1536 J. Am. Chem. Soc. 1987, 109, 1536-1540

Outer-Sphere One-Electron Reductions of Arenediazonium Salts

Michael P. Doyle,*[1a] Judith K. Guy,[1a] Kathlynn C. Brown,[1a] Surendra N. Mahapatro,[1a] Craig M. VanZyl,[1a] and Jack R. Pladziewicz*[1b]

Contribution from the Department of Chemistry, Trinity University, San Antonio, Texas 78284, and the Department of Chemistry, University of Wisconsin, Eau Claire, Wisconsin 54701.
Received August 6, 1986

Abstract: Arenediazonium tetrafluoroborate salts undergo facile reduction by both potassium ferrocyanide and decamethylferrocene. Their reaction rates are characteristically second order, and rate constants for the ferrocyanide reductions of substituted benzenediazonium ions ranging from *p*-nitro to *p*-methoxy span five orders of magnitude. Linear correlation between log (k_X/k_H) and Hammett σ-values is obtained with $\rho = +4.7$ for reactions with ferrocyanide and $\rho = +3.3$ for reactions with decamethylferrocene. Similar correlations are observed with the polarographic half-wave potentials of these diazonium salts. Marcus theory has been applied to these electron-transfer reactions to obtain estimates of the apparent self-exchange rate constants of arenediazonium ions. Their values are relatively low, and they exhibit a substantial unexpected substituent dependence ($\rho = +6.4$). Application of Marcus theory to known electron-transfer reactions of diazonium ions using these apparent self-exchange rate constants demonstrates their suitability for the prediction of reaction rate constants and their usefulness for mechanistic evaluations.

Few classes of organic compounds are as susceptible to reduction as are arenediazonium salts.[2] The synthetic versatility of the Sandmeyer[3] and Meerwein reactions,[4] the Gomberg-Bachmann synthesis and Pschorr cyclization,[5] and a variety of related arylation and reduction reactions[6] is based on electron transfer to arenediazonium ions. Although the polarographic half-wave reduction potentials of a select number of arenediazonium salts are known[7,8] and their substituent dependence has been characterized,[8] few kinetic studies of their redox reactions, other than those describing relative rates, have been reported.[9-14]

Considerable controversy exists regarding the mechanism of the electron-transfer step in many transformations involving diazonium ions.[1,13-16] Two fundamental mechanisms, each resulting in the net transfer of an electron from a reducing agent (Red^-) to an arenediazonium ion, are employed to explain the electron-transfer process. They are described as outer-sphere (eq 1) and inner-sphere or bonded[17] (eq 2) electron transfer processes. When

$$ArN_2^+ + Red^- \rightarrow ArN_2^\bullet + Red^\bullet \qquad (1)$$

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

the intermediate complex **1** is observed, the formation of the aryldiazenyl radical is reasonably described as occurring by homolytic cleavage of **1**. However, when this intermediate is not detected, either mechanism may apply, and no satisfactory method has been devised to differentiate between them.

Table I. Second-Order Rate Constants for the Reduction of Arenediazonium Tetrafluoroborate Salts by Potassium Ferrocyanide and Decamethylferrocene at 25.0 °C

$ArN_2^+BF_4^-$ Ar =	$Fe(CN)_6^{4-}$ [a] $10^{-2}k_X$, $M^{-1}\,s^{-1}$	k_X/k_H	$(Me_5Cp)_2Fe$ [b] $10^{-3}k_X$, $M^{-1}\,s^{-1}$	k_X/k_H
$p\text{-}NO_2C_6H_4$	695	3.06×10^3	*c*	
$p\text{-}NCC_6H_4$	103	4.54×10^2	*c*	
$p\text{-}ClC_6H_4$	2.76	1.22×10	305	4.99
$p\text{-}FC_6H_4$	0.526	2.32	76.4	1.25
C_6H_5	0.227	1.00	61.1	1.00
$m\text{-}CH_3C_6H_4$	0.0843	0.371	34.0	0.556
$p\text{-}CH_3C_6H_4$	0.0206	9.25×10^{-2}	11.0	0.180
$p\text{-}CH_3OC_6H_4$	0.0071	3.13×10^{-2}	8.58	0.140

[a] Reactions performed in aqueous, phosphate-buffered (0.050 M) solution at pH 7.0. [b] Reactions performed in anhydrous acetonitrile. [c] Too fast to measure.

As an outer-sphere one-electron-transfer process, the reduction of arenediazonium ions should be amenable to treatment by Marcus theory.[18] Determination of the self-exchange rate constants for arenediazonium salts (eq 3) would not only provide a

$$ArN_2^+ + Ar^*N_2^\bullet \rightarrow ArN_2^\bullet + Ar^*N_2^+ \qquad (3)$$

suitable means of evaluating the mechanisms of their electron-transfer reactions but should also uncover the existence, if any, of a substituent dependence on this elementary process. In order

---

(1) (a) Trinity University. (b) University of Wisconsin, Eau Claire.

(2) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; Chapter 9.

(3) (a) Doyle, M. P.; Siegfried, B.; Dellaria, J. F., Jr. *J. Org. Chem.* **1977**, *42*, 2426. (b) Kochi, J. K. *J. Am. Chem. Soc.* **1957**, *79*, 2942. (c) Jenkins, C. L.; Kochi, J. K. *Ibid.* **1972**, *94*, 856. (d) Wulfman, D. S. In *The Chemistry of Diazonium and Diazo Groups*; Patai, S., Ed.; Wiley: New York, 1978; Part 1, Chapter 8.

(4) (a) Doyle, M. P.; Siegfried, B.; Elliott, R. C.; Dellaria, J. F. *J. Org. Chem.* **1977**, *42*, 2431. (b) Kochi, J. K. *J. Am. Chem. Soc.* **1955**, *77*, 5090. (c) Rondestvedt, C. S., Jr. *Org. React.* **1960**, *11*, 189.

(5) (a) Bachmann, W. E.; Hoffmann, R. A. *Org. React.* **1941**, *2*, 224. (b) Hey, D. H. *Adv. Free Radical Chem.* **1967**, *2*, 47. (c) Dermer, O. C.; Edmison, M. T. *Chem. Rev.* **1957**, *57*, 77. (d) Abramovitch, R. A. *Adv. Free Radical Chem.* **1967**, *2*, 87. (e) DeTar, D. F. *Org. React.* **1957**, *9*, 409. (f) Gadallah, F. F.; Cantu, A. A.; Elofson, R. M. *J. Org. Chem.* **1973**, *38*, 2386.

(6) (a) Sakakura, T.; Hara, M.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1545. (b) Cohen, T.; Lewarchik, R. J.; Tarino, J. Z. *J. Am. Chem. Soc.* **1974**, *96*, 7753. (c) Doyle, M. P.; Dellaria, J. F., Jr.; Siegfried, B.; Bishop, S. W. *J. Org. Chem.* **1977**, *42*, 3494.

(7) (a) Elofson, R. M.; Edsberg, R. L.; Mercherly, P. A. *J. Electrochem. Soc.* **1950**, *97*, 166. (b) Atkinson, E. R.; Warren, H. H.; Abel, P. I. *J. Am. Chem. Soc.* **1950**, *72*, 915. (c) Kochi, J. K. *J. Am. Chem. Soc.* **1955**, *77*, 3208.

(8) Elofson, R. M.; Gadallah, F. F. *J. Org. Chem.* **1969**, *34*, 3335.

(9) Doyle, M. P.; Mahapatro, S. N.; Tran, S. V. *Inorg. Chim. Acta* **1984**, *92*, 123.

(10) Doyle, M. P.; Mahapatro, S. N.; VanZyl, C. M.; Hester, M. R. *J. Am. Chem. Soc.* **1985**, *107*, 6136.

(11) Bisson, J. M.; Hanson, R.; Slocum, D. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1331.

(12) Jirkovsky, J.; Fojtik, A.; Becker, G. O. *Collect. Czech. Chem. Commun.* **1981**, *46*, 1560.

(13) Hegarty, A. F. In *The Chemistry of Diazonium and Diazo Groups*; Patai, S., Ed.; Wiley: New York, 1978; Part 2, Chapter 12.

(14) (a) Schwarz, W.; Zollinger, H. *Helv. Chim. Acta* **1981**, *64*, 513. (b) Besse, J.; Zollinger, H. *Ibid.* **1981**, *64*, 529.

(15) Zollinger, H. *Acc. Chem. Res.* **1973**, *6*, 335.

(16) Yasui, S.; Nakamura, K.; Ohno, A. *Tetrahedron Lett.* **1983**, *24*, 1983.

(17) The terms "non-bonded" and "bonded" electron-transfer processes were introduced by Littler as alternatives to "outer-sphere" and "inner-sphere" for organic systems: Littler, J. S. In *International Review of Science. Organic Chemistry*; Waters, W. A., Ed.; Butterworths: London; Series 1, Vol. 10, p 237. We have employed the term "bonded" as an appropriate designation for eq 2.

(18) Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79.

0002-7863/87/1509-1536$01.50/0

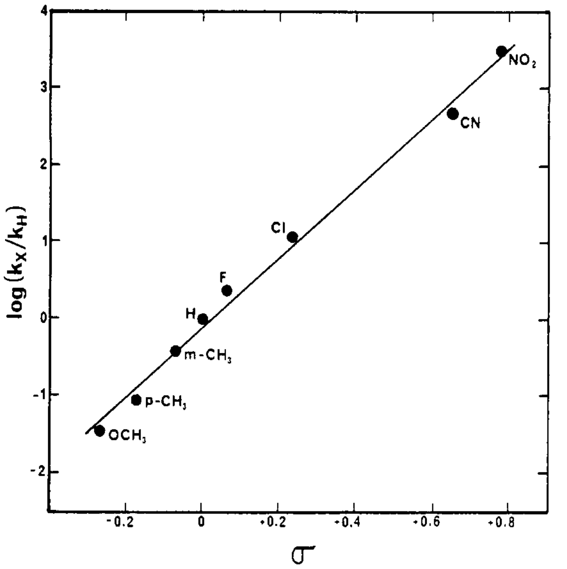


Figure 1. Hammett plot for reactions of substituted benzenediazonium tetrafluoroborate salts with potassium ferrocyanide in 0.05 M phosphate-buffered aqueous solution at 25.0 °C.

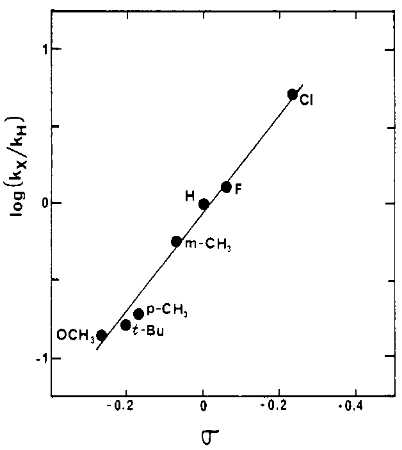


Figure 2. Hammett plot for reactions of substituted benzenediazonium tetrafluoroborate salts with decamethylferrocene in anhydrous acetonitrile at 25.0 °C.

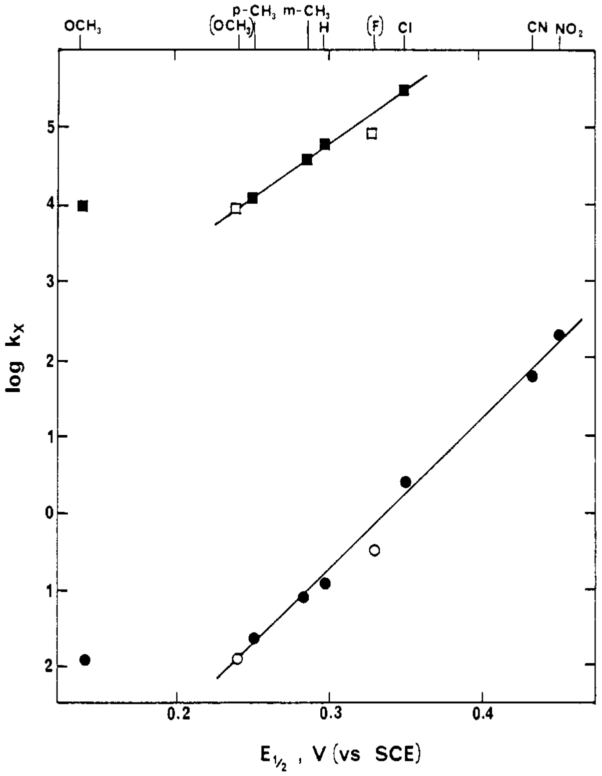


Figure 3. Correlations between measured half-wave reduction potentials of arenediazonium tetrafluoroborate salts and log k_X for reactions with ferrocyanide (●) and decamethylferrocene (■). The open points are estimated values obtained from the correlation between $E_{1/2}$ and σ-values.

to perform this evaluation, we have obtained kinetic data for the reactions of selected arenediazonium salts with two inorganic one-electron reducing agents whose oxidation potentials and self-exchange rate constants are well known and which characteristically undergo outer-sphere electron-transfer reactions. These results are applied to literature reports of rate constants for related electron-transfer reactions involving diazonium ions.

Results

Reduction by Ferrocyanide and Decamethylferrocene. Potassium ferrocyanide and decamethylferrocene were selected as potential reducing agents for arenediazonium ions because of their stability and because prior results suggested their suitability for these transformations.[19,20] Reductions by $Fe(CN)_6^{4-}$ were performed under nitrogen in aqueous phosphate-buffered solutions at pH 7.0 and 25.0 °C. Reaction products consisted of $Fe(CN)_6^{3-}$ and the arene corresponding to the diazonium ion employed. First-order kinetic dependence on both ferrocyanide and arenediazonium tetrafluoroborate concentrations were established, and second-order rate constants were calculated for the reactions of para-substituted benzenediazonium tetrafluoroborate salts whose reduction potentials were known or calculated from standard structure–reactivity correlations.[8] These results, spanning five orders of magnitude, are presented in Table I. Linear correlation is observed (Figure 1) between the log of the ratio of second-order rate constants for substituted to the unsubstituted benzenediazonium salts, log (k_X/k_H), and σ^{21} with a ρ-value of +4.7.[10]

Decamethylferrocene reductions of diazonium salts were investigated in anhydrous acetonitrile at 25.0 °C under nitrogen. Quantitative production of decamethylferrocenium tetrafluoroborate and arene according to the stoichiometry of eq 4 was

$$(Me_5Cp)_2Fe + ArN_2^+BF_4^- \xrightarrow{CH_3CN} (Me_5Cp)_2Fe^+BF_4^- + N_2 + ArH \quad (4)$$

observed. First-order kinetic dependence on both decamethylferrocene and arenediazonium tetrafluoroborate concentrations were established, and the second-order rate constants for these reduction reactions are listed in Table I. Reaction rates for these transformations were very rapid, even for measurement by stopped-flow methods, so that rate constants for reduction of those arenediazonium salts whose reactivities toward $(Me_5Cp)_2Fe$ were greater than that of the p-chloro derivative were not obtained. As was observed for reductions by $Fe(CN)_6^{4-}$, a distinct linear relationship exists between log (k_X/k_H) and Hammett σ-values (Figure 2) with ρ equal to +3.3.

Correlation with Reduction Potentials. The half-wave potentials of arenediazonium tetrafluoroborate salts reported by Elofson and Gadallah correlate with Hammett σ-values.[8] Although these $E_{1/2}$-values were obtained in the aprotic solvent sulfolane, linear correspondence with rate constants for electron-transfer reactions obtained in aqueous solutions have recently been reported.[12,23] Since the log of the rate constants for reduction of arenediazonium salts that we have obtained is linearly related to Hammett σ-values (Figures 1 and 2), it is not surprising that they should also correlate

---

(19) Ruchardt, C.; Merz, E.; Freudenberg, B.; Opgenorth, H.-J.; Tan, C. C.; Werner, R. *Spec. Publ.-Chem. Soc.* **1970**, *No. 24*, 51.

(20) (a) Rosenblum, M.; Howells, W. G.; Banerjee, A. K.; Bennett, C. *J. Am. Chem. Soc.* **1962**, *84*, 2726. (b) Pauson, P. L. *Q. Revs.* **1955**, *9*, 391.

(21) Jaffe, H. H. *Chem. Rev.* **1953**, *53*, 191.

(22) The second-order rate constant for p-$(CH_3)_3CC_6H_4N_2^+BF_4^-$ reduction by $(Me_5Cp)_2Fe$ is 9.44×10^3 M^{-1} s^{-1}.

(23) Galli, C. *J. Chem. Soc., Perkin Trans. 2* **1984**, 897.

Table II. Calculated Self-Exchange Rate Constants from Cross-Reactions for the Reduction of Arenediazonium Tetrafluoroborate Salts by Ferrocyanide and Decamethylferrocene

$ArN_2^+BF_4^-$		k_{22}, $M^{-1}\ s^{-1}$ (calcd)			
Ar =	$E_{1/2}$,[a] V	$Fe(CN)_6^{4-}$ [b]	$(Me_5Cp)_2Fe$ [c]	av k_{22}, $M^{-1}\ s^{-1}$	k_X/k_H [d]
p-$NO_2C_6H_4$	+0.450	9.1		9.1	7.6×10^4
p-NCC_6H_4	+0.433	3.3×10^{-1}		3.3×10^{-1}	2.8×10^3
p-ClC_6H_4	+0.350	4.2×10^{-3}	1.8×10^{-4}	2.2×10^{-3}	1.8×10
p-FC_6H_4	+0.328	3.3×10^{-4}	2.0×10^{-5}	1.8×10^{-4}	1.5
C_6H_5	+0.295	2.1×10^{-4}	3.7×10^{-5}	1.2×10^{-4}	1.0
m-$CH_3C_6H_4$	+0.285	4.2×10^{-5}	1.5×10^{-5}	2.9×10^{-5}	2.4×10^{-1}
p-$CH_3C_6H_4$	+0.250	9.2×10^{-6}	4.8×10^{-6}	7.0×10^{-6}	5.8×10^{-2}
p-$CH_3OC_6H_4$	+0.240[e]	1.6×10^{-6}	4.1×10^{-6}	2.9×10^{-6}	2.4×10^{-2}

[a] Reduction potentials vs. SCE in sulfolane (ref 8). [b] The reduction potential for $Fe(CN)_6^{3-/4-}$ vs. SCE at pH 7 is +0.168 V (ref 29), and k_{11} is $2 \times 10^4\ M^{-1}\ s^{-1}$ (ref 27). [c] The reduction potential for $Fe(CpMe_5)_2^{1+/0}$ in acetonitrile vs. SCE is −0.12 V (ref 30), and k_{11} is $4.4 \times 10^7\ M^{-1}\ s^{-1}$ (ref 28). [d] From av k_{22} values. [e] Estimated value (Figure 3). When the published value of +0.14 V is used, k_{22} is calculated to be $7.5 \times 10^{-5}\ M^{-1}\ s^{-1}$ (from reactions with $Fe(CN)_6^{4-}$) and $1.2 \times 10^{-4}\ M^{-1}\ s^{-1}$ (from reactions with decamethylferrocene).

with measured reduction potentials (Figure 3). The only exception is the p-methoxy derivative which, in both of these cases and in correlations with rate constants for semiquinone reductions of arenediazonium salts,[12] shows substantial deviation.

In their fit of half-wave reduction potentials to σ, Elofson and Gadallah used σ^+-values for para substituents capable of resonance electron donation.[8] This adjustment provided a reasonable linear correspondence to $E_{1/2}$ values for p-methoxy and p-dimethylamino-substituted diazonium salts, but other $E_{1/2}$ values for diazonium salts with electron-donating substituents fit equally well to either σ or σ^+. We suspect that the measured $E_{1/2}$ potentials for the p-methoxy- and p-(dimethylamino)benzenediazonium salts are too low and that they should have values corresponding to those predicted from the fit with σ. If this adjustment is made for the p-methoxy substituent, its $E_{1/2}$ value would be +0.24 V (vs. SCE) and, as seen in Figure 3, this value is in close agreement with that predicted from the rate data.[24]

Discussion

That the reductive transformations which we have investigated are due to outer-sphere electron transfer to arenediazonium salts has ample precedent,[19,20] but perhaps the strongest evidence comes from reactions with decamethylferrocene. Here electrostatic effects are relatively unimportant, and $(Me_5Cp)_2Fe$ is well established as a facile outer-sphere electron-transfer agent with no precedent for forming bonds to oxidants.[25] Moreover, there is no evidence of which we are aware that suggests that ferrocyanide forms bonds to organic molecules during electron transfer, but there is ample precedent for it reacting by nonbonded mechanisms with organic molecules.[18]

The Marcus equation[26] for outer-sphere electron-transfer processes (eq 5) is being used with increasing frequency to interpret

$$k_{12} = (k_{11}k_{22}k_{12}f)^{1/2}$$
$$\ln f = (\ln K_{12})^2/[4 \ln (k_{11}k_{22}/Z^2)] \qquad (5)$$

the redox reactions of organic compounds.[18] Its applications, particularly to reactions between organic compounds and typical one-electron redox reagents, have demonstrated that Marcus theory is a tool of increasing importance for mechanistic interpretations. However, its direct application requires knowledge of individual reactant self-exchange rate constants (k_{11} and k_{22}) as well as their redox potentials under the conditions of the kinetic measurements. While this information is often available for inorganic reactants, it is less well known for many classes of organic compounds. This is the case for arenediazonium tetrafluoroborate salts whose self-exchange rate constants are not available and whose half-wave reduction potentials have been determined in sulfolane,[8] whereas reaction kinetics are commonly performed in aqueous media or in acetonitrile. However, sufficient data are available in this study for an estimate of the apparent self-exchange rate constants for electron-transfer reactions of arenediazonium salts. Equation 5 can be rearranged (eq 6)[27] so that the apparent self-exchange rate constant of one reactant can

$$\ln k_{22} = (\ln k_{12} - \tfrac{1}{2} \ln K_{12} + \ln Z) - \ln k_{11} - [(\ln Z - \ln k_{12})^2 + \ln K_{12}(\ln Z - \ln k_{12})]^{1/2} \qquad (6)$$

be calculated if all other information is available. Apparent arenediazonium ion self-exchange rate constants, k_{22}, are estimated from the measured second-order rate constants, k_{12} (k_X in Table I), the reaction equilibrium constants, K_{12}, and the reducing agent's self-exchange rate constant, k_{11}.[28,29] Equilibrium constants are computed from the reduction potentials for arenediazonium tetrafluoroborate salts[8] and the ferrocyanide and decamethylferrocene potentials.[30,31] The collision frequency, Z, is taken to be $10^{11}\ M^{-1}\ s^{-1}$ in these calculations. The use of eq 6 assumes an outer-sphere electron transfer.

Half-wave potentials for arenediazonium salts in aqueous solution[7] are more negative by between 0.03 and 0.2 V than those measured in sulfolane,[8] but they are influenced by adsorptive effects. Moreover, half-wave potentials obtained in aqueous solution failed to exhibit normal substituent effects.[7c] According to Elofson and Gadallah,[8] $E_{1/2}$ values in acetonitrile are only "somewhat more negative" than those in sulfolane, but exact values have not been reported. Consequently, the $E_{1/2}$ values available in sulfolane[8] are the only reliable data for apparently reversible electron transfers with arenediazonium salts, and they were employed to determine equilibrium constants for calculations with eq 6.[32] However, that for the p-methoxybenzenediazonium salt was estimated from the correlations depicted in Figure 3 rather than with use of the measured value.[33] The $E_{1/2}$ value for p-fluorobenzenediazonium tetrafluoroborate was calculated from the equation relating half-wave potentials to Hammett σ-values.[8]

The calculated arenediazonium ion self-exchange rate constants derived from the arenediazonium ion reactions with decamethylferrocene and ferrocyanide (Table II) are in good agreement considering the approximate nature of these calculations. Their close correspondence provides evidence of the nonbonded mech-

---

[24] Similar agreement is found with rate data for reductions of arenediazonium ions by p-benzosemiquinone.[12]

[25] Carney, M. J.; Lesniak, J. S.; Likar, M. D.; Pladziewicz, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 2565.

[26] (a) Marcus, R. A.; Sutin, N. *Inorg. Chem.* **1975**, *14*, 213. (b) Marcus, R. A. *J. Phys. Chem.* **1963**, *67*, 853; **1965**, *43*, 679. (c) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

[27] Pladziewicz, J. R.; Espenson, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 56; *J. Phys. Chem.* **1971**, *75*, 3381.

[28] Campion, R. J.; Deck, D. F., Jr.; Wahl, A. C. *Inorg. Chem.* **1967**, *6*, 672.

[29] Yang, E. S.; Chan, M. S.; Wahl, A. C. *J. Phys. Chem.* **1975**, *79*, 2049; **1980**, *84*, 3094.

[30] Kolthoff, I. M.; Tomsicek, W. I. *J. Phys. Chem.* **1935**, *39*, 945.

[31] Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882.

[32] A reviewer pointed out the possibility that the redox potentials for the arenediazonium salts used in these calculations[8] are compromised by slow heterogeneous electron transfer and rapid successive reactions during the polarographic studies. If this is true, then our calculated self-exchange rate constants must be modified. However, we know of no published work which refutes or questions these data.

[33] That the measured value of $E_{1/2}$ is smaller than expected is consistent with interference from the coupled chemical reaction caused by consumption of the arenediazenyl radical in the time scale of the measurement.[18]

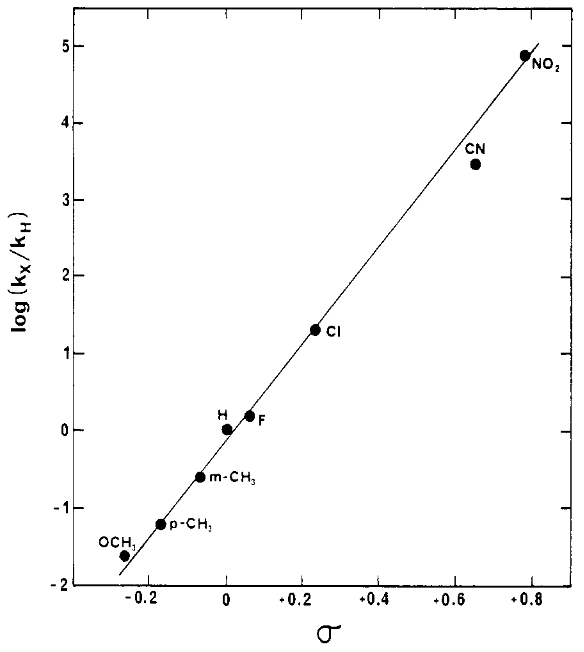


Figure 4. Hammett plot for calculated self-exchange rate constants of arenediazonium ions.

anism for electron transfer with these reducing agents. The slightly higher self-exchange values calculated from the ferrocyanide reactions as compared to those derived from the decamethylferrocene reactions are not surprising since work terms were ignored in these calculations. This approximation is justified for reactions with the uncharged decamethylferrocene but could result in erroneously high values for reactions involving reagents of opposite charge.

Two features of these self-exchange rate constants are noteworthy. First, the self-exchange rate constants are rather low when compared to constants from other organic redox systems, although substantial variation does exist.[18] A second intriguing feature is the striking systematic variation of self-exchange rate constants (10^4- to 10^6-fold differences) for only a 0.20 V variation in redox potential. Correlation of log (k_X/k_H) from averaged k_{22} values is observed with Hammett σ-constants (Figure 4), yielding a ρ-value of +6.4. The large substituent effect is surprising. In fact, it is often assumed in calculations of this type that a single self-exchange rate applies for a related series of compounds.[18] A system for which detailed self-exchange rates have been measured directly by NMR methods[29] and indirectly by an extensive series of cross-reactions[27] is that of ferrocene and ten of its derivatives. In this series, the self-exchange rate constants vary only by 20-fold (from about 2 to 40 × 10^6 M^{-1} s^{-1}), while their redox potentials span a range of more than 0.6 V.

Other examples involving exclusively aromatic organic anion and cation radicals include the series of nitriles, phenothiazines, and related compounds[34,35] wherein small changes in self-exchange rate constants (typically 10- to 20-fold) are found for large changes in redox potentials. In these systems, the self-exchange rate constants, typically 10^8 to 10^{10} M^{-1} s^{-1}, and redox potentials correlate with the energies of the highest occupied molecular orbital of the neutral parent for cation-radical exchanges. In systems where much lower self-exchange rates are observed, such as the electron transfer between cyclooctatetraene and its anion radical,[36] significant structural changes that accompany electron transfer are proposed to be responsible. It may also be that a large variation in self-exchange rate constants for a series of related compounds, such as we have observed here, only occurs when the barrier for electron transfer is relatively large. However, too few one-electron outer-sphere systems with high activation barriers have been studied to adequately address this point, and more data are needed.

Attempts to fit the observed cross-reaction rate constants to free energy functions derived from Marcus theory ($\Delta G^{\dagger}_{12}$ vs. $\Delta G^{\circ\prime}_{12}$ or ln k_{12} vs. $\Delta G^{\circ\prime}_{12}$)[37] gave poor agreement between the observed cross-reaction rate constants (Table II) and the predicted values. However, application of Marcus theory in these two forms assumes, as already mentioned, that the self-exchange free energy of activation, $\Delta G^{\dagger}_{22}$, is not subject to significant variation for compounds in a related series. This clearly is not the case for the arenediazonium ions studied here. The self-exchange free energies of activation apparently exhibit substantial substituent dependence.

Since the work terms should be near zero for the reactions of the uncharged decamethylferrocene, it is possible to estimate the reorganizational energy, λ, for arenediazonium ion–arenediazenyl radical self-exchange reactions from the decamethylferrocene–arenediazonium ion data in Table II with eq 7. For the self-exchange reactions, $\Delta G^{\circ\prime}$ is zero and λ is simply $4\Delta G^{\dagger}$. Reorganizational energies range from 80 kcal/mol for the *p*-chloro derivative to 89 kcal/mol for the *p*-methoxy derivative. These high energies, like the low self-exchange rate constants from which they are derived, suggest that the structures of the diazonium ion and its corresponding diazenyl radical differ considerably. This same conclusion has been previously offered to explain the significantly greater substituent dependence on electron affinities[38] relative to half-wave reduction potentials,[8] and the aryldiazenyl radical has been suggested[38] to be closer in structure to bent azo compounds than to linear diazonium ions.[39]

$$k = Ze^{-\Delta G^{\dagger}/RT} \qquad \text{where } \Delta G^{\dagger} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^{\circ\prime}}{\lambda}\right)^2 \qquad (7)$$

In his recent report of substituent effects of diazonium tetrafluoroborate salts in the Sandmeyer reaction, Galli employed an activation free energy value of 2.5 kcal/mol for the self-exchange reaction between the *p*-methoxybenzenediazonium ion and its corresponding diazenyl radical.[23] However, this value is only an estimate and, based on our work, is clearly much too low. We have also tried unsuccessfully to repeat his calculations in the Appendix of this paper for the second-order rate constants of ferrous ion reductions of two arenediazonium ions.[40] By repeating these calculations with use of the average of our self-exchange rate constants (Table II) and experimental data provided by Galli,[23] cross-reaction rate constants of 9.8 × 10^{-6} M^{-1} s^{-1} and 1.3 M^{-1} s^{-1} were calculated for the values observed by Galli of 7.9 × 10^{-2} M^{-1} s^{-1} and 3.3 M^{-1} s^{-1}, respectively, for the ferrous ion reductions of the *p*-methoxy- and *p*-nitrobenzenediazonium ions.[41] Corrections for work terms are not included since they would change the calculated values very little.

To test the validity of the self-exchange rate constants reported in Table II for the prediction of reaction rate constants, we have applied them to the fast electron-transfer reactions between the *p*-benzosemiquinone radical anion ($Q^{\bullet-}$) and arenediazonium tetrafluoroborate salts (eq 8).[12] Experimentally determined rate

$$Q^{\bullet-} + ArN_2^+ \rightarrow Q + ArN_2^{\bullet} \qquad (8)$$

constants from reactions performed in 64% aqueous acetonitrile are compared in Table III with values calculated with eq 5, average self-exchange rate constants for the diazonium salts from Table II, a value of +0.161 V (vs. SCE) for the $Q^{\bullet-}/Q$ potential calculated from the equations of Rich and Bendall,[42] and a semi-

---

[34] Malachesky, P. A.; Miller, T. A.; Layloff, T.; Adams, R. M. *Exch. React., Proc. Symp.* **1965**, 151.

[35] Rowert, B. A.; Marcoux, L.; Bard, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 5538.

[36] Katz, T. J. *J. Am. Chem. Soc.* **1960**, *82*, 3785.

[37] For example, see eq 65 and 70 in ref 18.

[38] Kampar, R. E.; Kokars, V. R.; Neiland, O. Y. *Zh. Obshch. Khim.* **1977**, *47*, 858.

[39] Rømming, Chr. *Acta Chem. Scand.* **1963**, *17*, 1444.

[40] The redox potentials for the reacting ions appear to have been incorrectly applied.

[41] The Hammett σ-value for this redox system was obtained from a relative rate study and is a surprisingly low +1.0.[25] Experimental rate constants were determined in the presence of cupric chloride.

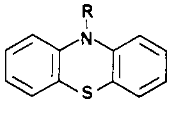
Table III. Observed and Calculated Cross-Reaction Rate Constants for Semiquinone Reduction of Arenediazonium Tetrafluorobrate Salts

$ArN_2^+BF_4^-$ Ar =	k_{11},[a] $M^{-1}\ s^{-1}$	k_{22},[b] $M^{-1}\ s^{-1}$	$E°$,[c] V	k_{12}(obsd),[d] $M^{-1}\ s^{-1}$	k_{12}(calcd), $M^{-1}\ s^{-1}$	k_{12}(obsd)/ k_{12}(calcd)
p-NO_2	5×10^7	9.1	0.611	9.4×10^9	3.1×10^8	30
p-Cl	5×10^7	2.2×10^{-3}	0.511	3.2×10^7	1.9×10^6	17
H	5×10^7	1.2×10^{-4}	0.456	8.0×10^6	2.2×10^5	36
p-CH_3	5×10^7	7.0×10^{-6}	0.411	5.2×10^6	2.7×10^4	192
p-OCH_3	5×10^7	2.9×10^{-6}	0.401	1.2×10^6	1.5×10^4	80

[a] Reference 41. [b] This work. [c] Reference 12 and Table II. [d] Reference 12.

quinone–quinone self-exchange rate constant of $5 \times 10^7\ M^{-1}\ s^{-1}$.[43] Except for the reaction with *p*-methylbenzenediazonium tetrafluoroborate, calculated rate constants are only 17- to 80-times lower than those observed. Since both the semiquinone self-exchange rate constant and its oxidation potential are estimated values, this is reasonably agreement considering the uncertainties involved in these calculations.

With the thought of using these calculations in making mechanistic choices between outer-sphere and bonded pathways, the expected rate constants for outer-sphere electron transfer from phenothiazine (**2a**) and 10-methylphenathiazine (**2b**) to the *p*-methoxybenzenediazonium ion were calculated by using the diazonium ion self-exchange rate constant in Table II and the published[35] phenothiazine potentials and self-exchange rate constants. These two reactions have been examined and, based on spectroscopic evidence for an initial rapid increase in absorbance followed by a slower, but much more pronounced, increase which resulted in the production of the cation radical of **2**, they have been reported to occur by bonded mechanisms.[11] The observed rate constants are 0.122 and $2.91 \times 10^{-3}\ M^{-1}\ s^{-1}$ for reduction of the *p*-methoxybenzenediazonium ion by phenothiazine and its 10-methyl derivative. The calculated values are 0.076 and $2.0 \times 10^{-3}\ M^{-1}\ s^{-1}$, respectively. This close agreement suggests that these reactions are not occurring by eq 2, as has been offered,[11] but that they are outer-sphere electron-transfer processes. The initial rapid increase in absorbance observed prior to electron transfer may in fact be due to the formation of a charge-transfer complex[44] rather than to an azo intermediate.



2

Although we must assume that electron-transfer reactions of arenediazonium salts with ferrocyanide and decamethylferrocene occur by outer-sphere mechanisms, this assumption is a good one given the known chemical reactivities of these two reductants, and the close correspondence between self-exchange rate constants obtained from each of these reaction systems adds credibility. Self-exchange rate constants for arenediazonium ions are low compared to those for other organic systems, suggesting a considerable structural difference between the diazonium ion and diazenyl radical. The large substituent dependence may be related to the high energy barrier for electron transfer, and additional efforts are needed to clarify the cause of this dependence. Application of Marcus theory using these self-exchange rate constants provides a surprisingly high degree of predictability for the determination of reaction rate constants and offers a useful probe for mechanistic evaluations.

Experimental Section

Materials. Arenediazonium tetrafluoroborate salts were prepared, recrystallized from acetone–hexane, and characterized by the standard procedure.[45] Reagent grade potassium ferrocyanide and decamethylferrocene (Strem Chemical Co.) were employed. Acetonitrile was distilled from calcium hydride; double-distilled water was used. Stock solutions of the diazonium salts and of decamethylferrocene were prepared in acetonitrile and maintained under nitrogen. Concentrated solutions of ferrocyanide were prepared in deoxygenated phosphate buffer (0.050 M, pH 7.0) and kept under nitrogen.

Reductions by Ferrocyanide. With the exception of the *p*-nitro- and *p*-cyanobenzenediazonium tetrafluoroborate salts, whose rates were followed by stopped-flow methods, reactions were initiated with the injection, using a gas-tight syringe, of 20–40 μL of the stock solution of the diazonium salt (2×10^{-2} M) into 3.00 mL of the ferrocyanide solution in 0.050 M phosphate buffer at pH 7.0 contained in a standard spectrophotometer cell thermostated to 25.0 °C. Initial reactant concentrations of ferrocyanide were 3–6 × 10^{-3} M, and those for diazonium salts were 1–2 × 10^{-4} M. Rates of reaction were determined by monitoring the increase in absorbance of ferricyanide at 460 nm with time with use of a Pye Unicam SP8-200 or a Cary 118 spectrophotometer. 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. Reactions were carried out under pseudo-first-order conditions. The resultant time courses were fitted to an integrated single exponential process from which the pseudo-first-order rate constants were calculated. Linearity in semilog plots was observed through a minimum of 3 half-lives. The kinetic dependence on the reactants was established by varying the molar ratio of ferrocyanide to the diazonium ion and, with *p*-cyanobenzenediazonium tetrafluoroborate, by performing the reaction under second-order conditions. Averaged second-order rate constants from a minimum of 3 kinetic determinations, or 16 in stopped-flow measurements, are reported with average deviations of ±4%.

The production of ferricyanide was monitored spectrophotometrically. Quantitative evolution of dinitrogen based on a 1:1 stoichiometry was observed. *p*-Nitrobenzenediazonium tetrafluoroborate yielded nitrobenzene (>80%) and minor amounts of *p*-nitrobenzonitrile (<2%) upon treatment with ferrocyanide under anaerobic conditions, and these reduction products were identified in reaction mixtures from kinetic determinations by HPLC analyses. Increasing the percentage of acetonitrile in the reaction mixture reduced and eventually eliminated the benzonitrile product. Both *p*-nitrophenol (37% yield) and nitrobenzene (13% yield) were obtained from reactions performed in dioxygen-saturated solutions, and the yield of nitrobenzene was dependent on the amount of acetonitrile in the reaction solution. Neither 4,4′-dinitrobiphenyl nor the corresponding azo compound was a product of these reactions.

Reductions by Decamethylferrocene. All kinetic experiments were performed by stopped-flow measurements. Standard kinetic determinations employed stock solutions of the diazonium salt (1–4 mM) and decamethylferrocene (0.2–0.8 mM) in acetonitrile under nitrogen. Solutions were thermostated at 25.0 °C, and reactions were initiated by equal-volume injection of each stock solution into the mixing chamber. Rates of reaction were determined by monitoring the increase in absorbance of the decamethylferricinium ion at its absorption maximum of 778 nm.[25] Reactions were performed under pseudo-first-order conditions, and linearity in semilog plots was observed through 4 half-lives. Reaction order was established as previously described. Averaged second-order rate constants from between 8 and 24 measurements were obtained, and values are reported with average deviations of ±5%. Control experiments showed that second-order rate constants were independent of added tetrabutylammonium tetrafluoroborate.

The production of decamethylferrocenium tetrafluoroborate[25] was monitored spectrophotometrically. Quantitative production of nitrobenzene, based on a 1:1 reactant stoichiometry, was determined by HPLC analyses of reaction mixtures from reductions of *p*-nitrobenzenediazonium tetrafluoroborate by $(Me_5Cp)_2Fe$ in anhydrous acetonitrile.

Acknowledgment. Support for this research from the National Science Foundation through Grant CHE-8418168 to M. P. Doyle and Grant CHE-8511729 to J. R. Pladziewicz and to J.R.P. from the donors of Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

---

(42) Rich, P. R.; Bendall, D. S. *Biochim. Biophys. Acta* **1980**, *592*, 506.

(43) Pelizzetti, E.; Mentasti, E.; Baiacchi, C. *J. Phys. Chem.* **1976**, *80*, 2979.

(44) Koller, S.; Zollinger, H. *Helv. Chim. Acta* **1970**, *53*, 78.

(45) Doyle, M. P.; Bryker, W. J. *J. Org. Chem.* **1979**, *44*, 1572.