

## On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. III. Applications to Data on the Rates of Organic Redox Reactions\*

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A recently developed theory of oxidation-reduction reactions (Part I) is used to calculate the rates of organic redox reactions whose mechanism involves the transfer of an electron from one reactant to the other. The theory can be used to discuss factors affecting the rates of these reactions. These factors include a standard free energy of reaction, the Coulombic interaction of the ionic charges of the reactants, and the solvation of the charged reactants. Attention is focused on the relation between the rate of the redox step in the over-all process and the standard free energy change,  $\Delta F^\circ$ , of this step, rather than on the more usual but less fundamental one between the corresponding quantities of the over-all process itself.

An approximate method is described for applying the theory to a molecule whose charge is not located at its center. Essentially all organic molecules lie in this category.

As an example of these considerations, several typical reactions are discussed. These reactions involve the oxidation of a series of hydroquinones by ferric ions and of a series of leucoindophenols by dissolved oxygen. They are assumed to possess electron transfer, rather than atom transfer, mechanisms. Free energies and entropies of activation of the redox step are calculated using the theoretical equation. The calculated results are considered to be in reasonable agreement with the experimental data, no adjustable parameters being employed.

### INTRODUCTION

IN the preceding paper of this series<sup>1</sup> reactions were discussed in which the standard free energy change of the elementary electron transfer step in a redox reaction was zero. Studies of these reactions permitted the importance of several other factors to be evaluated, factors such as Coulombic repulsion of ionic reactants and<sup>2</sup> the solvation of these ions. On the other hand, this leaves unconsidered a question of considerable chemical interest, namely the relation between the chemical structure and the reactivity of each member of a series of chemically related compounds toward some reagent.<sup>3</sup> One of the purposes of the present paper is to discuss the qualitative and quantitative theoretical features of such a reaction series. In general the over-all reaction may involve several steps, one of which is the redox step. Attention will be focused on the relation between the rate constant of this elementary redox step and the standard free energy of that step, rather than on the more usual but less fundamental relation between the rate constant of the over-all reaction and the over-all standard free energy change. The discussion will be based on the theory of electron transfer reactions developed in a preceding paper of this series.<sup>4</sup>

For the purposes of this discussion it is desirable to select a redox reaction of a series of chemically related organic compounds whose kinetics has been studied in

detail. The choice of reaction is somewhat restricted by the fact that many organic redox reactions do not possess an electron transfer mechanism. Accordingly, some current ideas on the mechanism of organic redox reactions will first be mentioned briefly.

One major contribution to the understanding of these reactions was made by Michaelis in his studies on the oxidation of hydroquinones to quinones. In these reactions two electrons are ultimately transferred from the organic compound to the oxidizing agent. It was formerly believed that this could only happen in one step. However, Michaelis and his co-workers<sup>5</sup> obtained considerable evidence for the intermediate formation of free radicals, semiquinones, which arise from the loss of only one electron by the organic compound. On the basis of this evidence, he formulated his theory of "compulsory univalent oxidation," which postulated that reactions proceed by way of univalent oxidation steps. Various kinetic data on the oxidation of hydroquinones support this postulate for these systems.<sup>6-8</sup>

Nevertheless, it is now known that *many other types* of organic redox reactions proceed by way of a hydride transfer.<sup>9</sup> This involves the simultaneous transfer of two electrons plus a proton, and no intermediate free radical is produced. It is clear that Michaelis' postulate does not have general applicability. It has been remarked that

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<sup>1</sup> R. A. Marcus, *J. Chem. Phys.* **26**, 867 (1957), hereinafter referred to as Part II.

<sup>2</sup> W. F. Libby, *J. Phys. Chem.* **56**, 863 (1952).

<sup>3</sup> A summary of references on the empirical relation between the over-all reaction rate and some quantity loosely related to the standard free energy of the over-all reaction has been given by J. H. Baxendale and S. Lewin, *Trans. Faraday Soc.* **42**, 126 (1946).

<sup>4</sup> R. A. Marcus, *J. Chem. Phys.* **24**, 966 (1956), hereinafter referred to as Part I.

<sup>5</sup> See review articles: L. Michaelis and M. P. Schubert, *Chem. Revs.* **22**, 437 (1938); L. Michaelis, *Trans. Electrochem. Soc.* **71**, 107 (1939); *Ann. N. Y. Acad. Sci.* **40**, 39 (1940). E. A. H. Friedheim and L. Michaelis, *J. Biol. Chem.* **91**, 355 (1931); B. Elema, *Rec. trav. chim.* **50**, 807 (1931); *ibid.*, **52**, 569 (1933).

<sup>6</sup> J. H. Baxendale and S. Lewin, *Trans. Faraday Soc.* **42**, 126 (1946).

<sup>7</sup> Baxendale, Hardy, and Sutcliffe, *Trans. Faraday Soc.* **47**, 963 (1951).

<sup>8</sup> J. H. Baxendale and H. R. Hardy, *Trans. Faraday Soc.* **50**, 808 (1954).

<sup>9</sup> See P. D. Bartlett and J. D. McCollum, *J. Am. Chem. Soc.* **78**, 1441 (1956), and references contained therein.

his postulate is strongly supported where free radical intermediates are probable and where the redox potential can be measured electrochemically.<sup>10</sup>

As in Part II, a major question of interest is whether the redox step in the reaction involves the transfer of an atom (or groups of atoms) between the reactants or whether an electron transfer is involved. Hydride transfers fall in the former category. Representative examples of other types of organic reactions in this category have recently been discussed.<sup>11</sup> The numerous atom abstraction reactions of free radicals in the gas phase and in solution can be classed as redox reactions.

On the other hand, there are a number of organic redox reactions for which an electron transfer mechanism is likely and a number for which it is not unreasonable. Some of these are listed below.

The electron exchange rate between Würster's blue and its one electron reduction product has been reported and was measured using nuclear magnetic resonance spectroscopy.<sup>12</sup> Analogous measurements for the exchange reaction between naphthalene and its negative ion have also been made with the aid of an electronic paramagnetic resonance method.<sup>13</sup> The reduction of aromatic hydrocarbons, triaryl ketones and some other compounds by metallic sodium in certain solvents to form the corresponding anions and sodium ions may be another example.<sup>14,15</sup> The electron exchange reaction of one of the resultant homogeneous solutions with added aromatic hydrocarbons<sup>15</sup> is presumably another. Indeed, the latter process has recently been used to prepare block copolymers.<sup>16</sup> An electron transfer mechanism may obtain in the reduction of various organic compounds, such as aldehydes,<sup>17</sup> peroxides,<sup>18</sup> and carbonium ions,<sup>19</sup> by heavy metal cations, although in the first two cases a plausible group transfer mechanism can also be suggested. In each of these three reactions an organic free radical is produced; at least one of these systems serves as a redox catalyst for polymerization.<sup>18</sup> Other possible examples of electron transfer reactions include the reduction of hydrazinium and aminium salts by

heavy metal cations.<sup>20</sup> Barron has recently discussed certain biological oxidations, including some induced by radiation, on the basis of an electron transfer mechanism.<sup>21</sup> Again, hydroquinone- and quinone-like compounds have frequently been assumed to be active electron transfer agents. They form thermodynamically reversible half-cells with electrodes, and have been used as a diagnostic tool for testing whether a reaction has an electron transfer mechanism.<sup>10</sup>

In the present paper the theory of redox reactions described in Part I will be applied to two reaction series involving the oxidation of hydroquinone-like compounds by molecular oxygen and by ferric ions. These reactions have been studied kinetically in considerable experimental detail. It will be seen that the theory provides a reasonable quantitative interpretation of the data.

It has not yet been possible to demonstrate experimentally whether an atom transfer or whether an electron transfer mechanism prevails in the two reaction series considered here. Nevertheless it should be fruitful in such cases to apply a quantitative theory, atom transfer or electron transfer, to the results, for this suggests various experimental tests and various correlations of data on widely different processes, and in these ways may serve to suggest further lines of research. The present theory,<sup>4</sup> for example, makes predictions which can be tested experimentally.

It would be of particular interest to compare this analysis of these series of reactions with one based on a similarly fundamental atom transfer theory. However, at present there is no atom transfer theory which could be used to calculate the reaction rate without the use of adjustable parameters. Indeed, it is regrettable but nevertheless a fact that absolute rate theories concerned with the problem of transfer or exchange of atoms and groups of atoms in related reactions are almost invariably semiempirical in nature because of the computational complexities arising from such atomic migrations.

## THEORETICAL EQUATIONS

The basic theoretical equations employed in this paper will be those used in Part II. These expressed the rate constant of the redox step in terms of  $\Delta F^*$  and  $\Delta S^*$ , the excess free energy and entropy of activation [Eqs. (1) and (6) there], and related the  $\Delta F^*$  and  $\Delta S^*$  to  $\Delta F^0$ , the standard free energy change of the redox step, and to  $a_1$  and  $a_2$ , the polarizing radii of the reactants [Eqs. (2) and (5) of Part II].

It will also be useful to deduce a simple, approximate theoretical expression for  $\Delta S^*$ , and to derive a simple relation for the dependence of  $\Delta F^*$  on  $\Delta F^0$  in a given reaction series. Using the symbols defined in Part II,

<sup>20</sup> See survey by W. A. Waters, *Chemistry of Free Radicals*, (Oxford University Press, Oxford, 1948), second edition, Chap. 4.

<sup>21</sup> E. S. G. Barron, paper presented at the Conference on Unstable Species, New York Academy of Sciences, March 15 and 16, 1956; to be published in *Ann. N. Y. Acad. Sci.*

<sup>10</sup> See W. von E. Doering and T. C. Aschner, *J. Am. Chem. Soc.* **75**, 393 (1953).

<sup>11</sup> F. H. Westheimer, *The Mechanism of Enzyme Action*, edited by W. D. McElroy and B. Glass, p. 321. (Johns Hopkins Press, Baltimore, 1954). The mechanism of some related reactions has also been discussed recently by L. S. Levitt, *J. Org. Chem.* **20**, 1297 (1955).

<sup>12</sup> Bruce, Norberg, and Weissman, *J. Chem. Phys.* **24**, 473 (1956).

<sup>13</sup> R. L. Ward and S. I. Weissman, *J. Am. Chem. Soc.* **76**, 3612 (1954).

<sup>14</sup> See review by A. J. Birch, *Quart. Revs.* **4**, 69 (1950).

<sup>15</sup> Paul, Lipkin, and Weissman, *J. Am. Chem. Soc.* **78**, 116 (1956).

<sup>16</sup> Szwarc, Levy, and Milkovich, *J. Am. Chem. Soc.* **78**, 2656 (1956).

<sup>17</sup> See review by J. R. McNesby and C. A. Heller, Jr., *Chem. Revs.* **54**, 325 (1954).

<sup>18</sup> See review by R. G. R. Bacon, *Quart. Revs.* **9**, 287 (1955).

<sup>19</sup> Conant, Small, and Taylor, *J. Am. Chem. Soc.* **47**, 1959 (1925). J. B. Conant and N. M. Bigelow, *ibid.*, **53**, 676 (1931).

Eqs. (5) and (2) of that paper<sup>1</sup> can be written as

$$\Delta S^* = \frac{1}{2} \Delta S_r^0 \left( 1 + \frac{\Delta F_r^0}{\lambda} \right) - \frac{e_1^* e_2^*}{r} \frac{d}{dT} \left( \frac{1}{D_s} \right) - \frac{1}{4} \left[ 1 - \left( \frac{\Delta F_r^0}{\lambda} \right)^2 \right] \frac{d\lambda}{dT}, \quad (1)$$

where  $\Delta S_r^0$  is  $-\partial \Delta F_r^0 / \partial T$  and  $\Delta F_r^0$  equals  $\{\Delta F^0 + (e_1 e_2 - e_1^* e_2^*) / D_s r\}$ . In Eq. (1) the last term is generally very small and we then have as an approximate equation for  $\Delta S^*$ ,

$$\Delta S^* \approx \frac{1}{2} \Delta S_r^0 \left( 1 + \frac{\Delta F_r^0}{\lambda} \right) - \frac{e_1^* e_2^*}{r} \frac{d}{dT} \left( \frac{1}{D_s} \right). \quad (2)$$

From Eqs. (2) to (4) of Part II a simple dependence of  $\Delta F^*$  on  $\Delta F^0$  can be deduced for the reaction of some reagent with a series of compounds chemically similar to each other and differing only in some substituent such that the charged part of the molecule remains the same throughout the series. Two such series are discussed later in this paper. The polarizing radius of each member of a series will be taken to be the same, since each has the same charged group; it is the charged part of the molecule which causes the electrical polarization of the medium. It will therefore be seen from Eq. (4) of Part II that  $\lambda$  is the same for each member of the series. Accordingly, we are interested in the dependence of  $\Delta F^*$  upon  $\Delta F^0$  at a given  $\lambda$ , i.e., in  $(\partial \Delta F^* / \partial \Delta F^0)_\lambda$ . We find from Eqs. (2) to (4) of Part II that

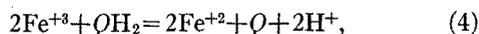
$$\left( \frac{\partial \Delta F^*}{\partial \Delta F^0} \right)_\lambda = \frac{1}{2} \left( 1 + \frac{\Delta F_r^0}{\lambda} \right). \quad (3)$$

This predicts that when  $\Delta F_r^0 / \lambda$  is very small, a plot of  $\Delta F^*$  vs  $\Delta F^0$  should be a straight line with a slope of  $\frac{1}{2}$ . When  $\Delta F_r^0 / \lambda$  is large, a plot of  $\Delta F^*$  vs  $\Delta F^0$  will be approximately linear for small changes in  $\Delta F^0$ ; the slope will be about unity if  $\Delta F_r^0 / \lambda$  is as large as unity.

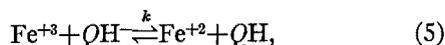
## OXIDATION OF HYDROQUINONES BY FERRIC ION

### Mechanism

The over-all reaction for the oxidation of a hydroquinone by ferric ions is given by Eq. (4).



where  $\text{QH}_2$  and  $\text{Q}$  denote the hydroquinone and quinone, respectively. The rate of this reaction has been measured<sup>7,8</sup> as a function of the concentrations of the various reactants and products. One mechanism consistent with the data involves<sup>7,8</sup> the ionization of  $\text{QH}_2$  to  $\text{QH}^-$ , followed by an electron transfer between  $\text{QH}^-$  and  $\text{Fe}^{+3}$ , reaction (5).



where  $\text{QH}$  denotes the semiquinone. This step was in turn followed by the ionization of  $\text{QH}$  to  $\text{Q}^-$  and then by the latter's oxidation to  $\text{Q}$ .

We shall be concerned here with the experimental and theoretical value of  $k$ , the rate constant for the forward reaction in Eq. (5). The experimental  $k$  can readily be computed<sup>22</sup> from the known<sup>8</sup> over-all bimolecular rate constant  $k_1$  and the known<sup>23,8</sup> first ionization constant of  $\text{QH}_2$ ,  $K_1$ . It is given later in Table I. The various quantities needed for the theoretical calculation of  $k$  are computed in the following sections.

### Standard Free Energy Change of the Redox Step, $\Delta F^0$

The standard free energy of reaction (5),  $\Delta F^0$ , has not been measured directly but can be estimated from  $K_1$ , and from  $K$  and  $K_s$ , the equilibrium constants of reactions (4) and (6), respectively,



It is readily verified that  $\Delta F^0$  is given by

$$\Delta F^0 = -RT \ln(KK_s/K_1^2)^{\frac{1}{2}}. \quad (7)$$

The values of  $K$  and  $K_1$  have been determined experimentally.<sup>8,23</sup> Numerous data on the formation constants of semiquinones  $K_s$  have also been obtained. When, as in reaction (6), all three compounds in this equilibrium are uncharged, or have the same charge, the free energy of this reaction is found to be practically independent of the chemical structure of these compounds.<sup>24</sup> The standard free energy change of reaction (6),  $-RT \ln K_s$ , is found to be<sup>24</sup> about 2.3 kcal mole<sup>-1</sup>.

With these values of  $K$ ,  $K_1$  and  $K_s$ , the values of  $\Delta F^0$  given in Table I were calculated from Eq. (7).

### Effective Radii

The nature of the effective radii  $a$  which appear in the basic theoretical equation for  $\Delta F^*$ , Eq. (2) of Part II, has been reviewed in Part II. However, the organic ions which will be considered here introduce two new features. First, the ion is far from being spherical and, second, it is possible that the effective radius  $a$  could be quite different when this particle is a charged reactant and when it is an uncharged product. This is discussed in the appendix, where it is inferred from entropy data

<sup>22</sup> The reaction rate of the forward step in Eq. (6),  $k(\text{Fe}^{+3})(\text{QH}^-)$ , was written<sup>8</sup> as  $k_1(\text{Fe}^{+3})_s(\text{QH}_2)_s$ , where the subscript  $s$  denotes stoichiometric concentration and where  $k_1$ , a pseudo-rate constant, was found to be inversely proportional to  $(\text{H}^+)$ . Values of  $k_1$  were reported,<sup>8</sup> rather than those of  $k$ . Under the pH conditions used,  $(\text{QH}_2)_s \cong (\text{QH}_2)$ ,  $(\text{Fe}^{+3})_s \cong (\text{Fe}^{+3})$ , and, therefore,  $k = k_1(\text{H}^+) / K_1$ ,  $K_1$  being the ionization constant of  $\text{QH}_2$ .

<sup>23</sup> J. H. Baxendale and H. R. Hardy, *Trans. Faraday Soc.* **49**, 1140 (1953).

<sup>24</sup> This can be inferred from a detailed analysis of data on the pH dependence of the first and the second oxidation potentials of many hydroquinone-like compounds. The results of this analysis will be submitted for publication. Compare also a remark by G. Schwarzenbach, *Inst. intern. chim. Solvay 8e Conseil chim., Univ. Bruxelles Mechanisme de oxydation*, *Rapp. et. disc.* **47** (1950).

that the effective polarizing radius of a hydroquinone-like ion such as  $\text{HOC}_6\text{H}_4\text{O}^-$  is about the same as that of the hydroxyl ion. It is further suggested that the dielectric saturation around this group when it is a charged particle be neglected as a first approximation, and that  $a$  equals the crystallographic radius of the oxygen group 1.4 Å. This approximation can be removed by a refinement of the theory.

As discussed in the preceding paper<sup>2</sup> the value of  $a$  for the  $\text{Fe}^{2+}-\text{Fe}^{3+}$  particle is 3.44 Å.

### Excess Free Energy of Activation

Experimental values of  $\Delta F^*$  were calculated from the rate constants  $k$  given in Table I, using Eq. (1) of Part II and setting  $Z$  equal<sup>25</sup> to  $10^{13}$  liter mole<sup>-1</sup> sec<sup>-1</sup> in that equation. These values are reported in Table I.

Using the effective radii and the  $\Delta F^0$ 's deduced in the preceding section and setting  $D_{op}=1.8$  and  $D_s=78.5$  at 25°C, values of  $\Delta F_{\text{calc}}^*$  were obtained with the aid of Eqs. (2) to (4) of Part II, and are given in Table I. These results will be discussed in detail later.

### Excess Entropy of Activation

Experimental values for the excess entropy of activation of reaction (5),  $\Delta S_{\text{expt}}^*$ , were calculated<sup>26</sup> from the data. The values of  $\Delta S_{\text{calc}}^*$  were computed from Eq. (1) using the previously determined radii and  $\Delta F^0$ , and using the calculated<sup>27</sup>  $\Delta S^0$ . In this way  $\Delta S_{\text{expt}}^*$  was found to be 46, 57, 47 and 44 cal mole<sup>-1</sup> deg<sup>-1</sup>, and  $\Delta S_{\text{calc}}^*$ , to be 36, 38, 36, and 31 entropy units, for the 2,6-dichloro, benzo, tolu and duro hydroquinones, re-

TABLE I. Kinetic and thermodynamic data for  $\text{Fe}^{2+}+\text{QH}^-$  reaction at 25°C.<sup>a</sup>

Hydroquinone	$k \times 10^{-9}$ (liter mole sec)	$\Delta F^0$	$\Delta F_{\text{expt}}^*$	$(\Delta F_{\text{calc}}^* - \Delta F_{\text{expt}}^*)$			
				$\Delta F_{\text{calc}}^*$	Expt	Calc	
2,6-dichloro-	0.023	-9.3	7.7	7.5	0	0	
benzo-	3.3	-13.2	4.8	5.9	2.9	1.6	
tolu-	24	-14.9	3.6	5.2	4.1	2.3	
duro-	270	-20.5	2.1	3.2	5.6	4.3	

<sup>a</sup> All free energy units are in kcal mole<sup>-1</sup>.

<sup>b</sup> x denotes the 2,6-dichloro compound and y denotes any other compound.

<sup>25</sup> See A. A. Frost and R. G. Pearson, *Kinetics and Mechanism* (John Wiley and Sons, Inc., New York, 1953).  $Z$  is the collision number in solution.

<sup>26</sup> The pseudo-rate constant  $k_1$  defined previously<sup>22</sup> has an activation energy  $E_1$ , say, and a frequency factor  $A_1$  so that  $k_1 = A_1 \exp(-E_1/RT)$ . Values of  $A_1$  were determined experimentally. The frequency factor of  $k_1$ ,  $A_1$ , say, can be calculated from the known<sup>8</sup>  $A_1$  and the known<sup>23</sup> entropy of ionization of  $\text{QH}_2$ ,  $\Delta S_1$ , say. It is found that  $A = A_1(\text{H}^+) \exp(-\Delta S_1/R)$ . According to Eq. (6) of Part II  $\Delta S_{\text{expt}}^*$  is then found by setting  $Z \exp(\Delta S^*/R) = A$ ,  $Z$  being<sup>25</sup>  $10^{13}$  liter mole<sup>-1</sup> sec<sup>-1</sup>.

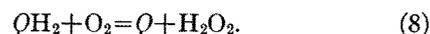
<sup>27</sup>  $\Delta S^0$  equals  $-\partial \Delta F^0 / \partial T$  and therefore according to Eq. (7) it equals  $\frac{1}{2} \Delta S + \frac{1}{2} \Delta S_S - \Delta S_1$  where  $\Delta S$  and  $\Delta S_S$  are the standard entropy changes in reactions (4) and (6), respectively.  $\Delta S$  and  $\Delta S_1$  have been determined experimentally.<sup>8,23</sup> Since the sum of the translational, rotational and vibrational entropies of the reactants and of the products of reaction (6) should be about the same, it may be assumed that  $\Delta S_S$  is essentially zero.

spectively. The average of the former group of values is 49 and that of the latter is 35. Values of  $\Delta S_{\text{calc}}^*$  were also computed from the approximate equation, Eq. (2). They agreed well with the exact calculated values, within about one and a half entropy units.

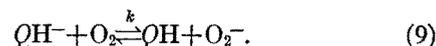
## AEROBIC OXIDATION OF THE LEUCOINDOPHENOLS

### Excess Free Energy of Activation

The over-all reaction of the leucoindophenols with dissolved oxygen is represented by Eq. (8), where  $\text{QH}_2$  denotes a leucoindophenol such as  $\text{HOC}_6\text{H}_4\text{NHC}_6\text{H}_4\text{OH}$ , and  $Q$  denotes the corresponding indophenol,  $\text{HOC}_6\text{H}_4\text{NC}_6\text{H}_4\text{O}$ .



A mechanism<sup>6</sup> consistent with the data<sup>6</sup> involved the ionization of  $\text{QH}_2$  to  $\text{QH}^-$ , which then transferred an electron to  $\text{O}_2$ :



This was followed by reactions of  $\text{QH}$  and  $\text{O}_2^-$ . As in the preceding reaction series discussed in this paper, the rate constant  $k$  for the forward reaction in Eq. (9) can be inferred from the over-all bimolecular rate constant  $k_1$  and the first ionization constant  $K_1$  of  $\text{QH}_2$ . ( $k = k_1(\text{H}^+)/K_1$ ). The  $k$ 's and the values of  $\Delta F_{\text{expt}}^*$  calculated from them using Eq. (1) of Part II are given in Table II.

It can be shown that the  $\Delta F^0$  of reaction (9), needed for the estimation of  $\Delta F_{\text{calc}}^*$ , is given by Eq. (10).

$$\Delta F^0 = -F(E_{\text{QH}_2^0} - E_{\text{O}_2^-}) + RT \ln K_1 / K_S \frac{1}{2} \quad (10)$$

where  $E_{\text{QH}_2^0}$  is the standard oxidation potential of  $\text{QH}_2$  ( $\text{QH}_2 = \text{Q} + 2\text{H}^+ + 2e$ ),  $E_{\text{O}_2^-}$  is that of  $\text{O}_2^-$  ( $\text{O}_2^- = \text{O}_2 + e$ ),  $F$  is the Faraday, and  $K_S$  is the equilibrium constant of reaction (6) for the formation of semiquinones of indophenols. The  $\Delta F^0$ 's of Table II were estimated using the known<sup>28</sup>  $E_{\text{QH}_2^0}$ , the estimated<sup>29</sup>  $E_{\text{O}_2^-}$ , the value of  $-RT \ln K_S$  discussed in the previous section (2.3 kcal mole<sup>-1</sup>) and the known<sup>6</sup>  $K_1$ .

Introducing into Eq. (2) of Part II, these  $\Delta F^0$ 's and the effective radii deduced in the appendix the  $\Delta F_{\text{calc}}^*$  values of Table II were computed.

### Excess Entropy of Activation

All the entropy data needed for the estimation of  $\Delta S_{\text{expt}}^*$  and  $\Delta S_{\text{calc}}^*$ , the experimental and the calculated

<sup>28</sup> See *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1929) Vol. 6, p. 333. These values were multiplied by  $-1$ , in conformity with current convention.

<sup>29</sup> W. M. Latimer, *Oxidation Potentials* (Prentice-Hall, Inc., New York, 1952). Latimer suggested a value of 0.56 volt for  $E_{\text{O}_2^-}$  and stated that it can hardly be more positive but that it could be as much as 0.2 volt less positive (compare his discussion of the perhydroxyl-hydrogen peroxide couple, p. 47). Evans, Hush, and Uri [*Quart. Revs.* 6, 186 (1952)] have estimated the free energy of solvation of  $\text{O}_2^-$  theoretically, and have shown it to be consistent with Latimer's assignment for  $E_{\text{O}_2^-}$ . However, such a calculation is subject to considerable error.

TABLE II. Kinetic and thermodynamic data for  $O_2 + QH^-$  reaction at 30°C.<sup>a</sup>

Indophenol	$k$ ( $\frac{\text{liter}}{\text{mole sec}}$ )	$\Delta F^0$	$\Delta F_{\text{expt}}^*$	$\Delta F_{\text{calc}}^*$	$(\Delta F_y^* - \Delta F_x^*)^0$	
					Expt	Calc
unsubstituted	47	15.9- $\alpha^b$	15.7	23.7 <sup>b</sup>	0	0
o-chloro	5.1	17.7- $\alpha$	17.0	24.9 <sup>b</sup>	1.3	1.2
o-bromo	6.1	17.4- $\alpha$	16.9	24.7 <sup>b</sup>	1.2	1.0
2,6-dibromo	0.23	19.7- $\alpha$	18.9	26.2 <sup>b</sup>	3.2	2.5

<sup>a</sup> All free energy units are in kcal mole<sup>-1</sup>.

<sup>b</sup> There is an appreciable uncertainty in  $-E_{O_2}^0$ , and therefore in  $\Delta F^0$ , of an amount  $\alpha$ , where  $\alpha$  may be about 0 to +5 kcal mole<sup>-1</sup> according to Latimer.<sup>29</sup> This introduces a corresponding uncertainty in the  $\Delta F_{\text{calc}}^*$ , which may be about 3 kcal mole<sup>-1</sup> less than those reported in this table.

<sup>c</sup>  $x$  denotes the unsubstituted compound and  $y$  denotes the substituted compound.

excess entropy of activation of the electron transfer step, Eq. (9), are not available. However, some estimates of the undetermined entropy values may be made.

For example, just as<sup>26</sup> in the case of the ferric-hydroquinone reaction,  $\Delta S_{\text{expt}}^*$  can be calculated from the frequency factor of the pseudo rate constant and the entropy of ionization of  $QH_2$ ,  $\Delta S_1$ . Assuming that  $\Delta S_1$  equals the value for the hydroquinones and for water (which in the appendix are shown to be equal) one finds in this way that  $\Delta S_{\text{expt}}^* \cong 7$  cal mole<sup>-1</sup> deg<sup>-1</sup>.

The term  $\Delta S_{\text{calc}}^*$  is seen from the approximate equation, Eq. (2), to be about  $\Delta S^0(1 + \Delta F^0/\lambda)/2$  since  $e_1e_2$  and  $e_1^*e_2^*$  are each equal to zero in reaction (9). In reaction (9) it is also expected that the translational, rotational, and vibrational entropies of the reactants are each about equal to those of the products. Accordingly, if the entropy change  $\Delta S^0$  of reaction (9) were appreciable, the main contributions to it would arise from possible differences in the entropy of solvation of  $QH^-$  and  $O_2^-$ . This would not be expected to be large, so that  $\Delta S^0/2$  should be relatively small. Further,  $\Delta F^0/\lambda$  is calculated to be only about 0.3, so we conclude that  $\Delta S_{\text{calc}}^*$  is small, in agreement with the estimated small value of  $\Delta S_{\text{expt}}^*$ .

## DISCUSSION

A comparison of Tables I and II shows that the rate constants of the redox step in the two series of reactions considered here differ from each other by a factor of  $10^9$  on the average. This difference stems from the considerable difference in the standard free energy change  $\Delta F^0$  of the redox step in the two cases, one being about -13 kcal mole<sup>-1</sup>, the other perhaps lying between +17 and +12 kcal mole<sup>-1</sup>, depending on the correct value of  $E_{O_2}^0$ . This difference in turn is related principally to the differences between standard oxidation potentials of the ferrous ion and of the oxygen molecule ion.

According to the theory developed in Part I, the standard free energy change affects the reaction rate in the following way. During an electron transfer step there is first a reorganization of the solvent molecules about the reacting ions prior to the jump of an electron

from one reactant to the other. Now, for a given  $\Delta S^0$ , the more positive  $\Delta F^0$  is, the greater would be the energy of the state of the system just after the jump. Therefore, the energy of the system just before the jump, which is equal to this, would also have to be greater. This simply means that there is a greater energy barrier to forming from the isolated reactants a suitable collision complex in which the electron can jump. Conversely, the more negative  $\Delta F^0$ , the less is this energy barrier.

In spite of the extremely favorable value of  $\Delta F^0$ , the redox step of the ferric ion-hydroquinone ion reaction is seen from Table I not to proceed at every collision. According to the theory, this is because of the preliminary solvent reorganization prior to the electronic jump. However, it is of interest that the rate constant of the redox step in the ferric ion-hydroquinone reaction is much larger, on the average, than those of the isotopic exchange electron transfer reactions having zero standard free energy change, considered in the preceding paper<sup>2</sup> in this series. The major reasons for this difference lie in the Coulombic attraction of the  $Fe^{+3}-QH^-$  reactants, as compared with the Coulombic repulsion of the reactants in those isotopic exchange reactions, and in the large negative value of  $\Delta F^0$  in the former reaction as compared with the zero value in the latter.

While the general agreement between the calculated and experimental results is satisfactory, the type of agreement obtained in Table II for the absolute value of  $\Delta F^*$  in the reaction of ferric and hydroquinone ions is partly fortuitous. Two compensating approximations were employed: The  $a$  value chosen for the iron ion assumed complete dielectric saturation in the innermost hydration layer of this ion and, as in the preceding paper,<sup>2</sup> tends to make  $\Delta F_{\text{calc}}^*$  too small. The  $a$  value for the oxygen group correctly assumed no dielectric saturation around the uncharged reactant but made the same assumption when it was charged. This tends to make  $\Delta F_{\text{calc}}^*$  too large.

In the oxygen-leucoindophenol reaction, only the second of these two approximations was involved and therefore there is no compensation. This may be the reason why the absolute value of  $\Delta F^*$  is somewhat larger than  $\Delta F_{\text{expt}}^*$  in Table II.

In Table I it is observed that the rate constant for the electron transfer step of the durohydroquinone is very high, namely  $2.7 \times 10^{11}$  liter mole<sup>-1</sup> sec<sup>-1</sup>. This value is about the maximum value that a rate constant can have in solution. The maximum corresponds to the situation in which the probability of reaction per collision is so high that the slow process in the reaction becomes the diffusion of the reactants toward each other. Using a formula of Debye<sup>30</sup> we estimate that the rate constant for a diffusion-controlled reaction between two ions of charges +3 and -1 is about  $5 \times 10^{10}$  liter mole<sup>-1</sup> sec<sup>-1</sup>. Within the error of the various determinations this is about equal to the rate constant  $k$  of the electron

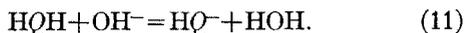
<sup>30</sup> P. Debye, Trans. Electrochem. Soc. **82**, 265 (1942).

transfer step for the durohydroquinone reaction. If a hydroquinone could be found which apparently gave a larger value for the rate constant, then at least for this compound the mechanism could not be represented by reaction (5), unless this occurred via a long-lived intermediate.<sup>31</sup>

#### APPENDIX. IONIC RADII

The negative charge on a hydroquinone ion such as  $\text{HOC}_6\text{H}_4\text{O}^-$  or  $\text{HOC}_6\text{H}_4\text{NHC}_6\text{H}_4\text{O}^-$  is largely on the oxygen. Thus it is this atom which polarizes the dielectric. Accordingly, the appropriate polarizing radius  $a$  to be used for this charged center may be the same as that for another negatively charged oxygen, such as the  $\text{OH}^-$  ion. It is true that the organic residue will prevent the close approach of some of the solvent molecules and hence reduce their polarization. On the other hand, this residue is itself polarized by the charged oxygen, atomic polarization being induced, although it is less strongly polarized than in the solvent. In this way the organic residue and the solvent play analogous roles.

A similarity between the hydroquinone ion and the hydroxyl ion in their extent of solvation, and therefore in their effective polarizing radius  $a$ , can be inferred from the standard entropy change of reaction (11).



In such a reaction, the translational and rotational entropies of each of the two products would be expected to be about the same as those of the corresponding two reactants. Moreover, the sum of the vibrational entropies of the products should be about equal to the sum of the reactants. If there is an appreciable entropy change in the reaction it would be expected to arise from differences in the ability of the  $\text{OH}^-$  and the  $\text{HQ}^-$  ions to polarize the solvent molecules and therefore to vary in their entropy of solvation. Now the standard entropy change of reaction (11) is readily shown to equal the difference in entropy of ionization of water and of  $\text{QH}_2$ . The entropy of ionization of  $\text{QH}_2$  for the various hydroquinones in Table I is,<sup>23</sup> in the respective order in which they occur in that table,  $-26$ ,  $-32$ ,  $-29$  and  $-25$  entropy units, with an average value of  $-28$ . The entropy of ionization of water is<sup>32</sup>  $-26.7$  eu. Accordingly,

<sup>31</sup> The formation of such an intermediate, e.g. one in which the ferric ion was bonded to the charged oxygen of the hydroquinone ion, would of course necessitate a more elaborate (or different) theoretical treatment for this reaction. It would be desirable to study the oxidation of hydroquinones by suitable metal ions under conditions inhibiting the formation of such an intermediate. This might be done by adding a reagent which forms a strong complex with both valence states of the aquo metal ion.

<sup>32</sup> H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions* (Reinhold Publishing Corporation, New York, 1950), Chap 15.

the entropy change of reaction (11) is seen to be zero within the experimental error. This therefore provides some basis for assuming that  $\text{QH}^-$  and  $\text{OH}^-$  have about the same polarizing radius,  $a$ .

Another question discussed in the text concerned the relative abilities of  $\text{QH}^-$  and  $\text{QH}$  to dielectrically saturate the neighboring water molecules. The  $\text{QH}$  molecule, being uncharged, cannot saturate the dielectric. The former, being charged, could. Thus  $a$  would apparently be different for  $\text{QH}^-$  and  $\text{QH}$ , contrary to an assumption made in the derivation of Eq. (2) (Part II) for  $\Delta F^*$ . However, it is possible that this dielectric saturation by the anion is relatively small. For example, studies<sup>33</sup> of the dielectric constant of aqueous salt solutions indicate less dielectric saturation in the vicinity of anions, as compared with cations. It is of interest, too, though not necessarily significant, that the "experimental" free energies of solvation of anions agree reasonably well<sup>34</sup> with those calculated theoretically from the Born<sup>35</sup> formula. The Born formula assumes that the dielectric is unsaturated.

In the interest of simplicity, we shall assume that as a first approximation there is little dielectric saturation in the vicinity of the  $\text{QH}^-$  ion. Accordingly, it follows that  $a$  will be the crystallographic radius of the oxygen group, which is<sup>36</sup> about 1.4 Å. In a later paper we plan to remove the assumption of absence of dielectric saturation.

The  $\text{O}_2^-$  may be regarded as an ellipsoid of revolution whose<sup>37</sup> semimajor axis was found crystallographically to be 2.02 Å and whose semiminor axis is 1.51 Å. As a first approximation this molecule will be treated as a sphere of radius 1.7 Å, which has the same volume as the ellipsoid. This "crystallographic" radius will be taken as the value of  $a$  for  $\text{O}_2^-$ , for the same reasons given previously for the choice of the crystallographic radius as the  $a$  value of the oxygen atom in the hydroquinone ion.

<sup>33</sup> Hasted, Ritson, and Collie, *J. Chem. Phys.* **16**, 1 (1948). A possible explanation of this has been given by D. H. Everett and C. A. Coulson, *Trans. Faraday Soc.* **36**, 633 (1940).

<sup>34</sup> See Latimer, Pitzer, and Slansky, *J. Chem. Phys.* **7**, 108 (1939); W. M. Latimer, *ibid.*, **23**, 90 (1955). These authors found that for anions, the radius inferred by introducing the "experimental" free energy of hydration into the Born formula and solving for the effective radius, was but 0.1 Å greater than the crystallographic radius.

<sup>35</sup> M. Born, *Z. Physik* **1**, 45 (1920).

<sup>36</sup> The van der Waals' radius of each charged oxygen atom in inorganic oxy-anions was estimated to have this magnitude (see appendix of reference 2). This is also essentially equal to the radius of the hydroxide ion, the  $\text{O}^{2-}$  ion, and the water molecule. Values of these radii are given by A. F. Wells, *Structural and Inorganic Chemistry* (Oxford University Press, 1950).

<sup>37</sup> A. Helms and W. Klemm, *Z. anorg. u. allgem. Chem.* **241**, 97 (1939).