ON THE THEORY OF OXIDATION-REDUCTION REACTIONS AND OF RELATED PROCESSES*

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Recent years have witnessed the elucidation of the mechanisms of many organic and inorganic chemical reactions. Several principal factors have contributed to this development. Among these may be listed the detailed kinetic study of numerous reactions, and the use of isotopic tracers, in some cases, to map the migration of specific atoms between the reacting molecules. Another factor is the deep insight into reaction mechanisms afforded by qualitative application of the ideas of modern valence theory, such as those embodied in the conception of the activated complex.

Oxidation-reduction reactions provide typical examples of this trend. Detailed kinetic studies have shown that they frequently involve a number of successive reaction steps. Attention has become focused on the rates and mechanisms of these elementary reactions, some of which are equilibria involving the formation, or disappearance, of the species participating in the actual redox step.

Similar remarks apply to electrode processes, whose slow rate is one cause of overvoltage and of polarographic irreversibility. Detailed studies of the mechanism of these processes, frequently by alternating current techniques, are comparatively fewer, but they have begun to reveal the complexities and trends involved.[1-6] These processes, too, may involve several successive steps, some of which are associated with the formation or disappearance of the reacting particle undergoing electron or atom transfer with the electrode. Isotopic tracer techniques have been employed here also.

Tentatively, one may draw from the studies of redox processes several generalizations that are especially pertinent to the ensuing discussion:

(1) In a homogeneous oxidation of a series of chemically related compounds differing only in some substituent, some correlation usually exists between differences in over-all reaction rate and differences in the standard free energy change of the reaction.[7]

(2) The study of reactions having zero standard free energy change permits a closer evaluation of other factors affecting the reaction rate. Excellent examples of such processes are isotopic exchange reactions[8]

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*This paper, illustrated with lantern slides, was presented at a meeting of the Section on February 5, 1957.

The research described in this paper was supported in part by the Office of Naval Research under Contract No. Nonr 839(09). Reproduction in whole or in part is permitted for any purpose by the United States government.

between ions differing only in their valence state, such as those in EQUATIONS 1 and 2:

$$\mathrm{Fe(H_2O)_6^{*+2} + Fe(H_2O)_6^{+3} = Fe(H_2O)_6^{*+3} + Fe(H_2O)_6^{+2}} \qquad (1)$$

$$\mathrm{Fe(CN)_6^{*-4} + Fe(CN)_6^{-3} = Fe(CN)_6^{*-3} + Fe(CN)_6^{-4}} \qquad (2)$$

(The asterisk in these equations denotes a radioactive ion.) It appears from these studies that ionic size, Coulombic repulsion, and differences in corresponding interatomic distances in the two reactants affect the reaction rate.

(3) Some parallelism appears to exist between the rate at which a material undergoes electrolysis at a given overvoltage and the rate at which it undergoes an isotopic exchange redox reaction. For example, the rate of the isotopic exchange reaction between small hydrated cations is smaller than that between the complex iron cyanide ions.[9-11] Correspondingly, the former form systems less reversible electrochemically.[12] Similarly, the isotopic exchange reaction between the cobalt ammines is slower than that between cobalt ethylenediamines[13] and, again, the former form electrochemically less reversible systems.[14,15]

The mechanism of the actual redox step in a process may be one of electron or atom transfer between the reactants. Generally the reaction kinetics alone cannot distinguish between these two paths. Isotopic tracers have established an atom transfer mechanism in several cases,[16,17] but their use is limited to reactions in which no alternative nonredox path is available for the transfer. For example, the method is inapplicable if the atom, such as the phenolic hydrogen in hydroquinones, is highly labile.

Nevertheless, several approaches based on recent theoretical developments can be tentatively suggested for distinguishing between these two mechanisms in such cases. These will be considered later.

We shall first examine a possible electron transfer mechanism and some of its consequences.

In 1952 Libby[18] applied the Franck-Condon principle to isotopic exchange electron transfer reactions, pointing out that the atoms did not have time to move during the rapid electronic jump. This line of reasoning focused attention on the role played by the co-ordination shells and hydration atmospheres of the two reactants. The more similar the two reactants were in this respect, the less would be the energy barrier to reaction. These ideas were explored in more detail by the present writer, who later formulated a quantitative theory for electron transfer processes. The results of this investigation are outlined in the succeeding paragraphs.

In most chemical reactions, bonds are formed and broken in the critical collision, or activated, complex, and this will generally require a large interaction of the electronic structures of the two reactants. In contrast, only a weak electronic interaction of the reacting molecules may be necessary to couple the reactants electronically and so permit an electron transfer process to occur.

Assuming that these electronic orbitals interact but slightly in the activated complex, I have shown[19] that the latter proceeds through two successive states. These have the same energy and the same atomic configuration, but the first has the electronic configuration of the reactants, and the second has that of the products. This restriction of constant energy is far-reaching and does not obtain in reactions having a large interaction of the orbitals of the two reactants. In those reactions, the electronic configuration of the critical collision complex can sometimes be approximately regarded as consisting of a "quantum mechanical resonance" between two strongly interacting electronic structures (that of the reactants and that of the products). These two resonance structures have the same atomic configuration but, usually, they do not have the same energy.

It followed from the atomic configuration-energy restriction that a reorganization of the entire atomic configuration is necessary to form a collision complex satisfying this restriction. To compute the free energy of reorganization, and hence the probability of formation of the reorganized state, expressions were first deduced for the properties of such nonequilibrium systems. The usual electrostatic formulas could not be used, and equations appropriate for these "disorganized" states of dielectric medium were derived.[20] An infinite number of atomic configurations can satisfy the restriction. The most probable set of configurations was obtained by minimizing the free energy of reorganization, subject to the restriction of constant energy. This information permitted the determination of the properties of the most probable state of the critical collision complex, including its free energy of formation from the reactants.

The expression obtained for the rate constant k of the electron transfer step is given by the following set of equations:[19]

$$k = pZe^{-\Delta F^*/RT} \tag{3}$$

where Z is the collision frequency of two uncharged molecules in solution and p is the probability of occurrence of an electron transfer during the lifetime of the activated complex (10^{-13} sec.). The quantity p was assumed to be of the order of unity in preliminary applications and some evidence in favor of this was cited. ΔF^* is given by:

$$\Delta F^* = m^2\lambda + e_1^* e_2^* / D_s r \tag{4}$$

where

$$2m + 1 = -[\Delta F^\circ + (e_1 e_2 - e_1^* e_2^*)/D_s r]/\lambda \tag{5}$$

and

$$\lambda = \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right)(\Delta e)^2 \left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \tag{6}$$

In these equations, e_1^* and e_2^* are the charges of the reactants, e_1 and e_2 are those of the products. As a result of reaction, the change in charge of reactant 1, Δe, is $(e_1 - e_1^*) = (e_2^* - e_2)$. The effective radii of the reactants, a_1 and a_2, were discussed. For complex ions and small hydrated metal cations they are the radii of spheres enclosing the first co-ordination shell. The standard free energy change of the electron transfer step in the reaction is $\Delta F°$. The factor r, the distance between the centers of the reactants in the collision complex, was discussed and set equal to its minimum value $(a_1 + a_2)$. D_{op} is the square of the refractive index of the solvent, while D_s is the static dielectric constant.

Application[21] of these equations to isotopic exchange reactions was particularly instructive. The agreement between the experimental and theoretical results using no adjustable parameters was excellent for tightly knit covalently bound ions. For example, $\Delta F^*_{expt.}$ was[9] 12.7 kcal. mol^{-1} for the $Fe(CN)_6^{-4}$ – $Fe(CN)_6^{-3}$ reaction, while the calculated value was 10.1 kcal. mol^{-1}. In the MnO_4^{-2} – MnO_4^{-1} reaction $\Delta F^*_{expt.}$ was[22] 12.8 kcal. mol^{-1} and $\Delta F^*_{calc.}$ was 9.2 kcal. mol^{-1}. On the other hand, the agreement for small hydrated cations was reasonable, but not as good. For $Fe(H_2O)_6^{+2}$ – $Fe(H_2O)_6^{+3}$, $\Delta F^*_{expt.}$ equals[10] 16.3 and $\Delta F^*_{calc.}$ is 9.8 kcal. mol^{-1}. For $Co(H_2O)_6^{+2}$ – $Co(H_2O)_6^{+3}$, $\Delta F^*_{expt.}$ equals[11] 16.4 and $\Delta F^*_{calc.}$ is 9.9 kcal. mol^{-1}.

In the derivation of these equations each ion was treated as a sphere, inside of which no changes in interatomic distances occurred during the reaction. This assumption appears to be a reasonable one when the central atom in the ion is covalently bound to its ligands in both valence states, and therefore is less valid for the aquo ions. More recently, this assumption was eliminated[23] and a more detailed calculation was made incorporating, in a basic way, these changes in interatomic distances in the formation of the activated complex. The approximate *a priori* value computed for $\Delta F^*_{calc.}$ for both the $Fe(H_2O)_6^{+2}$ – $Fe(H_2O)_6^{+3}$ and $Co(H_2O)_6^{+2}$ – $Co(H_2O)_6^{+3}$ reactions was 18 kcal. mol^{-1}.

Experiments measuring the difference between the rate constants of an isotopic exchange reaction in water and in heavy water have been of particular interest. It was found experimentally[24] that the rate constants of the exchange reactions $Fe(H_2O)_6^{+2}$ – $Fe(H_2O)_6^{+3}$ and $Fe(H_2O)_6^{+2}$ – $Fe(H_2O)_5OH^{+2}$ were about twice as fast in water as in heavy water. An appreciably higher rate constant in water was also observed[25] for the NpO_2^+ – NpO_2^{+2} reaction. Since the two solvents have similar values of both D_s and D_{op}, a reason for this behavior must be sought elsewhere.

Two explanations can immediately be offered; one of these[21] is an application of the refinement of the theory discussed previously. Some change must occur in the interatomic O-H distances in these processes. (The NpO_2^+ and NpO_2^{+2} ions are also partially hydrated.) It can be shown that such changes occur more easily for O-H bonds than they do for O-D bonds because of the former's larger zero-point vibrational energy. However, a hydrogen (deuterium) atom transfer mechanism would also be consistent[24] with the data. These considerations were used[21] to propose tentatively a diagnostic test for distinguishing a small-overlap electron transfer mechanism from an atom transfer process where the atom transferred was not a hydrogen. Probable examples of such systems included halide ion-catalyzed isotopic exchange reactions between metal aquo ions.

Recently, a theory of overvoltage has been formulated[26] using the same basic assumptions as those employed in the redox theory, but taking into account the special conditions prevailing at electrode interfaces. The final equations deduced for the rate constant of the electron transfer step at the electrode bear a strong resemblance to EQUATIONS 3 to 6. The major differences are that Z becomes the number of collisions per second of an uncharged particle with unit area of the electrode; the Coulombic terms $e_1^* e_2^*/D_s r$ and $e_1 e_2/D_s r$ are replaced by appropriate terms for the work required to transport the central ion in its initial and in its final states to the electrode-solution interface; ΔF° is replaced by the "activation" overvoltage (the part of the overvoltage due to the slowness of the electron transfer step), λ has one-half its value in EQUATION 6, and a_1 equals a_2. Any changes in interatomic distances within the central ion during the entire process can be incorporated into the theory in a way similar to that employed[23] for homogeneous redox reactions.

When there is no concentration polarization this expression immediately gives the absolute value of the current density as a function of overvoltage. Application[26] to some redox systems, including the conversion of ferrous to ferric ion and of ferrocyanide to ferricyanide ion, gave satisfactory quantitative agreement with recent data.

There is a very strong parallelism between the theoretical equations noted earlier for electrode processes and those for homogeneous redox reactions, when the former occurs at zero overvoltage and the latter is an isotopic exchange having zero ΔF° (and a_1 equal to a_2). This suggests that it will be interesting to explore more quantitatively the relationship between the rates of various isotopic exchange reactions and of electrode processes involving corresponding ions. Some data available for such a comparison have been referred to earlier, and preliminary results in this direction are encouraging. A detailed and extensive comparison would be particularly desirable. Should this parallelism, modified by the small difference in theoretical equations, be established extensively, then this would be suggestive evidence for a "small-overlap"[19] electron transfer mechanism for both processes.

Evidence has been presented to show that the electrochemical reduction[27,1] and oxidation[28] of some organic compounds occur via an electron transfer with the electrode, rather than as the result of reaction with nascent hydrogen or oxygen, which might be present at the electrode surface. Nevertheless, it seems likely that with certain possible exceptions the *homogeneous* oxidation-reduction of most organic compounds will possess an atom transfer mechanism.[29,30] Tracer studies have definitely established a mechanism of this nature in a number of cases.[17] Some possible exceptions are those organic redox reactions in which each of two reactants forms a more-or-less reversible electrochemical system. This has been assumed[31] on occasion. Partly for this reason, the recent detailed kinetic studies[7,32,33] of the homogeneous oxidation of a series of hydroquinone-like compounds by various oxidizing agents such as ferric ion or molecular oxygen have been of particular interest. In both cases, the data were consistent with two postulated reaction sequences. The redox step in one was an electron transfer; that in the other, an atom transfer. Application of EQUATIONS 3 to 6 to these systems is rather approximate since the charge distribution on the organic compound is far from spherical (in the electron transfer mechanism the active reagent is the negatively charged hydroquinone ion). The extension of the theory to such molecules has been discussed elsewhere.[34] The agreement between the experimental and calculated results is reasonable, but additional refinements are in progress. In these reactions, too, it would seem desirable to study in a detailed, comparative way the rates of homogeneous and electrochemical redox processes.

Crystallographic studies have also contributed to the understanding of redox reactions. For example, utilizing Libby's application of the Franck-Condon principle to electron transfer reactions, Brown[35] has pointed out that the slowness of the $Co(NH_3)_6^{+2} - Co(NH_3)_6^{+3}$ exchange reaction may be due to the large difference in Co-N bond lengths in the two reactants. A theoretical computation of the contribution of this effect on the reaction rate involves a knowledge not only of the interatomic bond distances, but also of the force constants of these bonds. Neither of these properties is known for most of the reagents whose isotopic exchange reactions have been investigated. Crystallographic and spectroscopic studies of these systems promise to be of definite interest.

A major question in electron transfer reactions is the ease with which an electron can jump from one reactant to the other when there exists a suitable atomic configuration satisfying the constant energy restriction. Some calculations[21] based upon earlier estimates[36] have suggested that this process could occur with relative ease, that is, that p in EQUATION 3, for example, was of the order of 1 to 0.01. However, a more direct estimate would be desirable. The electron transferred from an occupied electronic orbital of one reactant to a vacant electronic orbital of the other. The rate at which this process occurs in an appropriate atomic configuration depends upon the extent of overlap of the two orbitals. Some measure of this can perhaps be inferred from the interaction of two occupied orbitals in adjacent hydrated ions in a crystal lattice. A quantitative measure of this interaction is derived from the interaction of the electron spins in the two ions, which in turn determines certain magnetic properties. Thus, an adequate quantitative theory for the latter phenomena may effectively contribute to the solution of the electron transfer problem.

One other example of electron transfer processes may be singled out for special mention. The visible and ultraviolet absorption spectra of halide ions in aqueous solution differ quite markedly from those in crystals. The absorption process was interpreted[37] in terms of an electron transfer from the ion to the adjacent solvent. Applying the Franck-Condon principle and detailed electrostatic considerations to the problem, Platzman and Franck[37] obtained excellent agreement between experimental and calculated positions of the absorption bands. This theory is also indirectly pertinent to the theory of the transfer of an electron from a univalent anion to an oxidizing agent,[34] since both quantitative formulations have certain assumptions in common.

In conclusion, it can be said that an understanding of electron transfer processes certainly will not be gained by the application of a single technique. Instead, the use of kinetic, electrochemical, crystallographic, magnetic, and spectroscopic methods will each contribute to the solution of the problem. This general field, therefore, promises to be a fruitful one for increased co-operation between physical chemists, organic chemists, and physicists.

References

1. BOCKRIS, J. O'M. 1954. Electrode kinetics. *In* Modern Aspects of Electrochemistry. : 180-276. J. O'M. Bockris, Ed. Academic Press. New York, N. Y.
2. KIVALO, P. 1954. Polarographic Processes Involving Chemical Reaction of the Product of the Electron Transfer Reaction. Thesis. Abo Akademi. Abo, Finland.
3. KIVALO, P. 1955. Polarographic processes involving chemical reaction of the product of the electron transfer reaction. Acta Chem. Scand. **9**: 221.
4. KIVALO, P., K. B. OLDHAM & H. A. LAITINEN. 1953. Verification of a theory of irreversible polarographic waves. J. Am. Chem. Soc. **75**: 4148.
5. DELAHAY, P. J. 1953. Unified theory of polarographic waves. J. Am. Chem. Soc. **75**: 1430.
6. EVANS, M. G. & N. S. HUSH. 1952. Ionogenic reactions involving bond breaking at electrodes. J. chim. phys. **49**: C159.
7. BAXENDALE, J. H. & S. LEWIN. 1946. The aerobic oxidation of leuco phenolindophenols. Trans. Faraday Soc. **42**: 126. These authors also summarize earlier correlations.
8. ZWOLINSKI, B. J., R. J. MARCUS & H. EYRING. 1955. Inorganic oxidation-reduction reactions in solution. Electron transfers. Chem. Revs. **55**: 157.
9. WAHL, A. C. & C. F. DECK. 1954. Rate of the ferrocyanide-ferricyanide exchange reaction. J. Am. Chem. Soc. **76**: 4054.
10. SILVERMAN, J. & R. W. DODSON. 1952. The exchange reaction between the two oxidation states of iron in acid solution. J. Phys. Chem. **56**: 846.
11. BONNER, N. A. & J. P. HUNT. 1952. The exchange reaction between cobaltous and cobaltic ions in perchloric acid solution. J. Am. Chem. Soc. **74**: 1866.

12. RANDLES, J. E. B. & K. W. SOMERTON. 1952. Kinetics of rapid electrode reactions. Part 3. Electron exchange reactions. Trans. Faraday Soc. **48**: 937.
13. LEWIS, W. B., C. D. CORYELL & J. W. IRVINE, JR. 1949. The electron transfer between cobaltous and cobaltic ammine complexes. J. Chem. Soc. Suppl. No. 2. : 386.
14. LAITINEN, H. A. & P. KIVALO. 1953. Polarographic reduction of hexamminecobalt (III) ion. II. The effect of complexing agents. J. Am. Chem. Soc. **75**: 2198.
15. GRIEB, M. W. 1953. Ph.D. Thesis. Univ. Ill. Urbana, Ill.
16. TAUBE, H. 1955. Anions as bridging and nonbridging ligands in reactions of Co (III) compounds with Cr^{++}. J. Am. Chem. Soc. **77**: 4481.
17. BARTLETT, P. D. & J. D. MCCOLLUM. 1956. Hydride transfer mechanisms in strongly acid media. The reduction of carbonium ion by alcohols and an evaluation of the basic strength of isopropyl alcohol. J. Am. Chem. Soc. **78**: 1441.
18. LIBBY, W. F. 1952. Theory of electron exchange reactions in aqueous solution. J. Phys. Chem. **56**: 863.
19. MARCUS, R. A. 1956. On the theory of oxidation-reduction reactions involving electron transfer. I. J. Chem. Phys. **24**: 966.
20. MARCUS, R. A. 1956. Electrostatic free energy and other properties of systems having nonequilibrium polarization. I. J. Chem. Phys. **24**: 979.
21. MARCUS, R. A. 1957. On the theory of oxidation-reduction reactions involving electron transfer. II. Applications to data on the rates of isotopic exchange reactions. J. Chem. Phys. In press.
22. SHEPPARD, J. C. & A. C. WAHL. 1953. Rate of the electron-transfer exchange reaction between manganate and permanganate ions. J. Am. Chem. Soc. **75**: 5133.
23. MARCUS, R. A. 1956. On the theory of oxidation-reduction reactions. Paper presented at the Southwide Chem. Conf. Am. Chem. Soc. Memphis, Tenn.
24. HUDIS, J. & R. W. DODSON. 1956. Rate of ferrous-ferric exchange in D_2O. J. Am. Chem. Soc. **78**: 911.
25. HINDMAN, J. C. 1956. Kinetics of the exchange reactions between Np(V) and Np(VI) ions. Paper presented at the Southwide Chem. Conf. Am. Chem. Soc. Memphis, Tenn.
26. MARCUS, R. A. 1957. On the theory of overvoltage and of polarographic irreversibility. J. Chem. Phys. To be submitted for publication.
27. STACKELBERG, M. VON & P. WEBER. 1952. Does cathodic reduction (hydrogenation) of organic compounds in aqueous solution occur through atomic hydrogen or through electrons? Z. Elektrochem. **56**: 806.
28. MUKAIBO, T. & M. OIKAWA. 1952. Electrolysis of organic substances. I. Electrolytic oxidation of lactose in the presence of bromide salts. J. Electrochem. Soc. Japan. **20**: 108.
29. WESTHEIMER, F. H. 1954. "One-electron" and "two-electron" oxidation-reduction reactions in inorganic and organic chemistry. *In* Mechanism of Enzyme Action. : 321-352. W. D. McElroy & B. Glass, Eds. Johns Hopkins Univ. Press. Baltimore, Md.
30. LEVITT, L. S. 1955. The common basis of organic oxidations in acidic solution. J. Org. Chem. **20**: 1297.
31. DOERING, W. VON E. & T. C. ASCHNER. 1953. Mechanism of the alkoxide-catalyzed carbinol-carbonyl equilibrium. J. Am. Chem. Soc. **75**: 393.
32. BAXENDALE, J. H., H. R. HARDY & L. H. SUTCLIFFE. 1951. Kinetics and equilibria in the system ferrous ion + ferric ion + hydroquinone + quinone. Trans. Faraday Soc. **47**: 963.
33. BAXENDALE, J. H. & H. R. HARDY. 1954. Kinetics and equilibria in solutions containing ferrous ion, ferric ion and some substituted hydroquinones and quinones. Trans. Faraday Soc. **50**: 808.
34. MARCUS, R. A. 1957. On the theory of oxidation-reduction reactions involving electron transfer. III. Applications to data on the rates of organic redox reactions. J. Chem. Phys. In press.
35. BROWN, H. C. 1952. (In a discussion to a symposium on electron transfer reactions.) J. Phys. Chem. **56**: 868.

36. MARCUS, R. J., B. J. ZWOLINSKI & H. EYRING. 1954. The electron tunnelling hypothesis for electron exchange reactions. J. Phys. Chem. **58**: 432.

37. PLATZMAN, R. & J. FRANCK. 1954. The role of the hydration configuration in electronic processes involving ions in aqueous solution. Z. Physik. **138**: 411.