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ELECTROCHEMISTRY

Edited by

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bimolecular rate constant is about 10^9 liter mole^{-1} sec^{-1}.

While most of the work reported to date has involved organic compounds, Maki and Geske[15] demonstrated rather early the existence of the free radicals in lithium or sodium perchlorate in anhydrous acetonitrile which had been subjected to electrooxidation within the cavity of an EPR spectrometer. Most likely the spectrum observed is that of the perchlorate radical ($\cdot ClO_4$). Hopefully the next several years will see investigations involving free radicals derived electrochemically from a large number of inorganic compounds.

The existence of good commercial EPR spectrometers and accessories which lend themselves well to this kind of work, coupled with recent appearance of advertisements extolling the virtues of these techniques, lends support to the hope that the work of Maki, Geske, Adams, *et al*, described here, has laid foundations for the rapid growth of these techniques.

References

1. Wertz, J. E., *Chem. Rev.*, **55,** 820 (1955).
2. Ingram, D. J. E., "Spectroscopy at Radio and Microwave Frequencies," London, Butterworths, 1955.
3. Galkin, A. A., *et al*., *J. Exptl. Theoret. Phys.* (*USSR*), **32,** 1581 (1957).
4. Austin, D. E. G., Gwin, J. H., Ingram, D. J. E., and Peover, M. E., *Nature*, **182,** 1784 (1958).
5. Geske, D. H., and Maki, A. H., *J. Am. Chem. Soc.*, **82,** 2671 (1960).
6. Maki, A. H., and Geske, D. H., *J. Am. Chem. Soc.*, **83,** 1852 (1961).
7. Van Bekkum, H., Verkade, P. E., and Wepster, B. M., *Rev. Trav. chim.*, **78,** 815 (1959). Taft, R. W., Jr., and Lewis, I. C., *J. Am. Chem. Soc.*, **81,** 5343 (1959).
8. Anderson, D. H., Frank, P. J., and Gutowsky, H. S., *J. Chem. Phys.*, **32,** 196 (1960).
9. Maki, A. H., and Geske, D. H., *J. Chem. Phys.*, **33,** 825 (1960).
10. Geske, D. H., and Ragle, J. L., *J. Am. Chem. Soc.*, **83,** 3532 (1961).
11. Piette, L. H., Ludwig, P., and Adams, R. N., *J. Am. Chem. Soc.*, **83,** 3909 (1961), and *Anal. Chem.*, **34,** 916 (1962).
12. Melchior, M. T., and Maki, A. H., *J. Chem. Phys.*, **34,** 471 (1961).
13. Lee, H. Y., and Adams, R. N., *Anal. Chem.*, **34,** 1587 (1962).
14. Ludwig, P., an Adams, R. N., *J. Chem. Phys.*, **37,** 828 (1962).
15. Maki, A. H., and Geske, D. H., *J. Chem. Phys.*, **30,** 1357 (1959).

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ELECTRON SPIN RESONANCE SPECTROSCOPY.

See ELECTRON PARAMAGNETIC RESONANCE IN STUDIES OF ELECTRODE PROCESSES

ELECTRON TRANSFERS AT ELECTRODES

An electrode immersed in a solution containing oxidizable or reducible ions or molecules will acquire electrons from or donate electrons to them. These electron transfers occur at suitable collisions of the species with the electrode, and the probability that such an electron transfer will occur depends on factors such as various differences in the chemical structures of the oxidized and reduced forms, the electrode-solution potential difference, the electrode material, the temperature, and the nature of the electrolyte medium, e.g.[1, 2]

In typical systems the net rate of electron transfer occurring per unit area of electrode is $p_1Z_1c_1 - p_2Z_2c_2$, where c_1 and c_2 are the concentrations of the oxidized and reduced species very near the electrode, Z_1 and Z_2 are collision frequencies (i.e., numbers of collisions of these species with unit area of electrode per unit time when their concentrations are unity), and p_1 and p_2 are the probability factors just mentioned.[1, 3, 4] When several types of oxidizable and reducible species undergo electron transfer with the electrode, terms for each similar to the above should be added.

The measurement of the rate constants, $k_1(=p_1Z_1)$ and $k_2(=p_2Z_2)$, and the understanding of their magnitudes are subjects of principal interest here. These k's normally depend exponentially on the electrode-solution potential difference and, thereby, on the cell potential, E:[3]

$$k_1 = k_1' \exp\,[-\alpha n\mathrm{F}(E - E')/RT]$$

$$k_2 = k_2' \exp\,[(1 - \alpha)n\mathrm{F}(E - E')/RT]$$

where k_1' is the value of k_1 when E equals any particular value of E, E'; n is the number of electrons transferred per collision with the electrode, T is the absolute temperature, α is the transfer coefficient (the slope of the Tafel plot), F and R are universal constants, the Faraday and the gas constant.

The net current, written cathodically, is i_c,

$$i_c = n\mathrm{F}A(k_1c_1 - k_2c_2)$$

where A is the electrode area. By setting i_c equal to zero at equilibrium, one obtains a kinetic derivation of the Nernst equation, $E = E^{\circ\prime} + (RT/n\text{F}) \ln c_1/c_2$, with $E^{\circ\prime}$ (the formal potential) equal to a term independent of concentration, $E' + (RT/n\text{F}) \ln k_1'/k_2'$. If E' is selected to be $E^{\circ\prime}$, k_1' evidently equals k_2' and one denotes their corresponding value by k'. (The Nernst equation (q.v.) itself can be derived more rigorously on thermodynamic grounds alone, of course.)

Determination of these all-important constants, k_1 and k_2, from the experimental data requires some information about c_1 and c_2. When the migration of oxidized and reduced species to and from the electrode is sufficiently fast, their concentrations equal those in the bulk of the solution and there is no difficulty from this source. But often this migration is not fast enough and a variety of techniques is used to overcome this obstacle.[3, 5–9]

Methods used to study the rates of electrode processes include (1) those designed to speed up the migration (rotating electrodes or rapid flow of solution past electrode), (2) those employing pulsed or alternating currents or potentials, (3) those using stationary or dropping electrodes and direct current techniques, and (4) various combinations of these.

Sometimes, the ion or molecule actually undergoing electron transfer is not one of the initial reactants but is formed from it by homogeneous chemical reaction. This case of consecutive processes, coupled with migration, can be handled formally, and in favorable cases in practice, by solving the appropriate differential equations. Such kinetic studies provide detailed knowledge of the reaction mechanism, its intermediates, and its various rate constants.

Conditions are simpler when these additional homogeneous reactions are highly reversible chemical equilibria. Consider, for example, the following system:

$$xA + yB \underset{\text{rapid}}{\rightleftharpoons} C_1 \xrightarrow[\text{electrode}]{ne} C_2$$

where A and B are two of the major constituents in the solution, x and y describe the stoichiometry, and C_1 and C_2 are the oxidized and reduced species. c_1 then equals Ka^xb^y, K being the chemical equilibrium constant and a is the concentration of A near the electrode. The net rate of electron transfer now equals $k_1Ka^xb^y - k_2c_2$. Appropriate measurements in which a and b are varied then yield values of x and y (the "reaction orders"). The establishment of the rate law provides detailed insight into the overall mechanism. The measurement of electrochemical reaction orders has been described in detail.[10]

The electron transfer step sometimes involves no rupture of chemical bonds. Sometimes, however, it is accompanied by rupture and simultaneous transfer of an atom between this reacting species and the electrode. The atoms or free radicals then undergo subsequent reactions. One example is the reduction of H_3O^+ ions to form hydrogen atoms adsorbed on the electrode and, eventually, to form hydrogen molecules.[11] Often, ruptures are slow compared with the pure electron transfers, but notable exceptions exist.

The vigorous development of techniques for the study of fast electrode reactions has permitted the study of many rapid electron transfers. Several related compilations of the data in this expanding field exist.[1b, 5, 12] Principally, values of α, i_0 (the exchange current density), and of the temperature coefficient of i_0 are listed. i_0 is the value of $n\text{F}k_1c_1$ measured at $E = E^{\circ\prime}$ and at local electrochemical equilibrium. It is readily shown to be $n\text{F}k'c_1(c_2/c_1)^\alpha$. The value at unit concentration, $n\text{F}k'$, is of particular interest. Very recently a comparison of these k''s for a series of reactions with the rate constants of intimately related homogeneous electron transfer reactions (ones involving "isotopic exchange") has been made using a theoretically based equation, with encouraging results.[1b, 13] Again, the coefficients α are often about 0.5 for these "simple" electron transfers, in accordance with theoretical expectations when double layer penetration effects are small.[1b]

The actual mechanism of electron transfer, both in the presence and absence of bond ruptures, has been discussed from the fundamental modern viewpoint of quantum and statistical mechanics. In each type of transfer the electrochemical process is accompanied by a change from a fairly stable arrangement of the atoms of the entire initial system (oxidized species, surrounding medium, electrode) to a fairly stable atomic arrangement of the final system (reduced species, etc.). In the purely electron transfer type of process,[1] this change of atomic configuration (i.e., of atomic position) occurs inside and outside the inner coordination shell of the reacting species. Each bond in the reacting species will have a somewhat different equilibrium length in the oxidized and reduced forms of the species. Since the ionic charge also differs (by n electronic charges) the average degree of orientation of solvent molecules

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in the vicinity differs for the two forms, as does the average degree of proximity of other ions of the medium. Accordingly, changes of bond lengths, reorientation of solvent molecules, and some adjustments of ion atmosphere must occur during the reaction.

Fluctuations in these bond lengths, orientations, and ionic positions occur continually. Thereby, an arrangement of the atomic positions that is a fairly stable one for the final reacting system (reduced molecule, the electrolyte medium, plus charged electrode) can be formed from one which is a fairly stable arrangement for the initial system (oxidized molecule, electrolyte medium, electrode). This fluctuation can cause an electron transfer only if a sufficiently strong coupling of the electronic orbitals of the reactant with those of the electrode exists. This coupling is in fact negligible when the reactant is far from the electrode. For appreciable coupling their distance apart should be no more than a molecular diameter or so. Accordingly, a suitably close approach of the species, coupled with the other fluctuations listed above, can cause an electron transfer.[1]

Statistical mechanical calculation of the probabilities of these fluctuations occurring, plus quantum mechanical calculation of the electronic coupling and appropriate combination of these ingredients, then yields an expression for the electron transfer rate. For convenience, assumptions are usually made analogous to those of absolute reaction rate theory.[1, 14]

In the case of electron transfers accompanied by simultaneous bond rupture[10] the major fluctuation of interest is in the position of the atom being transferred from reactant to electrode (or vice versa). Theoretical descriptions of these rupture-type electron transfers have focused attention on this particular fluctuation; an improved approximation would take cognizance of the other, less important, fluctuations, too. Analogous remarks apply to electrode processes involving deposition of metal cations.

The probability of finding a reactant or product near the electrode is influenced by interaction of the species with the charges in the electrode double layer (q.v.). The interaction also alters the relative stability of the two forms of the electrochemically active species there, and provides a second effect on the rate of formation of one from the other. Some detailed studies have been made of the influence of the double layer and interpreted largely on the basis of the Frumkin equation.[2, 6] There is therefore a considerable connection between the extensive studies of double layer phenomena at interfaces and those of salt effects on electron transfer rates at the electrode.

When the electron transfer is of the bond rupture-atom transfer type, it is expected to be a sensitive function of the electrode material, for this affects the strength of the metal-atom bond. At any given current, the hydrogen overpotential (q.v.) depends markedly on the electrode material, for example. On the other hand, in the case of electron transfers not involving bond ruptures the theoretical prediction has been made that the exchange current density should be relatively insensitive to the electrode material, provided specific adsorption and electric double layer effects, surface contamination and the presence of oxide layers can be avoided or the data suitably corrected for such phenomena.[1b]

In any field as rapidly expanding as the present one, divergent points of views of authors may often be found. The true experimental test comes as widely different techniques yield similar values for the same rate constants. From the point of view of the developing theory of these processes, any approach should be examined in the light of deductions from quantum and statistical mechanics. Often in treatments of these complicated systesm *ad hoc* assumptions are unwittingly introduced, without being examined from more basic points of view. Fortunately, the ensuing controversies have often given way to profitable clarification of the concepts.

References

1. (a) Cf. Marcus, R. A., "A Theory of Electron Transfer Processes At Electrodes" in Ref. 2, p. 239; (b) *J. Phys. Chem.*, 67, 853 (1963), and references cited therein; (c) Abstracts, 145th National ACS Meeting, New York City (1963).
2. Cf. articles in "Trans. Symposium Electrode Processes, Philadelphia, Pa., 1959," E. Yeager, Ed., New York, John Wiley & Sons, Inc., 1961.
3. E.g., articles in "Modern Aspects of Electrochemistry," Vol. 1, J. O'M. Bockris, Ed., New York, Academic Press, 1954.
4. The equation is based on a first order rate equation for the elementary step of electron transfer. (One instance of a second order equation which has been reported and listed in Ref. 5 is for $2I^- \rightarrow I_2 + 2e$.) Adsorption effects can complicate the law and a measurement of the adsorption isotherm is then needed.
5. Jordan, J., and Stalica, N. R., "Handbook of Analytical Chemistry," L. Meites, Ed., p. 38, New York, McGraw-Hill Book Co., 1963.

6. Cf. articles in "Advances in Electrochemistry and Electrochemical Engineering," Vol. 1, P. Delahay, Ed., New York, Interscience, 1961.
7. Gerischer, H., *Ann. Rev. Phys. Chem.*, 12, 227 (1961).
8. Levich, V. G., "Physicochemical Hydrodynamics," Englewood Cliffs, N. J., Prentice Hall, Inc., 1962.
9. Reinmuth, W. H., in "Advances in Analytical Chemistry and Instrumentation," Vol. 1, C. N. Reilley, Ed., p. 241, New York, Interscience, 1960.
10. Vetter, K. J., "Elektrochemische Kinetische," Berlin, Springer-Verlag, 1961.
11. E.g., Horiuti, J., in Ref. 2; Glasstone, S., Laidler, K. J., and Eyring, H., "The Theory of Rate Processes," New York, McGraw-Hill Book Co., 1941.
12. Tanaka, N., and Tamanushi, R., "Kinetic Parameters of Electrode Reaction," a report to I.U.P.A.C., 1961; copies obtainable from H. Fischer, Dept. of Electrochemistry, Inst. of Technology, Karlsruhe, Germany.
13. See Sutin, N., *Ann. Rev. Nuclear Sci.*, 12, 285 (1962) for a recent review of the data on homogeneous electron transfer reactions.
14. For references to theoretical work of Hush and of Levich and Dogonadze, see *Trans. Faraday Soc.*, 57, 557 (1961) and *Collection Czechoslov. Chem. Communs.*, 26, 193 (1961) (O. Boshko, translator, University of Ottawa, Ont.).

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Cross-references: *Electrode Double Layer; Electrode Reactions, Kinetics; Exchange Current; Nernst Equation; Overvoltage; Tafel Lines; Transfer Coefficient.*

ELECTRO-ORGANIC CHEMISTRY

Electro-organic chemistry is the borderline field between electrochemistry and organic chemistry in which reactions of organic compounds are carried out by means of electrolysis. In the past and today electro-organic processes have been attractive for specific advantages offered. Thus, they have been particularly useful for reactions which cannot be easily carried out by other methods, for example, currently, the fluorination of hydrocarbons (q.v.) and anodic or cathodic coupling reactions or, previously for several years, the reduction of sugar to sugar alcohols (q.v.), which was a commercial process until a catalytic method was developed. A second major advantage of the electrolytic method is the precise control of reaction conditions, notably temperature, time of exposure of the organic reactants in the reaction zone, electrode material and potential, and composition of electrolyte. Perhaps the third major advantage of electro-organic technique is the relative ease of recovery of pure products. For example, in preparing reduction products which are difficult to separate from metal salts, the electrolytic method provides a means of effecting reduction with substantially no contamination of products by metallic reductants.

Experimental apparatus for carrying out electro-organic reactions is very simple, a cell containing two electrodes immersed in the electrolyte, usually with means of agitation and of preventing contact of the products formed at one electrode with the opposite electrode. The electrode at which the reaction is to take place should either be surrounded by the other electrode and equidistant from it at all points, as a cylindrical cathode around a rod anode, or be placed between two electrodes of opposite sign, as a working electrode in the form of a sheet or plate, between two nonworking plates. Agitation is most simply effected by a stirrer within the cell; the electrode may itself be used as stirrer. Such an arrangement is particularly advantageous when stirring at high speeds is desired. Use of a stationary porous electrode, through which electrolyte can be passed into or out of the cell, is equivalent to stirring and sometimes is more effective than simple agitation. In most reductions it is necessary to prevent the products from making contact with the anode at which they may be reoxidized. Commonly this is accomplished by separating the anode and cathode with a porous diaphragm, often Alundum or similar ceramic. On the other hand, the reduction of an oxidation product may be prevented simply by using an inactive cathode, or by setting the current density at a level such that the compound is not reduced. In reactions involving the use of inorganic intermediates, such as hypohalites, reduction may be prevented by the use of calcium or chromium salts which form hydroxides at the cathode. These precipitates behave as diaphragms.

A variety of organic reactions can be carried out electrolytically. Thus, organic compounds themselves may be electrolyzed to form coupled products at the anode as in the case of some salts of aliphatic acids, $2RCOOM + 2F \rightarrow R{-}R + 2CO_2$ (Kolbe synthesis), or to form