and to poorer iron content. Crystal field parameters are probably such that the iron ions are less strongly bound to the lattice. This would explain the lower iron content found by ESCA.

In compounds where the $Fe-O_2$ is more ionic, the O_2^- radical which is formed is at the origin of other reactions, in particular the irreversible formation of hydrogen peroxide.

Looking at the results reported here, we anticipate that further studies on the initial or model compounds of these systems will shed light on these mechanisms.

Acknowledgment. Special thanks are due to our colleagues of the Laboratoire de Catalyse and in particular to Professor E. G. Derouane for assistance in obtaining and interpreting EPR spectra and also to the Laboratoire d'Analyses par Rêactions Nuclêaires (Namur) and to the Central Laboratory of the Solvay Co. (Brussels) for providing spectral analyses of the samples, as well as to Professor P. Caro (CNRS, Bellevue) for stimulating comments on this work. The authors wish to thank their colleagues at the Laboratoire de Spectroscopie Electronique for many helpful discussions and especially Dr. Joseph Riga. We dedicate this work to the memory of Mr. Vincent Van Uytvanck, a chemistry student at this Faculty, who collaborated on the project. S.M. is indebted to IRSIA (Belgium) for a doctoral fellowship; financial support to M.S. by the French–Belgian Cultural Exchange program is gratefully acknowledged.

Registry No. PcFe monomer, 132-16-1; PcFe dimer, 70728-85-7; PcFe polymer, 70728-87-9; O_2, 7782-44-7.

References and Notes

(1) J. P. Collman, J. I. Brauman, and S. Suslick, *J. Am. Chem. Soc.*, **97**, 7185 (1975).
(2) (a) G. B. Boreskov, A. P. Dzisyak, and L. A. Kasatkina, *Kinet. Katal.*, 381 (1962); (b) G. B. Boreskov, W. Poporsky, and V. C. Sazonor, *Porous Struct. Catal. Transp. Processes Heterogeneous Catal., Symp.*, 590 (1968).
(3) W. J. Wallace and W. S. Caughey, *Biochem. Biophys. Res. Commun.*, **61**, 635 (1974).
(4) A. J. Appleby, J. Fleisch, and M. Savy, *J. Catal.*, **44**, 281 (1976).
(5) M. Savy, C. Bernard, and G. Magner, *Electrochim. Acta*, **20**, 383 (1975).
(6) E. V. Dose, M. A. Hoselton, N. Sutin, M. F. Tweedle, and L. J. Wilson, *J. Am. Chem. Soc.*, **100**, 1141 (1978).
(7) (a) P. Caro, M. Faucher, and M. Savy, XVIIIth IUPAC Conference, Sao Paulo, Brazil, 1977; (b) P. Caro, M. Faucher, M. Savy, and H. Pankowska, *J. Chem. Phys.*, **68**, 1045 (1978).
(8) A. J. Appleby and M. Savy, *Electrochim. Acta*, **21**, 576 (1976).
(9) M. Savy, P. Andro, and C. Bernard, *Electrochim. Acta*, **19**, 403 (1974).
(10) W. C. Drinkard and J. C. Bailar, Jr., *J. Chem. Soc.*, **81**, 4795 (1959).
(11) J. J. Pireaux, *Appl. Spectrosc.* **30**, 219 (1976).
(12) H. Höchst, A. Goldmann, S. Hufner, and H. Malter, *Phys. Status Solidi B*, **76**, 559 (1976).
(13) Y. Niwa, H. Kobayashi, and T. Tsuchiya, *J. Chem. Phys.*, **60**, 799 (1974).
(14) Y. Niwa, H. Kobayashi, and T. Tsuchiya, *Inorg. Chem.*, **13**, 2891 (1974).
(15) M. Barber and D. T. Clark, *J. Chem. Soc. D*, 24 (1974).
(16) H. Inoue, Y. Kida, and E. Imoto, *Bull. Chem. Soc. Jpn.*, **40**, 184 (1967).
(17) S. K. Sen, *Ann. Soc. Sci. Bruxelles Ser. 1*, **90**, 125 (1976).
(18) A. Dedieu, M. Rohmer, H. Veillard, and A. Veillard, *Bull. Soc. Chim. Belg.*, **85**, 953 (1976).
(19) S. P. Kowalczyk, Ph.D. Thesis, University of California, Berkeley, 1976.
(20) A. M. Schäffer, M. Gouterman, and E. R. Davidson, *Theor. Chim. Acta*, **30**, 9 (1973).
(21) J. Riga, J. J. Pireaux, and J. Verbist, *Mol. Phys.*, **34**, 131 (1977).
(22) (a) M. C. Hayoit de Termicourt, Mêmoire de Licence, Namur, 1977; (b) J. Riga, M. C. Hayoit de Termicourt, J. Leblanc-Lepêre and J. Verbist, to be submitted for publication.
(23) U. Gelius in "Electron Spectroscopy", D. A. Shirley, Ed., North-Holland Publishing Co., Amsterdam, 1972, p 487.
(24) F. L. Battye, A. Goldmann, and L. Kasper, *Phys. Status Solidi B*, **80**, 425 (1977).
(25) B. W. Dale, R. J. P. Williams, P. R. Edwards, and C. E. Johnson, *J. Chem. Phys.*, **49**, 3441 (1968).
(26) J. H. Scofield, *J. Electron Spectrosc. Relat. Phenom.*, **8**, 129 (1976).
(27) L. Pauling and C. D. Coryell, *Proc. Natl. Acad. Sci. USA*, **22**, 210 (1936).
(28) (a) L. Pauling, "Haemoglobin", Butterworths, London, 1949, p 57; (b) L. Pauling, *Nature (London)*, **203**, 182 (1964); (c) J. J. Weiss, *ibid.*, **202**, 83 (1964); (d) *ibid.*, **203**, 183 (1964).
(29) J. S. Griffith, *Proc. R. Soc. London, Ser. A*, **235**, 23 (1956).
(30) (a) G. A. Rodley and W. T. Robinson, *Nature (London)*, **235**, 438 (1972); (b) J. P. Collman, H. Takaya, B. Winkler, L. Libit, S. K. Seah, G. A. Rodley, and W. T. Robinson, *J. Am. Chem. Soc.*, **95**, 1656 (1973); (c) J. P. Collman, R. R. Gagne, C. A. Reed, T. R. Albert, G. Lang, and W. T. Robinson, *ibid.*, **97**, 1427 (1975).
(31) (a) R. Hoffmann, M. M. L. Chen, M. Elian, A. R. Rossi, and D. M. P. Mingos, *Inorg. Chem.* **13**, 2666 (1974); (b) E. Ochiai, *J. Inorg. Nucl. Chem.*, **35**, 3375 (1973).
(32) (a) P. Fantucci, V. Valenti, F. Cariati, and I. Fragala, *Inorg. Nucl. Chem. Lett.*, **11**, 585 (1975); (b) J. H. Burness, J. G. Dillard, and L. T. Taylor, *J. Am. Chem. Soc.*, **97**, 6080 (1975).
(33) A. Dedieu, M. M. Rohmer, and A. Veillard, *J. Am. Chem. Soc.*, **98**, 5789 (1976).
(34) G. A. Allen, M. T. Curtis, A. J. Hooper, and P. H. Trucker, *J. Chem. Soc., Dalton Trans.*, **14**, 1525 (1974).
(35) K. Asami, K. Hashimoto, and S. Shimodaira, *Corros. Sci.*, **16**, 33 (1976).
(36) N. S. McIntyre, D. G. Zetaruk, *Anal. Chem.*, **49**, 1521 (1977).

Contribution from the Department of Chemistry,
Texas Tech University, Lubbock, Texas 79409

Reduction of the Bis(2,9-dimethyl-1,10-phenanthroline)copper(II) Ion by Substituted Hydroquinones

JOHN D. CLEMMER, GILBERT K. HOGABOOM, and ROBERT A. HOLWERDA*

Received March 9, 1979

Anaerobic stopped-flow kinetic studies of the reduction of the bis(2,9-dimethyl-1,10-phenanthroline)copper(II) ion ($Cu(dmp)_2^{2+}$) by 16 monosubstituted hydroquinones (H_2Q-X) have been performed ($\mu = 0.2$ M (acetate)). In each case, the rate law was found to be $d[Cu(dmp)_2^+]/dt = (k_1 + (k_2/[H^+]))[H_2Q\text{-X}][Cu(dmp)_2^{2+}]$ within the range pH 4–6 at 25 °C. The data are consistent with a mechanism involving reduction of $Cu(dmp)_2^{2+}$ by both the un-ionized and monoionized forms of H_2Q-X. For hydroquinone, rate constants (25 °C) and activation parameters associated with reduction of $Cu(dmp)_2^{2+}$ by H_2Q and HQ^- are 1.2×10^2 M^{-1} s^{-1} ($\Delta H^{\ddagger} = 15.6$ kcal/mol, $\Delta S^{\ddagger} = +3$ cal/(mol deg)) and 2.5×10^7 M^{-1} s^{-1} ($\Delta H^{\ddagger} = 12.5$ kcal/mol, $\Delta S^{\ddagger} = +18$ cal/mol deg), respectively. It is shown that Marcus theory for outer-sphere electron transfer accounts reasonably well for the dependence of rate on thermodynamic driving force in the reactions of both H_2Q-X and $(HQ\text{-X})^-$ with $Cu(dmp)_2^{2+}$. Marcus theory calculations further demonstrate that the 10^5-fold reactivity difference between H_2Q-X and $(HQ\text{-X})^-$ is entirely attributable to the more favorable standard free energy exchange for the latter substrate. Finally, comparisons are made between the electron-transfer reactivities of substituted hydroquinones with $Cu(dmp)_2^{2+}$ and the type 1 copper site in the metallo enzyme laccase.

Introduction

We have recently been interested in the factors governing the electron-transfer reactivity of substituted hydroquinones with copper-containing metallo enzymes and with low molecular weight transition-metal ion oxidants. Of particular interest is the relationship between rate and thermodynamic driving force in these systems. According to Marcus theory for outer-sphere electron transfer, the excess free energy of

0020-1669/79/1318-2567$01.00/0 © 1979 American Chemical Society

activation for a cross reaction (ΔG^*_{12}) varies with the standard free energy change for the redox step (ΔG°_{12}) as in eq 1 and 2,[1] where ΔG^*_{11} and ΔG^*_{22} are the activation free energies

$$\Delta G^*_{12} = W_r + \lambda\left(1 + \frac{\Delta G^\circ_{12}}{\lambda}\right)^2/4 \qquad (1)$$

$$\lambda = 2(\Delta G^*_{11} + \Delta G^*_{22}) \qquad (2)$$

for the self-exchange electron-transfer reactions of the redox partners. The W_r term accounts for the work required to bring the reactants into the activated complex. This equation has now been used successfully in correlating ΔG^*_{12} and ΔG°_{12} values for electron transfer from hydroquinone and its derivatives to a number of one-electron transition-metal ion oxidants, including $Fe(phen)_3^{3+}$,[2] $IrCl_6^{2-}$,[3] Np(VI),[4] Fe(III),[4] $Mo(CN)_8^{3-}$,[5] and the 12-tungstocobaltate(III) ion.[6]

Recently completed mechanistic studies of the oxidation of substituted hydroquinones (H_2Q-X) by the type 1 copper site of *Rhus vernicifera* laccase, a polyphenol oxidase, have shown that rate constants for electron transfer within the enzyme–substrate complex do not exhibit the dependence on thermodynamic driving force expected from eq 1; for most substrates this rate constant is in fact essentially independent of the nature of the substituent X (average value for ten substrates is 30 ± 10 s^{-1}; 25 °C, pH 7.0, μ = 0.5 M (phosphate)).[7] On this basis it was concluded that protein-dependent activation requirements overshadow the Franck–Condon rearrangement contributions for type 1 Cu(II) and the substituted hydroquinone. This conclusion rests upon the assumption that the Marcus equation is obeyed in reactions of H_2Q-X with copper(II) species under conditions where activation requirements associated with the electron transfer act are dominant.

Kinetic results for the oxidation of 16 monosubstituted hydroquinones by the bis(2,9-dimethyl-1,10-phenanthroline)copper(II) ion ($Cu(dmp)_2^{2+}$) are reported in this paper, and the dependence of rate on thermodynamic driving force is examined. Rate constants are given for the reactions of $Cu(dmp)_2^{2+}$ with both the un-ionized and monoionized ($(HQ\text{-}X)^-$) forms of these substrates, and the relative electron-transfer reactivity of these two species is discussed.

Experimental Section

Reagents. Copper acetate monohydrate was recrystallized from water before use, and 2,9-dimethyl-1,10-phenanthroline (G. F. Smith) was used as received. Ionic strength 0.2 M sodium acetate buffers prepared with triply distilled water were used for all kinetic studies. Anaerobic solutions of $Cu(dmp)_2^{2+}$ and substituted hydroquinones were prepared in serum-capped bottles by purging with oxygen-free N_2 for a minimum of 30 min. Solutions of $Cu(dmp)_2^{2+}$ were stored in the dark to protect against photoinduced reduction to $Cu(dmp)_2^+$.

Hydroquinone, bromohydroquinone, and 2,5-dihydroxybenzoic acid were used as supplied by Eastman. Methoxyhydroquinone, methylhydroquinone, hydroxyhydroquinone, and hydroquinonesulfonic acid (potassium salt) obtained from Aldrich also were used without further purification. Practical chlorohydroquinone (Eastman) and *tert*-butylhydroquinone (Aldrich) were purified by vacuum sublimation. Fluorohydroquinone and (trifluoromethyl)hydroquinone were prepared by the method of Feiring and Sheppard.[8] The reaction of tri-*n*-butylborane with *p*-benzoquinone in diethyl ether was used to prepare *n*-butylhydroquinone.[9] Kvalnes' procedure was followed for the most part in synthesizing iodohydroquinone.[10] The iodobenzoquinone intermediate was purified through vacuum sublimation and reduced to the hydroquinone with $SnCl_2$. Pure iodohydroquinone was obtained by recrystallization from $CHCl_3$. The method of Wallenfels et al.[11] was followed to prepare cyanohydroquinone. The methyl ester of 2,5-dihydroxybenzoic acid was obtained by refluxing the parent acid in CH_3OH saturated with HBr.[12] Nitrohydroquinone was obtained through the nitration of hydroquinone monobenzoate, followed by saponification of the ester in basic solution.[13]

Vacuum sublimation was the final purification step for all compounds synthesized except *n*-butylhydroquinone and iodohydroquinone. The purity of all compounds except H_2O-SO_3K was confirmed through comparisons of melting points with the literature values. Literature infrared spectra, where available, were found to be in excellent agreement with those measured for hydroquinones used in our kinetic studies, and proton NMR spectra of methyl 2,5-dihydroxyphenyl benzoate and *n*-butylhydroquinone confirmed the presence of $COOCH_3$ and C_4H_9 substituents, respectively. The purity of hydroquinonesulfonic acid (potassium salt) was determined to be >98% through a ceric titration using ferroin as the indicator.

Determination of Hydroquinone Ionization Constants. Room-temperature first ionization constants (K_a^1) for H_2Q-F, H_2Q-Br, H_2Q-I, H_2Q-CF_3, H_2Q-CN, H_2Q-$C(CH_3)_3$, H_2Q-SO_3^-, and H_2Q-n-C_4H_9 were determined spectrophotometrically by the method of Baxendale and Hardy.[14] Ultraviolet spectra of the substituted hydroquinones in anaerobic, ionic strength 0.2 M sodium phosphate buffers (pH 4–11) were recorded in the range 280–350 nm. K_a^1 values were derived from the least-squares slopes of $(A - A_0)[H^+]$ vs. A plots, where A represents the absorbance at a particular wavelength and hydrogen ion concentration and A_0 corresponds to the absorbance at the same wavelength measured under conditions where essentially all of the hydroquinone is present as the un-ionized form (ca. pH 4). Slopes of $(A - A_0)[H^+]$ vs. A plots for several wavelengths were averaged to give the reported K_a values.

Stoichiometric Measurements. The stoichiometry of the reaction between hydroquinone and $Cu(dmp)_2^{2+}$ was determined spectrophotometrically by mixing H_2Q with excess oxidant anaerobically in a serum-capped bottle with Hamilton gastight syringes and by measuring the absorbance change at 454 nm, λ_{max} for the $Cu(dmp)_2^+$ product. The number of moles of $Cu(dmp)_2^+$ produced per mole of H_2Q consumed was obtained by using $\epsilon_{454} = 1.09 \times 10^4$ M^{-1} cm^{-1}, the value measured for $Cu(dmp)_2^+$ under the experimental conditions (pH 6.0, μ = 0.2 M (acetate)) by completely reducing a known amount of $Cu(dmp)_2^{2+}$ with sodium ascorbate. The absorbance of the organic product (1,4-benzoquinone) at 454 nm was shown to be negligible compared with that of $Cu(dmp)_2^+$.

Kinetic Measurements. Formation of $Cu(dmp)_2^+$ was followed at 454 nm with a Durrum D-110 stopped-flow spectrophotometer. Pseudo-first-order conditions for $Cu(dmp)_2^{2+}$ were employed, holding the oxidant concentration constant at 10 μM and varying the reductant concentration from 0.1 to 40 mM. Anaerobic solutions of $Cu(dmp)_2^{2+}$ were transferred to the stopped-flow apparatus through Teflon needles to avoid contamination with iron. A minimum of 30 min was allowed for temperature equilibration to occur before kinetics runs were performed. Most runs were performed with solutions of cupric acetate containing sufficient dmp to give a $[dmp]/[Cu(II)]_{tot}$ ratio of 25 after taking protonation of dmp to $dmpH^+$ into account ($pK_a(dmpH^+)$ = 5.85; 25 °C, μ 0.1 M).[15] With Irving and Mellor's formation constants for $Cu(dmp)^{2+}$ and $Cu(dmp)_2^{2+}$ it is easily shown that >99% of all Cu(II) in solution is present as $Cu(dmp)_2^{2+}$ under these conditions.

Observed first-order rate constants (k_{obsd}) were derived as usual from the least-squares slopes of linear ln $(A_\infty - A_t)$ vs. time plots. Absorbance–time data were obtained as photographs of oscilloscope traces (Tektronix Model 564 B) or as output from a Hewlett-Packard 7004 B X-Y recorder. Reported rate constants are the average of at least three determinations.

Instrumentation. Infrared spectra (KBr pellet) were recorded with a Perkin-Elmer 457 spectrophotometer, and NMR spectra (acetone-d_6 solvent) were obtained with a Varian A-60 spectrometer. All UV–visible spectral data were acquired on a Cary 17 spectrophotometer. A Metrhom/Brinkmann pH-103 meter calibrated with pH 4, 7, and 9 standards was used to make pH measurements (±0.02-unit accuracy). The final pH of reaction solutions was always within experimental error of that for the acetate buffer alone.

Results

Stoichiometric results for the oxidation of hydroquinone by excess $Cu(dmp)_2^{2+}$ indicate that 2.06 ± 0.06 mol of $Cu(dmp)_2^+$ are produced/mol of H_2Q consumed, consistent with the overall process of eq 3, where Q represents 1,4-benzoquinone.

$$H_2Q + 2Cu(dmp)_2^{2+} \rightarrow 2Cu(dmp)_2^+ + Q + 2H^+ \qquad (3)$$

Plots of ln $(A_\infty - A_t)$ vs. time based on 454-nm data for the reduction of $Cu(dmp)_2^{2+}$ by H_2Q and substituted hydroquinones invariably were found to be linear for >95%

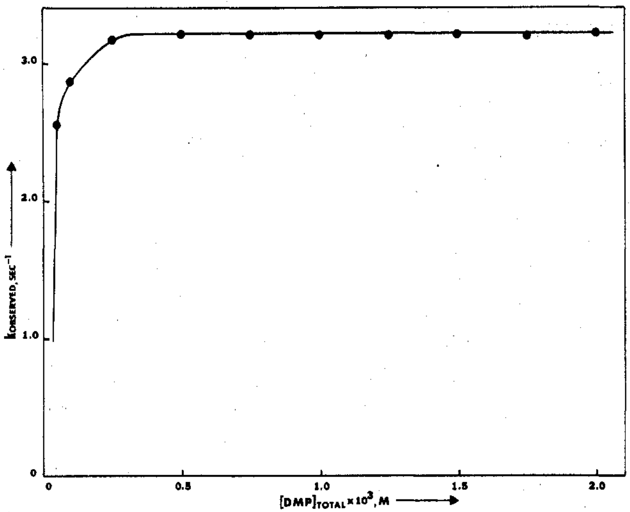

Figure 1. Dependence of k_{obsd} on [dmp] for $[H_2Q] = 1.0 \times 10^{-3}$ M; 25.0 °C, pH 6.0, $\mu = 0.2$ M (acetate).

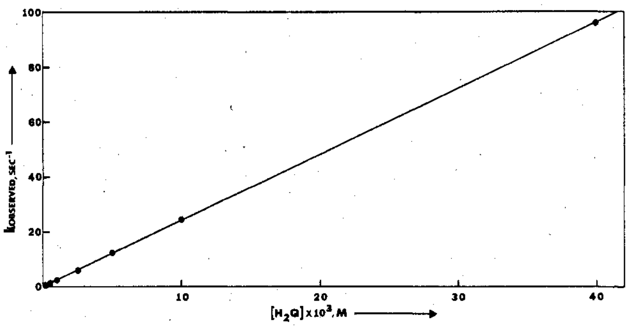

Figure 2. Plot illustrating the first-order reducing-agent dependence in the reaction of H_2Q with $Cu(dmp)_2^{2+}$; 25.0 °C, pH 5.81, $\mu = 0.2$ M (acetate).

of the reactions, indicating a first-order $Cu(dmp)_2^{2+}$ dependence in each case. The dependence of k_{obsd} on $[dmp]_{tot}$ at constant $[H_2Q]$ and pH was examined to confirm that $Cu(dmp)_2^{2+}$ is the predominant Cu(II) species in solution under our conditions. Figure 1 shows that k_{obsd} reaches a limiting value above $[dmp]_{tot} = 2.5 \times 10^{-4}$ M, indicating that a 25-fold excess of dmp (including both dmp and $dmpH^+$) is adequate to fully convert all of the copper in solution to $Cu(dmp)_2^{2+}$ at pH 6. It seems clear, therefore, that $Cu(dmp)_2^{2+}$ predominates also under our standard conditions for kinetic measurements (25-fold excess of *free* dmp over Cu(II)).

Kinetic data describing the variation of k_{obsd} with [H_2Q-X] at constant pH are assembled in Table I,[16] and concentration dependence data for the reaction of H_2Q with $Cu(dmp)_2^{2+}$ at pH 5.81 are illustrated in Figure 2. The reactions of $Cu(dmp)_2^{2+}$ with all 15 substrates examined are first order with respect to the hydroquinone; 10–20-fold concentration ranges were covered in most cases. Concentration-dependence studies were not carried out for the reaction of H_2Q-NO_2 with $Cu(dmp)_2^{2+}$, as the high absorbance of this substrate at 454 nm exceeded the offset capability of the stopped-flow apparatus for $[H_2Q\text{-}NO_2] > 5 \times 10^{-4}$ M. It is assumed that a first-order reducing-agent dependence pertains for this substrate as well. The k_{obsd} vs. $[H_2Q\text{-}COO^-]$ plot (pH 5.61) shows a slight deviation from simple first-order behavior, as a nonzero intercept (1.4 s^{-1}) is obtained from the linear least-squares analysis. While this intercept might be assigned to a reducing-agent-independent term in the rate law, its small contribution to k_{obsd} makes its kinetic significance doubtful.

Table II[16] summarizes the results of kinetic studies in which the dependence of k_{obsd} on pH (4 < pH < 6) was examined at constant H_2Q-X concentration. A plot of k_{obsd} vs. $[H^+]^{-1}$ for the H_2Q–$Cu(dmp)_2^{2+}$ reaction (Figure 3) shows that the complete rate law is as shown in eq 4, where $k_1 = 1.2 \times 10^2$ M^{-1} s^{-1} and $k_2 = 3.5 \times 10^{-3}$ s^{-1} at 25 °C. Analogous plots based on pH-dependence results for the substituted hydroquinones also are consistent with a rate law containing both an inverse first-order term in H^+ and an H^+-independent term. In some cases, however, the intercept terms (k_1) are so small as to be within experimental error of zero. The parameters k_1 and k_2, obtained from the least-squares analysis of k_{obsd} vs. $[H^+]^{-1}$ plots, are given in Table III along with pK_a^1 values for H_2Q-F, H_2Q-Br, H_2Q-I, H_2Q-CF_3, H_2Q-CN, H_2Q-$C(CH_3)_3$, H_2Q-SO_3^- and H_2Q-n-C_4H_9.

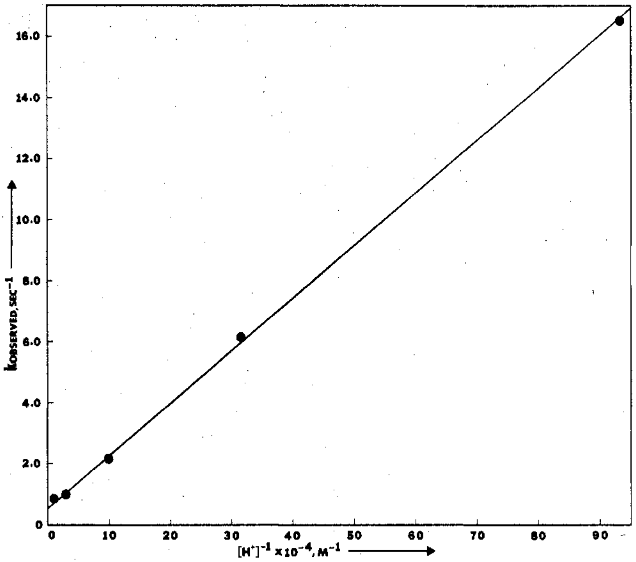

Figure 3. Plot illustrating the relationship $k_{obsd} = (k_1 + (k_2/[H^+]))[H_2Q]$ for the reaction of $Cu(dmp)_2^{2+}$ with hydroquinone; $[H_2Q] = 5.0 \times 10^{-3}$ M, 25.0 °C, $\mu = 0.2$ M (acetate).

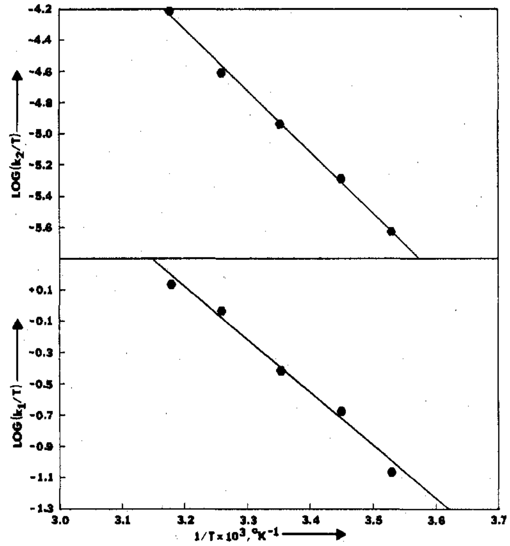

Figure 4. Eyring plots based on the rate parameters k_1 and k_2 for the H_2Q–$Cu(dmp)_2^{2+}$ reaction; $\mu = 0.2$ M (acetate).

$$\frac{d[Cu(dmp)_2^{+}]}{dt} = \left(k_1 + \frac{k_2}{[H^+]}\right)[H_2Q][Cu(dmp)_2^{2+}] \quad (4)$$

The pH-dependence of rate constants for the reduction of $Cu(dmp)_2^{2+}$ by hydroquinone was examined at five temperatures between 10.2 and 41.5 °C in order to obtain the activation parameters associated with k_1 and k_2. The relationship $k_{obsd} = (k_1 + (k_2/[H^+]))[H_2Q]$ pertains over the entire temperature range, and excellent linear Eyring plots of log

Table III. Rate Parameters for the Oxidation of Substituted Hydroquinones by $Cu(dmp)_2^{2+}$ [a,b]

substrate	$10^{-2}k_1$, M^{-1} s^{-1}	10^2k_2, s^{-1}	$10^{-7}k_2'$, M^{-1} s^{-1} [c]	$pK_a^1(H_2Q\text{-}X)$ [d]	$E°(Q\text{-}X)$, V
H_2Q	1.2 (0.2)	0.349 (0.011)	2.5	9.85[e]	0.699[i]
H_2Q-F	2.7 (1.4)	1.89 (0.062)	0.86	8.66 (0.04)	0.693[j]
H_2Q-Cl	5.1 (3.9)	5.16 (0.17)	4.1	8.90[f]	0.712[i]
H_2Q-Br		6.24 (0.20)	2.1	8.53 (0.05)	0.712[i]
H_2Q-I	1.2 (0.8)	5.64 (0.18)	3.6	8.81 (0.05)	0.706[k]
H_2Q-OH	84.9 (4.1)	7.57 (0.25)	9.1	9.08[g]	0.601[g]
$H_2Q\text{-}OCH_3$	66.5 (4.3)	14.47 (0.47)	118	9.91[f]	0.594[l]
$H_2Q\text{-}COO^-$	2.4 (0.4)	0.856 (0.028)	27	10.50[h]	0.674[m]
$H_2Q\text{-}COOCH_3$		0.300 (0.010)	1.3	9.63[g]	0.794[g]
$H_2Q\text{-}CH_3$	7.0 (0.6)	1.12 (0.04)	13	10.05[e]	0.643[i]
$H_2Q\text{-}CF_3$		0.801 (0.026)	0.37	8.66 (0.06)	0.776[j]
$H_2Q\text{-}n\text{-}C_4H_9$	16.9 (0.4)	1.46 (0.05)	26	10.25 (0.05)	0.639[m]
$H_2Q\text{-}C(CH_3)_3$	7.6 (0.3)	0.954 (0.031)	16	10.22 (0.07)	0.628[m]
H_2Q-CN		7.89 (0.26)	0.25	7.50 (0.03)	0.747[m]
$H_2Q\text{-}NO_2$		3.41 (0.11)	0.10	7.47[g]	0.752[g]
$H_2Q\text{-}SO_3^-$		0.171 (0.006)	0.61	9.55 (0.03)	0.787[n]

[a] 25.0 °C, $\mu = 0.2$ M (acetate). [b] Uncertainties shown in parentheses. [c] $k_2' = k_2/K_a^1(H_2Q\text{-}X)$. [d] Based on first ionization constant for the phenolic OH group. [e] 25.0 °C (H_2Q), 25.1 °C ($H_2Q\text{-}CH_3$), $\mu = 0.65$ M.[14] [f] 25 °C, $\mu = 0.375$ M: C. A. Bishop and L. K. J. Tong, *J. Am. Chem. Soc.*, 87, 501 (1965). [g] 20 °C, $\mu = 0.1$ M: J. Sunkel and H. Staude, *Ber. Bunsenges. Phys. Chem.*, 72, 567 (1968). [h] "Lange's Handbook of Chemistry", J. A. Dean, Ed., 11th ed., McGraw-Hill, New York, 1973. [i] W. M. Clark, "Oxidation-Reduction Potentials of Organic Systems", Williams and Wilkins, Baltimore, MD, 1960. [j] Estimated from half-wave potential.[8] [k] Reference 10. [l] L. F. Fieser, *J. Am. Chem. Soc.*, **52**, 5204 (1930). [m] Extrapolated from a plot of $E°(Q\text{-}X)$ vs. $pK_a^1(H_2Q\text{-}X)$, following the method described in ref 3. [n] Reference 2.

(k_1/T) and log (k_2/T) vs. $1/T$ (Figure 4) were derived from the temperature-variation data. The activation parameters obtained from the slopes and intercepts of these Eyring plots are as follows: k_1, $\Delta H^\ddagger = 15.6 \pm 1.1$ kcal/mol, $\Delta S^\ddagger = +3 \pm 1$ cal/(mol deg); k_2, $\Delta H^\ddagger = 18.0 \pm 0.6$ kcal/mol, $\Delta S^\ddagger = -9.6 \pm 0.5$ cal/(mol deg).

Discussion

Our kinetic results for the reduction of $Cu(dmp)_2^{2+}$ by substituted hydroquinones are readily understood in terms of a mechanism involving electron transfer to the oxidant from both the un-ionized and monoionized ($(HQ\text{-}X)^-$) forms of the hydroquinone reductants (eq 5). Disproportionation of the

$$H_2Q\text{-}X + Cu(dmp)_2^{2+} \xrightarrow{k_1} (HSQ\text{-}X)^+ + Cu(dmp)_2^+$$

$$2(HSQ\text{-}X)^+ \rightarrow H_2Q\text{-}X + Q\text{-}X + 2H^+ \quad \text{fast}$$

$$H_2Q\text{-}X \overset{K_a^1}{\rightleftharpoons} (HQ\text{-}X)^- + H^+ \quad \text{fast} \qquad (5)$$

$$(HQ\text{-}X)^- + Cu(dmp)_2^{2+} \xrightarrow{k_2'} SQ\text{-}X + Cu(dmp)_2^+$$

$$2SQ\text{-}X \rightarrow H_2Q\text{-}X + Q\text{-}X \quad \text{fast}$$

semiquinone one-electron oxidation products of H_2Q-X ($(HSQ\text{-}X)^+$) and $(HQ\text{-}X)^-$ (SQ-X) must be very fast, as no evidence was obtained for subsequent reaction of these species with $Cu(dmp)_2^{2+}$. The rate law (eq 6) expected on the basis

$$\frac{d[Cu(dmp)_2^+]}{dt} = \left(k_1 + \frac{K_a^1 k_2'}{[H^+]}\right)[H_2Q\text{-}X][Cu(dmp)_2^{2+}] \qquad (6)$$

of this mechanism is consistent with the experimental result, considering that H_2Q-X is only slightly ionized to $(HQ\text{-}X)^-$ between pH 4 and 6. On this basis, the experimental rate constant for the $[H^+]^{-1}$ term, k_2, is equivalent to $K_a^1k_2'$; k_2' values calculated from this relationship are given in Table III.

Davies et al. have suggested that there is at least one water molecule in the first coordination sphere of $Cu(dmp)_2^{2+}$(aq) and estimate an upper limit for the ionization constant of this complexed H_2O molecule at 4×10^{-10} M (25 °C).[17] A kinetically indistinguishable alternative to the above mechanism (eq 7) requires competitive reduction of $Cu(dmp)_2^{2+}$(aq) and

$$H_2Q\text{-}X + Cu(dmp)_2^{2+} \xrightarrow{k_1} (HSQ\text{-}X)^+ + Cu(dmp)_2^+$$

$$2(HSQ\text{-}X)^+ \rightarrow H_2Q\text{-}X + Q\text{-}X + 2H^+ \quad \text{fast}$$

$$Cu(dmp)_2^{2+}(aq) \overset{K_h}{\rightleftharpoons} Cu(dmp)_2OH^+ + H^+ \quad \text{fast} \qquad (7)$$

$$H_2Q\text{-}X + Cu(dmp)_2OH^+ \xrightarrow{k_2''} SQ\text{-}X + Cu(dmp)_2^+$$

$$2SQ\text{-}X \rightarrow H_2Q\text{-}X + Q\text{-}X \quad \text{fast}$$

$Cu(dmp)_2OH^+$ by H_2Q-X. In this case, the relationship $k_2 = K_hk_2''$ would pertain. Rate constants derived from the H_2Q-X and $Cu(dmp)_2^{2+}$(aq) ionization mechanisms are comparable (i.e., for H_2Q: $k_2' = 2.5 \times 10^7$ M^{-1} s^{-1}, $k_2'' \leq 9 \times 10^6$ M^{-1} s^{-1}; 25 °C), and there is, unfortunately, no basis for unambiguously excluding either possibility. Nevertheless, several considerations lead us to prefer the H_2Q-X ionization mechanism. First, inverse first-order terms in H^+ have been identified in the rate laws of hydroquinone reactions for which there is little possibility that ionization of the oxidant is responsible. Thus, $[H^+]^{-1}$ terms predominate in the reaction of H_2Q with the metalloproteins ferricytochrome *c*,[18] *Rhus vernicifera* laccase,[19] and parsley plastocyanin[20] under conditions similar to ours, and in each case the H_2Q-X ionization mechanism is preferred. Second, it is important to note that the rate constant k_2' (or k_2'') typically is larger than k_1 by a factor of ca. 10^5 throughout the entire series of monosubstituted hydroquinones. This large reactivity difference is difficult to understand in terms of the $Cu(dmp)_2^{2+}$(aq) ionization mechanism but may be readily accounted for considering the difference in thermodynamic driving force for the oxidation of H_2Q-X and $(HQ\text{-}X)^-$ (vide infra).

Correlating the rate constants in Table III with literature two-electron reduction potentials for Q-X reveals that there is a definite relationship between k_1 or k_2' values and the oxidizability of the hydroquinone substrate. Thus, rate constants for the reduction of $Cu(dmp)_2^{2+}$ by $(HQ\text{-}X)^-$ span a 10^3-fold range (1.0×10^6–1.2×10^9 M^{-1} s^{-1}), corresponding to a difference in $E°$ of 0.158 V between $Q\text{-}NO_2$ and $Q\text{-}OCH_3$. It is of interest, therefore, to determine whether ΔG^*_{12} values for the oxidation of the various un-ionized and monoionized hydroquinone substrates exhibit the dependence of $\Delta G°$

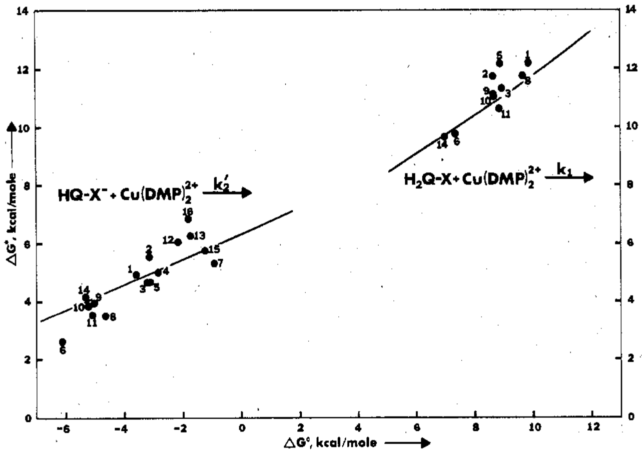

Figure 5. Correlation of activation free energy with standard free energy change for the oxidation of un-ionized and monoionized hydroquinones by $Cu(dmp)_2^{2+}$; 25.0 °C, $\mu = 0.2$ M (acetate). The least-squares lines have been drawn on the basis of eq 1, neglecting the work term W_r. Substrate key: 1, H_2Q; 2, H_2Q-F; 3, H_2Q-Cl; 4, H_2Q-Br; 5, H_2Q-I; 6, H_2Q-OCH_3; 7, H_2Q-$COOCH_3$; 8, H_2Q-COO^-; 9, H_2Q-CH_3; 10, H_2Q-$C(CH_3)_3$; 11, H_2Q-*n*-C_4H_9; 12, H_2Q-CF_3; 13, H_2Q-CN; 14, H_2Q-OH; 15, H_2Q-SO_3^-; 16, H_2Q-NO_2.

predicted by the equation from Marcus theory. The excess free energy of activation is related to the rate constant k_{12} by eq 8, where the collision frequency Z is taken to be 10^{11} M^{-1} s^{-1}.[1] For the reactions of monoionized hydroquinones, the standard free energy change for the redox step ($\Delta G°_{12}$) is that for reaction 9. It is easily shown that the equilibrium constant K_{12} may be calculated from eq 10, where K_0 and K_{SQ}, respectively, are equilibrium constants for reactions 11 and 12.

$$\Delta G^*_{12} = -RT \ln (k_{12}/Z) \qquad (8)$$

$$(HQ\text{-}X)^- + Cu(dmp)_2^{2+} \overset{K_{12}}{\rightleftharpoons} SQ\text{-}X + Cu(dmp)_2^+ \qquad (9)$$

$$K_{12} = (K_0 K_{SQ})^{1/2}/K_a^1 \qquad (10)$$

$$H_2Q\text{-}X + 2Cu(dmp)_2^{2+} \rightleftharpoons 2H^+ + Q\text{-}X + 2Cu(dmp)_2^+ \qquad (11)$$

$$H_2Q\text{-}X + Q\text{-}X \rightleftharpoons 2SQ\text{-}X \qquad (12)$$

K_0 has been calculated from the standard reduction potential for Q-X (Table III) and for $Cu(dmp)_2^{2+}$ (+0.640 V).[21] The semiquinone formation constant K_{SQ} has been estimated by using eq 13,[3] where K_{SQA} is the semiquinone formation constant based on the fully ionized forms of the hydroquinone, quinone, and semiquinone; K_a^2 and $K_a^2(SQ)$ are the second ionization constants of the hydroquinone and the semiquinone, respectively. The values of K_{SQA}, K_a^2, and $K_a^2(SQ)$ were extrapolated from graphs of these quantities vs. $E°$(Q-X) by following the procedure of Pelizzetti et al.[3] and by using literature data cited by these workers. When available, experimental values for these quantities were used in calculating K_{SQ}.

$$K_{SQ} = K_{SQA} K_a^1 K_a^2 (K_a^2(SQ))^{-2} \qquad (13)$$

The result of a nonlinear least-squares fitting of ΔG^*_{12}, $\Delta G°_{12}$ pairs to eq 1, treating only λ as a variable, is shown in Figure 5. Considering the rather large uncertainties in $\Delta G°_{12}$ values, owing principally to the extrapolations employed in calculating K_{SQ}, the observed fit is reasonably good. Only two of 16 substrates ($(HQ\text{-}NO_2)^-$ and $(HQ\text{-}OCH_3)^-$) deviate markedly from the least-squares curve over an interval of ca. 5 kcal/mol in $\Delta G°_{12}$. On this basis we conclude that the Marcus relationship does in fact successfully correlate rate with thermodynamic driving force in reactions of monoionized hydroquinones with $Cu(dmp)_2^{2+}$.

Marcus calculations have also been carried out for the reactions of un-ionized hydroquinones with $Cu(dmp)_2^{2+}$. The standard free energy change for the redox step is assumed to be that for reaction 14, and the equilibrium constant K_{12}' has been calculated from the relationship in eq 15. The nonlinear least-squares fit of $\Delta G^*_{12}(k_1)$, $\Delta G°_{12}'$ pairs to eq 1 (Figure 5) is not particularly good, possibly owing to the large uncertainties in k_1 values. The variation of ΔG^*_{12} with $\Delta G°_{12}'$ clearly is compatible with the Marcus theory equation, however, over the narrow interval in $\Delta G°_{12}'$ (3 kcal/mol) covered by the ten substrates for which k_1 could be determined.

$$H_2Q\text{-}X + Cu(dmp)_2^{2+} \overset{K_{12}'}{\rightleftharpoons} (HSQ\text{-}X)^+ + Cu(dmp)_2^+ \qquad (14)$$

$$K_{12}' = (K_0 K_{SQ})^{1/2} \qquad (15)$$

It is interesting to note that the Franck–Condon reorganizational factors (λ) derived from the least-squares fits for the reactions of $(HQ\text{-}X)^-$ (25.4 ± 0.6 kcal/mol) and H_2Q-X (23 ± 2 kcal/mol) are comparable in value, with λ for H_2Q-X actually being slightly smaller than that for monoionized hydroquinone substrates. This implies that the observed 10^5-fold advantage in electron-transfer reactivity for $(HQ\text{-}X)^-$ relative to that for H_2Q-X is entirely attributable to the $\Delta G°_{12}$ term. Indeed, Figure 5 makes it clear that the thermodynamic driving force for the reactions of monoionized hydroquinones ($-6 < \Delta G°_{12} < -1$ kcal/mol) greatly exceeds that for the reactions of the un-ionized substrates ($7 < \Delta G°_{12}' < 10$ kcal/mol).

The activation free energy of the hydroquinone/semiquinone self-exchange electron-transfer reaction has been estimated at ca. 4.5 kcal/mol.[3] Substituting this value into eq 2 and using the λ value derived for the $(HQ\text{-}X)^-$–$Cu(dmp)_2^{2+}$ reaction, we estimate the room-temperature activation free energy and rate constant for the $Cu(dmp)_2^{2+/+}$ self-exchange reaction at ca. 8 kcal/mol and 1×10^5 M^{-1} s^{-1}, respectively. This estimate of the inherent redox reactivity of the $Cu(dmp)_2^{2+/+}$ couple agrees reasonably well with that calculated by Augustin and Yandell from kinetic results for the reduction of $Cu(dmp)_2^{2+}$ by ferrocytochrome *c* ($k(Cu(dmp)_2^{2+/+}) = 1.2 \times 10^4$ M^{-1} s^{-1}; pH 6.1, $\mu = 0.1$ M, 25 °C).[22] Such a high electron-transfer reactivity seems reasonable on consideration of the small inner-sphere rearrangement barrier expected for the conversion of $Cu(dmp)_2^{2+}$, a flattened tetrahedral species,[23] to the tetrahedral[23] $Cu(dmp)_2^+$ ion.

To better understand the large reactivity difference between H_2Q-X and $(HQ\text{-}X)^-$ it is useful to compare activation parameters for their reactions with $Cu(dmp)_2^{2+}$. Activation parameters pertaining to the oxidation of HQ^- may be obtained from the relationships in eq 16 using Baxendale et al.'s thermodynamic parameters for the ionization of hydroquinone ($\Delta H°(K_a^1) = 5.5$ kcal/mol, $\Delta S°(K_a^1) = -28$ cal/(mol deg)).[24] On this basis we obtain the values $\Delta H^*(k_2') = 12.5$ kcal/mol and $\Delta S^*(k_2') = +18$ cal/(mol deg). Comparing these parameters with those for the oxidation of un-ionized hydroquinone reveals that favorable adjustments in both activation parameters are responsible for the 2×10^5-fold enhancement in k_2' relative to k_1; ΔH^* decreases by 3.1 kcal/mol, while ΔS^* increases by 15 cal/(mol deg).

$$\Delta H^*(k_2') = \Delta H^*(k_2) - \Delta H°(K_a^1)$$
$$\Delta S^*(k_2') = \Delta S^*(k_2) - \Delta S°(K_a^1) \qquad (16)$$

The activation parameters for the HQ^-–$Cu(dmp)_2^{2+}$ reaction clearly show that the large rate constant for this reaction may be attributed to an unusually favorable activation entropy for a bimolecular process; by contrast, the enthalpic activation barrier is substantially higher than that encountered for most fast electron-transfer processes. Desai and Milburn have shown that large positive entropies of formation are largely responsible for the stability of iron(III)–phenolate complexes; $\Delta H_f°$ values in this system are negligibly small compared with $-T\Delta S_f°$.[25] For example, $\Delta H_f°$ and $\Delta S_f°$ values for the $C_6H_5O^-$–Fe(III) reaction in aqueous solution ($\mu = 0.1$ M) are −0.5 kcal/mol and +33 cal/(mol deg), respectively.[25] Release of water molecules bound by the phenolate anion evidently provides much of the driving force for the formation of this type of complex. It seems likely, therefore, that changes in substrate–solvent interactions accompanying formation of the activated complex in the HQ^-–$Cu(dmp)_2^{2+}$ reaction are primarily responsible for the $\Delta S^‡$ value of +18 cal/(mol deg). The data do not by any means prove the existence of an inner-sphere intermediate complex between HQ^- and $Cu(dmp)_2^{2+}$, however, as disordering of water molecules of hydration would be expected even for the formation of an outer-sphere complex between oppositely charged species. The reasonable adherence to the Marcus relationship exhibited by the $(HQ\text{-}X)^-$–$Cu(dmp)_2^{2+}$ system provides good support for the conclusion that these reactions involve outer-sphere electron transfer.

Our kinetic results for reactions of substituted hydroquinones with $Cu(dmp)_2^{2+}$ demonstrate that the poor correlation between rate and thermodynamic driving force observed for electron transfer from these substrates to laccase type 1 Cu(II) is the exception rather than the rule for Cu(II) oxidants. The laccase and $Cu(dmp)_2^{2+}$ systems also differ in that exceptionally high enzyme-substrate complex formation constants are found in the enzyme's reactions with many hydroquinones having substituents possessing at least one lone pair of electrons.[7] These substituents evidently stabilize the precursor complex by functioning as ligands toward either the type 2 or type 3 copper site. By contrast, substituents provide no special stabilization of the precursor complex in the $Cu(dmp)_2^{2+}$–H_2Q-X system, as the rate saturation expected with the formation of a strong intermediate complex was not observed for any of the substituted hydroquinones. Experiments are now under way to determine the importance of hydroquinone substituents as ligands and bridging groups in reactions with other transition-metal ion oxidants.

Acknowledgment. We thank the Robert A. Welch Foundation for their support of this research (Grant D-735). Purchase of the stopped flow spectrophotometer was made possible through a Cottrell Research Grant from the Research Corp.

Registry No. $Cu(dmp)_2^{2+}$, 14875-91-3; H_2Q, 123-31-9; H_2Q-F, 55660-73-6; H_2Q-Cl, 615-67-8; H_2Q-Br, 583-69-7; H_2Q-I, 23030-43-5; H_2Q-OH, 533-73-3; H_2Q-OCH_3, 824-46-4; H_2Q-COO^-, 490-80-2; H_2Q-$COOCH_3$, 2150-46-1; H_2Q-CH_3, 95-71-6; H_2Q-CF_3, 577-10-6; H_2Q-*n*-C_4H_9, 4197-69-7; H_2Q-$C(CH_3)_3$, 1948-33-0; H_2Q-CN, 4640-29-3; H_2Q-NO_2, 16090-33-8; H_2Q-SO_3^-, 68864-98-2.

Supplementary Material Available: Tables I and II, listing observed rate constants for the reduction of $Cu(dmp)_2^{2+}$ by substituted hydroquinones (6 pages). Ordering information is given on any current masthead page.

References and Notes

(1) R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968).
(2) E. Mentasti and E. Pelizzetti, *Int. J. Chem. Kinet.*, **9**, 215 (1977).
(3) E. Pelizzetti, E. Mentasti, and C. Baiocchi, *J. Phys. Chem.*, **80**, 2979 (1976).
(4) K. Reinschmiedt, J. C. Sullivan, and M. Woods, *Inorg. Chem.*, **12**, 1639 (1973).
(5) E. Pelizzetti, E. Mentasti, and E. Pramauro, *Inorg. Chem.*, **17**, 1688 (1978).
(6) Z. Amjad, J.-C. Brodovitch, and A. McAuley, *Can. J. Chem.*, **55**, 3581 (1977).
(7) J. D. Clemmer, B. L. Gilliland, R. A. Bartsch, and R. A. Holwerda, *Biochim. Biophys. Acta*, **568**, 307 (1979).
(8) A. E. Feiring and W. A. Sheppard, *J. Org. Chem.*, **40**, 2543 (1975).
(9) M. F. Hawthorne and M. Reintjes, *J. Am. Chem. Soc.*, **86**, 951 (1964).
(10) D. E. Kvalnes, *J. Am. Chem. Soc.*, **56**, 667 (1934).
(11) K. Wallenfels, D. Hofmann, and R. Kern, *Tetrahedron*, **21**, 2213 (1965).
(12) N. H. Beaugeard and J. Mattis, *Bull. Soc. Chim. Fr.*, 1612 (1956).
(13) F. Kehrmann, M. Sandoz, and R. Monnier, *Helv. Chim. Acta*, **4**, 941 (1921).
(14) J. H. Baxendale and H. R. Hardy, *Trans. Faraday Soc.*, **49**, 1140 (1953).
(15) H. Irving and D. H. Mellor, *J. Chem. Soc.*, 5237 (1962).
(16) Supplementary material.
(17) G. Davies, R. Higgins, and D. J. Loose, *Inorg. Chem.*, **15**, 700 (1976).
(18) G. R. Williams, *Can. J. Biochem. Physiol.*, **41**, 231 (1963).
(19) R. A. Holwerda and H. B. Gray, *J. Am. Chem. Soc.*, **96**, 6008 (1974).
(20) P. M. Wood, *Biochim. Biophys. Acta*, **357**, 370 (1974).
(21) G. S. Patterson and R. H. Holm, *Bioinorg. Chem.*, **4**, 257 (1975).
(22) M. A. Augustin and J. K. Yandell, *J. Chem. Soc., Chem. Commun.*, 370 (1978).
(23) J. R. Hall, N. K. Marchant, and R. A. Plowman, *Aust. J. Chem.*, **16**, 34 (1963).
(24) J. H. Baxendale, H. R. Hardy, and C. H. Sutcliffe, *Trans. Faraday Soc.*, **47**, 963 (1951).
(25) A. G. Desai and R. M. Milburn, *J. Am. Chem. Soc.*, **91**, 1958 (1969).

Contribution from the Rocketdyne Division, Rockwell International, Canoga Park, California 91304,
and the Science Center, Rockwell International, Thousand Oaks, California 91360

Formation and Decomposition Mechanism of NF_4^+ Salts

KARL O. CHRISTE,* RICHARD D. WILSON, and IRA B. GOLDBERG

Received February 12, 1979

The thermal decompositions of NF_4BF_4 and NF_4AsF_6 were studied in a sapphire reactor at different temperatures by total-pressure measurements. It was found that the rates, previously reported by Solomon and co-workers for NF_4AsF_6, significantly differ from those of the present investigation, although both studies result in a $^3/_2$ reaction order. From the temperature dependence of the observed decomposition rates, the following values were obtained for the global activation energies: $E_{NF_4BF_4} = 36.6 \pm 0.8$ kcal mol^{-1} and $E_{NF_4AsF_6} = 44.7 \pm 4.2$ kcal mol^{-1}. The suppression of the decomposition rates by NF_3, F_2, and BF_3 or AsF_5 was measured. A critical evaluation of all experimental data available on the NF_4^+ salt formation and decomposition suggests the following reversible reaction mechanism: $F_2 \rightleftarrows 2\dot{F}$; $\dot{F} + NF_3 \rightleftarrows \dot{N}F_4$; $\dot{N}F_4 + AsF_5 \rightleftarrows \dot{N}F_3^+AsF_6^-$; $\dot{N}F_3^+AsF_6^- + \dot{F} \rightleftarrows NF_4^+AsF_6^-$. A Born–Haber cycle calculated for NF_4BF_4 shows that the global decomposition activation energy and the heat of the formation reaction are identical within experimental errors and that the second step of the above mechanism is approximately thermochemically neutral. The rate of the thermal formation of NF_4SbF_6 at 250 °C was also studied.

Introduction

The formation and decomposition reactions of NF_4^+ salts are of significant theoretical and practical interest. From a theoretical point of view, the question arises as to whether $\dot{N}F_4$ or NF_5 is produced as an unstable intermediate. This would be highly unusual because second-row elements generally do not form hypervalent molecules. From a practical point of view, a better knowledge of the formation and the decom-

---

* To whom correspondence should be addressed at the Rocketdyne Division, Rockwell International.