Snellings-Desmarais for the mass spectrum of the deuteriated cyclohexanedione.

Registry No. **2**, 628-41-1; **3**, 24560-92-7; **4**, 24560-93-8; **5**, 99-85-4; **6**, 35934-83-9; **7**, 114693-81-1; **8**, 114693-82-2; tetracyanoethylene, 670-54-2; 1,3-cyclohexanedione, 504-02-9; 2,2-dimethyl-1,3-cyclohexanedione, 562-13-0; *cis*-2,2-dimethyl-1,3-cyclohexanediol, 77613-91-3; *trans*-2,2-dimethyl-1,3-cyclohexanediol, 114693-83-3; *cis*-2,2-dimethyl-1,3-cyclohexanediol bis(*p*-toluenesulfonate), 114693-84-4.

Reduction of Arenediazonium Salts by Hydroquinone. Kinetics and Mechanism for the Electron-Transfer Step

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Received January 13, 1988

Arenediazonium tetrafluoroborate salts undergo facile electron transfer reactions with hydroquinone in aqueous phosphate-buffered solutions containing the hydrogen donor solvent acetonitrile. Reaction rates are first-order in hydroquinone and arenediazonium ion concentrations, and they exhibit inverse first order dependence on the hydrogen ion concentration over the pH range of 1.0–9.5. Benzoquinone and arene are the principal products, but arylation of acetonitrile and benzoquinone are competitive in a reaction process that exhibits a 2:1 stoichiometric relationship between the arenediazonium ion salt and hydroquinone. Rate constants for reduction of substituted benzenediazonium ions by the monoanion of hydroquinone correlate with σ constants yielding a ρ value of 3.5. Reactions performed in deuterium oxide show kinetic isotope effects that reflect the solvent isotope effect on the acidity constant for hydroquinone, and levels of isotope incorporation by deuterium abstraction from deuterium oxide and/or acetonitrile-d_3 demonstrate that neither water nor hydroquinone are hydrogen atom donors to intermediate aryl radicals. Reduction of arenediazonium ions involves a rate-limiting single electron transfer from the monoanion of hydroquinone followed by a rapid single electron transfer from the semiquinone intermediate to the diazonium ion. Application of Marcus theory provides calculated rate constants for electron transfer from the hydroquinone monoanion to arenediazonium ions. These rate constants, together with the absence of evidence for a diazo ether intermediate and rate constants for diazotate formation, suggest that electron transfer occurs by an outer-sphere mechanism.

Hydroquinone/*p*-benzoquinone is a classic example of a redox-reversible organic system,[1,2] capable of undergoing the net two-electron transfer in one elementary step[3] or in two one-electron steps.[4–6] Both mechanistic events have been reported in extensive investigations of hydroquinone oxidations by a variety of metal complexes.[3–7] These reactions generally conform to outer-sphere electron transfer processes, although inner-sphere reactions have also been reported.[8]

Arenediazonium salts are highly susceptible to reduction[9] via one-electron transfer processes that may take either of two dynamic forms: a "nonbonded" outer-sphere mechanism involving the direct transfer of one electron from a reducing agent (Red:$^-$) to the diazonium ion (eq 1) and a "bonded" inner-sphere mechanism involving the formation of an intermediate complex (1) which undergoes homolytic cleavage (eq 2).[10] Both pathways result in the same products, and rapid loss of dinitrogen from the aryldiazenyl radical provides these pathways with their characteristic irreversibility. Unlike hydroquinone oxidations, whose reaction mechanisms are relatively well defined, there are few thorough kinetic investigations of the reductions of arenediazonium salts,[11–14] despite their synthetic uses.[15–17] Most reductive transformations of arenediazonium salts that have been investigated in detail are portrayed by inner-sphere mechanisms.[18] However, we have recently defined the characteristics of their outer-sphere electron-transfer processes through redox reac-

$$\mathrm{ArN_2^+ + Red{:}^- \rightarrow ArN_2^{\bullet} + Red^{\bullet}} \qquad (1)$$

$$\mathrm{ArN_2^+ + Red{:}^- \rightleftharpoons \underset{1}{ArN{=}NRed} \rightarrow ArN_2^{\bullet} + Red^{\bullet}} \qquad (2)$$

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Table I. Product Analyses from Reactions of *p*-Nitrobenzenediazonium Tetrafluoroborate with Hydroquinone at 25 °C[a]

10^4[H_2Q], M	10^5[pNBDT], M	pH	% CH_3CN (v/v)	yield, % Q	yield, % $PhNO_2$	yield, % **4**	yield, % **5**	($PhNO_2$ + **4** + **5**)[b] / (Q + **4**)
9.64	9.66		100	42	75	1	20	2.2
9.83	9.82	7.0	40	32	66	2	9	2.3
9.69	9.60	7.0	2	31	62	2	4	2.1
9.61	9.63	3.2	40	40	57	2	24	2.0
9.66	9.69	3.2	2	34	42	1	18	1.7

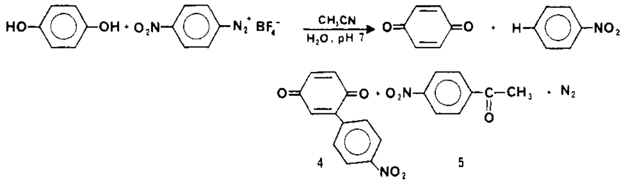
[a] Except for the reaction performed in 100% acetonitrile where no buffer was employed, reactions were run in 0.050 M phosphate. [b] Total yield of nitrophenyl products divided by the total yield of quinone products.

tions with potassium ferrocyanide and decamethylferrocene from which self-exchange rate constants for arenediazonium ions were obtained,[19] and Marcus theory was applied with these self-exchange rate constants for mechanistic predictions.

Reactions of phenolic compounds with arenediazonium ions have received limited attention,[20,21] but both the inner-sphere[22] and outer-sphere[21] pathways (eq 1, 2) have been proposed to explain the involvement of aryl radicals in product formation. Although diazo ethers (**1**, Red = Ar′O) are reactive compounds presumed to be intermediates in diazo coupling reactions,[23,24] evidence has recently been reported that is inconsistent with this reaction pathway for diazo coupling.[25] The majority of products obtained from diazo ethers appear to result from free radical intermediates formed by either eq 1 or eq 2. However, there is insufficient data on these processes to offer a convincing choice between the mechanistic alternatives. We now report detailed kinetic investigations of the reductions of arenediazonium salts by hydroquinone and application of Marcus theory which allows a choice among these mechanistic alternatives.

Results

Product Analysis and Reaction Stoichiometry. Treatment of hydroquinone (H_2Q) with *p*-nitrobenzenediazonium tetrafluoroborate (pNBDT) in 0.05 M phosphate-buffered aqueous solutions containing 2% acetonitrile (v/v) at pH 7.0 under a nitrogen atmosphere resulted in the rapid evolution of dinitrogen and the production (eq 3) of 1,4-benzoquinone (Q), nitrobenzene, *p*-nitrophenyl-1,4-benzoquinone (**4**), *p*-nitroacetophenone (**5**), and an intractable material that was not characterized.



(3)

Benzoquinone and nitrobenzene were the major products. Reactions performed with (1–2) × 10^{-5} M pNBDT and a 10-fold molar excess of H_2Q produced nitrobenzene and benzoquinone in molar yields ranging from 53 to 67% and 25 to 31%, respectively, from multiple experiments based upon the limiting reagent. Increasing the concentration of reactants lowered product yields. Similarly, conducting these reactions in the absence of acetonitrile resulted in a dramatic decrease in the yield of nitrobenzene (13%), but the yield of benzoquinone (35%) was not affected in the same manner. However, use of acetonitrile as a cosolvent in the reaction solution increased product accountability (Table I). *p*-Nitroacetophenone, which is formed by arylation of acetonitrile,[26] was also a well-defined product of reactions performed in the presence of acetonitrile. *p*-Nitrophenyl-1,4-benzoquinone, the product from arylation of benzoquinone,[27] was a minor component of the reaction mixtures.

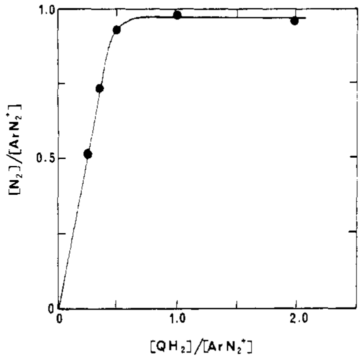


Figure 1. Stoichiometry of nitrogen evolution from the reduction of *p*-nitrobenzenediazonium tetrafluoroborate by hydroquinone at pH 7.0 and 25 °C in 0.05 M phosphate-buffered solution.

The composite data from product analyses, which show that the molar yield of *p*-nitrophenyl products is twice that of benzoquinone, suggest a 2:1 [pNBDT]:[H_2Q] stoichiometry. Nitrogen evolution from reactions performed with variable molar ratios of H_2Q to pNBDT under these conditions also defines a 2:1 reactant stoichiometry (Figure 1). Similar results were obtained with benzenediazonium tetrafluoroborate under the same reaction conditions.

Phenolic products that could arise from diazonium salts by direct displacement of dinitrogen by water or from reactions initieated by the association of aryl radicals with dioxygen[11b] were not observed, nor were fluoroarenes arising from fluoride capture from tetrafluoroborate. Similarly, azobenzenes and biaryls were not formed in detectable amounts from reactions performed with 10^{-4}–10^{-5} M concentrations of reactants. However, succinonitrile, the product from radical combination of the hydrogen atom abstraction product from acetonitrile, was obtained in 1–2% yield.

Rate Law and Spectral Characteristics. Reductions of a representative series of arenediazonium tetrafluoroborate salts by hydroquinone were conducted at pH 7.0

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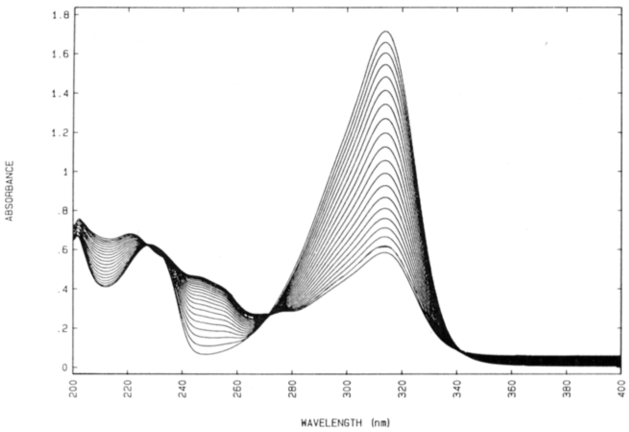

Figure 2. Time course for the reaction between *p*-methoxybenzenediazonium tetrafluoroborate (6.70×10^{-5} M) and hydroquinone (3.45×10^{-5} M) at pH 7.0 and 25.0 °C in 0.050 M phosphate-buffered aqueous solution containing 2% (v/v) acetonitrile. Individual spectra were taken over a period of 1 h at 3-min intervals.

and 25.0 °C under nitrogen in aqueous phosphate-buffered solutions containing 2% acetonitrile (v/v). Hydroquinone was used in amounts ranging from 5-fold to 20-fold molar excess over the diazonium salt. Rates were followed by monitoring the decrease in absorbance at the λ_{max} of the arenediazonium salt, and stopped-flow measurements were employed for all diazonium salts except the *p*-methoxy derivative. First-order kinetic dependence on the concentration of the diazonium salts, normally extending through more than 3 half-lives, was established under these conditions. The kinetic dependence on hydroquinone, obtained from the linear relationship between the experimental pseudo-first-order rate constant and the concentration of hydroquinone at constant diazonium concentration, was also first order. Thus these reactions are second order overall, first order in the concentration of the arenediazonium salt and first order in the concentration of H_2Q. By separately monitoring absorptions from the *p*-nitrobenzenediazonium ion (λ = 276 nm) and 1,4-benzoquinone (λ = 314 nm), the rate for arenediazonium ion decomposition at pH 6.9 was established to be approximately double that for 1,4-benzoquinone production ($k_{pNBDT} = 3.74 \times 10^4$ M^{-1} s^{-1}; $k_{H_2Q} = 1.86 \times 10^4$ M^{-1} s^{-1}), which is precisely the result anticipated from stoichiometric determinations. In the presence of dioxygen, the rate constant for reduction of *p*-nitrobenzenediazonium tetrafluoroborate at pH 7.0 in 2% aqueous acetonitrile was approximately twice that in the absence of dioxygen.

Addition of the arenediazonium salt to hydroquinone did not produce a spectral change beyond that from addition of absorbances of the two spectrally distinct reactants. *p*-Methoxybenzenediazonium tetrafluoroborate showed no spectral shift associated with the development of a reaction intermediate during the time course of its reduction by H_2Q (Figure 2). Isospestic points are observed at 227, 273, and 341 nm. Similarly, the absorption spectrum of Variamine Blue RT (*p*-anilinobenzenediazonium hydrogen sulfate), which exhibits a spectrally distinct λ_{max} at 377 nm and whose half-life for reduction was longer than 3 h under the conditions employed, did not change upon addition of H_2Q. Spectral changes attributed to the formation of an intermediate complex (**1**) have been reported for the oxidation of phenothiazines by the *p*-methoxybenzenediazonium ions,[14] but we have previously stated that they are more likely due to charge-transfer complexes than bonded intermediates such as **1**.[19]

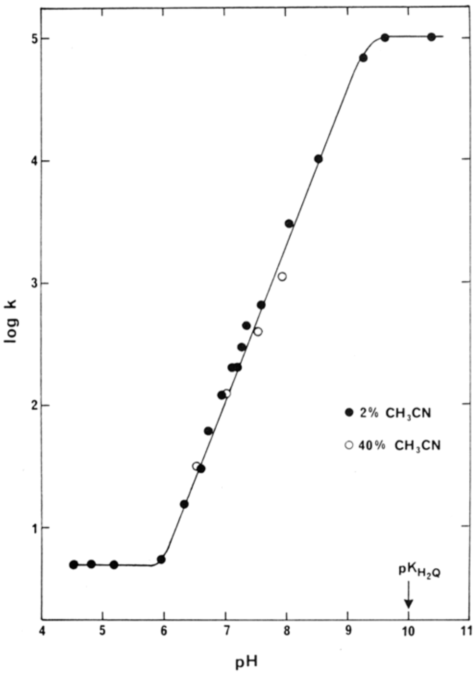

Figure 3. pH–rate profile for the reduction of *p*-chlorobenzenediazonium tetrafluoroborate by hydroquinone at 25.0 °C in 0.05 M phosphate-buffered aqueous solution.

pH Dependence. Rate constants for the reaction between *p*-chlorobenzenediazonium tetrafluoroborate and hydroquinone were obtained over the pH range of 4.5–10.3, and the resulting pH–rate profile is shown in Figure 3. Changing the buffer from phosphate to borate did not influence the rate of reaction at pH values greater than 9. Procedures were employed that minimized complications arising from diazotate formation[18] at pH values greater than 8.0, although at pH >9 diazotate formation becomes competitive with the redox reaction. Diazotates were unreactive toward hydroquinone.

Figure 3 is the composite of data from reactions performed in 2% aqueous acetonitrile and in 40% aqueous acetonitrile. As is evident from this data, there is no substantial difference in rate constants from reactions performed in these two media. The resulting curve approaches, as its upper limit, the first ionization constant for hydroquinone ($pK_a = 10.0$ at $\mu = 0.04$, 25 °C).[28] The slope of the line in the apparent linear relationship from pH 6 to pH 9 is 1.24. Taken alone, the data for reactions performed in 40% aqueous acetonitrile show a linear dependence on pH with a slope of 1.0, which defines exactly an inverse first-order dependence on the hydrogen ion concentration.

Acetonitrile is an effective hydrogen donor solvent for carbon radicals,[14b] and we assumed that its use eliminated radical chain reactions that could render our observed rates constants uninterpretable. That nearly identical rate constants were observed in 2% and 40% aqueous acetonitrile is consistent with the relative unimportance of radical chain processes under the reaction conditions that we have employed. As a further test of this assumption, acrylonitrile, which is even more effective than acetonitrile as a radical trap for carbon radicals,[29] was also employed. With [acrylonitrile] equal to 0.10 M, the second-order rate constant for reduction of *p*-nitrobenzenediazonium tetrafluoroborate at pH 6.9 was 3.52×10^4 M^{-1} s^{-1}, which is less

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Table II. Second-Order Rate Constants for the Reduction of Arenediazonium Tetrafluoroborate Salts by Hydroquinone at 25.0 °C[a]

	pH 4.5		pH 7.0		
$ArN_2^+BF_4^-$, Ar =	k_X, M^{-1} s^{-1}	k_X/k_H	$10^{-2}k_X$, M^{-1} s^{-1}	k_X/k_H	$k_{7.0}/k_{4.5}$
$p\text{-}NO_2C_6H_4$	392	1.66×10^3	490	3.71×10^2	125
$p\text{-}NCC_6H_4$	124	4.70×10^2	140	1.06×10^2	113
$p\text{-}ClC_6H_4$	5.00	2.12×10	2.88	2.19	58
$p\text{-}FC_6H_4$	0.741	2.39	1.65	1.25	223
C_6H_5	0.453	1.00	1.32	1.00	291
$m\text{-}CH_3C_6H_4$			0.50	0.379	
$p\text{-}CH_3C_6H_4$	0.064	0.198	0.213	0.161	333
$p\text{-}CH_3OC_6H_4$	0.027	0.077	0.089	0.068	330

[a] Reactions were performed in aqueous 0.050 M phosphate-buffered solutions.

than the rate constant obtained in 2% aqueous acetonitrile (3.74×10^4 M^{-1} s^{-1}) by a factor of only 1.06. Rapid polymerization of acrylonitrile precluded its use at lower pH values.

The rate constant for oxidation of H_2Q by the *p*-chlorobenzenediazonium ion at pH 7.0 was also observed to increase with increasing ionic strength. The second-order rate constant, which is 288 M^{-1} s^{-1} in 0.050 M phosphate buffer, increased linearly to 370 M^{-1} s^{-1} in 0.10 M phosphate buffer. The equilibrium constant for ionization of hydroquinone is also dependent on ionic strength,[28,30] which, as was noted by Holwerda and Gray in their investigation of the reduction of laccase by hydroquinone,[31] is the probable cause of this increase.

The leveling of the second-order rate constant for reduction of *p*-chlorobenzenediazonium tetrafluoroborate at pH values less than 6 could be attributed to a contribution from H_2Q to the rate for oxidation of HQ^-. This explanation is consistent with the pH profile of Figure 3. However, when this same reaction was performed at pH 1.0, a rate constant identical with that obtained at pH 4.5 was not observed; instead, the rate constant for oxidation of H_2Q was so low as to be imperceptible. Consequently, these investigations were extended from pH 7.0 to pH 0 with *p*-nitrobenzenediazonium tetrafluoroborate in 1.0 M perchlorate and/or 0.050 M phosphate buffer solution. A second pH–rate profile was identified from pH 6 to pH 0 (curve A in Figure 4) for reactions performed in aqueous solution containing 2% (v/v) of acetonitrile. Rate constants for reduction of *p*-nitrobenzenediazonium tetrafluoroborate decreased from nearly 400 M^{-1} s^{-1} at pH 4.5 to 0.5 M^{-1} s^{-1} at pH 0 with a slope of 1.14 in the pH range of 0–2.

The unexpectedly complex pH dependence observed between pH 6 and 0 was resolved when the same reactions were performed in 40% aqueous acetonitrile. Under these conditions the log values of the second-order rate constants exhibited a linear dependence on pH throughout the range from 7 to 1 (curve B of Figure 4) with a slope of 1.0. When this data is joined to that of Figure 3, the inverse first order rate dependence on the hydrogen ion concentration throughout the pH range of 1.0–9.5 is substantiated.

Substituent Effects. Second-order rate constants were obtained for reactions of a series of substituted arenediazonium tetrafluoroborate salts with hydroquinone, and their values, extending over 3 orders of magnitude, are reported in Table II. These data were determined at both pH 7.0 and 4.5 in 0.05 M phosphate buffer containing 2% acetonitrile by volume. The calculated second-order rate constants, k_X, obtained at pH 7.0 were assumed to have the same inverse dependence on the hydrogen ion concentration as was found for *p*-chloro- and *p*-nitrobenzenediazonium salts. Consequently, the second-order rate constants obtained at pH 4.5 could be employed as one-point measures of deviation from the inverse hydrogen ion concentration dependence for all of the substituted benzenediazonium salts. The ratio of rate constants, $k_{7.0}/k_{4.5}$, should be 316 if deviations from this relationship, as described by the data in Figures 3 and 4, do not occur. However, as can be seen from the calculated values of $k_{7.0}/k_{4.5}$ in Table II, substantial deviations exist for all but the least reactive of the arenediazonium salts.

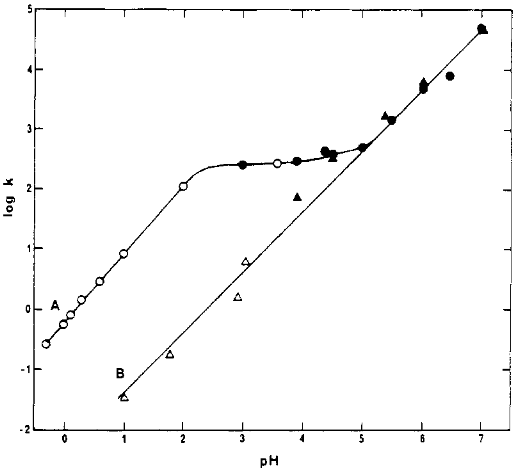

Figure 4. pH–rate profile for the reduction of *p*-nitrobenzenediazonium tetrafluoroborate by hydroquinone at 25.0 °C in aqueous solutions containing: A, 2% (v/v) acetonitrite (○, ●) and B, 40% (v/v) acetonitrile (△, ▲). Open points (○, △) refer to 0.10 M $HClO_4/ClO_4^-$; closed points (●, ▲) are from 0.050 M $H_2PO_4^-/HPO_4^{2-}$.

Isotope Effects. Rate constants were obtained for reactions between *p*-nitrobenzenediazonium tetrafluoroborate and hydroquinone performed in deuterium oxide containing 2% acetonitrile at pD 4.5 and 7.0. Under these conditions hydroquinone exists as its dideuterio derivative, and its K_a value in D_2O is 4.16 times less than that of its protonated analogue in H_2O.[32] The isotope effect on the acidity constant for hydroquinone is reflected in the kinetic isotope effects obtained at pH 7.0 ($k_{H_2O}/k_{D_2O} = 3.6$) and at pH 4.5 ($k_{H_2O}/k_{D_2O} = 3.9$) for its oxidation.

The nature of the hydrogen-transfer step resulting in the formation of nitrobenzene was evaluated from studies of deuterium incorporation in reactions between *p*-nitrobenzenediazonium tetrafluoroborate and hydroquinone. No deuterium incorporation (<3%) was observed for reactions performed at pD 4.5 and 7.0 in D_2O containing 2% acetonitrile, but 72% deuterium incorporation was observed for reactions performed in D_2O containing CD_3CN. At pH 7.0 in H_2O containing 2% CD_3CN, these reactions

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Table III. Calculated Second-Order Rate Constants, k_{HQ^-}, for the Reduction of Arenediazonium Tetrafluoroborate Salts by Hydroquinone at 25.0 °C

$ArN_2^+BF_4^-$, Ar =	k_{HQ^-},[a] $M^{-1} s^{-1}$	$k_{Q\cdot^-}$,[b] $M^{-1} s^{-1}$	$ArN_2^+BF_4^-$, Ar =	k_{HQ^-},[a] $M^{-1} s^{-1}$	$k_{Q\cdot^-}$,[b] $M^{-1} s^{-1}$
p-$NO_2C_6H_4$	2.45×10^7	9.4×10^9	C_6H_5	6.60×10^4	8.0×10^6
p-NCC_6H_4	7.00×10^6		m-$CH_3C_6H_4$	2.25×10^4	
p-ClC_6H_4	1.44×10^5	3.2×10^7	p-$CH_3C_6H_4$	1.06×10^4	5.2×10^6
p-FC_6H_4	8.26×10^4		p-$CH_3OC_6H_4$	4.47×10^3	1.2×10^6

[a] Calculated from eq 10. [b] Data taken from ref 16; reactions performed in 64% aqueous acetonitrile.

resulted in a similar degree of deuterium incorporation (66%). However, at pH 4.5 deuterium incorporation amounted to only 49%.

Discussion

The composite data for rate dependence on the concentrations of the arenediazonium ion, hydroquinone, and hydronium ion in the pH range of 1.0–9.5 are consistent with the generalized rate law:

$$\frac{-d[ArN_2^+]}{dt} = k_{HQ^-}[ArN_2^+][HQ^-] \tag{4}$$

where $[ArN_2^+]$ and $[HQ^-]$ are the molar concentrations of the diazonium salt and the monobasic form of hydroquinone, respectively, and k_{HQ^-} is the corresponding reaction rate constant. This rate law fits the mechanism depicted in Scheme I, which is presented without identifying the electron-transfer step as either an outer-sphere or inner-sphere process. Prior investigations of hydroquinone oxidation by inorganic reducing agents have confirmed the existence of pH-dependent and pH-independent pathways for electron transfer,[4,33] but our data are only consistent with the pH-dependent reaction. The semiquinone radical anion ($Q^{\cdot-}$) and its protonated analogue, the semiquinone radical ($HQ^\cdot$), are themselves susceptible to further oxidation by arenediazonium salts (eq 7, 8) in exceedingly fast electron transfer reactions.[13]

Scheme I

$$H_2Q \xrightleftharpoons{K_{H_2Q}} HQ^- + H^+ \tag{5}$$

$$HQ^- + ArN_2^+ \xrightarrow{k_{HQ^-}} Q^{\cdot-} + ArN_2^\cdot + H^+ \text{ (or } HQ^\cdot + ArN_2^\cdot\text{)} \tag{6}$$

$$HQ^\cdot + ArN_2^+ \xrightarrow{k_{HQ\cdot}} Q + ArN_2^\cdot + H^+ \tag{7}$$

$$Q^{\cdot-} + ArN_2^+ \xrightarrow{k_{Q\cdot^-}} Q + ArN_2^\cdot \tag{8}$$

If further decomposition of $ArN_2^\cdot$ occurs independently of H_2Q, as appears to be the case, the net 2:1 stoichiometry determined kinetically and by product analyses at pH 7.0 is established by the operation of the composite of eq 5–8 (eq 9). The absence of deuterium incorporation into nitrobenzene for reactions performed in D_2O (with 2% CH_3CN) demonstrates that hydroquinone does not serve as a hydrogen (or deuterium) donor in these reactions. Furthermore, the match of kinetic results obtained at pH 7 for reactions performed in the presence of 2% and 40% acetonitrile or acrylonitrile suggests the absence of radical chain processes.

$$H_2Q + 2ArN_2^+ \rightarrow Q + 2ArN_2^\cdot + 2H^+ \tag{9}$$

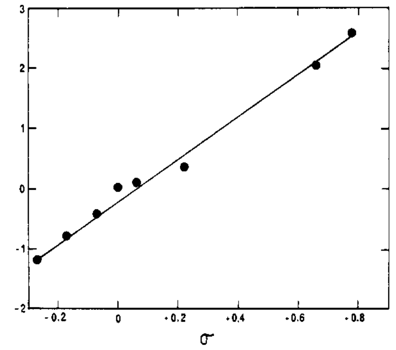

Figure 5. Hammett plot for reactions of substituted benzenediazonium tetrafluoroborate salts with hydroquinone in 0.05 M phosphate-buffered aqueous solution at pH 7.0 and 25.0 °C.

By applying the relationship for total hydroquinone, $[THQ] = [H_2Q] + [HQ^-]$, the acid dissociation relationship $K_{H_2Q} = [H^+][HQ^-]/[H_2Q]$, and the steady-state approximation for $[Q^{\cdot-}]$,[34] equation 4 becomes

$$\frac{-d[ArN_2^+]}{dt} = k_{obsd}[ArN_2^+][THQ] \tag{10}$$

where the observed second-order rate constant, k_{obsd}, is

$$k_{obsd} = \frac{2k_{HQ^-}K_{H_2Q}}{[H^+] + K_{H_2Q}} \tag{11}$$

At high $[H^+]$, eq 11 becomes $k_{obsd} = 2k_{HQ^-}K_{H_2Q}/[H^+]$, and as $[H^+]$ approaches K_{H_2Q}, k_{obsd} approaches k_{HQ^-}. When $[H^+] \ll K_{H_2Q}$, $k_{obsd} = 2k_{HQ^-}$. The kinetic expression of eq 11 is consistent with the experimentally determined 2:1 relationship between the rate for reduction of the diazonium ion and the rate for oxidation of hydroquinone.

The rate constant k_{HQ^-} for reduction of p-chlorobenzenediazonium tetrafluoroborate calculated from application of eq 11 is 1.44×10^5 $M^{-1} s^{-1}$, which is a factor of 6 more than the limiting experimental rate constant obtained between pH 9.5 and 10.3 (Figure 3). This discrepancy is due to the competitition between diazotate formation at these high pH values ($k = 1.6 \times 10^4$ $M^{-1} s^{-1}$ under comparable conditions)[36] and electron transfer to the arenediazonium ion. The calculated rate constant is assumed to be the more accurate value, and the rate constants for hydroquinone reduction of substituted arenediazonium salts are presented in Table III together with comparative data for reductions by the semiquinone radical anion.[16] Linear correlation is observed (Figure 5) between the log of the second-order rate constants for substituted benzenediazonium salts obtained at pH 7.0 and σ^-[37] with a ρ value of 3.5.

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(33) Clemmer, J. D.; Hogaboom, G. K.; Holwerda, R. A. *Inorg. Chem.* **1979**, *18*, 2567.

(34) The value of the acid dissociation constant $K_{HQ\cdot}$ for p-benzosemiquinone is $(5 \pm 3) \times 10^{-5}$ M at 20 °C,[16,27,35] which is consistent with our assumption that $[HQ^\cdot] \ll [Q^\cdot]^-$ at pH >5.

(35) (a) Patel, K. B.; Willson, R. L. *J. Chem. Soc., Faraday Trans. 1* **1973**, 814. (b) Adams, G. E.; Michael, B. D. *Trans. Faraday Soc.* **1967**, *63*, 1171.

(36) Ritchie, C. D.; Wright, D. J. *J. Am. Chem. Soc.* **1971**, *93*, 6574.

Table IV. Calculated Second-Order Rate Constants for Outer-Sphere Electron Transfer from the Monoanion of Hydroquinone to Arenediazonium Tetrafluoroborate Salts

$ArN_2^+BF_4^-$, Ar =	$k_{22}(ArN_2^+)$,[a] $M^{-1}\ s^{-1}$	k_{19}(calcd),[b] $M^{-1}\ s^{-1}$	k_{HQ^-}/k_{19}[c]	k_{21}(calcd),[b] $M^{-1}\ s^{-1}$	$10k_{HQ^-}/k_{21}$[c]
p-$NO_2C_6H_4$	9.1	9.6×10^5	26	4.1×10^8	0.60
p-NCC_6H_4	3.3×10^{-1}	1.4×10^5	50	8.1×10^7	0.86
p-ClC_6H_4	2.2×10^{-3}	2.7×10^3	53	2.7×10^6	0.53
p-FC_6H_4	1.8×10^{-4}	5.1×10^2	1.6×10^2	6.2×10^5	1.3
C_6H_5	1.2×10^{-4}	2.2×10^2	3.0×10^2	3.1×10^5	2.1
m-$CH_3C_6H_4$	2.9×10^{-5}	9.0×10^1	2.5×10^2	1.4×10^5	1.6
p-$CH_3C_6H_4$	7.0×10^{-6}	2.3×10^1	4.7×10^2	4.0×10^4	2.6
p-$CH_3OC_6H_4$	2.9×10^{-6}	1.2×10^1	3.7×10^2	2.2×10^4	2.0

[a] Average self-exchange rate constants from ref 19. [b] Calculated from eq 18. [c] Values for k_{HQ^-} taken from Table III.

The treatment just described assumes that disproportionation of the semiquinone radical[38] is not competitive with electron transfer to arenediazonium ions. The validity of this assumption has recently been confirmed by kinetic determinations of rate constants for eq 7 and 8 (see Table III).[13] The aryldiazenyl radical can undergo hydrogen abstraction with subsequent dinitrogen extrusion (eq 12) or loss of dinitrogen and subsequent hydrogen abstraction from the hydrogen-donor solvent (eq 13). However,

$$ArN_2^\bullet \xrightarrow{CH_3CN} ArN{=}NH \rightarrow ArH + N_2 \qquad (12)$$

$$ArN_2^\bullet \xrightarrow{-N_2} Ar^\bullet \xrightarrow{SolH} ArH \qquad (13)$$

competitive hydrogen abstraction by the diazenyl radical is suggested by the partial deuterium incorporation into nitrobenzene that is observed for reactions performed in H_2O containing CD_3CN. Huang and Kosower also observed only partial deuterium incorporation from decomposition of 2-phenyldiazene-*1-d* (73%) in acetonitrile, but no definitive hydrogen source was identified.[39] As can be seen from the spectral time course of Figure 2, diazene intermediates are not evident, but this is understandable in view of the known oxidative capability of 1,4-benzoquinone toward phenyldiazene.[39] That hydrogen transfer from water or hydroquinone (eq 14) does not occur is

$$Ar^\bullet + H_2O\ (\text{or } HQ^-) \rightarrow ArH + HQ^\bullet\ (\text{or} Q^{\bullet -}) \qquad (14)$$

demonstrated by the absence of deuterium incorporation into nitrobenzene when p-nitrobenzenediazonium tetrafluoroborate was reacted with hydroquinone in D_2O containing CH_3CN.

Deviation from inverse first-order dependence on $[H^+]$ that is observed (Figure 4A) for reactions performed in 2% acetonitrile is presumably caused by a pH-dependent chain reaction. Increasing the concentration of acetonitrile allows the redox reaction to occur with "normal" inverse dependence on $[H^+]$. However, the reason for this deviation is not obvious. Except for p-nitroacetophenone, product yields at pH 3.2 are similar to those observed at pH 7.0 (Table I), and both the kinetic isotope effect and the percentage incorporation of deuterium into nitrobenzene at lower pH values do not clarify the mechanism. One explanation may be that the product from arylation of acetonitrile at pH values less than 6 is protonated (eq 15)[26a] and, thereby, susceptible to reduction by the hydroquinone monoanion (eq 16). Semiquinone then undergoes electron transfer with the arenediazonium ion (eq 7) to produce quinone and the arenediazenyl radical which continues the radical chain process. Increasing the concentration of acetonitrile diminishes the competitiveness of **2** for HQ^- relative to hydrogen abstraction from this hydrogen donor (eq 17). In support of this mechanism, increasing the

$$Ar^\bullet + CH_3CN \rightarrow ArC(CH_3){=}N^\bullet \overset{H^+}{\rightleftharpoons} \underset{\mathbf{2}}{ArC(CH_3){=}NH^{\bullet +}} \qquad (15)$$

$$\mathbf{2} + HQ^- \rightarrow ArC(CH_3){=}NH + HQ^\bullet \qquad (16)$$

$$\mathbf{2} + CH_3CN \rightarrow ArC(CH_3){=}NH_2^+ + {}^\bullet CH_2CN \qquad (17)$$

concentration of hydroquinone at pH 3.0 increases the rate of reaction, and decreasing the concentration of hydroquinone at the same pH value decreases the redox rate in 2% aqueous acetonitrile.

Marcus theory for outer-sphere electron transfer reactions is being applied with increasing frequency to evaluate the mechanisms of redox reactions involving organic compounds.[40] The success of these applications is dependent on the availability of individual reactant self-exchange rate constants as well as redox potentials for the reacting substrates under the conditions of their kinetic measurements. Since consistent self-exchange rate constants for arenediazonium ions from cross reactions with decamethylferrocene and ferrocyanide have recently been obtained[19] and the estimated value for the hydroquinone self-exchange rate constant is also known,[5c] we have employed the Marcus equation[41] (eq 18) to predict the rate constants for outer-sphere electron transfer from the hydroquinone monoanion to arenediazonium ions (eq 19).

$$k_{mn} = (k_{mm}k_{nn}K_{mn}f)^{1/2}$$

$$\ln f = (\ln K_{mn})^2/[4 \ln (k_{mm}k_{nn}/Z^2)] \qquad (18)$$

$$HQ^- + ArN_2^+ \xrightarrow{k_{19}} HQ^\bullet + ArN_2^\bullet \qquad (19)$$

Previous investigations of the redox reactions of hydroquinone have found explicit evidence for outer-sphere electron transfer[4,5] when these reactions were performed in 1 M mineral acid with oxidants whose self-exchange rate constants were at least 3 orders of magnitude greater than those of arenediazonium ions. Application of the self-exchange rate constants for diazonium salts has provided cross reaction rate constants[19] that were generally less than 2 orders of magnitude lower than those observed for semiquinone oxidation,[13] and they were within a factor of 2 lower for phenothiazine oxidations.[14]

Calculated rate constants for the reductions of arenediazonium ions by HQ^- (eq 19) are listed in Table IV. Although self-exchange rate constants for arenediazonium ions are estimates, based on cross reactions, the k_{HQ^-}/k_{19}

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ratios for reactions performed with *p*-nitro-, *p*-cyano-, and *p*-chlorobenzenediazonium ions are in reasonably close agreement with a predicted outer-sphere electron transfer process. Those for diazonium salts with electron-donating substituents do not agree as well, but their deviations from the ideal ratio are not substantially different from those for reduction by the semiquinone radical anion (e.g., $k_{Q^{\bullet -}}(\mathrm{obsd})/k_{Q^{\bullet -}}(\mathrm{calcd}) = 192$ for *p*-$CH_3C_6H_4N_2^+$).[19] We have used a value of −0.240 V (vs SCE) for the $HQ^-/HQ^\bullet$ potential calculated from the equations of Rich and Bendall,[7] and this value is appropriate for calculations of rate constants for eq 19. However, $HQ^\bullet$ is relatively strong acid ($K_a \simeq 5 \times 10^{-5}$ M)[13,27,35] and could be expected to undergo proton loss during the electron transfer (eq 20). In this

$$HQ^- + ArN_2^+ \xrightarrow{k_{20}} Q^{\bullet -} + ArN_2^\bullet + H^+ \qquad (20)$$

case, the $HQ^-/(Q^{\bullet -} + H^+)$ potential is pH–dependent, and the Marcus relationship would not be strictly applicable. One can estimate an upper limit of rate constants for eq 20 by calculating the values predicted by Marcus theory for reduction of diazonium salts by Q^{2-} (k_{21}, eq 21), these

$$Q^{2-} + ArN_2^+ \xrightarrow{k_{21}} Q^- + ArN_2^\bullet \qquad (21)$$

values, which are only factors of between 19 and 3 times greater than k_{HQ^-}, are also given in Table IV. Despite these complications, the values of k_{HQ^-} and k_{19} differ by no more than a factor of 500, which is remarkable for the reaction system that has been investigated and suggests outer-sphere electron transfer between arenediazonium salts and hydroquinone. The absence of any evidence for associated intermediates (1) further implicates, but does not confirm, the outer-sphere pathway for electron transfer. Finally, the rate constants for oxidation of the hydroquinone monanion by arenediazonium salts are between 10 and 100 times greater than those for association with hydroxide,[42] which is both more basic and more nucleophilic than phenoxide. Consequently, the inner-sphere mechanism for electron transfer (eq 2) is an unlikely alternative to the outer-sphere electron transfer mechanism.

Experimental Section

Materials. Arenediazonium tetrafluoroborate salts were prepared from the corresponding anilines by treatment with *tert*-butyl nitrate and boron trifluoride etherate,[43] and they were recrystallized from acetone–hexane. Reagent grade hydroquinone was employed. Acetonitrile was distilled from calcium hydride, and double-distilled water was used. Stock solutions of the diazonium salts were prepared in acetonitrile and maintained under nitrogen. Concentrated solutions of hydroquinone were prepared in deoxygenated phosphate buffer (0.050 M) and kept under nitrogen.

Product Analyses. Products from reactions between pNBDT and 1,4-hydroquinone were determined by HPLC analyses of reaction solutions at concentrations similar to those employed for kinetic determinations. Reactions were run under nitrogen in 0.05 M phosphate buffer with molar reactant ratios ($[H_2Q]/[\mathrm{pNBDT}]$ extending from 5 to 20, but only those whose reactant ratio was 10 are reported in Table I. Analyses were performed with a 25-cm C-18 column at 254 nm with a ternary solvent consisting of (v/v) 68% H_2O/26% CH_3CN/6% HOAc, and external standards of the authentic products were employed for quantitative determinations. Succinonitrile was analyzed by capillary GC following continuous extraction of reaction mixtures with ether.

Deuterium incorporation into nitrobenzene was performed under similar conditions with 99.8 atom % deuterium oxide and/or 99 atom % acetonitrile-d_3. Nitrobenzene was isolated from the reaction mixtures by 24-h continuous extractions and analyzed by GC/MS with a HP 5995C quadrupole mass spectrometer. The percentage of deuterium incorporation was obtained from the molecular ions of the isotopic components with appropriate corrections for isotopic abundances. Duplicate runs were performed to determine the precision of analyses which were ±3%.

Nitrogen evolution was monitored on a standard gas buret. Reactions were performed at 10^{-3}–10^{-2} M in reactants, and duplicate measurements were obtained. The precision of analyses was ±5%.

Kinetic Determinations. Except for reactions at pH 7.0 with *p*-methoxybenzenediazonium tetrafluoroborate, which were monitored by conventional methods, kinetic experiments were performed under nitrogen by stopped-flow measurements with stock solutions of the diazonium salt (0.2 mM) and hydroquinone (2–5 mM) in 0.050 M phosphate buffer. Rapid mixing experiments were carried out in a Dionex Model 110 stopped-flow spectrophotometer interfaced to a high speed, 12-bit A/D converter (OLIS, Inc.) and a microcomputer system. Solutions were thermostated at 25.0 °C, and reactions were initiated by equal-volume injection of each stock solution into the mixing chamber. Except for the fast reactions of *p*-nitro- and *p*-cyanobenzenediazonium tetrafluoroborate, kinetic measurements at pH 4.5 were performed by conventional methods on a Cary 118 spectrophotometer. Rates of reaction were determined by monitoring the decrease in absorbance at the absorption maximum of each diazonium salt:[42] 266 nm (*p*-NO_2), 265 nm (*p*-CN), 280 nm (*p*-Cl), 264 nm (*p*-F), 261 nm (*p*-H), 266 nm (*m*-CH_3), 278 nm (*p*-CH_3), and 315 nm (*p*-CH_3O). The production of 1,4-benzoquinone was monitored at 318 nm. Reactions were performed under pseudo-first-order conditions, and linearity in semilog plots was generally observed through 3 half-lives. The kinetic dependence on hydroquinone was established by varying its molar ratio with respect to the diazonium salt. Average second-order rate constants from a minimum of four conventional determinations, or eight in stopped-flow measurements, are reported with average deviations of ±3%.

The pH–rate profile was compiled from data obtained in 0.050 M phosphate buffer and, for pH values greater than 9, were duplicated in 0.050 borate buffer. To ensure that diazotate formation did not compete with electron transfer from hydroquinone, an equal volume injection of the diazonium salt in unbuffered water was delivered with hydroquinone in 0.10 M phosphate (or borate) buffer into the mixing chamber for kinetic determinations at pH values greater than 8. Reactions at pH values less than 3.0 were performed in 1.0 M perchlorate solutions containing requisite amounts of perchloric acid and sodium perchlorate. There was no appreciable change in rate resulting from the use of perchlorate or phosphate at the same pH (3–4.5). Sodium acetate/acetic acid formed a stable complex with pNBDT at pH values between 3 and 6, believed to the covalent azo compound 1 (Red = OAc), and could not be used as a buffer solution in these investigations. Neither phosphate nor perchlorate exhibited similar behavior as monitored by UV/visible spectroscopy.

Kinetic isotope effects were determined with the use of 99.8 atom % deuterium oxide under reaction conditions identical with those employed for reactions in H_2O. The pH of the phosphate-buffered solutions was adjusted with deuteriated acid or base in D_2O. At least two separate series of kinetic determinations were used to obtain the reported values (±4%).

Acknowledgment. Support for this research from the National Institutes of Health (Grant GM37469) is gratefully acknowledged. The National Science Foundation provided partial support for the acquisition of the GC/MS system.

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