Free Energy and the Rate of Chemical Reactions The Relation Between the Rate and OxidationReduction Potentials

Harold Gershinowitz

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The Relation Between the Rate and Oxidation-Reduction Potentials

HAROLD GERSHINOWITZ, *Department of Chemistry, Columbia University*
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The theories of the rates of chemical reactions previously developed by Eyring, Rice and the author give a relationship between the rate of reaction and the free energy of formation of the activated state. With the aid of this relation it is possible to explain the experimental data which have shown that there is a connection between the rates of oxidation-reduction reactions and the potentials of the reagents used.

I. INTRODUCTION

SOME years ago, Conant and his co-workers[1] pointed out that there was a definite relationship between the rate of an irreversible oxidation-reduction reaction and the oxidation-reduction potentials of the reagents that are used. With the aid of some assumptions concerning the mechanism of such reactions, they were able to derive an equation relating the relative rates of reaction with two different reagents with the normal potentials of these reagents. It was found that the agreement with experimental data was satisfactory. The studies of Conant and his collaborators have been continued and extended by Chow,[2] who also has found that a relationship between oxidation reduction potentials and the rates of some reactions can be expressed by a simple empirical equation. This work has made it evident that there exists some connection between the kinetic rate constant and thermodynamic quantities. Such a conclusion is also indicated by the data in the fields of acid and basic catalysis.

Until quite recently, there seemed to be no theoretical justification of the existence of such relationships. The collision theory of the rates of chemical reactions had no connection with thermodynamics. Within the past year, however, Eyring, Rice and the author[3] have developed theories of the absolute rates of chemical reactions which serve to relate the data of kinetics with thermodynamic quantities. O. K. Rice and the author have shown how one may determine the absolute rates of unimolecular decompositions and bimolecular associations from the entropy change involved in the reactions. Wynne-Jones and Eyring[4] have related the abnormal rates of some reactions in solution to the entropy of formation of an "activated complex." The rate can also be simply related to the free energy change involved in the formation of an activated state. Since the free energy change and the e.m.f. are directly proportional, it is possible to obtain a theoretical derivation of a relation between the rate of a reaction and the oxidation-reduction potentials of the reagents involved. In the following, we shall borrow freely from the notation and terminology of Eyring and his co-workers as well as those of Rice and the author, in accordance with the method used in reference 3c.

II. THE RELATION BETWEEN THE SPECIFIC RATE CONSTANT AND OXIDATION-REDUCTION POTENTIALS

It has been shown that the rate of a chemical reaction is given by the concentration of the reacting systems in a certain fraction of the total phase space that is available to the systems, multiplied by the velocity with which the systems are passing through this region.[3] The configuration of the reacting molecules which corresponds to this region of phase space may be called the activated complex. That is, if one wishes to describe the particles in the systems by

[1] Conant, Chem. Rev. **3**, 1 (1926); Conant and Pratt, J. Am. Chem. Soc. **48**, 3178, 3220 (1926), and earlier papers.
[2] Chow and Kammerling, J. Biol. Chem. **104**, 69 (1934); Chow, J. Am. Chem. Soc. **56**, 894 (1934); ibid. **57**, 1437, 1440 (1935).
[3] (a) Eyring, J. Chem. Phys. **3**, 307 (1935); (b) O. K. Rice and H. Gershinowitz, ibid. **2**, 857 (1934) and (c) ibid. **3**. 479 (1935).

[4] (a) Wynne-Jones and Eyring, J. Chem. Phys. **3**, 492 (1935); see also (b) Evans and Polanyi, Trans. Faraday Soc. **21**, 875 (1935).

means of their coordinates and momenta, the concept of position in phase space is used. If one prefers to describe the particles by means of their coordinates and potential energies, one speaks of the activated complex. It has been shown that the two methods give the same results. The velocity of these systems or activated complexes, expressed in units of cells of phase space of size h per second, is kT/h, where T is the absolute temperature and k and h are the Boltzmann and Planck constants, respectively. If (C) is the concentration of activated complexes per unit length h, the specific rate of any reaction is given by

$$k_1 = (C)kT/h = (C) \cdot v, \tag{1}$$

where we write v for kT/h in order to simplify the writing of subsequent equations.

Now if we represent the equilibrium reaction by which the activated complex is formed as

$$nA + mB \rightleftharpoons C \tag{2}$$

the equilibrium constant for the reaction is

$$K = (C)/(A)^n(B)^m. \tag{3}$$

At unit concentration of reactants $K = (C)$ and the specific rate constant becomes[4]

$$k_1 = K \cdot v. \tag{4}$$

From thermodynamics we get the relation

$$\ln K = -\Delta F^*/RT, \tag{5}$$

where ΔF^* is the free energy of formation of the activated state. Substituting for K in (4),[5]

$$k_1 = \exp(-\Delta F^*/RT) \cdot v. \tag{6}$$

In general, ΔF^* is not the same as ΔF, the free energy change for the total reaction. The calculations of the absolute rates of unimolecular decompositions and bimolecular associations in the gas phase[3b, c] indicated that the entropy change for the formation of the activated state is, in most cases, equal to zero for the decompositions and equal to the entropy change for the total reaction in the case of the associations, i.e., the activated state has approximately the same entropy as the normal associated molecule. The calculations of Wynne-Jones and Eyring[4]

show that for many reactions in solution, also, the entropy change for the formation of the activated complex is equal to the total entropy change in the reaction. For the free energy change in such reactions to be equal to the free energy of formation of the activated complex, it would be necessary that the energy of formation of the activated state be equal to the energy of the reaction. This will be so only if the energy of activation of the reverse reaction is zero, since the energy change for the reaction is equal to the difference of the activation energies of the forward and reverse reactions.[6] We see, therefore, that the free energy of formation of the activated state will rarely be equal to the free energy change for the total reaction.[7] It is this fact that has obscured the relation between free energy and the rate of reaction.

For a reversible reaction, we have the relation

$$\Delta F^* = -nFE^*, \tag{7}$$

where n is the number of equivalents, F the Faraday and E^* the e.m.f. for the reaction by which the activated complex is formed. Substituting (7) in (6) we have, finally,

$$k_1 = \exp(nFE^*/RT) \cdot v. \tag{8}$$

With Eq. (8) as a basis, we can now determine the relation between the potential of a reagent and the rate of a reaction. For organic oxidations, Conant and Pratt proposed the following mechanism

$$ROH + B \rightleftharpoons RO^- + BH$$
$$RO^- \rightarrow R = 0. \tag{9}$$
$$|$$
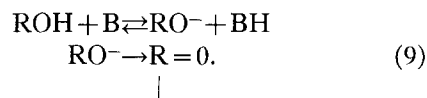
This type of reaction can readily be treated by the theoretical method that we have just proposed. An added advantage of such a treatment is that, in order to obtain relative rates, it is not necessary to assume as particular a mechanism

[5] A similar relation between the free energy and the reaction rate has been obtained by V. K. La Mer (J. Chem. Phys. 1, 291 (1933), Eq. (10) et seq.), by means of thermodynamic analogies from Tolman's general expression for the temperature coefficient of the rate of reaction. The most important difference lies in the fact that in the expression we have derived there is no arbitrary constant, since we have obtained directly the integrated form of the expression for the specific rate constant so that there is no question of an undetermined constant of integration.

[6] Gershinowitz and Rice, J. Chem. Phys. 2, 273 (1934).

[7] There does seem to be at least one reaction for which the free energy change that determines the rate of the reaction is the same as the total change in free energy. This is the autoxidation of hydroquinone, catalyzed by manganous salts in acid solutions, studied by La Mer and Temple (Proc. Nat. Acad. Sci. 15, 191 (1929)).

as that which Conant and Pratt used to explain the relation between e.m.f. and the rate of reaction. If one does however, postulate a definite mechanism, it becomes possible to calculate not only the relative rates, but also the absolute values of the rate constants. It is also possible to extend the theoretical equations to include the more complex systems studied by Chow.

Let us assume that we have a substance A which is to be oxidized by some reagent B, and that the activated complex C consists of some oxidized form of A, say A', and B', the reduced form of B. At this point it is not necessary to know the further mechanism of the reaction, or whether the oxidized form of the molecules A is a single molecule or a polymolecular complex. All that we need know is that the rate determining step for the reaction is the passing of this complex through a certain region of phase space, no matter whether the motion represents a unimolecular rearrangement or some bimolecular or polymolecular change. The change in potential involved in the formation of the activated state is

$$E^* = E_{A'} - E_A + E_{B'} - E_B. \qquad (10a)$$

At unit concentration of reactants

$$E_{B'} - E_B = E_{0B}, \qquad (10b)$$

where E_{0B} is the normal oxidation-reduction potential of B. Hence, from Eq. (7),

$$k_1 = \exp\ (nF(E_{A'} - E_A + E_{0B})/RT) \cdot v. \qquad (11)$$

If instead of B, we used some other oxidizing agent D, the rate would be given by

$$k_1' = \exp\ (mF(E_{A'} - E_A + E_{0D})/RT) \cdot v. \qquad (12)$$

If $n = m$,

$$k_1/k_1' = \exp\ [(E_{0B} - E_{0D})nF/RT] \qquad (13a)$$

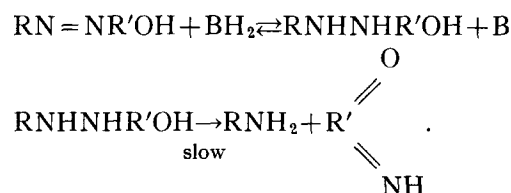or $\quad \ln\ (k_1/k_1') = [E_{0B} - E_{0D}] \cdot nF/RT. \qquad (13b)$

By substituting numerical values for the universal constants, and letting $n = 2$, as in some cases studied by Conant and Pratt,

$$0.03 \log\ (k_1/k_1') = E_{0B} - E_{0D}. \qquad (14)$$

This equation is identical with Eq. (11) of Conant and Pratt, which was found to give satisfactory agreement with the experimental

data. We see that this relationship is a direct consequence of the new theories of the absolute rate of chemical reactions, and that it may be derived without assuming the unimolecular mechanism that Conant *et al.* found it necessary to use.

An essential distinction between the method we have used and that employed by Conant and his co-workers is involved in the nature of the equilibrium processes. Conant and Pratt,[8] for example, assume the following mechanism for the reduction of an azo dye,

$$RN = NR'OH + BH_2 \rightleftharpoons RNHNHR'OH + B$$

$$RNHNHR'OH \xrightarrow[\text{slow}]{} RNH_2 + R' \overset{\displaystyle O}{\underset{\displaystyle NH}{\big\backslash\!\!\backslash}}\ .$$

The second of these reactions is the one that may be considered to go through an activated complex. But according to the method that we have used, it does not matter how many intermediate steps there are between this step and the initial reactants. As long as the activated complex is the same, the rate of the reaction will depend only on the potential of the reducing agent. Rice[9] has made clear the distinction between flux equilibrium and "back and forth" equilibrium. In the theory of the activated complex the complex is in flux equilibrium with the normal reactants. This is why an apparently equilibrium method can give information about rates of reactions that are not in equilibrium. It is the free energy of the state of the system that is in flux equilibrium that determines the rate of the reaction. All the intermediate configurations that are in "back and forth" equilibrium will drop out of the calculation. It is thus clear that the method of the activated complex is more complete and rigorous than that used by Conant, which is a special case, and that it will explain all the data that the latter will. This explicit definition of the nature of the activated complex also distinguishes this treatment from that based on the Bronsted-Bjerrum type of complex, which is not rigorously defined.

Chow has found that it is possible to explain

[8] Conant and Pratt, J. Am. Chem. Soc. **48**, 2464 (1926).
[9] O. K. Rice, J. Phys. Chem. **4**, 53 (1936).

the experimental data for the kinetics of various oxidation-reduction reactions by means of a simple empirical relationship which he has proposed, namely

$$\text{rate} \propto \exp{(nFE/3RT)}. \tag{15}$$

Using this equation, he has obtained good agreement with the data on the catalytic absorption of oxygen by linseed oil, and the oxidation of formate and oxalate ions by halogens in the dark. While the general form of this relation is that which would be expected from Eq. (8), it seems rather difficult to construct a mechanism for the formation of the activated complex which would give the exact dependence on the potential that is given by Chow. It is possible to construct several mechanisms that give the relation, rate $\propto \exp{(nFE/2RT)}$, but while these give good constants within a run, they do not give good results from run to run. From the data it would seem that a dependence on $(nFE/3RT)$ is actually demanded. Such a relation can be obtained from a mechanism which demands the formation of a complex from three equivalents of the reagent. It would seem that more data are needed to help decide what is the nature of the activated complex. A step in this direction is afforded by the recent work of Abel and Schmid,[10] who have obtained indirect spectroscopic evidence of the presence of the ion $[CO_2CO_2^-]$ in the oxidation of oxalate ion by iodine.

III. DISCUSSION

Bancroft and Magoffin[11] have recently discussed the role played by excited energy levels in electrochemical processes. The method which they have used may be correlated with that of Conant by means of the approach used above. They state that the concept of an intermediate energy level which they use is quite different from the assumptions of a reversible electrolytic process and a practically irreversible nonelectrolytic one made by Conant and his collaborators. From the treatment we have given, however, it may be seen that both methods are essentially the same, being qualitative descriptions, in different words, of the fact that the rate of reaction is determined by the concentration of an intermediate configuration of the system, which is in equilibrium with the reactants.

The development of rigorous thermodynamics and the kinetic theory explanation of the rates of chemical reactions served to discredit the idea, prevalent since the time of van't Hoff, that the rate of a reaction should be determined by the free energy change. The theories of reactions recently developed, which take into account all the degrees of freedom of the reacting molecules, especially in the form developed by Eyring, which makes explicit use of an activated complex, show that the rate of a reaction is determined by a free energy change, which is usually not the same as the free energy change for the total reaction. The theory of Bronsted and Bjerrum, which introduced an intermediate complex, explained some of the relationships between rates and quantities usually associated with equilibrium measurements. La Mer has shown the relation between the free energy change and the concept of the critical complex.[5] In these treatments, however, there still remained arbitrary constants. Wynne-Jones and Eyring and Evans and Polanyi[4] have shown quantitatively the relation between the theory of Bronsted and Bjerrum and the general theory of the activated complex which applies to gas phase reactions, as well as to reactions in solution. The regularities observed for oxidation-reduction reactions and for acid and basic catalysis should no longer be considered as isolated phenomena, but as being manifestations of the existence of some critical configuration of the·reactants. This relation between the two types of reaction helps to explain why Abel and Hilferding[12] were able to describe formally the reaction between oxalate ion and iodide ion as either an oxidation-reduction reaction or a reaction catalyzed by H^+. Also, as Bancroft and Magoffin have remarked, there is no need to make any fundamental distinction between hydrogenation and reduction. It should now be possible to treat all reactions, homogeneous or heterogeneous, by the same theoretical methods.

[10] Abel and Schmid, Naturwiss. **23**, 501 (1935).
[11] Bancroft and Magoffin, J. Am. Chem. Soc. **57**, 2561 (1935).

[12] Abel and Hilferding, Zeits. f. physik. Chemie **A172**, 353 (1935).