Discussion

Table III gives the limiting conductances and the conductance–viscosity products for the four ions.[23] It is at once apparent that while the Walden rule (as might be expected) is not obeyed, the variation in the product on passing from methanol to ethanol is considerably less than on passing from water to methanol, and is moreover not as great for the three cations as for chloride.

In Table IV are the limiting conductance ratios for the ions in water at 25 and 45° and in the two alcohols. It was earlier pointed[5b] out that viscosity effects on passing from one solvent to another should cancel to some extent in the ratio, if the ions compared were of the same sign and charge. A glance at Table IV shows at once, however, that no simple generalization as to the conductance ratio can be made. In all cases, there is an increase in the ratio of the conductance of the slower to the faster cation with rise in temperature, *i.e.*, with decrease in dielectric constant, and the same is true on going from water to methanol. On passing from methanol to ethanol, a solvent of still lower dielectric constant, however, the $\mathrm{Na}^+/\mathrm{K}^+$ ratio is unaltered, while that for $\mathrm{Li}^+/\mathrm{Na}^+$ actually decreases. Thus there does not seem any obvious dependence of the ratio on solvent dielectric constant, and this of itself would seem to bargain out any purely electrostatic picture of solvent dipole–cation interaction. It is true that the use of the macroscopic dielectric constant[24] as a rough measure of solvent–ion interaction and consequently of the ion size effective in transport is a gross and possibly unjustifiable simplification. A more sophisticated treatment such as that used by Gilkerson[25] in his recent study of the effect of solvent properties, in particular the dipole moment, on the ion-pair dissociation constant, however, does not seem hopeful, since it would involve assumptions as to the local dielectric constant effective in the interaction between the ion and the innermost layer of solvent dipoles. It should also be noted that while there is a definite trend in the ratio $\mathrm{Na}^+/\mathrm{Cl}^-$, this is not the case for $\mathrm{K}^+/\mathrm{Cl}^-$. If as relatively simple a quantity as the limiting conductance ratio for a pair of noble gas type ions, shows such individualistic behavior with three solvents as closely related as water and the two alcohols, it indicates (we believe) that any satisfactory answer to the problem of ionic mobility as a function of solvent properties is still remote.

Finally, it should be noted, however, that the ion-pair dissociation constants for the three salts lie in the order expected, *i.e.*, the salt with the smallest crystallographic and consequently the largest solvated radius for the cation shows the smallest tendency toward ion-pair formation.

In conclusion, we wish to express our thanks to the National Research Council of Canada for the award of studentships to J. R. G. and G. S. K.

---

[23] The water and methanol data are from Tables IV and V of ref. 5b; see also Benson and Gordon, *J. Chem. Phys.*, **13**, 473 (1945).

[24] P. Van Rysselberghe and R. M. Fristrom, THIS JOURNAL, **67**, 680 (1945).

[25] W. R. Gilkerson, *J. Chem. Phys.*, **25**, 1199 (1956).

TORONTO, ONTARIO, CANADA

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

Adsorption Kinetics and Electrode Processes

BY PAUL DELAHAY AND ISAAC TRACHTENBERG[1,2]

RECEIVED DECEMBER 11, 1956

The kinetics of adsorption on electrodes is studied for substances which are not reduced or oxidized at the electrode. Adsorption rates are derived for the plane electrode with control by semi-infinite linear diffusion, the streaming mercury electrode, and electrodes in stirred solution. Adsorption at the dropping mercury electrode is also considered briefly. To simplify the treatment it is assumed either (a) that the concentration of adsorbate is so low as to allow linearization of the isotherm, or (b) that the concentration of adsorbate is so large as to correspond to full coverage. In the range of concentrations in which the isotherm can be linearized, adsorption with diffusion control is a slow process and the equilibrium surface concentration is reached only after a long time (perhaps 30 min.). This conclusion is verified experimentally by differential capacity measurements for the adsorption of *n*-hexyl alcohol on a hanging mercury drop in 1 *M* potassium nitrate. Conversely, the streaming mercury electrode is essentially free of adsorbate. Implications are discussed for double layer capacity measurements, electrocapillary curves studies, electrochemical kinetics and polarography. Maxima and minima and other features of current–time curves during drop life in polarographic reductions in presence of an adsorbable species are accounted for; and the dependence of limiting currents on the head of mercury is interpreted. Experimental results are given for the reduction of Cu(II) in 0.5 *M* sodium citrate in presence of quinoline. Experimental methods are discussed, and a simple and accurate bridge for differential capacity measurements without isolation transformer is described.

Introduction

The characteristics of electrode processes often are affected by the adsorption of substances not directly involved in the electrode reaction. For instance, the exchange current and the transfer coefficient for the discharge of cadmium ion on cadmium amalgam vary when hexyl alcohol is added to the cadmium ion solution. The partial coverage of the electrode by the adsorbed substance causes an increase in actual current density and a concomitant increase in overvoltage. The variation of kinetic parameters and the increase in actual current density account for the distortion of current–potential curves which results from the addition of an adsorbable species such as a polar organic substance. If the exchange current is large enough, current–potential curves may not be altered because the decrease in the rate of the electrochemical reaction is not sufficient to cause a

---

[1] Paper presented at the 15th International Congress of Pure and Applied Chemistry, Lisbon, September 9–16, 1956.

[2] Predoctoral fellow 1955–1957.

departure from so-called reversible behavior.[3] Another effect of adsorption of polar organic substances is the decrease of limiting currents which otherwise would be mass transfer controlled.

These effects have been studied in detail[4-13] but, if one excepts studies of adsorption by electrolysis with superimposed alternating current[14-16] (no claim to a comprehensive literature survey is made), mass transfer of the adsorbate has generally not been considered, and it has been assumed tacitly that there is no concentration "polarization" of the adsorbate. In other words it is generally assumed that the surface concentration has the equilibrium value corresponding to the concentration of adsorbable substance in the bulk of the solution far from the electrode. This assumption often cannot be made[17] as will be apparent from this work, and a study of the kinetics of adsorption with mass transfer control is of interest. This study is reported here (a) for control by linear diffusion, (b) for the dropping mercury electrode, (c) for the streaming electrode and (d) for stirred solution. Implications in double layer capacity measurements, electrocapillary curve studies, electrochemical kinetics, and polarography are considered.

Control by Semi-infinite Linear Diffusion

Boundary Value Problem.—We consider the adsorption of a substance on a plane electrode with mass transfer controlled by semi-infinite linear diffusion. The surface of the electrode is supposed to be uncovered initially; the modification in treatment for a partially covered electrode at time zero is trivial. The surface concentration Γ of adsorbable substance at time t is obtained by integrating the flux of adsorbate from 0 to t, *i.e.*

$$\Gamma = \int_0^t D(\partial C/\partial x)_{x=0}\,\mathrm{d}t \qquad (1)$$

where D is the diffusion coefficient of the adsorbate, C the concentration of this substance, and x the distance from the electrode. If it is assumed that the adsorption process is so rapid that there is solely diffusion control, the surface concentration Γ is related to the volume concentration at the electrode surface, $C_{x=0}$, by the adsorption isotherm. This simplification is quite justified since it has been found by the alternating current method[14-16] that the adsorption of many polar organic substances on a mercury electrode is purely diffusion controlled. For other metals there might be partial control by the kinetics of adsorption, but this complication will not be considered here. Thus

$$\Gamma = \frac{\Gamma_m C}{a + C} \qquad (2)$$

where Γ_m is the surface concentration for maximum coverage, and a is a parameter which is characteristic of the isotherm.

The combination of (1) and (2) yields the boundary condition for which Fick's equation must be solved. Furthermore, one has $C = C^0$ for $x \geqslant 0$ and $t = 0$; and $C \rightarrow C^0$ for $x \rightarrow \infty$ and $t \geqslant 0$, C^0 being the bulk concentration of adsorbate.

Solutions are discussed below for the following two cases: (a) The adsorption isotherm can be linearized,[18] *i.e.*

$$\Gamma = KC \text{ with } K = \Gamma_m/a \qquad (3)$$

and (b) the case in which C^0 is so large that $\Gamma \approx \Gamma_m$ even when $C_{x=0} \ll C^0$. The general case is not treated because of mathematical difficulties. A general solution could be obtained by means of computer calculations, but the essential ideas can be presented in a simple treatment.

Variations of Concentration for the Linearized Isotherm.—The ratio of concentrations C/C^0, as obtained by Laplace transformation[19] is

$$\frac{C}{C^0} = 1 - \exp\left[\frac{x}{K} + \frac{Dt}{K^2}\right]\operatorname{erfc}\left[\frac{x}{2D^{1/2}t^{1/2}} + \frac{D^{1/2}t^{1/2}}{K}\right] \qquad (4)$$

where "erfc" represents the complement of the error function. Variations of C/C^0 with the distance from the electrode are shown in Fig. 1 for different times after the beginning of the adsorption process and for the values $D = 0.5 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ and $K = 5 \times 10^{-3}$ cm. (see Experimental Verification). The concentration in the immediate vicinity of the electrode approaches the bulk concentration C^0 only after a long time (1000 sec. or more), and *adsorption equilibrium is slowly attained.* The qualitative interpretation is simple: the gradient of concentration of adsorbate decreases continuously as adsorption proceeds, and the rate of diffusion drops accordingly.

---

(3) Reversible waves are observed in polarography when the rate constant at the standard potential for the electrode reaction is larger than 10^{-2} cm. sec.$^{-1}$. See P. Delahay, THIS JOURNAL, **75**, 1430 (1953); P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience, New York, N. Y., 1954, pp. 83–85.

(4) J. Heyrovsky, F. Sorm and J. Foretj, *Collection Czechoslov. Chem. Communs.*, **12**, 11 (1947).

(5) K. Wiesner, *ibid.*, **12**, 594 (1947).

(6) M. Matyas, *ibid.*, **16**, 496 (1951).

(7) J. Koryta, *ibid.*, **18**, 206 (1953).

(8) J. Heyrovsky, *ibid.*, **19**, S 58 (1954); contains several references to previous work by this investigator and co-workers; see also references to studies of the effect of gelatin and similar substances.

(9) (a) M. A. Loshkarev and A. A. Kryukova, *Doklady. Akad. Nauk SSSR*, **62**, 97 (1948); (b) *Zhur. Fiz. Khim.*, **23**, 209, 221, 1457 (1949); (c) **26**, 731 (1952).

(10) L. Gierst and D. Bermane, paper presented at the National Meeting of the Electrochemical Society, San Francisco, 1956; D. Bermane, Thesis, Brussels, 1955.

(11) V. V. Losev, *Doklady Akad. Nauk SSSR*, **107**, 432 (1956).

(12) For detailed reviews see A. N. Frumkin, *Z. Elektrochem.*, **59**, 807 (1955); *Doklady Akad. Nauk SSSR*, **85**, 373 (1952). Translation of the latter paper was made available by the Naval Research Laboratory, Washington, D. C.

(13) We do not consider the case in which the overvoltage is decreased by the addition of a foreign substance, as for hydrogen evolution upon addition of certain alkaloids.

(14) (a) A. N. Frumkin and V. I. Melik-Gaikazyan, *Doklady Akad. Nauk SSSR*, **77**, 855 (1951); (b) V. I. Melik-Gaikazyan, *Zhur. Fiz. Khim.*, **26**, 560, 1184 (1952). English translations kindly supplied by Dr. D. C. Grahame of Amherst College.

(15) T. Berzins and P. Delahay, *J. Phys. Chem.*, **59**, 906 (1955).

(16) W. Lorenz and F. Möckel, *Z. Elektrochem.*, **60**, 507 (1956).

(17) This does not necessarily invalidate conclusions previously derived because a systematic error on surface concentration may be unimportant.

(18) A linearized adsorption isotherm has been used in the treatment of electrolysis at constant current for an adsorbable reducible (or oxidizable) substance; see W. Lorenz, *Z. Elektrochem.*, **59**, 730 (1955).

(19) Set $u = C^0 - C$. The transform of the solution of Fick's equation is $\bar{u} = A \exp[-(s/D)^{1/2}x]$, A being an integration constant, and s the parameter of the transform. The constant A is determined from the transform of (3), and there results $\bar{u} = C^0 \exp[-(s/D)^{1/2}x]/s^{1/2}[(D^{1/2}/K) + s^{1/2}]$. The inverse transform is available in tables; see R. V. Churchill, "Modern Operational Mathematics in Engineering," McGraw–Hill Book Co., Inc., New York, N. Y., 1944.

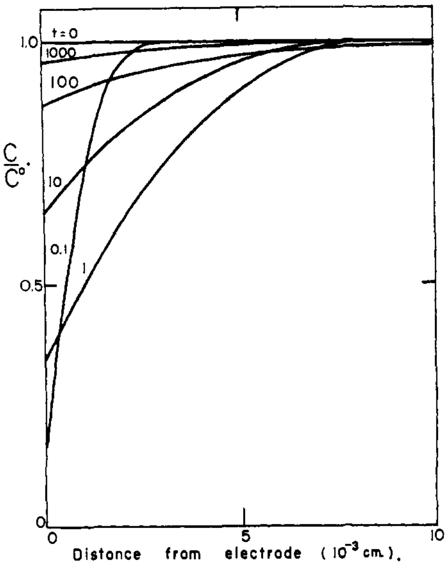


Fig. 1.—Variations of C/C^0 with distance from electrode for different times (in seconds) after the beginning of adsorption and for control by semi-infinite linear diffusion (data in text).

The surface concentration Γ_t at time t is readily obtained from (4) by noting that, according to (3), $\Gamma_t = KC_{x=0}$. Thus

$$\frac{\Gamma_t}{\Gamma_e} = 1 - \exp\left(\frac{Dt}{K^2}\right)\operatorname{erfc}\left(\frac{D^{1/2}t^{1/2}}{K}\right) \tag{5}$$

where Γ_e is the equilibrium surface concentration for the bulk concentration C^0, *i.e.*, $\Gamma_e = KC^0$ (see eq. 3). The function in (5) is tabulated in Carslaw and Jaeger.[20] The ratio Γ_t/Γ_e, which is equal to zero for $t = 0$, approaches unity as t tends to infinity. The value of the argument for which there is virtually complete coverage is readily deduced from (5). For instance, $\Gamma_t/\Gamma_e \geqslant 0.99$ when $D^{1/2}t^{1/2}/K \geqslant 56.5$; *i.e.*, for $t > 1.6 \times 10^4$ sec. for the data of Fig. 1. Actually, convection interferes and shortens the time necessary to attain adsorption equilibrium.

The ratio Γ_t/Γ_e given by (5) is independent of the bulk concentration of adsorbable substance because the adsorption isotherm is linearized in this treatment. Thus, the rate of diffusion is doubled when C^0 is changed to $2C^0$, but Γ_e is also doubled and, consequently, Γ_t/Γ_e is independent of C^0. Actually, one would find that the time required to reach a given value of Γ_t/Γ_e decreases as C^0 increases if the *complete* adsorption isotherm (equation 2) were used.

Variations of Concentration for the Case in which $\Gamma_e \approx \Gamma_m$ even for $C_{x=0} << C^0$.—This case can be treated readily by the Ilkovic equation, as written for the case of semi-infinite linear diffusion.[21,22] It is assumed that the rate of diffusion is the same as for a process in which $C_{x=0} = 0$ for $t >$ and $C_{x=0} = C^0$ for $t = 0$. This major *simplification* is justified when the bulk concentration of adsorbate, C^0, is so large that the maximum coverage Γ_m is reached even when the volume concentration of adsorbate at the electrode surface is much smaller than $C°$. One then has[23] per unit area

$$\left(\frac{\partial C}{\partial x}\right)_{x=0} = \frac{C^0}{(\pi Dt)^{1/2}} \tag{6}$$

and in view of (1)

$$\Gamma_t = \frac{2D^{1/2}C^0}{\pi^{1/2}}t^{1/2} \tag{7}$$

Equation 7 holds only for values for t for which $\Gamma_t \leqslant \Gamma_m$. The time τ at which $\Gamma_t = \Gamma_m$ is readily computed from (7). Actually, the value Γ_m is approached asymptotically and τ should be infinite, but a finite value is obtained in this very approximate derivation. Note that τ is inversely proportional to the square of the bulk concentration C^0.

Experimental Verification.—The differential capacity of an electrode is markedly changed by the adsorption of polar organic substances. The double layer can be represented by an equivalent circuit composed of two capacities in parallel: one capacity for the covered fraction of the electrode, and the other capacity for the uncovered fraction. On the basis of this model one can write

$$c = c_{\theta=1} + (c_{\theta=0} - c_{\theta=1})(1 - \theta) \tag{8}$$

θ being the electrode coverage. Equation 8 holds for the range of potentials in which $c_{\theta=0} > c_{\theta=1}$. At time t, one has $\theta = \Gamma_t/\Gamma_m$, Γ_m being the maximum surface concentration of adsorbate. Likewise, $\theta = \Gamma_e/\Gamma_m$ for $t \rightarrow \infty$. Hence

$$\frac{\Gamma_t}{\Gamma_e} = \frac{c_{\theta=0} - c_t}{c_{\theta=0} - c_{t\rightarrow\infty}} \tag{9}$$

Relationship 9 was applied to the adsorption of *n*-hexyl alcohol on a mercury hanging drop in 1 *M* potassium nitrate. Differential capacities were measured with an a.c. bridge (see Experimental). Values of $c_{t\rightarrow\infty}$ measured at −0.700 v. (*vs.* S.C.E.) are shown in Fig. 2. These values were reached after 30 to 60 minutes. The curve and the asymptote were traced to fit a Langmuir isotherm ($\Gamma_m = 8 \times 10^{-10}$ moles cm.$^{-2}$, $a = 2 \times 10^{-8}$ moles cm.$^{-3}$, see eq. 2). The capacity c_t was followed during adsorption, and the corresponding values of Γ_t/Γ_e (Fig. 3) were computed from (9).

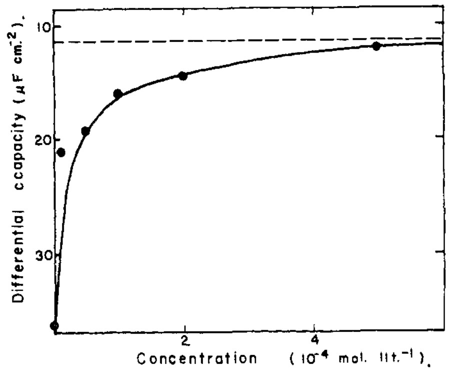


Fig. 2.—Differential capacity of hanging mercury drop in 1 *M* potassium nitrate with varying amounts of *n*-hexyl alcohol. Capacities were measured at −0.700 v. (*vs.* S.C.E.) and 25°.

The theoretical curve deduced from eq. 5 is also traced in Fig. 3 for the value $D^{1/2}/K = 0.05$ sec.$^{-1/2}$, *i.e.*, for $K = 4 \times 10^{-2}$ cm. with $D = 0.4 \times 10^{-5}$ cm.^{2} sec.$^{-1}$. This value of K corresponds to $\Gamma = \Gamma_m$ for $C = 2 \times 10^{-8}$ moles cm.$^{-3}$ for the linearized isotherm (Fig. 2). The value $\Gamma_m = 8 \times 10^{-10}$ mole cm.$^{-2}$, used in the calculation of K, was computed from the coverage of 21×10^{-16} cm.^{2} per molecule quoted by Adam[24] for the adsorption of an aliphatic alcohol with no compression of the film.

The marked departure from theory in Fig. 3 is to be expected since the theoretical curve corresponds to linear dif-

---

(20) H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Oxford University Press, London, 1947, p. 373.

(21) Private communication from Dr. J. E. B. Randles of the University of Birmingham, England.

(22) P. Corbusier and L. Gierst, *Anal. Chim. Acta*, **15**, 254 (1956), also evaluated the surface coverage on the dropping mercury electrode by application of the Ilkovic equation. See also ref. 7.

(23) (a) D. Ilkovic, *Collection Czechoslov. Chem. Communs.*, **6**, 498 (1934); (b) *J. chim. phys.*, **35**, 129 (1938).

(24) N. K. Adam, "The Physics and Chemistry of Surfaces," 3rd ed., Oxford University Press, London, 1941, p. 50.

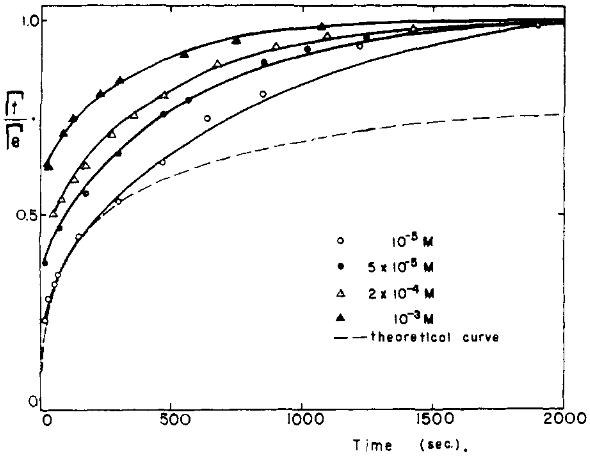


Fig. 3.—Variations of Γ_t/Γ_e with time for the conditions of Fig. 2. The theoretical curve is for the plane electrode.

fusion whereas the experimental results were obtained with a spherical electrode. The disagreement is in the right direction since the rate of diffusion for a spherical electrode is higher than for a plane electrode, all other conditions being the same. Convection also increased the rate of mass transfer of *n*-hexyl alcohol. Similar experiments were made with a mercury pool electrode, but the results were unreliable probably because of wetting of the mercury in contact with the wall of the container.

Figure 3 also shows that Γ_e is reached more rapidly when the bulk concentration of adsorbate is increased, *e.g.*, when the isotherm departs markedly from the linearized form (Fig. 2).

Although this experimental study is only semi-quantitative it definitely bears out the conclusion that adsorption with diffusion control is a slow process. Further work on the verification of eq. 5 by means of radiotracers is now being done by Mr. J. Truemper in this Laboratory.

Control by Diffusion at the Dropping Mercury Electrode

The derivation of the surface concentration for the dropping mercury electrode is the same as above, in principle, but the mathematical treatment is more involved. Fick's equation, as modified by Ilkovic for a moving boundary[23b]

$$\partial C/\partial t = D\partial^2 C/\partial x^2 + (2/3)(x/t)\partial C/\partial x \qquad (10)$$

is applied, and eq. 1 is rewritten to take into account the expansion of the drop (with $t^{2/3}$)

$$\Gamma = \frac{1}{t^{2/3}}\int_0^t Dt^{2/3}(\partial C/\partial x)_{x=0}\,\mathrm{d}t \qquad (11)$$

This problem possibly could be solved by computer calculations or by making the same transformations that Smutek[25] used in his elegant treatment of irreversible polarographic waves. Calculations would be laborious, and only a simple analysis will be made here.

The rate of diffusion is increased because of the expansion of the drop, and Γ_t/Γ_e approaches unity more rapidly than eq. 5 predicts for linear diffusion. However, the time required to reach a given Γ_t/Γ_e should be of the same order of magnitude in both cases. From (5) one deduces that $\Gamma_t/\Gamma_e \approx 1$ for $(Dt)^{1/2}/K > 20$, *i.e.*, $D^{1/2}/K > 10$ sec.$^{-1/2}$ for a normal drop time of 4 sec. Since D is of the order of 0.5×10^{-5} cm.^{2} sec.$^{-1}$ in most cases (not for polyelectrolytes), the preceding condition becomes $K < 2 \times 10^{-4}$ cm. If one takes the realistic approximate value of $\Gamma_m = 10^{-9}$ mole cm.$^{-2}$ (see Experimental Verification), the above limit of K corresponds, *for the linearized isotherm*, to full coverage for $C = 5 \times 10^{-6}$ mole/cm.$^{-3}$. In most cases, $\Gamma \approx \Gamma_m$ for much lower concentrations than 5×10^{-6} mole/cm.$^{-3}$ (linearized isotherm), and K ($\Gamma_m = KC$, see eq. 3) is appreciably larger than the upper limit of 2×10^{-4} cm. prescribed above. As a result,[26] *the surface concentration of adsorbate during drop life is much smaller than the equilibrium value in the range of low concentrations corresponding to the linearized isotherm.*

The ratio Γ_t/Γ_e at the end of drop life increases with the bulk concentration of adsorbate above concentrations corresponding to the linearized isotherm. This can be shown by transposing eq. 7 to the case of the dropping mercury electrode. The value of $(\partial C/\partial x)_{x=0}$ in (6) is multiplied[23] by $(7/3)^{1/2}$, and the result is introduced in (11). Thus

$$\Gamma_t = \frac{6}{7}\left(\frac{7}{3}\right)^{1/2}\frac{1}{\pi^{1/2}}C^0D^{1/2}t^{1/2} \qquad (12)$$

with t such that $\Gamma_t \leqslant \Gamma_m$. From (12) one calculates that the time τ at which $\Gamma_t = \Gamma_m$ is 0.3 sec. for $D = 0.4 \times 10^{-5}$ cm.^{2}/sec.$^{-1}$ and $C^0 = 10^{-6}$ mole/cm.$^{-3}$. This calculation which is *very* approximate corresponds to the most favorable conditions for equilibrium attainment.

Control by Mass Transfer at the Streaming Mercury Electrode

The electrode surface is continuously renewed at the streaming mercury electrode, and it is of interest to determine to what extent the mercury surface is free of adsorbable substance and can be regarded as "clean" in applications in electrochemical kinetics.

The surface concentration of adsorbate will be derived by adaptation of the result for linear diffusion as was done by Koryta[27] in his treatment of the limiting current for the streaming mercury electrode. On the basis of the assumptions listed below, Koryta obtained the simplified form of the equation for the limiting current which had been derived more rigorously by Rius and co-workers.[28,29]

The following assumptions are made: (a) the layer of solution which is adjacent to the mercury column moves at the same velocity as mercury; (b) this layer is thicker than the diffusion layer; (c) there is virtually no concentration gradient in this layer in the direction parallel to the axis of the mercury jet; (d) diffusion in the layer in the immediate vicinity of the mercury column is treated by Fick's equation for linear diffusion.

The number of moles adsorbed on the electrode is

$$N = \int_0^L D\left(\frac{\partial C}{\partial x}\right)_{x=0} 2\pi r\,\mathrm{d}l \qquad (13)$$

where L is the length of the mercury column (supposed to be cylindric), l is the distance from the

---

(25) M. Smutek, *Collection Czechoslov. Chem. Communs.*, **20**, 247 (1955); see also H. Matsuda and Y. Ayabe, *Bull. Chem. Soc. Japan*, **28**, 422 (1955).

(26) One deduces from (5) that $\Gamma_t/\Gamma_e = 0.10$ for $D^{1/2}/K = 0.05$ sec.$^{-1/2}$ and $t = 4$ sec. This corresponds to the data used in the calculation of the theoretical curve in Fig. 3.

(27) J. Koryta, *Collection Czechoslov. Chem. Communs.*, **19**, 433 (1954).

(28) A. Rius, S. Polo and J. Llopis, *Anal. fis. y quim. (Madrid)*, **45**, 1029 (1949).

(29) For a more precise analysis than that of Rius *et al.*, see J. R. Weaver and R. W. Parry, THIS JOURNAL, **76**, 6258 (1954); **78**, 5542 (1956).

tip of the capillary to the annular zone of height dl and r is the radius of the mercury jet. The gradient of concentration $(\partial C/\partial x)_{x=0}$ in (13) is evaluated from (4). The latter contains the variable t which is converted to l by noting that $t = l/v$ where v is the velocity (assumed to be uniform) of mercury. Thus, for $l = L$ one has

$$N = 2\pi rLKC^0\left\{1 - \exp\left(\frac{DL}{K^2v}\right)\operatorname{erfc}\left[\frac{1}{K}\left(\frac{DL}{v}\right)^{1/2}\right]\right\} \tag{14}$$

The value of N_e for adsorption equilibrium is in view of (3)

$$N_e = 2\pi rLKC^0 \tag{15}$$

and

$$\frac{N}{N_e} = 1 - \exp\left(\frac{DL}{K^2v}\right)\operatorname{erfc}\left[\frac{1}{K}\left(\frac{DL}{v}\right)^{1/2}\right] \tag{16}$$

The ratio N/N_e has the same form as the value Γ_t/Γ_e for linear diffusion, and the dimensionless parameter $(1/K)(DL/v)^{1/2}$ simply replaces the group $(Dt)^{1/2}/K$.

Because of the assumptions underlying eq. 16, this formula is only approximate but the order of magnitude of N/N_e can be evaluated from it. One has $N/N_e = 0.6\%$ for $D^{1/2}/K = 0.05$ sec.$^{-1/2}$ (see experimental part above), $L = 0.5$ cm., and $v = 50$ cm. sec.$^{-1}$. The electrode is thus essentially free of adsorbate. This could be advantageous in electrochemical kinetics where contamination of electrodes (even mercury or amalgam electrodes) is a serious obstacle to the precise determination of kinetic parameters for electrode processes.

The case in which the bulk concentration of adsorbable substance is so large as to correspond to virtual saturation of the electrode surface can be analyzed by following the same procedure as for linear diffusion. Details will not be given here because the result is of little practical value.

Control by Mass Transfer in Stirred Solution

The surface concentration of adsorbate is easily obtained on the basis of the concept of the Nernst diffusion layer. Thus

$$(\partial C/\partial x)_{x=0} = (C^0 - C_{x=0})/\delta \tag{17}$$

where δ is the thickness of the diffusion layer. By substituting in eq. 1 the gradient from (17) and by differentiating the result with respect to t, there follows a differential equation. The solution is

$$C = C^0\left[1 - \exp\left(-\frac{Dt}{K\delta}\right)\right] \tag{18}$$

Hence (see eq. 3), one has for the linearized isotherm

$$\frac{\Gamma_t}{\Gamma} = 1 - \exp\left(-\frac{Dt}{K\delta}\right) \tag{19}$$

The electrode is rather rapidly covered: $\Gamma_t/\Gamma_e = 0.98$ for $t = 120$ sec. and $D^{1/2}/K = 0.05$ sec.$^{-1/2}$ (see experimental part above), *i.e.*, for $D = 0.4 \times 10^{-5}$ cm.^{2} sec.$^{-1}$, and $\delta = 0.003$ cm. (an order of magnitude for not too vigorous a stirring).

Implications

Double Layer Capacity Measurements.—Double layer capacity measurements are somewhat in error when adsorption equilibrium is not attained for adsorbable species. This is the case in the study of the adsorption of polar organic molecules on mercury, when the differential capacity is measured with a dropping mercury electrode and the concentration of the organic substance is low. The correct dependence of the differential capacity on frequency is nevertheless obtained because the diffusion layer is much thicker than the layer in which the concentration of adsorbate varies periodically with time. However, the surface concentration of adsorbate is smaller than the equilibrium value corresponding to the bulk concentration. It is observed that the characteristic two desorption peaks in the curve differential capacity against potential disappear as the concentration of adsorbate is decreased. When adsorption equilibrium is not attained with the dropping mercury electrode, the peaks should disappear at higher concentrations than for curves obtained with the hanging mercury drop.

Likewise, differential capacities measured with the dropping mercury electrode for *low* electrolyte concentration (10^{-3} M or less) could be somewhat erroneous when the anion (or cation) is adsorbed. The theoretical analysis made above does not apply to this case because of complications resulting from migration and the structure of the double layer, but the conclusion about the slowness of adsorption is still qualitatively valid. The same comment can be made for polyelectrolytes.[30] Fortunately, most measurements of differential capacity for pure electrolytes are made at concentrations at which adsorption equilibrium is attained.

The value of the parameter $(Dt)^{1/2}/K$ for the system being investigated can serve as a guide in deciding whether adsorption equilibrium is attained: the condition $(Dt)^{1/2}/K > 20$ should be fulfilled (see eq. 5). A simpler test is to change the head of mercury and determine whether the differential capacity per unit area varies with drop time. When equilibrium is not attained, the coverage at the end of the drop life decreases with drop time (see section on Polarography below), and the differential capacity per unit area varies accordingly.

Non-attainment of adsorption equilibrium could be avoided by the use of a stationary mercury electrode, but progressive contamination of the electrode by traces of impurities might be very difficult to avoid. The hanging mercury drop is preferable to the mercury pool[31] because of better reproducibility of area. Another possible solution is the use of the rotating dropping mercury electrode developed for voltammetric studies by Stricks and Kolthoff.[32] However, the use of this electrode in precise measurements of differential capacities might not be practical.

Electrocapillary Curves.—The foregoing considerations can be transposed to the "drop weight" method for the determination of electrocapillary curves. Somewhat erroneous results can be expected particularly in studies at low concentration of electrocapillary active substances. Although results are then affected by a systematic error, they

---

(30) I. R. Miller and D. C. Grahame, THIS JOURNAL, **78**, 3577 (1956).

(31) A mercury pool electrode was recently used in differential capacity measurements: R. S. Hansen, R. E. Minturn and D. A. Hickson, *J. Phys. Chem.*, **60**, 1153 (1956).

(32) W. Stricks and I. M. Kolthoff, THIS JOURNAL, **78**, 2085 (1956).

can be precise and analytical application is possible.[22]

Electrochemical Kinetics.—In general, traces of adsorbed impurities strongly affect kinetic parameters for electrode processes (exchange current and transfer coefficient). This source of error often cannot be entirely eliminated by careful purification of solution, and electrodes in which contamination is minimized are advantageous. The streaming mercury electrode is the best in this respect, but it is not very practical. The dropping mercury (amalgam) electrode is better than the hanging mercury drop because of the short duration of measurements and the continuous renewal of the mercury surface. It is suggested that kinetic parameters be measured for different times of the drop life (synchronization system), and that results be extrapolated to zero time to minimize the effect of impurity adsorption. This procedure should prove useful in the application of relaxation methods (potential- or current-step methods, electrolysis with superimposed a.c. component). The extrapolation method probably would fail for electrode reactions with gas evolution (hydrogen or oxygen overvoltage) because of the necessity of attainment of a steady state for the electrode coverage by gas. The dropping mercury electrode cannot be utilized in such a case anyhow.

The advantage of the dropping mercury electrode over the hanging mercury drop can be inferred from the recent work of Gerischer and Staubach[33] on the kinetics of the mercurous ion–mercury electrode. These authors observed that exchange currents obtained with a dropping mercury electrode for different concentrations of mercurous ion were about three times larger than the values for the hanging mercury drop. Two different methods, a.c. electrolysis and the potential-step method, were applied in these two sets of measurements and this might account for the discrepancy on the exchange current values. However, the lesser contamination of the dropping mercury electrode may well be the explanation of the difference between the two sets of results.

Polarography.—The departure from adsorption equilibrium (with respect to the bulk concentration) at the dropping mercury electrode may be relevant in a variety of polarographic studies: maximum suppressors, catalytic waves of alkaloids, distortion of waves, and depression of limiting currents by adsorption of foreign substances, etc. Implications will be considered here for current–time curves for electrode reactions in presence of an adsorbable organic substance that is not reduced or oxidized. This study was made for the reduction of Cu(II) in 0.5 *M* sodium citrate in presence of quinoline. Tracings of current–potential curves (maximum current during drop life) are given in Fig. 4. The range of markedly cathodic potentials at which quinoline should be desorbed could not be explored because of reduction of this substance.[34] Current–time curves during drop life are shown in Fig. 5 with the pertaining data in Table I. The following effects will be discussed: effects of drop time, quinoline concentration, and potential.

Since the area of the mercury drop (sphere) increases with $t^{2/3}$, t being the time during drop life, the rate of drop growth depends on $t^{-1/3}$ and decreases continuously. In the initial stage of the drop life, the drop grows too rapidly to be fully covered and the faradaic current is not too markedly hindered. The drop becomes progressively covered with adsorbate, and the current decreases at the end of the drop life (Fig. 5A). If the drop time is long enough (perhaps 10 sec.), the decrease in current is soon over-compensated by the increase in area, and the current increases again (Fig. 5B).

The rate of adsorption increases with the volume concentration of adsorbate. Hence, the minimum in current–time curves is shifted toward shorter times as the concentration of adsorbate increases (Fig. 5C and 5D). The minimum in current–time curves disappears at large concentrations of adsorbable species.

The electrode coverage can be adjusted at will by variation of the potential,[35,36] all other conditions being identical; and the shape of current–time curves changes with potential.[37] If the potential is sufficiently close to one of the two desorption peaks of the differential capacity curve, the coverage is small, and the minimum in the current–time curves disappears (Fig. 5E). Compare plates B, D and E of Fig. 5 which were obtained under identical conditions except that the potential was changed.

If the limiting current is relatively small in comparison with the diffusion current which would be observed in the absence of adsorbed substance, "blocking" by the film primarily controls the current. There is little concentration polarization for the reducible substance, and the limiting current is essentially proportional to the electrode area. The limiting current then is practically independent of the head of mercury.[38] Conversely, when the limiting current is almost equal to the diffusion current, mass transfer is rate determining, and the limiting current virtually obeys the Ilkovic equation. Under these conditions, the limiting current is essentially proportional to the square root of the head of mercury. The intermediate behavior is more complex and corresponds to current–time curves with a minimum.

The foregoing conclusions are borne out experimentally, and it is observed that the relationship between maximum current during drop life and the head of mercury depends on the concentration of adsorbable substance (Fig. 6). Limiting currents of Fig. 6 were measured at the minimum of current–potential curves (see Fig. 4).

Experimental

Cell, Solutions and Procedure for Differential Capacity Measurements.—A hanging mercury drop similar to that developed by Gerischer was utilized.[39,40] Mercury drops were collected in a glass spoon and then, by rotation of the spoon, hung on a fine gold–plated platinum wire[41] sealed in a

---

[33] H. Gerischer and K. E. Staubach, *Z. physik. Chem.*, *N.F.*, **6**, 118 (1956).

[34] I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd ed., Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1952, p. 818.

[35] A. Frumkin, *Z. Physik*, **35**, 792 (1926).

[36] J. A. V. Butler, *Proc. Roy. Soc.* (*London*), **122A**, 339 (1929).

[37] Another reason is the current-time dependence for irreversible waves.

[38] The limiting current is proportional to $(mt)^{2/3}$, and m is proportional to H while t is inversely proportional to H, H being the head of mercury corrected for the back pressure.

[39] H. Gerischer, *Z. physik. Chem.*, **202**, 302 (1953).

[40] T. Berzins and P. Delahay, THIS JOURNAL, **77**, 6448 (1955).

[41] Instead of hanging the drop on a gold-plated platinum wire, one can use a mercury-plated platinum wire and thus prevent contamination of mercury by gold. This procedure was developed by J. W. Ross, R. D. DeMars and I. Shain, *Anal. Chem.*, **28**, 1768 (1956).

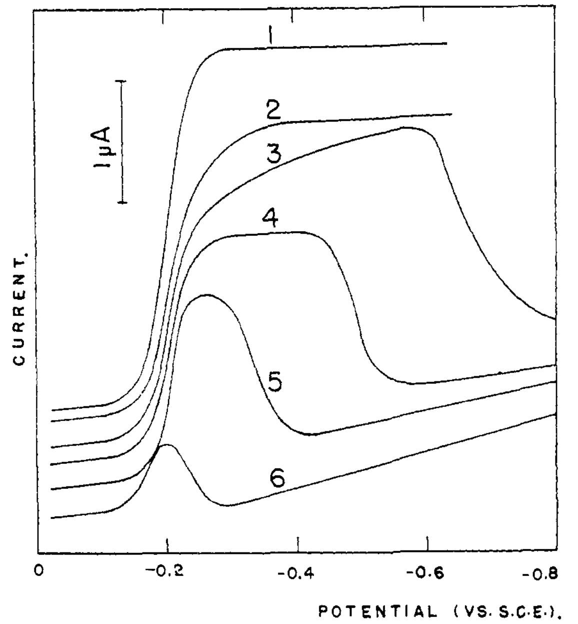


Fig. 4.—Polarograms of 1 millimolar Cu(II) in 0.5 *M* sodium citrate with varying amounts of quinoline. Millimolar concentrations of quinoline are: (1) 0; (2) 0.1; (3) 0.5; (4) 1; (5) 2.5; (6) 5; temperature, 25°

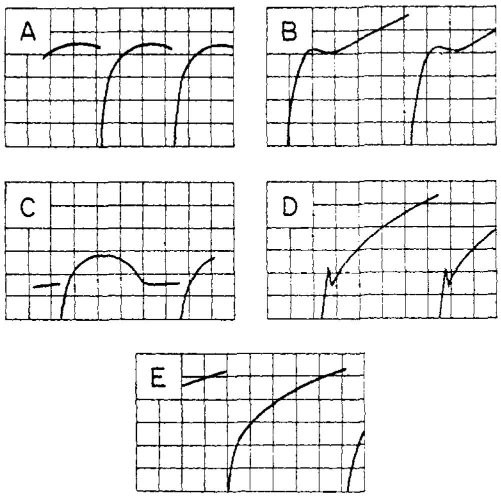


Fig. 5.—Current-time curves for 1 millimolar Cu(II) in 0.5 *M* sodium citrate. See data in Table I.

drawn-out glass tube. This method proved more practical than the one used by Gerischer. The tip of the glass tube was drawn out to avoid shielding of the mercury drop and the resulting dispersion of differential capacity with frequency. The cell was quite similar to that devised by Grahame.[42] The mercury drop was surrounded by a cylinder of platinum foil (diameter, 1 cm.; length 1.5 cm.) which was connected to the a.c. bridge. The potential of the mercury drop was adjusted against a saturated calomel electrode.

Solutions were freed of oxygen by nitrogen. To avoid evaporation of the substance being adsorbed on the electrode (*n*-hexyl alcohol), the pure electrolyte was first freed of oxygen, and a small volume (1 ml. in general) of an aqueous solution of *n*-hexyl alcohol was added afterwards. No nitrogen was passed through the solution after the addition of *n*-hexyl alcohol. Solutions were prepared with bidistilled water because traces of organic impurities interfered, especially at low concentrations (10^{-5} *M*) of *n*-hexyl alcohol.

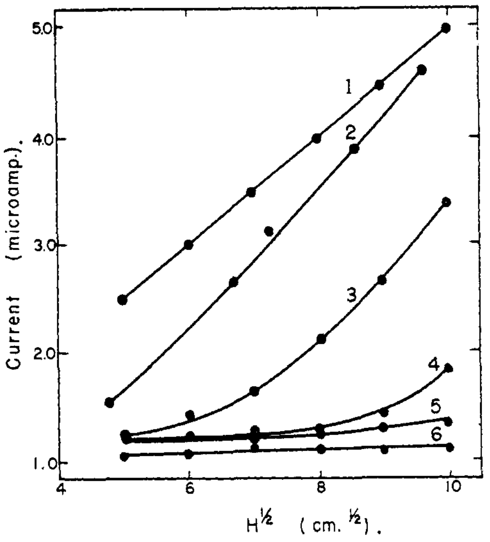


Fig. 6.—Limiting current at 25° against head of mercury for the reduction of 1 millimolar Cu(II) in 0.5 *M* sodium citrate in presence of quinoline. Millimolar concentrations of quinoline are: curve (1), 0; (2) 0.3; (3) 0.4; (4) 0.6; (5) 1; (6) 3.

The procedure was as follows. After preparation of the solution in the cell and proper setting of the potential of the mercury drop electrode (see bridge below), a mercury drop was rapidly hung and the differential capacity was measured within 20–30 sec. The bridge was set approximately at the correct resistance and capacity in advance to speed up measurements. The differential capacity was followed until a steady reading was obtained. This required at least 30 min. with the more dilute solution of hexyl alcohol.

Bridge.—The bridge of Fig. 7 was utilized.[43–45] It is described here because it is simpler than bridges with isolation transformers (in the input and detector circuits) often utilized in differential capacity measurements.[42]

Components were as follows: R_1 and R_2, matched 100 ohm resistances; R_3 and R_4, 1 megohm; R_5, 0–999.9 ohms decade box; R_6, 0–1 megohm variable resistance; C_1, 0.5 microfarad; C_2 and C_3, 0.05 microfarad; C_4, 0–11 microfarad decade box in 0.001 microfarad steps; C_5, 0–500 microfarads, adjustable; H, 32 henry inductance; POT, Leeds and Northrup student potentiometer; OSC, Hulett-Packard oscillator, Model 650A; AMP, Tektronix preamplifier, Model 122; CRO, Dumont oscilloscope, Model 304A; FIL, General Radio filter, Model 1231-P5.

TABLE I

DATA[a] FOR FIG. 5

Plate	*C*,[b] mmole. l.$^{-1}$	$-E$, v. *vs.* S.C.E.	*H*,[c] cm.	Abscissa scale, sec./square	Ordinate scale, mv./square	*R*[d],
A	0.6	0.588	81	1	1	800
B	.6	.588	25	2	1	2000
C	.3	.887	25	2	1	1000
D	.6	.816	25	2	1	2000
E	.6	.415	25	2	1	1500

[a] m = 2.23 mg. sec.$^{-1}$ at −0.80 volt (*vs.* S.C.E.) and for H = 81 cm. [b] Concentration of quinoline. [c] Head of mercury. [d] Resistance (in series with cell) connected to cathode-ray oscilloscope. [e] Temperature, 25°.

---

(42) D. C. Grahame, THIS JOURNAL, **71**, 2975 (1949).

(43) We are indebted to Dr. W. Vielstich, formerly Research Associate in this Laboratory, for having suggested the use of this simple bridge. See W. Vielstich, Thesis, Göttingen, 1954.

(44) For a general review of a.c. bridge measurements in electrochemistry see H. Gerischer, *Z. Elektrochem.*, **58**, 9 (1954).

(45) See also the bridge developed by J. E. B. Randles, *Trans. Faraday Soc.*, **50**, 1246 (1954).

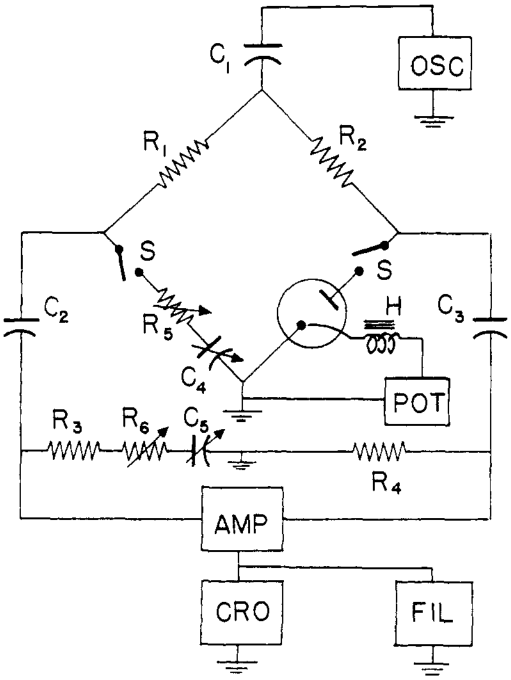


Fig. 7.—Bridge for differential capacity measurements.

The procedure was as follows: the voltage (peak voltage) applied to the bridge was set approximately at 5 mv. at 2000 c.p.s.; the earth compensation was first adjusted with R_6 and C_5 to achieve balance, switch S being open; the potential of the mercury drop was set with potentiometer POT, and S was closed; the bridge then was adjusted with R_5 and C_4. In general, results were precise within 0.1%.

Polarographic Measurements and Recording of Current-Time Curves.—Current-time curves were recorded by connecting a cathode-ray oscilloscope (Tektronix model 531 with preamplifier 53-54D) to a decade resistance box R in series with the cell. The ohmic drop in R did not exceed a few millivolts (Table I). Polarographic measurements followed conventional practice except for deaeration which was carried out by the procedure outlined in the previous section. Current-potential curves were recorded with a Sargent polarograph, Model XXI. The recorder of this instrument was replaced by a Brown recorder with fast response (1 sec. for full scale deflection).

Characteristics of capillary: for Fig. 4, m = 1.23 mg. sec.$^{-1}$, τ = 5.0 sec. (somewhat dependent on quinoline concentration) at −0.8 volt (*vs.* S.C.E.); for Fig. 6, m = 2.23 mg. sec.$^{-1}$ at −0.8 volt (*vs.* S.C.E.) for an uncorrected head of mercury of 81 cm.

Acknowledgment.—The investigation was begun with the support of the Humble Oil & Refining Company and was completed under the sponsorship of the Office of Naval Research. The generous help of these organizations is gladly acknowledged. Mr. Gleb Mamantov translated the Russian papers of reference 9 and discussed them in detail with us.

Added in proof.—Arrangements have been made with the Oak Ridge Institute of Nuclear Studies to carry out computer calculations for the complete isotherm for the plane electrode and the dropping mercury electrode.

Baton Rouge, Louisiana

[Contribution from the Department of Chemistry, Cornell University]

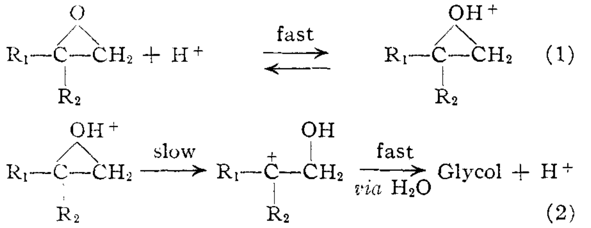
Entropies of Activation and Mechanism for the Acid-catalyzed Hydrolysis of Ethylene Oxide and its Derivatives[1]

By F. A. Long, J. G. Pritchard and Fred E. Stafford

Received January 17, 1957

The rates of the acid-catalyzed hydrolysis of ethylene, propylene, isobutylene and trimethylene oxides have been measured at several temperatures and the energies and entropies of activation have been calculated. The close similarity in the entropy of activation values strongly suggests that all of the oxides hydrolyze by the same A-1 mechanism, which has been proposed previously for epoxides. A survey of entropies of activation for other acid-catalyzed hydrolysis reactions indicates that within similar classes of compounds the A-1 mechanism is generally associated with a much more positive entropy of activation than the A-2 mechanism.

Recent studies on the acid-catalyzed hydrolysis of epoxides have led to the conclusion that this reaction follows an A-1 mechanism in which the rate-determining step is the formation of a carbonium ion.[2-4] In the case of 1,1-disubstituted oxides, the evidence for the A-1 mechanism is sufficient to exclude all others. Thus: (a) the preliminary equilibrium step (1) is established[4] from rate studies in deuterium oxide; (b) the rate-determining spontaneous opening of the epoxide ring in step (2) is shown by the fact that the rates of reaction of several epoxides in strong aqueous solutions of perchloric acid show a good correlation[3] with the Hammett acidity function, h_0; (c) H_2O^{18} has been shown to enter the isobutylene oxide molecule in the tertiary position in accord with step (2)[2]; and (d) the reaction rate is significantly faster for epoxides having electron releasing substituent groups, R_1 and R_2, and slower for those with electron withdrawing groups. The same points of evidence have also been established for monosubstituted oxides (R_2 = H). However, for the symmetrical parent compound, ethylene oxide (R_1 = R_2 = H), only items (a) and (b) have been established since



(1)

(2)

---

(1) Work supported in part by a grant from the Atomic Energy Commission.

(2) F. A. Long and J. G. Pritchard, This Journal, **78**, 2663 (1956).

(3) J. G. Pritchard and F. A. Long, *ibid.*, **78**, 2667 (1956).

(4) J. G. Pritchard and F. A. Long, *ibid.*, **78**, 6008 (1956).