be 25 to 30% larger than that for cyclobutane. From the available experimental data it cannot be ascertained whether this slightly faster rate is due mainly to a small decrease in the activation energy or to a change in the frequency factor. It is to be noted that with no change in frequency factor a decrease in the activation energy of 0.38 kcal./mole, which would be within the experimental error of the activation energy measurements, would produce a 30% increase in the rate.

The entropy of activation can be calculated by setting the expression $\kappa e(kT/h)e^{\Delta S^*/R}$ equal to the experimental frequency factor.[16] The calculated value of ΔS^* at 450°, with κ assumed to be unity, is $+ 8.9$ cal./deg. mole. This positive value which might be expected for a reaction of the type shown above involving ring cleavage is quite close to that found for cyclobutane.

Acknowledgment.—The authors wish to thank the Celanese Corporation of America for providing financial assistance, the National Advisory Committee for Aeronautics for supplying a sample of ethylcyclobutane, and Mr. Carl Whiteman for making the infrared measurements.

ROCHESTER, N. Y.

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[16] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 295.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Electrochemical Fission of the Carbon–Fluorine Bond. *p*H-Dependency of the Process

BY PHILIP J. ELVING AND JOSEPH T. LEONE

RECEIVED DECEMBER 4, 1956

Phenacyl fluoride gives two well-defined, diffusion-controlled cathodic polarographic waves, the first resulting from fission of the carbon–fluorine bond and the second from reduction of the acetophenone formed on fluorine removal. The former represents the first case of carbon–fluorine bond fission at the D.M.E. and the first instance where the carbon–halogen bond fission *per se* has been found to be *p*H-dependent. A mechanism involving induced polarization of the carbon–fluorine bond by the electrode and by hydrogen ion *via* the hydrogen fluoride bond in the transition state or species, has been postulated to explain the *p*H-dependence observed for the first wave below *p*H 6. With decreasing hydrogen ion concentration, the effect decreases and the first wave becomes *p*H-independent.

The electrochemical fission of carbon–halogen bonds has been studied extensively using polarography and electrolysis at constant potential.[1] However, the fission of a carbon–fluorine bond under polarographic conditions has not been previously reported, due apparently to the comparative rarity of fluorine-containing organic compounds and to the greater stability of the C–F bond compared to other carbon–halogen bonds.

The logical approach to the problem of C–F bond fission seemed to be the determination of which structures facilitated carbon–halogen bond fission and then the polarographic study of the fluorine-containing analog. Fluoroacetic acid was considered unsuitable since at about *p*H 1, where carbon–halogen bond fission should be most facile, iodo-, bromo- and chloroacetic acids have $E_{1/2}$ values *vs.* the S.C.E. of -0.16,[2a] -0.55[2a] and -1.64 v. (calculated),[2b] respectively; this would obviously place $E_{1/2}$ of fluoroacetic acid well out of the range of acidic buffers. Ethyl fluoroacetate seemed a more suitable compound for study since carbon–halogen bond fission in esters is *p*H-independent; the ester could be studied in alkaline buffers in which a more negative potential is available before background discharge. However, no wave was obtained at 0°, indicating either that the ester hydrolyzed too rapidly to permit study or that the C–F bond was not reducible in the ammonia and phosphate buffers used.

Since the first waves of tribromoacetic[2a] and trichloroacetic[3] acids occur at less negative potentials (-0.08 v. at *p*H 3.7, and -0.89 v. at *p*H 4.0, respectively), it was thought that trifluoroacetic acid might provide a sufficiently labile bond. The latter compound, however, was not reducible under normal polarographic conditions. In this connection, it is pertinent to note that the C–F bonds in F_2CH_2 and F_3CH are considerably shorter than that in FCH_3[4]; this is reflected in the greater stability of the polyfluoromethanes.[5] If this behavior is generally true of the trifluoromethyl group, the stepwise fission of the carbon–halogen bonds would not be observed as in the case of trichloro- and tribromoacetic acids, but all of the bonds would probably be ruptured in a single step at a potential more negative than that at which the one C–F bond in the monofluoro compound would be reduced.

Study of the polarographic behavior of phenacyl chlorides and bromides[6] showed that there is available an adequate potential span before carbonyl group reduction in which a more difficultly reducible C–F bond might be ruptured. Consequently, phenacyl fluoride was investigated. Fission of the C–F bond was observed: $E_{1/2}$ for the resulting cathodic wave is strongly *p*H-dependent below *p*H 6.

Discussion of Observed Results[7]

Phenacyl fluoride gives two well-defined diffusion-controlled cathodic polarographic waves over the *p*H range of 0.5 to 11.5 (Table I; Figs. 1 to 3).

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[1] P. J. Elving, *Rec. Chem. Progr.*, **14**, 99 (1953).

[2] (a) P. J. Elving, I. Rosenthal and M. K. Kramer, THIS JOURNAL, **73**, 1717 (1951); (b) I. Rosenthal, C.-S. Tang and P. J. Elving, *ibid.*, **74**, 6112 (1952).

[3] P. J. Elving and C.-S. Tang, *ibid.*, **72**, 3244 (1950).

[4] L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1948, p. 235.

[5] J. H. Simons, ed., "Fluorine Chemistry," Vol. I, Academic Press, New York, N. Y., 1950, pp. 351–353; E. Warhurst, *Proc. Roy. Soc.* (*London*), **A207**, 32 (1951).

[6] J. T. Leone, M.S. Thesis, The Pennsylvania State University, 1952.

[7] Detailed data are available from the authors.

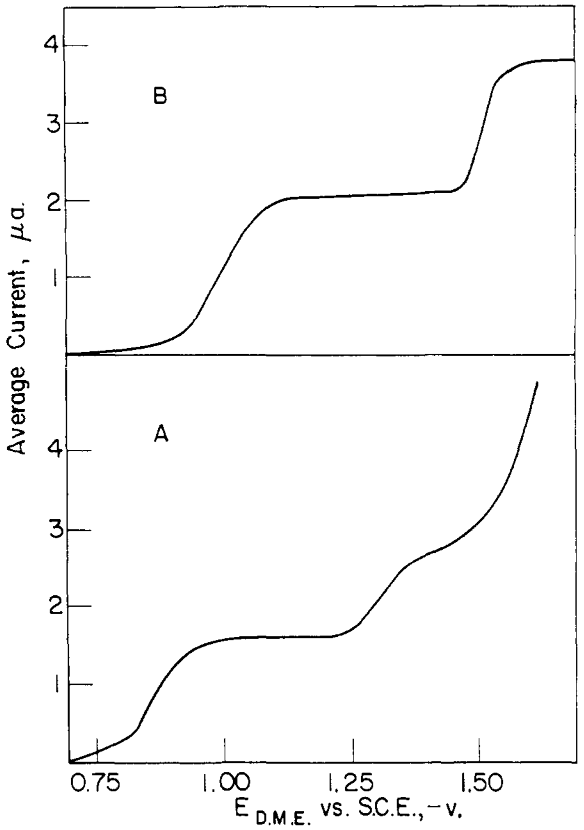


Fig. 1.—Tracings (average current) of polarograms of 0.481 m*M* phenacyl fluoride solutions: A, acetate buffer, *p*H 4.9; B, ammonia buffer, *p*H 9.5.

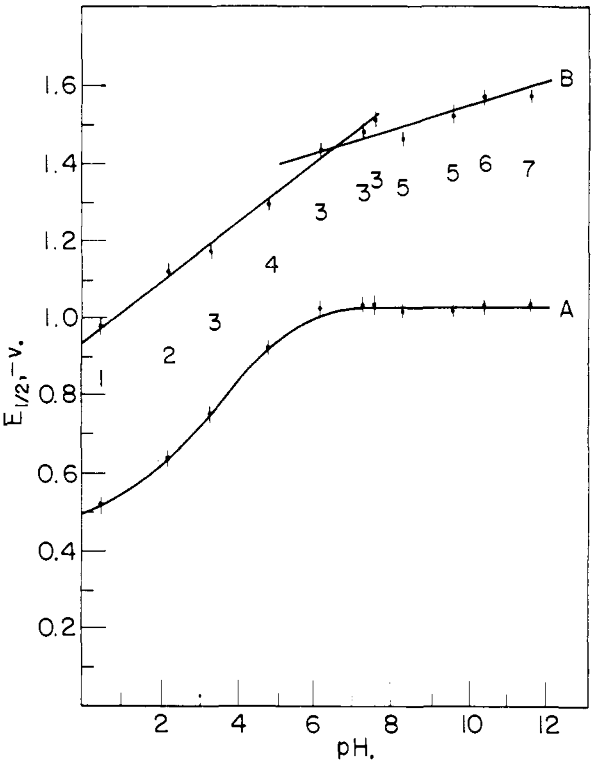
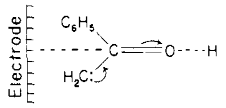


Fig. 2.—Variation of $E_{1/2}$ of phenacyl fluoride with *p*H: A, wave I, produced by carbon–fluorine bond fission; B, wave II, produced by carbonyl group reduction. The buffer systems used are designated by their code number (Table I).

The first wave is due to fission of the C–F bond: the second to reduction of the carbonyl group in the acetophenone produced by replacement of the fluorine by hydrogen in the first process.

Potential Phenomena.—$E_{1/2}$ of wave I is strongly *p*H-dependent below *p*H 6 and completely independent of *p*H above 6: $E_{1/2}$ of wave II is *p*H-dependent over the entire *p*H range (Fig. 2). The *p*H-dependent portion of the $E_{1/2}$–*p*H relation for wave I is sigmoid-shaped; the inflection point is at about *p*H 4.

Contrary to usual behavior, both reduction processes become more facile with decrease in temperature in the strongly *p*H-dependent region, while in the *p*H-independent or weakly dependent region there is little or no effect. Since the reduction of the acetophenone carbonyl group normally shows the opposite behavior,[8] the first wave reduction process may exert some influence on the second wave process, *i.e.*, some of the carbonyl group, being polarized at the electrode, may be in the carbanion, formed by C–F bond fission. This phenomenon may occur because combination of the anion with a proton is slower at the lower temperature. Since polarization of the carbonyl group would be easier in the carbanion than in the acetophenone, the carbanion carbonyl group would be reducible at a slightly less negative potential. This would result in a merged wave with an $E_{1/2}$ value slightly less negative than that of acetophenone.



(1)

Current Phenomena.—The magnitude of wave I is fairly constant over the entire *p*H range as has been previously observed for other carbon–halogen bond fission processes; the diffusion current constant, $I = i_d/Cm^{2/3}t^{1/6}$, is relatively constant (3.1 ± 0.2) over the *p*H range; fluctuations that do occur are probably due to modification of the diffusion coefficient by the different buffer components. *I* values for wave II show a bell-shaped variation with *p*H, characteristic of the alkyl phenyl ketones[8]; in the low acidic region (*p*H 0.5 to 4.8), *I* is fairly constant at 1.4, then increases rapidly to 3.1 (*p*H 8.2) and subsequently decreases to 2.6 (*p*H 11.5). Fluctuations which appear in the case of wave II are due not only to modifications of the diffusion coefficient of the phenacyl fluoride by the different buffer components, but also to the fact that this wave is produced by a combination of two processes[8]: a one-electron reduction to a free radical which dimerizes to pinacol, and a two-electron reduction through the free radical state to carbinol. Furthermore, in the acidic region the limiting current for wave II is rather steeply sloped and gradually merges into the background discharge, thus making measurements

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(8) J. T. Leone, Ph.D. Thesis, University of Michigan, 1956.

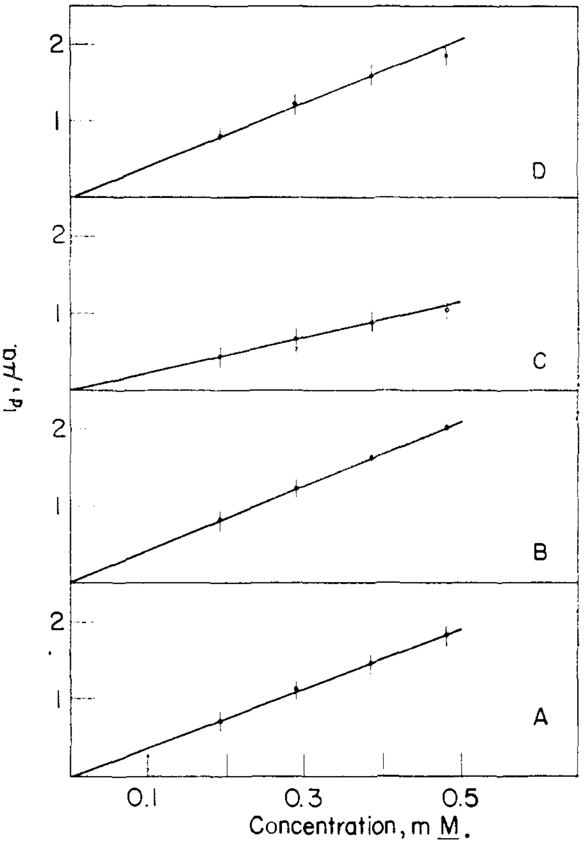

Fig. 3.—Variation of i_d of phenacyl fluoride with concentration: A and B, wave I in acetate and ammonia buffers of *p*H 4.9 and 9.5, respectively; C and D, wave II in acetate and ammonia buffers of *p*H 4.9 and 9.5, respectively.

of the actual average currents difficult. Consequently, wave II currents were determined in the acidic region by the usual geometric technique, even though the values obtained may in some cases be slightly smaller than the true ones. These additional difficulties are not encountered with wave I, which is well-defined over the entire *p*H range and is always produced by the same process (two-electron C–F bond fission).

Variations of the heights of both waves with drop-time (mercury height) and temperature in both acidic and alkaline media are those expected for a diffusion-controlled process.

Up to at least 0.4 m*M*, i_d for both waves is proportional to concentration (Fig. 3).

An *n* value of 1.9 ± 0.1 was calculated from the Ilkovic equation for the C–F bond fission by approximating the diffusion coefficient of phenacyl fluoride from that of *o*-hydroxybenzyl alcohol (0.72×10^{-5} cm.^{2}/sec. in water[9]). From a comparison of the magnitudes of waves I and II, *n* for wave II varies between 1 and 2 over the *p*H range, in accord with the gradual change from a one-electron pinacol to a two-electron carbinol process and back again as observed for acetophenone reduction.[8] Independent values of *n* could not be calculated since the diffusion coefficient of phenacyl fluoride is not known; the Stokes–Einstein diffusion equation could not be legitimately applied since the molecule does not conform to the specifications of being spherical[10a] and having a molecular weight in excess of 180.[10b]

The α values of wave I, calculated from the slope of the polarographic wave, tend to increase with increasing *p*H in a given buffer system (variation from 0.6 to 1.2). For wave II, α is slightly erratic but exhibits the same general behavior with regard to *p*H as does *I*, *i.e.*, α increases from about 1.0 to 1.9 and then decreases to 1.3.

Verification of Carbon–Fluorine Bond Fission.—Since $E_{1/2}$ for wave I of the other phenacyl halides[6] was *p*H-independent in the region *p*H 3 to 12, it seemed desirable to confirm the interpretation of C–F bond fission as the current-producing phenomenon. Accordingly, it was decided to investigate whether macro-scale electroreduction at a potential corresponding to the limiting current portion of wave I eliminated this wave and produced fluoride ion. Reduction of 0.4 mmole of phenacyl fluoride, using a coulometric technique, at −1.35 v. *vs.* the S.C.E. in 100 ml. of 0.45 *M* LiOH–LiCl solution containing 9.5% ethanol (*p*H 11.5), eliminated the species that produced the first wave and left only free acetophenone, which was identified polarographically. The first wave did not reappear after allowing the reduced solution to stand (*ca.* 1 hour). Subsequently, a portion of 1 g. of phenacyl fluoride was reduced under the same conditions.[11] After 7 hr. about two-thirds of the first wave (C–F bond activity) was destroyed. The solution was then extracted three times with ether to remove unreacted phenacyl fluoride and the water layer, which would contain any fluoride ion produced, was made slightly acidic with hydrochloric acid. Calcium chloride solution was added; the gelatinous precipitate produced was filtered, washed and dried; the residue gave a strongly positive etch test[12] for fluorine.

Mechanism of Carbon–Fluorine Bond Fission

Since fission of the C–F bond is strongly *p*H-dependent in the acidic region and independent of *p*H in the alkaline region, hydrogen ion must be involved in the potential-determining step. In all previous cases where carbon–halogen bond fission has been found to be *p*H-dependent, *e.g.*, α-haloalkanoic acids, the *p*H-dependence was observed in the vicinity of the acid–anion equilibrium, *e.g.*, the pK_a of the acids was contained in the steeply rising portion of the S-shaped $E_{1/2}$–*p*H relation.[13] This suggests that a similar system is operative in the electroreduction of the C–F bond in phenacyl fluoride. Such a system could arise from ionization of the enol form of the ketone or from association–dissociation of a species formed by hydrogen

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[9] E. W. Washburn, ed., "International Critical Tables," Vol. V, McGraw-Hill Book Co., New York, N. Y., 1929, p. 71.

[10] (a) A. Einstein, *Z. Elektrochem.*, **14**, 235 (1908); (b) L. Friedman and P. G. Carpenter, THIS JOURNAL, **61**, 1745 (1939).

[11] Only about 5 to 10% of the compound dissolved under these conditions; however, during the electrolysis much of the undissolved phenacyl fluoride went into solution and was subsequently reduced. The presence of undissolved phenacyl fluoride should not noticeably alter the course of the reduction.

[12] N. H. Furman, "Scott's Standard Methods of Chemical Analysis," 5th ed., Vol. I, D. Van Nostrand Co., New York, N. Y., 1948, p. 399.

[13] C. H. Albright, I. Rosenthal and P. J. Elving, *J. Electrochem. Soc.*, **99**, 227 (1952).

ion with the fissionable fluorine in the transition state.

Acetophenone exists exclusively in the keto form.[14] The presence of the α-fluorine would have little effect on enolization and might even make formation of the enol more difficult, since the prerequisite for enolization is the acquisition of a proton by the carbonyl oxygen,[15] *i.e.*, the fluorine would tend to pull the electrons away from the carbonyl oxygen.

On the other hand, no apparent difficulties are encountered if the hydrogen ion is considered as aiding the electrode in the polarization of the C–F bond. Since the pK_a of hydrofluoric acid (3.14) occurs in the steeply rising portion of the $E_{1/2}$–pH plot, the *p*H-dependence of the C–F bond fission very likely arises from an acid–anion relationship between hydrogen ion and the C–F bond, *i.e.*, hydrogen fluoride, hydrofluoric acid or an analogous species is involved in the transition state. This point of view is further supported by the shift of $E_{1/2}$ to less negative potentials with decrease in temperature; the decreased dissociation of hydrofluoric acid with decrease in temperature would tend to facilitate the C–F bond rupture.

A thorough discussion of the mechanism of ketonic carbonyl group reduction (origin of wave II)[8] is being prepared for publication.

Acidic Region.—In the acidic region, the process producing the first wave can be depicted as the result of a concerted push–pull attack on the C–F bond by both the electrode and hydrogen ions (Fig. 4). As the compound diffuses toward the electrode, it becomes oriented so that both the carbonyl oxygen and the fluorine are farthest away from the D.M.E., since a coulombic repulsion of increasing intensity is exerted on the oxygen and fluorine by the electrode. As the compound enters the region of the interphase, the electrode polarizes the C–F bond by attracting the carbon and repelling the fluorine; simultaneously, hydrogen ions in the vicinity of the fluorine attract it and repel the carbon. As the potential increases, the tendency of the electrons from the electrode to penetrate into the electronic cloud of the carbon atom increases simultaneously with the tendency of the fluorine to break away as hydrogen fluoride. The resulting transition state species then loses hydrofluoric acid or fluoride ion (depending on the *p*H) and produces a carbanion. Subsequently, the carbanion (α-carbon) rapidly picks up a proton from the solution to give acetophenone, which is reduced at a more negative potential (at reduced temperatures the pickup of the proton may be slowed sufficiently so that some acetophenone carbanion is also being reduced at the more negative potential). Hydrogen ions can also be considered as assisting the transfer of electrons to the α-carbon by inducing a positive charge on the side of the carbon nearest the electrode. The carbonyl group does not seem to influence the process except in the general manner of weakening the alpha C–F bond and facilitating orientation at the electrode.

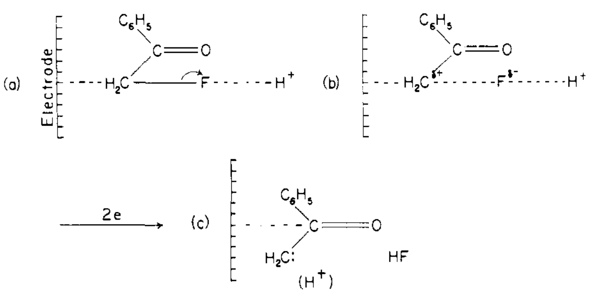

Fig. 4.—Reduction of phenacyl fluoride at the D.M.E. The approach of phenacyl fluoride to, and its orientation at, the electrode is represented by (a); its polarization and subsequent reduction are represented by (b) and (c), respectively.

The transition in the mechanism outlined is continuous; the process has been discussed in terms of individual steps for the sake of clarity. On the basis of this mechanism, $E_{1/2}$ for the C–F bond fission will become increasingly less negative as the *p*H decreases, due to the fact that the electrode has to furnish less energy (potential to transfer electrons) for the bond fission.

Alkaline Region.—In the alkaline region, the electrode process for the first wave is completely *p*H-independent, indicating that hydrogen ion does not materially contribute to the essential bond fission process and that the electrode must provide all the energy necessary for bond rupture. Fluoride ion will be produced and the acquisition of the proton by the carbanion formed will occur in a subsequent reaction with either the solvent or hydrogen ion.

Since C–F bond fission gives rise to a carbanion, the second wave may be produced not only by reduction of the acetophenone carbonyl group but also of some carbanion carbonyl group. The latter process would seem to be more favored in alkaline media and at reduced temperatures.

Experimental

Chemicals.—Phenacyl fluoride,[16a] obtained by a Friedel–Crafts synthesis (fluoroacetyl chloride[16b] on benzene), was purified by fractional distillation through a 1 × 28-cm. helices-packed column under reduced pressure; the product had b.p. 115–118° (26 mm.); n^{25}D 1.5315; and density 1.185 g./ml. at 22°. Buffer solutions (Table I) were prepared from C.P. grade chemicals. The nitrogen used for deoxygenating was purified and equilibrated by bubbling through sulfuric acid, alkaline pyrogallol solution, distilled water, and a portion of the test solution,

TABLE I

COMPOSITION OF BUFFER AND BACKGROUND SOLUTIONS[a]

Buffer no.	*p*H	Composition
1	0.3	Dilute HCl
2	2.2	HCl + KCl
3	3.0–8.0	$Na_2HPO_4 \cdot 7H_2O$ + citric acid monohydrate + KCl
4	3.8–5.7	NaOAc + HOAc
5	8.1–9.7	$NH_4Cl + NH_3$
6	9.2–9.9	$Na_2B_4O_7 \cdot 10H_2O$ + NaOH + KCl
7	9.7–12.4	$Na_2HPO_4 \cdot 7H_2O$ + NaOH

[a] All buffer solutions were used at an ionic strength of 0.45 *M* unless otherwise indicated.

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(14) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, New York, N. Y., 1941, p. 288.

(15) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 232.

(16) (a) W. E. Truce and B. H. Sack, THIS JOURNAL, **70**, 3959 (1948); (b) W. E. Truce, *ibid.*, **70**, 2828 (1948).

Apparatus.—A Leeds and Northrup Type E Electro-Chemograph was used with a thermostated H-cell[17] (25 ± 0.1°) containing a saturated calomel reference electrode. A Beckman Model G *p*H meter was used for *p*H measurement. All measuring apparatus were calibrated. The dropping mercury electrodes, prepared from Corning marine barometer tubing, had m and t values (open circuit, distilled water, 25°, 65 cm. uncorrected mercury head) for capillaries F and G of 0.966 and 0.982 mg./sec., and 5.85 and 5.78 sec., respectively. At 0°, m for capillary G was calculated[18] to be 0.89 mg./sec. The macro-scale electroreductions were conducted in a modified Lingane[19] coulometric apparatus maintained at 25 ± 0.1°.

Polarographic Procedure.—Stock solutions were prepared by dissolving a weighed amount of phenacyl fluoride in 95% ethanol. Test solutions were made by pipetting 5.00 ml. of stock solution into a 50-ml. volumetric flask and diluting with buffer solution. The test solution after transference to the polarographic cell was deoxygenated for 5 min. and then electrolyzed (10 min.) under a nitrogen atmosphere. The potentials reported are corrected for iR drop and are *vs.* S.C.E. All test solutions contained 9.5% ethanol and had an ionic strength of 0.45 *M;* the presence of the ethanol casts some doubt on the absolute validity of the *p*H measurements reported.

Acknowledgment.—The authors wish to thank the Atomic Energy Commission which helped support the work described.

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[17] J. C. Komyathy, F. Malloy and P. J. Elving, *Anal. Chem.*, **24**, 431 (1952).

[18] I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd ed., Interscience Publishers, New York, N. Y., 1952, pp. 91–92.

[19] J. J. Lingane, THIS JOURNAL, **67**, 1916 (1945).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Strontium Ion Association with Partially Neutralized Polyacids

BY FREDERICK T. WALL AND MICHAEL J. EITEL

RECEIVED MARCH 26, 1956

The association of strontium ions with polymeric acid anions has been studied by means of electrical transference and diffusion methods. The experiments were carried out on polymeric acids partially neutralized with strontium hydroxide. The degree of binding of strontium to the polymeric anions was computed from the amount of strontium that appeared to move with the anion during electrical transference. The fraction of free strontium ions could also be calculated from the apparent rate of diffusion of such ions in the presence of polymeric acid. The extents of binding calculated by the two methods were in substantial agreement and could be described adequately by use of certain empirical equations of a form compatible with a simple molecular model.

Introduction

The principal reason for the difference between the properties of polymeric ions and those of simple ions is that the charged groups of a polyelectrolyte cannot move entirely independently of each other because they are connected by the polymer chain. Thus the region which is effectively occupied by a coiling type polymer ion becomes one of much higher charge density than its surroundings. As a result, the counterions frequently penetrate into the polymer coil, and a considerable fraction of them becomes associated with the macroion because of electrostatic attraction. Previous studies[1–4] have demonstrated convincingly that the association of monovalent counterions with polymeric anions and cations is appreciable even for salts whose monomeric counterparts are almost completely ionized.

The purpose of this investigation was to study the association of divalent ions with partially neutralized aqueous polymeric acids as a function of the degree of neutralization, polymer concentration, temperature and degree of polymerization. Using radioactive strontium-89, the binding characteristics could be determined independently by means of transference experiments and diffusion measurements.

Divalent counterions interact with polyelectrolytes so much that flocculation results beyond low degrees of neutralization. This effect is attributable to the fact that divalent ions can associate with two binding sites, forming "bridges" between two polyions. In high neutralization ranges, an appreciable number of "bridges" can be formed, resulting in large aggregates of polymer which show a pronounced Tyndall effect in solution and which may even precipitate out.

Experimental

The methods employed in carrying out the Hittorf-type transference experiments have been described previously.[1,2] When a partially neutralized polymeric electrolyte, like polyacrylic acid, is electrolyzed, it is found that the polymeric anions move as expected toward the anode. Some of the cations migrate in the normal manner toward the cathode, but it is also observed that other cations move toward the anode. Such migration, apparently in the wrong direction, is explained by assuming that those cations are "bound" to the polymeric anion, or caught in the anionic sphere of influence, and hence constrained to move with the anion. A measure of the number of cations moving to the anode constitutes a transference determination of the extent of ion binding. The transport of counterions is most conveniently followed by radioactive counting, whereas the migration of polymer is determined gravimetrically.

Details of the diffusion method for determining ion binding have also been described previously.[1,2] In these experiments tracer ion diffusion takes place across a sintered glass frit from a well-mixed "hot" solution into a stirred, initially "cold," but chemically identical, solution. It is observed that polymeric anions tend to reduce the rate of diffusion of cations, a behavior attributed once again to ion binding. The extent of ion binding is determined by relating the reduced diffusion tendency of the ions in the presence of polymer to the rate of diffusion of the same ions in the absence of polymer. As a simplifying assumption, the diffusion rate of the bulky polymer ions is considered negligible compared to that of the smaller counterions.

Actually, the rate of exchange between bound and unbound counterions also influences the diffusion data. This

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[1] J. R. Huizenga, P. F. Grieger and F. T. Wall, THIS JOURNAL, **72**, 2636 (1950); **72**, 4228 (1950).

[2] F. T. Wall, J. J. Ondrejcin and M. Pikramenou, *ibid.*, **73**, 2821 (1951); F. T. Wall and R. H. Doremus, *ibid.*, **76**, 868 (1954); **76**, 1557 (1954).

[3] G. I. Cathers and R. M. Fuoss, *J. Polymer Sci.*, **4**, 121 (1949).

[4] A. Oth and P. Doty, *J. Phys. Chem.*, **56**, 43 (1952).