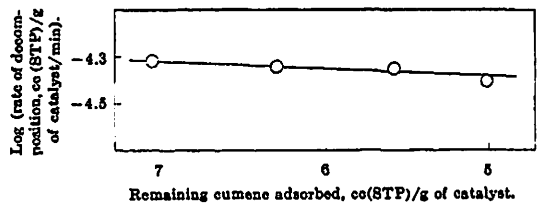

Figure 2. The rates of decomposition of cumene at 60°. The rate of decomposition at 40° for the cumene adsorbed of 4.17 cc was found to be 5.64×10^{-6} cc (STP)/g of catalyst, min. Comparison of the rates at both temperatures corresponding to the same amount adsorbed (4.17 cc) leads to an activation energy of 20.5 kcal/mole.

usual flow method, owing to a marked difference in the experimental conditions, *e.g.*, the reaction temperature or the coverage of cumene during the reaction.

Kinetics of Ferrocyanide Reduction of Quinones

by S. A. Levison[1a] and R. A. Marcus[1b]

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We describe here the kinetics of ferrocyanide reduction of 2,5-dichloro-, benzo-, and 2,5-dimethylquinones (denoted below by I, II, III) in 1 M KCl. Reagent materials were used where available and the hydroquinones of I and III were synthesized by $SnCl_2$ reduction and recrystallization. Slightly alcoholic solutions of quinones[2,3] in 1 M KCl were deoxygenated, placed in blackened vessels at 27°, and then in a 10-cm path Beckman cell. Buffered 1 M KCl ferrocyanide at 27° was added and the rate was measured from ferrocyanide diappearance at 420 mμ or disappearance of I at 275 mμ, using a Beckman.[4]

The acid dissociation constants of $H_2Fe(CN)_6^{2-}$ and $HFe(CN)_6^{3-}$ in 1 M KCl were measured with a Beckman (260–280 mμ) at concentrations of 0.4–4.5 × 10^{-5} M and found to be 0.32 ± 0.02 and (4.7 ± 0.2) × 10^{-3} M, respectively[1a] The equilibrium constant, K, of

$$Q + 2Fe(CN)_6^{4-} + 2H^+ \rightleftharpoons QH_2 + 2Fe(CN)_6^{3-} \quad (1)$$

was measured from the formal potentials E_0' of the two half-cells using a Leeds and Northrup potentiometer. The E_0' (relative to sce) of the ferrocyanide system in 1 M KCl was 0.22 V, and those for I, II, and III in 1 M KCl were 0.47, 0.44, and 0.34 V yielding K's of (2.8 ± 0.5) × 10^8, (3.1 ± 0.5) × 10^7, and (1.1 ± 0.2) × 10^4 M^{-2}, respectively. (The anions in (1) are largely paired with K^+; concentrations throughout this paper include all species, paired or unpaired.) E_0' for ferro–ferri was constant from pH 3.7 to 6.7 and E_0' for Q–QH_2 was constant from pH 2 to 6.7. (These E_0''s were defined by $E = E_0'$ and $E = E_0' + 2.3(RT/F)$pH, respectively, for the systems in the cited pH ranges, for equal concentration of oxidized and reduced forms.

The stoichoimetric equation (1) was confirmed spectrophotometrically by determining the amount of $Fe(CN)_6^{3-}$ formed in excess quinone and then in excess $Fe(CN)_6^{4-}$.[1a] The reaction order was investigated by (1) pseudo-first-order plots with ferrocyanide in large excess, and (2) when no reagent was in large excess, by determining best tangents to amount reacted *vs.* time plots. The slopes and known concentrations yielded apparent second-order k's [= rate/$(\text{ferro})_s(\text{Q})$, where s denotes stoichiometric].

All k's were constant at fixed $(\text{ferri})_s/(\text{ferro})_s$ at pH 2.74 to 4.74. Typical data for I and II are plotted in Figures 1 and 2.[5] The k's for III were constant in this range of ratios. The $(\text{ferro})_s$ was varied from 0.3 to 4, 0.2 to 2, and 1 to 10 (× 10^{-4} M), respectively, and the (Q)'s from 0.1 to 1, 1 to 5, and 1 to 10 (× 10^{-5} M). All data obeyed

$$\frac{1}{k} = \frac{1}{k_1'} + \frac{C\,(\text{ferri})_s}{(\text{ferro})_s} \quad (2)$$

and are summarized in Table I: k_1' is fairly insensitive to pH in the range (2.74 to 3.74) where it was measured.[6] $C \propto (H^+)^{-1}$ for I, and $C \propto (H^+)^{-1.4}$ for II.

Table I: Summary of Kinetic Data[a]

	I (2,5-Dichloro-quinone)		II (Benzoquinone)		III (2,5-Dimethyl-quinone)	
pH	$k_1' \times 10^{-4}$	$C \times 10^{3}$	$k_1' \times 10^{-3}$	$C \times 10^{3}$	k_1'	C
2.74	3.6	0.036	3.7	0.014	36	*b*
3.74	3.6	0.39	3.7	0.54	26	*b*
4.74	...	2.7	...	20.	...	5
5.74			...	390.		

[a] Units for k_1' and C^{-1} are (M min)$^{-1}$. [b] Not measured.[6]

(1) (a) S. A. Levison, Ph.D. Thesis, Polytechnic Institute of Brooklyn, June 1962. (b) Address correspondence to this author at Noyes Chemical Laboratory, University of Illinois, Urbana, Ill.

(2) I and III were dissolved in ethanol because of slow dissolution in water and were diluted to 1.0 to 0.01% alcoholic content, a variation without effect on potentials or reaction rates.

(3) Versene, 10^{-4} M, added to the ferrocyanide solution to remove a slight turbidity, perhaps due to $Pb_2Fe(CN)_6$, did not affect rates.

(4) In the kinetically important time of 10 min, a ΔT (0.7°) was estimated to cause a minor increase of 7% in rate.

(5) When $(\text{ferri})_s/(\text{ferro})_s$ changed during reaction in pseudo-first-order data, a mean was used. In ref 1a, C and E in Table 32 should be interchanged.

(6) A flow system would permit determination of k_1' at pH 4.74 and 5.74 by permitting measurements at very low conversions and hence at very low mean $(\text{ferri})_s/(\text{ferro})_s$ ratios. For compound III at pH 2.74 and 3.74, only initial rates were measured and no effort was made to determine C. Those initial rates were unchanged when $(\text{ferro})_s$ was increased from 1 to 10 × 10^{-4} M.

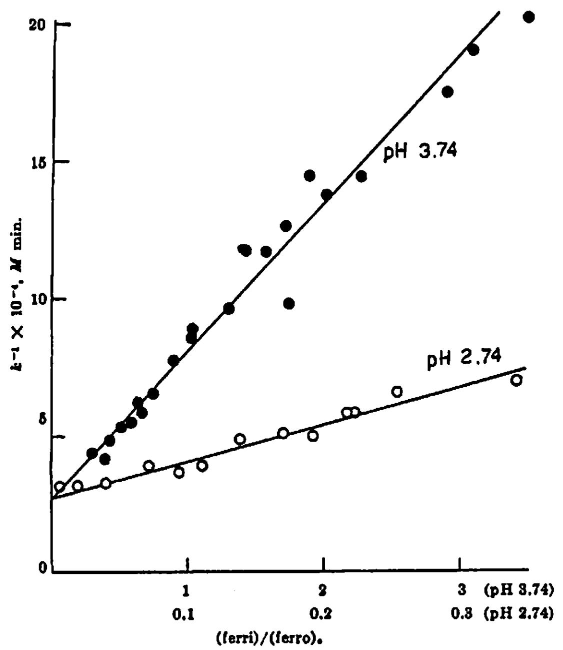

Figure 1. Depression of rate constants by ferricyanide at pH 2.74 and 3.74 (benzoquinone). At pH 2.74, (ferro) = 20 μM and (Q) = 50 μM. At pH 3.74, (ferro) = 20 and 10 μM and (Q) = 10 μM.

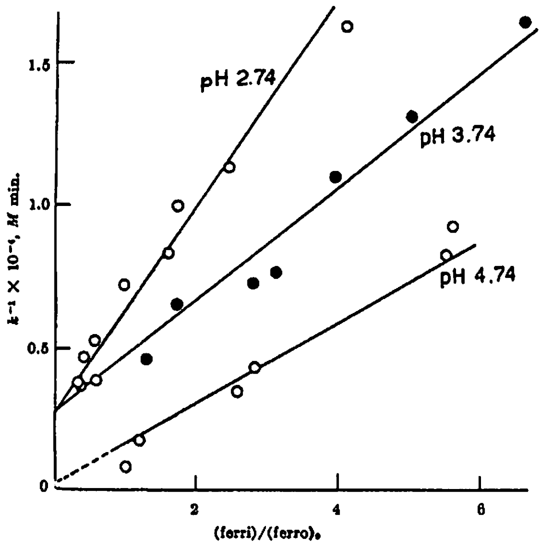

Figure 2. Depression of rate constants by ferricyanide at pH 2.74, 3.74, and 4.74 (2,5-dichloroquinone). For pH 4.74, the ordinate numerals should be mutliplied by 5. For pH 3.74 and 4.74, the abscissa numerals should be multiplied by $^1/_{20}$ and by $^1/_{40}$, respectively. Various values of (Q) and (ferro) were used.

With a pK of 2.3, the unprotonated form of ferro predominates ($\geq$70%) in pH 2.74 to 3.74 and, since k_1' was pH independent in this range, the principal elementary step involves unprotonated ferro and quinone. Thus, it cannot involve H-atom transfer. Using a steady-state treatment for

$$\text{ferro} + \text{Q} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{ferri} + \text{Q}^- \qquad (3)$$

and $\text{Q}^- + \text{H}^+ \rightleftharpoons \text{QH}^\cdot$, $\text{Ferro} + \text{QH}^\cdot \overset{k_2}{\rightleftharpoons} \text{QH}^- + \text{ferri}$, one obtains (2) with $k_1' = 2k_1$, and $C = k_{-1}K_{\text{QH}}/2k_1k_2(\text{H}^+)$, where K_{QH} is the acid dissociation constant for QH$^\cdot$. [(ferro)$_0$ = (ferro) in this range.] The mechanism agrees with $C \propto (\text{H}^+)^{-1}$ for I. To explain $C \propto (\text{H}^+)^{-1.4}$ for II, one can add reactions such as $\text{QH}^\cdot + \text{HFe(CN)}_6^{3-}$ or $\text{Q}^- + \text{H}_2\text{Fe(CN)}_6^{2-}$.

The $\Delta F^{\circ\prime}$ values in Table II were computed from

$$\Delta F^{\circ\prime} = -RT \ln (KK_{\text{QH}_2}K_{\text{QH}^-}\cdot K_{\text{S}^-})^{1/2} \qquad (4)$$

where K_{QH_2} and K_{QH^-} are acid dissociation constants of the hydroquinone and of its anion, and K_{S^-} refers to $\text{Q} + \text{Q}^{2-} \rightleftharpoons 2\text{Q}^-$. K was given earlier and the other constants in (4) are known.[8] The ΔF^*_{expt} in Table II were calculated from $k_1' = 10^{11} \exp(-\Delta F^*/RT)\ M^{-1}\ \text{sec}^{-1}$. For comparison with other data, we extrapolate these ΔF^*_{expt} to $\Delta F^{\circ\prime} = 0$ using[9]

$$\Delta F^* = \Delta F_0^*(1 + \Delta F^{\circ\prime}/4\Delta F_0^*)^2 \qquad (5)$$

The $\Delta F^*_{\text{calcd}}$ in Table II were obtained using $\Delta F_0^* =$ 8.4 kcal mole^{-1}.

Table II: Kinetic and Thermodynamic Data for $\text{Q} + \text{Fe(CN)}_6^{4-}$ Reaction 3

Quinone	k_1', $(M \text{ min})^{-1}$	$\Delta F^{\circ\prime}$, kcal mole^{-1}	ΔF^*_{expt}, kcal mole^{-1}	$\Delta F^*_{\text{calcd}}$, kcal mole^{-1}
2,5-Dichloro	1.9×10^4	5.7	11.7	11.5
Benzo	1.9×10^3	9.1	13.1	13.6
2,5-Dimethyl	1.3×10^1	12.5	16.1	15.8

We may compare this ΔF_0^* with that which we estimate from one-electron oxidation of the anion (IH_2^-) of 2,6-dichlorophenol indophenol by ferricyanide and one-electron reduction of a cation (IH_4^+) of leuco 2,3-dichlorophenol indophenol by ferrocyanide.[10] The

(7) $\Delta F^{\circ\prime}$ is the "ΔF°" of (3) for the given T and medium.

(8) C. A. Bishop and L. K. S. Tong, *J. Am. Chem. Soc.*, **87**, 501 (1965).

(9) This relation is motivated by the electron transfer theory in *J. Chem. Phys.*, **43**, 679 (1965), *J. Phys. Chem.*, **67**, 853 (1963), etc. As noted there, the theory does not exclude ion-paired systems. ΔF_0^* (*i.e.*, ΔF^* extrapolated to zero $\Delta F^{\circ}{}_r$) depends on intrinsic reorganization terms, $^1/_4\lambda$, on work terms, and now on ion-pair constants. This ΔF_0^*, according to theory, equals $^1/_2[\Delta F^*$ (ferro–ferri exchange) + ΔF^*(Q–Q$^-$ exchange)] when the work terms are small. (Compare eq A42, Appendix VIII, of the 1965 article. Our extrapolation based on (5) permitted the fulfillment of the linear $\Delta F^{\circ\prime}$ condition in that Appendix.) When the work terms are not small, this ΔF_0^* is still a useful property for characterizing intrinsic reactivities of different series of substrates towards a given reagent in a given medium.

(10) H. Diebler, *Z. Elektrochem.*, **67**, 396 (1963). (11° and μ = 0.1 M).

corresponding ΔF^*_{expt} are 4.6 and 2.8 kcal mole^{-1} and, we estimate,[11] the corresponding $\Delta F^{0\prime}$ are -1.8 and -3.2 kcal mole^{-1}. Thereby, the ΔF_0^* is *ca.* 5 kcal mole^{-1}. That is, the indophenols are intrinsically more reactive than the quinones. Several explanations could be offered, based on differences in molecular sizes and on a milder rearrangement of bond lengths for the larger conjugated system. However, comparisons with ΔF_0^*'s of related systems would be useful first.

(11) The $\Delta F^{0\prime}$'s for the IH_2^- and IH_3^+ reactions are $-RT \ln (K_s/K_a^2K)^{1/2}$ and $-RT \ln (K_sKK_a'^2)^{1/2}$, where K, K_a, K_s and K_a' refer to $IH + 2Fe(CN)_6^{4-} + 2H^+ \rightleftharpoons IH_3 + 2Fe(CN)_6^{3-}$, $IH_3 \rightleftharpoons IH_2^- + H^+$, $IH_3 + IH \rightleftharpoons 2IH_2{}^{\cdot}$ and $IH_3^+ \rightleftharpoons IH + H^+$, respectively. In ref 10, $K_a = 1 \times 10^{-7}\ M$ and $K_a' = 0.3\ M$. In O. Tomicek, "Chemical Indicators," Butterworth and Co. Ltd., London, 1951, p 156, $K = 3.6 \times 10^{8}\ M^{-2}$. K_s for phenol blue, an analog of the dichloro compound, is *ca.* 2×10^{-3}, using data in G. Schwarzenbach and L. Michaelis, *J. Am. Chem. Soc.*, 60, 1667 (1938).

Osmotic Coefficients of Tungstosilicic Acid[1]

by J. S. Johnson, Jr., and R. M. Rush

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The heteropolyacid $H_4SiW_{12}O_{40}$ has attracted considerable interest as one of the few known examples of a strong 1:4 electrolyte and as a well-characterized monodisperse solute of molecular weight between those of simple electrolytes and such large species as proteins. Some years back we measured the activity coefficients of tungstosilicic acid in dilute aqueous solution (0.004–0.04 *M*) by equilibrium ultracentrifugation and found that turbidities calculated from these activity coefficients agreed with our light scattering measurements.[2] These turbidities were substantially lower than some earlier measurements in the literature.[3] Since then, there have been reports of several other studies in related areas, and the controversy has, if anything, widened.

A group (KKOM)[4] associated with Kerker remeasured turbidities and included higher concentrations than our measurements. Their values fell between ours and those of Kronman and Timasheff.[3] They calculated water activities from turbidities, and claimed agreement with some preliminary values obtained isopiestically by Tyree and co-workers at the University of North Carolina (UNC). The turbidities they calculated from the isopiestic measurements were 6–10% lower than their measured values. However, differences between turbidities measured in the various laboratories are considerably greater.

Scatchard and Yoest at the Massachusetts Institute of Technology (MIT) also carried out some isopiestic measurements, and in collaboration with the UNC group, published[5] an analysis of both sets (MIT–UNC). They concluded that some early low concentration UNC points, which appeared to extrapolate to lower activity coefficient values than we obtained by ultracentrifugation, were in error, that the ultracentrifugation and isopiestic methods were in reasonably good agreement, and that their values were substantially different from KKOM over the entire concentration range.

Shortly before their paper appeared, a second Kerker group (KOK) published another study[6] of water activities of tungstosilicic acid solutions, this time measured with a vapor-phase osmometer. This set of values fell between KKOM and MIT–UNC. Pelzer and Schönert[7] have recently published osmotic coefficients of aqueous $HCl-H_4SiW_{12}O_{40}$ solutions. Although no two-component tungstosilicic acid solutions were included in their study, they concluded that their data indicated closer agreement at low concentrations with the preliminary UNC osmotic coefficients than with our ultracentrifugation values.

From this summary, it is apparent that there is no general agreement concerning the free energies of tungstosilicic acid–water solutions. Although equilibrium ultracentrifugation and the MIT–UNC study are consistent, the scatter of the data makes further study desirable, and the rejection of low-concentration points from the preliminary UNC study should be confirmed. Resolution of these conflicts with other laboratories is desirable, not only because of the widespread interest in this system, but also because a suggestion we made,[2] that $H_4SiW_{12}O_{40}$ solutions might be useful in calibration of light scattering photometers for measurements of aqueous solutions, depends on knowledge of the nonideality of the system. We have therefore carried out isopiestic measurements extending both higher and lower in concentration (from 0.02 to 1.3 *m*) than previously made by this technique.

Experimental Section

The isopiestic equipment and the techniques of measurement have been described previously.[8] Sodium chloride solutions were used as standards, and two cups were used for each solution and standard; the concentration of solutions in each of the duplicates for each

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corporation.

(2) J. S. Johnson, K. A. Kraus, and G. Scatchard, *J. Phys. Chem.*, 64, 1867 (1960).

(3) M. J. Kronman and S. N. Timasheff, *ibid.*, 63, 629 (1959).

(4) M. Kerker, J. P. Kratohvil, R. H. Ottewill, and E. Matijevic, *ibid.*, 67, 1097 (1963).

(5) S. Y. Tyree, Jr., R. L. Angstadt, F. C. Hentz, Jr., R. L. Yoest, and G. Scatchard, *ibid.*, 70, 3917 (1966).

(6) J. P. Kratohvil, L. E. Oppenheimer, and M. Kerker, *ibid.*, 70, 2834 (1966).

(7) H. Pelzer and H. Schönert, *Ber. Bunsenges. Physik. Chem.*, 70, 897 (1966).

(8) R. M. Rush and J. S. Johnson, *J. Chem. Eng. Data*, 11, 590 (1966).