize errors due to H_2^+ current.

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[11] J. O'M. Bockris, *Chem. Revs.*, **43**, 525 (1948).

[12] Obtained from the Stuart Oxygen Co. in 25-ml. vials and assayed by density measurements.

[13] A. O. Nier, M. G. Inghram, Stevens and Rustad, University of Minn. OEMar-149.

[14] W. Bleakney, *Phys. Rev.*, **41**, 32 (1932).

In Table II are shown sample experimental results with the mass spectrometer. The procedure employed is to first set the instrument for peak output by adjusting the accelerating and focusing potentials, the filament current, and by balancing the amplifiers. Standard gas is then flushed through the system, evacuated and admitted to a pressure corresponding to a given H_2^+ current which is read as a voltage drop across a fixed resistor. After an isotope ratio reading is taken the pressure is reduced and a second reading recorded at a lower H_2^+ current. This procedure is repeated for the unknown gas at the same H_2^+ currents. The time for completing measurements for both samples is limited to 15 minutes, an interval which had been previously determined as involving negligible drift of the DC amplifiers. The amplifiers are again balanced and the standard and unknown samples determined again, in reversed order.

(d) **Precision.**—The separation factor reported for each set of conditions of temperature and current density represents at least 6 determinations. In some instances about 30 samples from several different experiments were averaged. The accuracy of the separation factors, which is primarily limited by the instrument, is of the order of 2%. The precision of measurement for the separation factors at the two higher current densities is better than 2% and at the lower current densities about 1%.

TABLE II

SAMPLE DATA

Mass spectrometer: filament current = 4.0 amp., emission current = 10.0 ma., pressure = $<10^{-5}$ mm. Electrolyte: HDO/H_2O = 0.0341, 0.12 N H_2SO_4; standard sample: (V-6) HD/H_2 = 0.0120.

Sample	T, °C.	i, amp./cm.^{2}	$\overset{+}{V}_{H_2}$ (volts)	Ratio (HD/H_2)	S
(Background 25 mv. V_{H_2})					
D-72	25	2×10^{-3}	8.1	0.00997	3.66
			6.0	.00956	3.66
V-6			8.2	.01288	
			6.0	.01233	
V-6			8.0	.01317	
			6.0	.01270	
D-72			8.0	.00999	3.74
			6.0	.00945	3.82
(Refocus, background 20 mv.)					
D-121	80	10^{-3}	7.5	0.00982	3.60
			6.0	.00959	3.59
V-6			7.5	.01243	
			6.0	.01210	
(Refocus, background 20 mv.)					
D-151	25	2×10^{-3}	7.5	0.00956	3.70
			6.0	.00920	3.75
V-6			7.5	.01246	
			6.0	.01215	
(Refocus, background 20 mv.)					
V-6			7.5	0.01230	
			6.0	.01207	
D-151			7.5	.00933	3.74
			6.0	.00896	3.82

Current densities are accurate to about 3% for the lower values. At the higher current densities, where a decay of the current with time was observed, the variation from the initial (indicated) current density to the final, at the end of the generation interval, was as much as 10%.

(e) **Contamination.**—A criterion for acceptable data was that a separation factor obtained under a given set of conditions of temperature and current density at the inception of a run be reproduced under the same conditions at its termination. When this reproducibility was not realized the entire run was rejected. In such instances, almost without exception, the terminal values were lower than those found initially. In Fig. 2 are shown the variations of S with time at constant temperature and current density, i, in a rejected experiment. Three surfaces were successively let in and discarded. Figure 2 indicates the rate at which the clean mercury was contaminated by the electrolyte and shows that a rejected run tends toward a constant separation factor. This value of S approached by the curves in Fig. 2 bears a close relationship to the separation factor obtained from a cell which was deliberately contaminated with stopcock grease. In Table III are given the values of S at different temperatures for a cell deliberately contaminated with grease. These results were obtained by the addition of the grease into the anode chamber during a run which had hitherto been acceptable. The severe drop in S following the addition was immediately evident in the next gas sample removed from the cell.

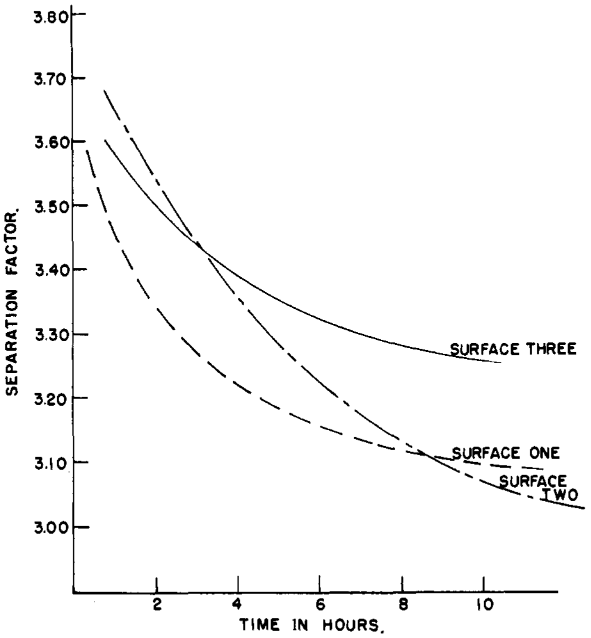

Fig. 2.—Variation with time of separation factor on three successive mercury surfaces from a contaminated solution.

TABLE III

SEPARATION FACTOR OF HYDROGEN AND DEUTERIUM WITH ADDITION OF STOPCOCK GREASE TO ELECTROLYTE

Electrolyte: 0.1 N H_2SO_4, D_2O = 1.73%, $i = 10^{-4}$ amp./cm.^{2}

T, °C.	5	25	48	74
S	2.84	2.91	2.89	2.80

Experimental Results

The data obtained in this investigation are summarized in Table IV. Examination of these data reveals a number of items of considerable interest.

TABLE IV

SEPARATION FACTOR OF HYDROGEN AND DEUTERIUM

Electrolyte: 0.1 N H_2SO_4, D_2O = 1.5 to 2.5%.

T, °C.	Current density, amp./cm.^{2}					
	10^{-4}	5×10^{-4}	10^{-3}	2×10^{-3}	5×10^{-3}	3×10^{-2}
0	3.83	3.76	3.72	3.73	3.32	2.96
25	3.79	3.74	3.72	3.68	3.42	3.14
40			3.67			
50	3.80	3.74	3.65		3.43	3.25
67				3.65		
74	3.75	3.70	3.67	3.64	3.37	3.30
80			3.65			
96.5	3.71	3.65	3.62	3.61	3.37	3.31

In the first place, they differ from the results obtained by all previous investigators. Although the agreement with Walton and Wolfenden's data is best, there is nevertheless a discrepancy of as much as -0.5 unit. It seems likely that contamination of the electrode surface by grease or other impurities could account for the low results.

Secondly, it is observed that for a fixed current density the fractionation factor is almost temperature independent within the limits of experimental uncertainty. Also the trend of the values with increasing temperature is downward at current densities of 10^{-4}, 5×10^{-4}, 10^{-3}, and 2×10^{-3}, while at 5×10^{-3} and 3×10^{-2}, the trend is upward. Indeed at 3×10^{-2} amp./cm.^{2} the variations are large enough so that they lie outside the range of experimental uncertainties. It is believed that this reversal of trend in these data is due to diffusion effects.

A further item of interest in Table IV is the effect of current density at fixed temperatures. The most striking fact which emerges is the sudden drop which occurs as the current density is increased beyond 10^{-3} amp./cm.^{2}. Although this current density is not particularly large, it nevertheless causes a depletion in the concentration of the hydrogen isotope relative to the deuterium isotope in the vicinity of the double layer. As a consequence the fractionation factor appears to decrease. Raising the temperature allows more rapid diffusion from the body of the solution to the solution–metal interface: therefore, the apparent diminution of the fractionation factor with current density is less pronounced at the higher temperature studied. That diffusion effects occur is evidenced by the drop in current in the course of a generation interval at the higher current densities.

Discussion of Results

The value of separation factor found in this determination is in good agreement with the factor calculated by Okamoto[15] using the electrochemical mechanism of Horiuti[16] and co-workers. In this proposed mechanism the configuration of the activated complex is considered to consist of a hydrogen atom and a hydrogen ion bounded in a colinear fashion by a mercury atom from the electrode and an oxygen atom from the electrolyte. The value for S at a mercury cathode at 20° was given as 3.4; however, in a later paper[17] using more recent values for the constants of water the value was reported at the same temperature as 3.8.

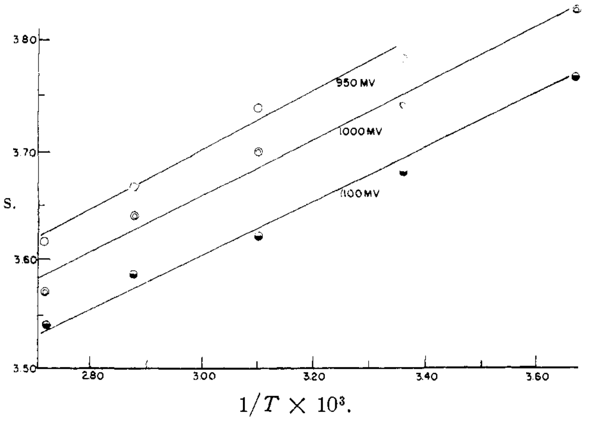

Fig. 3.—Variation of separation factor with temperature at constant overvoltage.

Separation Factor and Temperature.—Temperature dependence of S, in the form $S = A \exp(B/RT)$ is generally evaluated at constant overvoltage where the energy barrier is the same. By means of generalized Tafel[18] equations of overvoltage for hydrogen[4] and deuterium[5] and Table II, the separation factor at constant overvoltage was found. In Fig. 3, S is plotted at overvoltages of 950, 1000 and 1100 mv., as a function of the reciprocal of the absolute temperature. The value of B determined from the slope of these curves is 0.14 ± 0.01 kcal.

Using the same expression for the temperature dependence of S, Okamoto reported calculated values of B equal to 0.66 kcal. for mercury (electrochemical mechanism) and 1.20 kcal. for nickel (catalytic mechanism). The former value, though considerably smaller than the difference in zero point energy of the two isotopes is, nevertheless, much larger than the B found in Fig. 3.

The separation factors reported for mercury at two temperatures and at constant overvoltage by Walton and Wolfenden[8] are

T, °C.	15	95
$S =$	3.5_5	3.4

The overvoltage corresponds to a current density between 5×10^{-4} and 10^{-3} amp./cm.^{2} at the higher temperature and is in the neighborhood of 800 mv. B calculated from these values is 0.1 kcal. Agreement with the value of B determined in this investigation at overvoltages of 950, 1000 and 1100 mv. is good.

Separation Factor and Current Density.—The slope of the separation factor with current density is small but definitely negative. This slope remains constant except at high current densities where diffusion effects occur. The decrease in S at 15° was reported by Walton and Wolfenden[8] as 7% for a twenty-fold increase in current density (from 3×10^{-5} to 6×10^{-4} amp./cm.^{2}). At 95° the same authors reported no change in separation factor with the same variation in current density.

The variation in separation factor in this investigation was found to be three to 3.5% for a twenty-fold change in current density (from 10^{-4} to 2×10^{-3} amp./cm.^{2}) at all observed temperatures.

Separation Factor and Overvoltage Data.—By comparing the current density for hydrogen at a given overvoltage, temperature and cathode material with the current density for deuterium under the same conditions, an electrolytic separation factor may be predicted. This was done by Post and Hiskey[5] from overvoltage data at a mercury cathode. At 20° and an overvoltage of 1000 mv. they calculated a value of 3.1. In view of the large uncertainty inherent in this calculation the agreement with the experimental data is good. With a mean deviation of 2.4 in the slope of the Tafel equation for both isotopes, the precision of the calculated

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(15) G. Okamoto, *J. Fac. Sci. Hokkaido Imp. Univ.*, Ser. III, **2**, 115 (1938).

(16) J. Horiuti, G. Okamoto and K. Hirota, *Sci. Papers Inst. Phys. Chem.* (*Tokyo*), **29**, 223 (1936).

(17) J. Horiuti and T. Nakamura, *J. Chem. Phys.*, **18**, 395 (1950).

(18) J. Tafel, *Z. physik. Chem.*, **50**, 641 (1905).

separation factor is of the order of 35%. Because of the sensitivity of a calculated S with slight changes in overvoltage values, the converse prediction, *i.e.*, overvoltage differences from separation data, may be made with a high degree of precision. However, one qualification must be borne in mind: in overvoltage measurements the initial state of the discharged ion is isotopically homogeneous, either pure H_2O or pure D_2O being used, whereas in separation work (particularly from dilute isotope concentrations), the ground state of one of the isotopes is considerably different. This reservation must be made in correlating overvoltage and separation measurements.

Acknowledgment.—The authors wish to express their appreciation to Dr. Benjamin Post for his frequent aid and advice.

BROOKLYN, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Acid–Base Reactions in Non-dissociating Solvents. Acetic Acid and Triethylamine in Carbon Tetrachloride and Chloroform

BY GORDON M. BARROW AND E. ANNE YERGER

RECEIVED MAY 10, 1954

The reactions between acetic acid and triethylamine in carbon tetrachloride and chloroform, in the acid concentration range 0.001 to 1 molar, have been studied by infrared spectroscopy. The nature of the ion-pair products is clarified. The electronic structure, and infrared spectra, are dependent on the solvent interaction. Equilibrium constants are obtained for several reactions between the acid and the base in the two solvents.

Information on the reactions of acids and bases in non-ionizing solvents can be expected to be useful in understanding, separately, the dependence of acid and basic strengths on the structure of these compounds and on the solvation of the species present in the acid–base equilibrium. Such studies have been made by Davis and co-workers[1] and by Bell and Bayles[2] using an acid with absorption in the visible region.

By using changes in the infrared spectrum to follow the acid–base reaction it was hoped to obtain, in addition to acid–base equilibrium constants, some information about the nature of the ion-pair produced in these non-ionizing, or better "non-dissociating," solvents. That such reactions lead essentially only to ion-pairs has been shown by the dielectric constant studies of Davis and McDonald,[3] Maryott[4] and by Fuoss and Kraus.[5] Elucidation of the type of association between the ions does however not result from such measurements, whereas some information on this is furnished by changes in the infrared spectrum.

Acetic acid and triethylamine are spectroscopically convenient for this study and the use of chloroform as a solvent, in addition to carbon tetrachloride, provides an indication of the effect of solvent interaction which, however, probably does not lead to complete dissociation of the ion-pair.[6]

Before considering the acid–base equilibrium constants it was necessary to identify the reaction product species present at various concentrations in the two solvents.

Experimental

All spectra were obtained on a Baird Associates or a Beckman IR-2T instrument with rock salt optics, except for those of triethylammonium chloride, nitrate and picrate and the hydrochlorides of pyridine and aniline for which the latter instrument with a lithium fluoride monochromator was used. Beer's law was assumed and care was taken wherever possible to operate at fairly low absorptions so that no appreciable error would be introduced.

Cells of thickness 0.034, 0.095, 1.10 and 20.6 mm., as determined by interference effects for the thin cells and direct measurement for the thicker ones, were used for the different concentrations as follows: 1.0 molar in the 0.034, 0.5 to 0.1 molar in the 0.095, 0.02 molar in the 1.10, and 0.001 molar in the 20.6-mm. cell.

The reagents were prepared or purified in the following manner.

Triethylamine.—Eastman Kodak white label triethylamine was dried over KOH and distilled through a 30-cm. packed column. The product, $n^{20}\text{D}$ of 1.4003, was stored over KOH.

Triethylammonium Picrate.—Triethylamine was added to a concentrated solution of picric acid in 95% ethanol. After recrystallization from ethanol the melting point was 171–172°.

Triethylammonium Chloride and Triethylammmonium Nitrate.—These salts were obtained by evaporation of solutions of the reagent grade mineral acid and triethylamine. The products were dried under vacuum. The hydrochloride melted at 252–253°.

Anilinium Chloride.—Addition of aniline to an aqueous solution of reagent grade hydrochloric acid gave a product which was recrystallized from water and dried under vacuum. The neutral equivalent was 129 and the melting point was 198°.

Carbon Tetrachloride.—Reagent grade CCl_4 was stored over P_2O_5 and subsequently filtered into a distillation pot. A center cut of constant boiling point was taken from a 30-cm. packed column.

Chloroform.—J. T. Baker reagent grade chloroform was stored over $CaCl_2$ and Drierite, filtered into a distillation pot and distilled. A center cut consisting of about half the charge was taken and used immediately. Only for the very dilute solutions, 0.001 M of acetic acid in chloroform was there evidence of some impurity interacting with acetic acid. The monomer–dimer equilibrium data reported elsewhere showed large deviations from the constant obtained at higher concentrations when old or not carefully distilled chloroform was used.

I. Nature of the Intermediates and Products.—

To establish the absorption bands due to the salt, or ion-pair, formed from this acid and base the spectra of a number of salts of triethylamine were obtained. The spectra of the hydrochloride, nitrate

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[1] M. M. Davis and H. B. Hetzer, *Bur. Standards, J. Research*, **48**, 381 (1952), with references to previous work.

[2] R. P. Bell and J. W. Bayles, *J. Chem. Soc.*, 1518 (1952).

[3] M. M. Davis and E. A. McDonald, *Bur. Standards, J. Research*, **42**, 595 (1949).

[4] A. A. Maryott, *ibid.*, **41**, 1, 7 (1948).

[5] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 3614 (1933).

[6] M. M. Davis, *ibid.*, **71**, 3544 (1949).