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Cation Radicals of Phenothiazines. Electron Transfer with Aquoiron(II) and -(III) and Hexacyanoferrate(II) and -(III)

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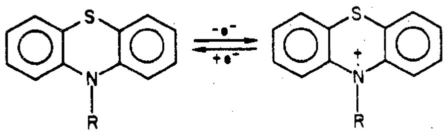
The rates of electron transfer of three different groups of reactions involving *N*-alkylphenothiazines (PTZ) have been obtained in aqueous perchloric acid medium by means of stopped-flow and *T*-jump spectrophotometric techniques: (1) the electron transfer between the cation radical and different PTZ derivatives; (2) the oxidation of PTZ by $Fe(H_2O)_6^{3+}$; (3) the oxidation of PTZ by $Fe(CN)_6^{3-}$. Electron transfers involving $Fe(CN)_6^{3-}$ are in agreement with the Marcus theory, while oxidation by Fe(III) shows an expected dependence of activation free energy on overall free energy change, although the calculated values are 300–500 times higher than the experimental ones.

Increasing interest has been recently devoted to the chemistry of organic cation radicals.[1] These species are intermediates in several oxidation processes; therefore it is useful to know some of their characteristic parameters such as the reduction potentials and the self-electron-exchange rates in solution as well as if their reaction kinetics can be treated in the light of most currently adopted electron-transfer theories,[2] particularly the Marcus theory,[3] which is one of the most frequently applied, since its form is conducive to experimental evaluation.

Cation radicals of *N*-alkylphenothiazines are known to be generated in solution by removal of one electron from their parent molecules,[4] according to



and to be long-lived in aqueous acidic medium. Almost all *N*-alkylphenothiazines are antipsychotic drugs, and their redox activity was related to the pharmaceutical properties (free radicals were in fact discovered as metabolites of phenothiazine-like drugs).[5a]

Unsubstituted phenothiazine attracted large interest also in photoionization studies performed for solar energy conversion purposes.[6] These investigations were performed in alcoholic solution or micellar phase owing to the poor solubility in water of phenothiazine (all of the present *N*-alkyl derivatives are, however, water soluble).

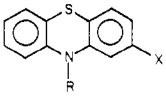
Besides, the photogalvanic effect of the thionine (a diamino derivative of phenothiazine)–iron system[7] is one of the most extensively studied because of the possibility of its use in the construction of photogalvanic cell.[8]

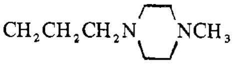
In this paper we present the results of our studies on the kinetics and mechanism of electron transfer between a series of *N*-alkylphenothiazines and $Fe(H_2O)_6^{3+/2+}$ and $Fe(CN)_6^{3-/4-}$ in acidic aqueous solution.

Experimental Section

Reagents. The *N*-alkylphenothiazines (later referred to as PTZ) in Chart I, obtained from Rhône-Poulenc, were investigated. The purity of the compounds was checked by elemental analysis as well

Chart I



compound	X	R
I	OH	$CH_2CH_2CH_2N(CH_3)_2$
II	H	 $CH_2CH_2CH_2N$ NCH_3
III	OCH_3	$CH_2CH_2CH_2N(CH_3)_2$
IV	H	$CH_2CH_2CH_2N(CH_3)_2$
V	Cl	$CH_2CH_2CH_2N(CH_3)_2$
VI	H	$CH_2CH_2N(C_2H_5)_2$
VII	H	$CH_2CH(CH_3)N(CH_3)_2$
VIII	H	$CH(CH_3)CH_2N(CH_3)_2$

as by mass spectrometry and NMR spectra.[5b] Iron(III) perchlorate (C. Erba) was used, and the solutions were standardized by complexometric titration. A solution of iron(II) perchlorate was prepared by dissolving pure iron wire in perchloric acid and was standardized by oxidimetric titration. Solutions of hexacyanoferrate(III) in perchloric acid were prepared immediately before use from a stock aqueous solution of hexacyanoferrate(III).

All other inorganic salts were analytical grade and their solutions were standardized according to usual titrimetric procedures. Water was doubly distilled.

Spectrophotometric Measurements. UV–visible spectra were measured using a Hitachi Perkin-Elmer EPS 3t spectrophotometer. Since all phenothiazine derivatives, with exception of I, are not quantitatively oxidized by Fe(III) or $Fe(CN)_6^{3-}$, spectra at increasing ratios of [Fe(III)]/[PTZ] (or $[Fe(CN)_6^{3-}]/[PTZ]$) were recorded in order to estimate both the molar absorptivities and the equilibrium quotients. The molar absorptivities were also verified by oxidizing PTZ with hexachloroiridate(IV), an oxidant which ensures the complete oxidation of PTZ: the values obtained are in good agreement. The wavelength region 520–560 nm proved particularly useful for following the course of the reactions because only the cation radicals have significant molar absorptivities.

Kinetic Measurements. A Durrum-Gibson stopped-flow spectrophotometer (with a 2-cm cell path) was employed for reactions of PTZ with Fe(III) and for some runs with $Fe(CN)_6^{3-}$. The measurements with Fe(III) were performed at [PTZ] = $(2\text{–}4) \times 10^{-5}$ M, while the choice of the concentrations of Fe(III) and Fe(II) was dependent on the phenothiazine derivative. The kinetic runs were performed in $[HClO_4]$ = 0.05–1.00 M (μ = 1.0 M ($LiClO_4$)) at different temperatures (10.0, 25.0, 37.0 °C).

Some kinetic runs for PTZ oxidation with $Fe(CN)_6^{3-}$ were followed by a *T*-jump spectrophotometer (Messanlagen) at the wavelength of maximum absorption of the cation radicals at $[HClO_4]$ = 1.00 M, μ = 1.0 M, and 25 °C.

Also electron exchanges between oxidized and reduced forms of different phenothiazines were followed by means of the *T*-jump technique.

Kinetic Data. The concentrations of reactants for reaction 1, from

$$\mathrm{Fe(III)} + \mathrm{PTZ} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Fe(II)} + \mathrm{PTZ}^{+}\cdot \qquad (1)$$

which rate law 2 results, were chosen in order to ensure pseudo-

$$-\mathrm{d[PTZ]}/\mathrm{d}t = k_1[\mathrm{Fe(III)}][\mathrm{PTZ}] - k_{-1}[\mathrm{Fe(II)}][\mathrm{PTZ}^{+}\cdot] \qquad (2)$$

first-order conditions; that is both Fe(III) and Fe(II) were added in relatively high concentrations with respect to PTZ. Under these conditions plots of ln ($A_\infty - A_t$) vs. time (where A_∞ and A_t represent the absorbance at equilibrium and at time *t*, respectively) were linear for at least 90% of the reaction. The slopes of the plots define pseudo-first-order rate constants for the approach to equilibrium (see eq 3). In order to evaluate the specific rate constants, k_{obsd}/[Fe(II)] was plotted against [Fe(III)]/[Fe(II)].

$$k_{\mathrm{obsd}} = k_1[\mathrm{Fe(III)}] + k_{-1}[\mathrm{Fe(II)}] \qquad (3)$$

The reactions between PTZ and $Fe(CN)_6^{3-}$ proceed similarly (eq 4). For measurements with the stopped-flow technique, owing to

$$\mathrm{Fe(CN)_6^{3-}} + \mathrm{PTZ} \underset{k'}{\overset{k}{\rightleftharpoons}} \mathrm{Fe(CN)_6^{4-}} + \mathrm{PTZ}^{+}\cdot \qquad (4)$$

Table I. Spectral Characteristics for Cation Radicals and Equilibrium Quotients for Reaction 1

compd	λ, nm	$10^{-3}\epsilon$, M^{-1} cm^{-1}	Q^a	E^0,[b] V
I	562	9.5 ± 0.3	80 ± 20	0.62_5
II	514	9.4 ± 0.4	1.9 ± 0.4	0.72
III	566	9.0 ± 0.4	2.5 ± 0.4	0.71
IV	513	9.2 ± 0.3	2.1 ± 0.4	0.71_5
V	525	10.2 ± 0.5	0.17 ± 0.03	0.78
VI	511	10.5 ± 0.4	$(4.0 \pm 0.7) \times 10^{-2}$	0.82
VII	515	9.3 ± 0.4	$(7.4 \pm 0.9) \times 10^{-3}$	0.86_5
VIII	524	8.8 ± 0.4	$(2.7 \pm 0.2) \times 10^{-3}$	0.89

[a] 25.0 °C, $[HClO_4]$ = 1.00 M, μ = 1.0 M. [b] For $PTZ^{+}\cdot$/PTZ, estimated by assuming E^0 for the Fe(III)/Fe(II) couple as 0.738 V (L. B. Magnusson and J. R. Huizenga, *J. Am. Chem. Soc.*, 75, 2242 (1953)).

the rapidity of the reactions, comparable concentrations were used, and consequently the integrated form of eq 5 takes the form of eq

$$\mathrm{d[PTZ^{+}\cdot]}/\mathrm{d}t = k[\mathrm{Fe(CN)_6^{3-}}][\mathrm{PTZ}] - k'[\mathrm{Fe(CN)_6^{4-}}][\mathrm{PTZ^{+}\cdot}] \qquad (5)$$

$$[R(1 - Q^{-1})]^{-1} \ln \left\{ \frac{X_e(Y + R)}{Y(X_e + R)} \right\} = kt \qquad (6)$$

6 (for $[Fe(CN)_6^{3-}]_0 \neq [PTZ]_0$, with $Fe(CN)_6^{4-}$ and $PTZ^{+}\cdot$ initially absent),[9] where the subscript e refers to equilibrium, $Y = X_e - X$ (where $X = A_t/l\epsilon$, being $A_0 = 0$), and $R = [1/(Q - 1)]\{Q^2([PTZ]_0 - [Fe(CN)_6^{3-}]_0)^2 + 4Q[PTZ]_0[Fe(CN)_6^{3-}]_0\}^{1/2}$. If the two reagents have equal initial concentrations, expression 7 holds (with $Fe(CN)_6^{4-}$ and

$$(Q^{1/2}/2[\mathrm{PTZ}]_0) \ln \left\{ \frac{X([\mathrm{PTZ}]_0 - 2X_e) + [\mathrm{PTZ}]_0 X_e}{[\mathrm{PTZ}]_0 Y} \right\} = kt \qquad (7)$$

$PTZ^{+}\cdot$ initially absent). The kinetic data for each run were fitted to eq 6 or 7, by using the values of *Q* listed in Table I.

In the *T*-jump experiments, a single relaxation time was observed. The relaxation times, τ, were obtained from logarithmic plots of absorbance deviations (arbitrary units) from the absorbance value gained at equilibrium. Three measurements were generally made for each solution and their relaxation times were within 10%. The rate constants were computed through relation 8 (when $[Fe(CN)_6^{3-}]_0 \neq [PTZ]_0$)[1d] or relation 9 (when $[Fe(CN)_6^{3-}]_0 = [PTZ]_0 = C_0$).

$$1/\tau = k[\mathrm{Fe(CN)_6^{3-}}][\mathrm{PTZ}] + k'[\mathrm{Fe(CN)_6^{4-}}][\mathrm{PTZ^{+}\cdot}] \qquad (8)$$

$$1/\tau = 2C_0k/Q^{1/2} \qquad (9)$$

With the *T*-jump technique we have also tried to follow the reactions between cation radicals and phenothiazines. Owing to the similar spectra of cation radicals some attempts failed with the exception of the reaction of $(IV)^{+}\cdot$ with III (by following the reaction at 560 nm) and of $(VII)^{+}\cdot$ with VIII (at 540 nm). $(IV)^{+}\cdot$ and $(VII)^{+}\cdot$ were generated by electrooxidation or by oxidation of an excess of PTZ with cerium(IV) sulfate (blank solutions did not show any relaxation). Equations 8 and 9 were used in order to obtain the rate constants.

Results

Spectral and Equilibrium Data. Table I collects the spectrophotometric characteristics of the cation radicals and the equilibrium quotients referred to eq 1.

Kinetic Data on PTZ/PTZ$^{+}\cdot$ Reactions. The equilibrium quotient of equilibrium 10a can be estimated from the

$$(\mathrm{IV})^{+}\cdot + \mathrm{III} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{IV} + (\mathrm{III})^{+}\cdot \qquad (10a)$$

equilibrium data obtained for each derivative with $Fe(CN)_6^{3-}$ to be 1.5 at 25 °C and $[HClO_4]$ = 1.00 M. The rate constants were determined by varying the reactant concentrations between 4×10^{-5} and 1×10^{-4} M. The value obtained was averaged on several measurements: $k_f = (3.5 \pm 0.5) \times 10^8$ M^{-1} s^{-1}. The rate constants were also evaluated at 12 °C by adopting the equilibrium constant extrapolated at this tem-

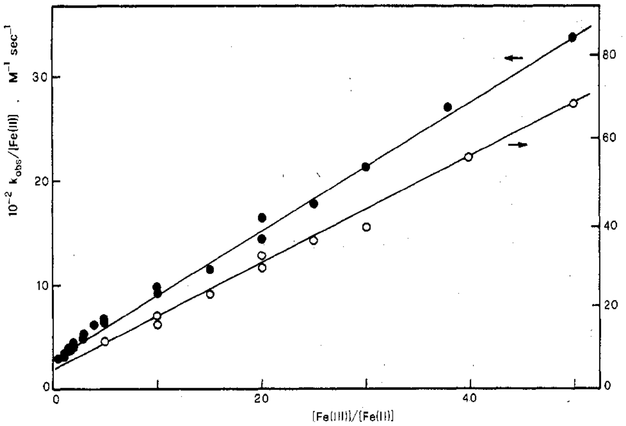


Figure 1. Plot of $k_{obsd}/[Fe(II)]$ as a function of $[Fe(III)]/[Fe(II)]$ for the reaction of V with Fe(III) at $[HClO_4]$ = 1.00 M: (●) 25.0 °C, (○) 37.0 °C.

Table II. Pseudo-First-Order Rate Constants (s^{-1}) for the Oxidation of III by Fe(III)[a]

	10^4[Fe(II)], M			
10^4[Fe(III)], M	2.0	4.0	20	40
2.0	0.032	0.046		
4.0	0.048	0.078	0.16	0.28
6.0	0.080	0.093	0.18	0.30
8.0	0.102	0.115	0.19_5	0.32
10.0	0.122	0.126	0.21_5	0.33_5
20	0.22	0.25		
40	0.43	0.41		
60	0.61	0.56		
80	0.85	0.88		
100	1.06	1.08		

[a] [III] = 2×10^{-5} M, $[HClO_4]$ = 1.00 M, μ = 1.0 M, 25.0 °C.

perature: $k_f = (3.2 \pm 0.7) \times 10^8\ M^{-1}\ s^{-1}$.

For reaction 10b at 25 °C, $k_f = (2.7 \pm 0.4) \times 10^8$ and, at

$$(VII)^{+\cdot} + VIII \underset{k_r}{\overset{k_f}{\rightleftharpoons}} VII + (VIII)^{+\cdot} \qquad (10b)$$

12 °C, $k_f = (2.6 \pm 0.5) \times 10^8\ M^{-1}\ s^{-1}$ ($[HClO_4]$ = 1.00 M).

Kinetic Data on PTZ/Fe(III) Reactions. The kinetics of the reactions of PTZ with Fe(III), depicted in eq 1, have been found to follow rate expressions 2 and 3. Figure 1 shows a plot according to eq 3, from which the values of k_1 and k_{-1} are derived. Table II collects the data referred to compound III for exemplification and Table III the specific rate constants together with activation parameters for the reactions of PTZ with Fe(III). The values of k_1/k_{-1} can be compared with the quotients derived spectrophotometrically showing, in most cases, a good agreement. Values of k_1 and k_{-1} were practically independent of hydrogen ion concentration in the range $0.05 \leq [HClO_4] \leq 1.00$ M. Small variations were attributed to medium effects.

Kinetic Data on PTZ/Fe(CN)$_6^{3-}$ Reactions. The second-order expressions given by eq 6 and 7 for stopped-flow runs as well as by eq 8 and 9 for *T*-jump experiments were in agreement with the reactions described by eq 4, as shown by the consistency of the rates obtained with different techniques and at different concentrations. The kinetic data concerning V are listed in Table IV. The rate constants k and k' (determined at 25 °C and $[HClO_4]$ = 1.00 M) are collected in Table V, together with the values of the equilibrium quotients spectrophotometrically determined.

Discussion

The Marcus Theory. The well-known Marcus theory[3] for adiabatic outer-sphere electron transfers relates the free energy of activation, ΔG^*_{12}, to the free energy of reaction, $\Delta G°_{12}$, through a reorganizational parameter, λ_{12}, which in turn is related to the free energy of activation for the self-exchange reactions, according to eq 11–14, where Z is the collision

$$k = Z \exp(-\Delta G^*_{12}/RT) \qquad (11)$$

$$\Delta G^*_{12} = w_{12} + \lambda_{12}(1 + \Delta G°_{12}'/\lambda_{12})^2/4 \qquad (12)$$

$$\lambda_{12} = 2(\Delta G^*_{11} - w_{11} + \Delta G^*_{22} - w_{22}) = 2(\Delta G^{**}_{11} + \Delta G^{**}_{22}) \qquad (13)$$

$$\Delta G°_{12}' = \Delta G°_{12} + w_{21} - w_{12} \qquad (14)$$

frequency in solution, assumed to be $10^{11}\ M^{-1}\ s^{-1}$, w_{12} and w_{21} are the work terms required to bring the reactants and products together, respectively, and w_{11} and w_{22} the work terms related to the self-exchange rates. Expressions for ΔH^*_{12} and ΔS^*_{12} may also be obtained[10,11] (see eq 15 and 16, where $\alpha = \Delta G°_{12}/4(\Delta G^*_{11} + \Delta G^*_{22})$).

$$\Delta H^*_{12} = \left(\frac{\Delta H^*_{11}}{2} + \frac{\Delta H^*_{22}}{2}\right)(1 - 4\alpha^2) + \frac{\Delta H°_{12}}{2}(1 - 2\alpha) \qquad (15)$$

$$\Delta S^*_{12} = \left(\frac{\Delta S^*_{11}}{2} + \frac{\Delta S^*_{22}}{2}\right)(1 - 4\alpha^2) + \frac{\Delta S°_{12}}{2}(1 - 2\alpha) \qquad (16)$$

From eq 12–14, under the assumption that the work terms for self-exchange reactions and cross-reactions tend to cancel, the Marcus cross-relationship takes the form of eq 17 where

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \qquad (17)$$

the following relationship holds:

$$\log f_{12} = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2) \qquad (18)$$

When $f_{12} \simeq 1$, eq 17 simplifies to give eq 19.

$$k_{12} \simeq (k_{11}k_{22}K_{12})^{1/2} \qquad (19)$$

The Marcus theory has found a wide applicability in the electron transfers involving metal ion complexes;[2,12] when ions of like charge are involved, eq 17–19 gave satisfactory results, but for ions of opposite charge, eq 12–14, which take into account the electrostatic effects, are more satisfactory.

The same treatment has been extended to excited-state reactions of complex ions.[13]

Table III. Specific Rate Constants and Activation Parameters for PTZ Oxidation by Fe(III)

compd	k_1[a]	$\Delta H^{\ddagger}_1$[b]	$\Delta S^{\ddagger}_1$[c]	k_{-1}[a]	$\Delta H^{\ddagger}_{-1}$[b]	$\Delta S^{\ddagger}_{-1}$[c]	k_1/k_{-1}
I	5.7×10^2	10.9	−10	12	7.3	−29	48
II	1.4×10^2	8.5	−20	80	5.8	−30	1.7_5
III	1.1×10^2	8.6	−20	65	4.4	−36	1.7
IV	1.3×10^2	9.9	−16	1.0×10^2	5.7	−30	1.3
V	60	11.9	−11	2.8×10^2	4.9	−31	0.21
VI	14	11.1	−16	4.7×10^2	5.1	−29	3.0×10^{-2}
VII	8.3	12.0	−14	1.1×10^3	6.0	−25	7.5×10^{-3}
VIII	7.6	11.9	−14	1.7×10^3	5.0	−27	4.5×10^{-3}

[a] In $M^{-1}\ s^{-1}$, $[HClO_4]$ = 1.00 M, μ = 1.0 M, 25.0 °C; the error is within ±10%. [b] In kcal mol^{-1}; the error is ±1.3 kcal mol^{-1}. [c] In cal $deg^{-1}\ mol^{-1}$; the error is ±4 cal $deg^{-1}\ mol^{-1}$.

Table IV. Kinetics of Equilibration of the Reaction of V with $Fe(CN)_6{}^{3-}$ [a]

$10^4[V]$, M	$10^4[Fe(CN)_6{}^{3-}]$, M	$10^3\tau$, s	$10^{-5}k$, M^{-1} s^{-1}
1.0	1.0	2.9	6.0
2.0	1.0	2.1	5.8
1.0	3.0	1.7	5.8
1.0	6.0	1.0_5	6.3
1.0	10.0	0.90	5.4

[a] $[HClO_4] = 1.00$ M, $\mu = 1.0$ M, 25.0 °C.

Table V. Specific Rate Constants and Equilibrium Quotients for the Oxidation of PTZ with $Fe(CN)_6{}^{3-}$ [a]

compd	$10^{-6}k$,[b] M^{-1} s^{-1}	Q[c]
II	2.1 ± 0.3	1.1 ± 0.2
III	1.6 ± 0.2	1.9 ± 0.2
IV	1.5 ± 0.3	1.3 ± 0.2
V	0.59 ± 0.06	0.12 ± 0.02

[a] $[HClO_4] = 1.00$ M, $\mu = 1.0$ M, 25,0 °C; the averages include both *T*-jump and stopped-flow measurements. [b] The errors represent the standard deviations. [c] Spectrophotometrically evaluated.

A wide applicability of the Marcus theory has been found also in electron transfer between organic molecules,[1d,e,14] as well as in organic biochemistry.[15] In recent papers we have attempted to apply the Marcus theory to the electron transfers between metal complexes and benzenediols or ascorbic acid.[16]

A recent work of Sutin et al. reviewed the Marcus theory application to the $Fe^{3+/2+}$ couple.[17] It is interesting to compare our present data in the light of their conclusions.

Self-Exchange Rate of PTZ. Since the free energy involved in the reaction of eq 10a is near zero, the rate constant of this system can be reasonably taken as the rate of self-exchange of $PTZ^{+}\cdot/PTZ$ systems. Then, if $\Delta G^{\circ}{}_{12}{}' \simeq 0$,

$$\Delta G^{*}{}_{11} = w_{11} + \lambda_{11}/4 \qquad (20)$$

The term w_{11} refers to the reaction between positively charged species,[5] but taking into account the present ionic strength and the difficulty in the evaluation of such terms in nonspherical reagents[18] with localized charges, we assume that this term is negligible. Thus $\Delta G^{**}{}_{11} = 3.3$ kcal mol^{-1}. Also the data for eq 10b are in agreement with this value.

The "intrinsic barrier" in these systems is very small because of the similarity of the molecular geometries of reduced and oxidized species. Values of rate constants for similar electron exchanges fall in the same order of magnitude; the literature data show that, for example, 1.3×10^8 M^{-1} s^{-1} has been found for triphenylmethyl cation radical exchange reaction in an acetic–trifluoroacetic acid mixture,[19] 2.2×10^9 M^{-1} s^{-1} for *N*-methylphenothiazine, and 3.6×10^8 M^{-1} s^{-1} for phenoxanthiin in acetonitrile.[20]

The large uncertainty which affects the rate constants of these electron transfers makes troublesome the estimation of the activation parameters. It is evident, however, that a small $\Delta H^{\ddagger}$ pertains to these systems. Values of activation energy in the range 1.4–1.7 kcal mol^{-1} have been found for the electron transfer between the parent phenothiazine and its cation radical, although in nonaqueous solvents.[21]

Reactions of PTZ with $Fe(CN)_6{}^{3-}$. The rates of reactions between PTZ and $Fe(CN)_6{}^{3-}$ can be estimated, according to the Marcus theory, using eq 11–14, better than eq 17–18, owing to the noncancellation of the work terms when differently charged species are involved.

However, some difficulties arise from the calculation of the work terms in self-exchange reactions, and different approaches have been reported.[22] We have recently investigated a series of benzenediol reactions with different oxidants[16,23] and, since benzenediols are uncharged molecules (then $w_{12} \simeq 0$), a "scale" of ΔG^{**} for the oxidants has been proposed (taking into account that $\Delta\Delta G^{**} = 1/2\Delta\lambda_{12}$ and assuming $IrCl_6{}^{2-/3-}$ as a reference system); satisfactory results have been obtained for the $Fe(CN)_6{}^{4-}/Mo(CN)_8{}^{3-}$ reaction system and other systems quoted in the literature.[23]

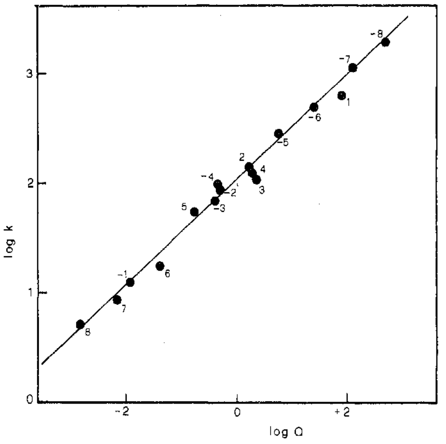


Figure 2. Plot of log *k* (specific constants of direct and reverse reactions in eq 1) as a function of log *Q* (spectrophotometric equilibrium quotients) for reactions between PTZ and Fe(III). The minus sign refers to the back-reactions.

With this treatment, $\Delta G^{**} = 8.5$ kcal mol^{-1} for $Fe(CN)_6{}^{3-/4-}$ has been suggested,[24] and then $\lambda_{12} = 23.6$ kcal mol^{-1}. In reaction 4, $w_{12} \simeq w_{21}$, and then $\Delta G^{\circ}{}_{12}{}' \simeq \Delta G^{\circ}{}_{12}$, while the term w_{12} can hardly be calculated (see above). If we tentatively neglect w_{12} (taking into account also the present high ionic strength), the values calculated are 2–3 times higher than the experimental ones, a discrepancy which is considered to be largely tolerated. Obviously, the introduction of values of w_{12} (as well as of lower values for ΔG for $Fe(CN)_6{}^{3-/4-}$) would lead to a higher discrepancy between calculated and experimental rates.

Reactions of PTZ with Fe(III). Tables I and III collect the equilibrium quotients determined both spectrophotometrically and kinetically. From these data, which are in satisfactory agreement, the reduction potentials of $PTZ^{+}\cdot/PTZ$ couples can be derived. These values are comparable with the $E_{1/2}$ determined in aqueous sulfuric acid.[25]

Another interesting feature is the practical invariance of the reaction rates in the acidity range $0.050 \leq [HClO_4] \leq 1.00$ M. Although in other oxidations the reacting species has been found to be mainly $FeOH^{2+}$,[26] in the present outer-sphere electron transfer Fe^{3+} is the main reactive species (being Fe(III) at $[HClO_4] = 0.050$ M present in ca. 3% as $FeOH^{2+}$; the specific rate for electron transfer to $FeOH^{2+}$ is not higher than the specific rate for Fe^{3+}). Similar behavior was previously noted in ferrocene oxidation by Fe(III) in propanol–water solution.[27]

The comparison between calculated and experimental rate constants for $Fe^{3+/2+}$ reactions, with the aid of the Marcus equations, is known to give calculated rate constants larger than the experimental ones of 1–3 orders of magnitude,[17] if the value $k_{22} = 4.0$ M^{-1} s^{-1} is adopted.[28]

In the present case the dependence of the logarithm of the rate constants as a function of the logarithm of equilibrium quotients is in perfect agreement with Marcus' prediction, being the slope 0.50 (see Figure 2). However, the calculated rate constants (by adopting eq 19, since the work terms probably compensated and $f \simeq 1$ in the present case) are about 300–500 times larger than the experimental one, as can be seen in Figure 3. The discrepancy is of the same order of magnitude observed for reactions of Fe^{2+} with $ML_3{}^{3+}$ complexes (where M = Os, Ru, and Fe and L is a phenanthroline-like ligand).[13,29]

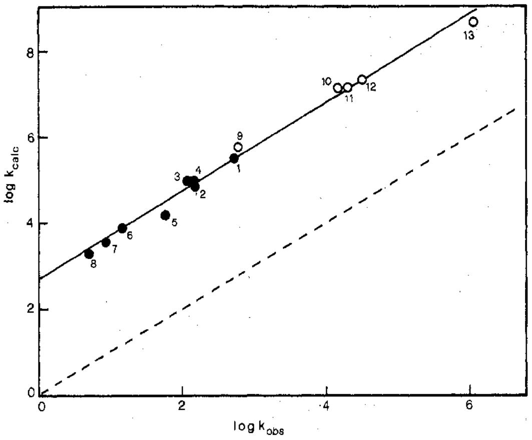


Figure 3. The correlation between the observed rate constants and the ones calculated according to the Marcus theory. Closed circles represent the PTZ data (calculated with λ_{12} = 35 kcal mol^{-1}) and the open circles refer to FeL_3^{3+}–Fe^{2+} systems[29] (calculated with λ_{12} = 33 kcal mol^{-1}). The other compounds reported are **9**, tris(4,4′-dimethyl-2,2′-bipyridyl)iron(III) (E^0 = 0.84 V), **10**, tris(2,2′-bipyridyl)iron(III) (E^0 = 1.02 V) (E^0 data for **9** and **10** are quoted in E. Mentasti and E. Pelizzetti, *Transition Met. Chem.*, **1**, 281 (1976)), **11**, tris(5-methyl-1,10-phenanthroline)iron(III) (E^0 = 1.02 V),[29] **12**, tris(1,10-phenanthroline)iron(III) (E^0 = 1.06 V),[29] and **13**, tris(5-nitro-1,10-phenanthroline)iron(III) (E^0 = 1.25 V).[29]

Table VI. Thermodynamic and Activation Parameters for PTZ/Fe(III) Reactions at 25.0 °C[a]

compd	$\Delta H°_{12}$[b]	$\Delta S°_{12}$[c]	$\Delta H^{\ddagger}_{12}$ (exp)[b]	$\Delta H^{\ddagger}_{12}$ (calcd)[b]	$\Delta S^{\ddagger}_{12}$ (exp)[c]	$\Delta S^{\ddagger}_{12}$ (calcd)
I	3.6	+19	10.9	6.7	−10	−11
II	2.7	+10	8.5	6.3	−20	−16
III	4.2	+16	8.6	7.1	−20	−13
IV	4.2	+14	9.9	7.1	−16	−14
V	6.0	+20	11.9	8.0	−11	−12
VI	6.0	+13	11.1	8.2	−16	−14
VII	6.0	+11	12.0	8.2	−14	−15
VIII	6.9	+13	11.9	8.8	−14	−14

[a] For Fe(III)/Fe(II), the values of $\Delta H^{\ddagger}$ = 9.3 kcal mol^{-1} and ΔS $\Delta S^{\ddagger}$ = −25 cal deg^{-1} mol^{-1} were adopted.[28] [b] In kcal mol^{-1}. [c] In cal deg^{-1} mol^{-1}.

It is also possible for the present systems to compare the experimental activation parameters with those predicted by eq 15 and 16. The data are collected in Table VI and have been calculated with ΔH^* = 1 kcal mol^{-1} and ΔS^* = −8 cal mol^{-1} K^{-1} for $PTZ^{+}\cdot$/PTZ self-exchange (see above). There is a good consistency for the values of $\Delta S^{\ddagger}_{12}$, while a discrepancy ranging between 2 and 4 kcal mol^{-1} is observed for $\Delta H^{\ddagger}_{12}$. Also this behavior resembles that observed for reactions of Fe^{2+} with $Ru(bpy)_3^{3+}$ and $Fe(bpy)_3^{3+}$.[10,17] Some possible explanations of this deviation have been attempted by several authors[27,30] and were recently discussed by Sutin et al.[17] Another attempt of testing eq 15 was previously carried out by Meyer et al. on $Fe^{3+/2+}$ reactions with mixed amine–pyridine and poly(pyridine) complexes of Ru.[31]

It seems interesting that also the present phenothiazine derivatives resemble in behavior the ML_3^{3+} complexes, whose self-electron-exchange parameter is very low (ΔG^{**} = 2.3 kcal mol^{-1}).[32] Probably also in the present case the cross-electron transfer cannot proceed with a pathway common to the exchange processes of the two reactants, and this can be reflected in the nonadiabaticity of the reaction (then appropriate factors should be included in eq 17–18).[10,17,33]

Conclusions

The applicability of the Marcus theory to the reactions of *N*-alkylphenothiazines and $Fe(CN)_6^{3-}$ has been proven to give satisfactory results. By working with aquoiron(III) as oxidant, we have assessed a correct dependence of rate constants on equilibrium quotients; the calculated rate constants are, however, about 300–500 times higher than the experimental ones. This behavior resembles the previously observed kinetic data on ML_3^{3+}/Fe^{2+} reactions.

The *N*-alkylphenothiazine cation radicals are, as reported above, unusually long-lived: this enables the use of the PTZ–metal ion system in photogalvanic cell studies.

The absorption maxima of PTZ and $PTZ^{+}\cdot$ are largely affected by the substituents on the aromatic ring[4] as well as the reduction potential of $PTZ^{+}\cdot$/PTZ couples and even by the length of side chain bonded to the N atom;[4] then, there is a large possibility to select a compound with its spectrum shifted toward the solar energy radiation and with the proper reduction potential.

An extension of this study, investigation of a N derivative with a long hydrophobic chain, is now in progress. These compounds can give rise to formation of aggregates, thus changing significantly their reactivity toward the oxidizing agents.

Registry No. I, 3926-64-5; II, 84-97-9; III, 61-01-8; IV, 58-40-2; V, 50-53-3; VI, 60-91-3; VII, 60-87-7; VIII, 303-14-0; $(I)^{+}\cdot$, 68457-22-7; $(II)^{+}\cdot$, 51982-38-8; $(III)^{+}\cdot$, 38878-35-2; $(IV)^{+}\cdot$, 34468-20-7; $(V)^{+}\cdot$, 34468-21-8; $(VI)^{+}\cdot$, 38878-37-4; $(VII)^{+}\cdot$, 38878-40-9; $(VIII)^{+}\cdot$, 68457-23-8; $Fe(H_2O)_6^{3+}$, 15377-81-8; $Fe(CN)_6^{3-}$, 13408-62-3.

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Flash Photolysis Studies of Ruthenium(II)–Ammine Complexes. 1. Transient Intermediates in the Photolysis of $Ru(NH_3)_5py\text{-}X^{2+}$ and Their Relationship to Photosubstitution Pathways

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Conventional flash photolysis of the ruthenium(II) complexes $Ru(NH_3)_5py\text{-}X^{2+}$ (where py-X is a substituted pyridine or related aromatic heterocycle) in aqueous solution leads to the formation of relatively long-lived transients for those species also showing net photoaquation of py-X. Since only those species which undergo significant photoaquation ($\phi_L > 0.01$ mol/einstein) display measurable transient formation and since these complexes are those previously concluded to have a ligand field (LF) state as the lowest energy excited state, it is concluded that this LF state is the immediate precursor of this transient. In this context, it is proposed that the transient is an intermediate (not an excited state) with the pyridine ring π bonded to the Ru(II) species $Ru(NH_3)_5^{2+}$ in a manner making the nitrogen lone pair free to be reversibly protonated. Rates of relaxation of the intermediate to starting material and to products are markedly pH dependent, indicating that the protonated intermediate is particularly long-lived but decays largely to form aquation products. A reaction scheme for formation and decay of these transients is proposed, and comparisons are made with relaxation rates and with quantum yields for net photoaquation.

Introduction

The quantitative photochemistry of ruthenium(II)–amine complexes in aqueous solution is a continuing research interest of these laboratories.[2–13] Although the majority of these studies have involved continuous photolysis techniques, preliminary flash photolysis studies have indicated[8,9,14] a rich chemistry of species produced transiently in these systems. In general, the phenomena resulting from flash photolysis can be separated into two categories. The first involves intermediates apparently related to the photosubstitution reactions of the hexacoordinate complexes, while the second involves intermediates derived from photoredox reactions in the presence of oxidants added to the reaction solutions. The latter reaction types have received considerable attention with regard to the excited-state chemistry of tris(bipyridyl)ruthenium(II) and analogues,[15] encouraged in part by the proposition that such species are possible mediators in the conversion of solar energy to chemical potential energy.[16] Clearly, these excited-state reaction types are interrelated, at least in the context that deactivation by substitution decreases the role of redox pathways and leads to decomposition. For example, even the relatively stable $Ru(bpy)_3^{2+}$ ion displays some photolability[17] which may diminish its usefulness in photocatalytic applications where long-term stability is desired.

This paper is concerned with the kinetic behavior of intermediates generated "unimolecularly" in the flash photolysis of the Ru(II) complexes $Ru(NH_3)_5py\text{-}X^{2+}$ in aqueous solution (where py-X is a substituted pyridine or a related aromatic nitrogen heterocycle). These species display intense metal-to-ligand charge-transfer (MLCT) absorption bands in their visible spectra, but the only reaction resulting from visible photolysis is ligand photoaquation. Understanding the behavior of the transient intermediates seen under flash irradiation is essential to the explanations of two features of the photoreaction behavior: first, the marked pH dependence on the pyridine aquation quantum yields for certain complexes in acidic solution,[4] and second, the discovery that the photoreactivities can be "tuned" by the choice of the substituent X.[10] The kinetic behavior of intermediates generated by flash photolysis of $Ru(NH_3)_5py\text{-}X^{2+}$ in the presence of added oxidants will be described separately.[11]

Experimental Section

Materials. The recrystallized $[Ru(NH_3)_5py\text{-}X](BF_4)$ salts were prepared from $[Ru(NH_3)_5Cl]Cl_2$ according to published procedures.[10,18] Aqueous solutions for photolysis were prepared from redistilled water with reagent sodium chloride used to maintain ionic strength. Solutions were deaerated with argon which had been passed through a chromous bubbler. Reinecke's salt used in actinometry was purchased from Eastman as $(NH_4)[Cr(NH_3)_2(SCN)_4]$ and converted to the potassium salt by recrystallizing from KNO_3 solution.

Flash Photolysis Procedures. Flash photolyses were carried out on a kinetic flash photolysis apparatus based on a Xenon Corp. Model A micropulser and a Model C trigger system. Filtered flash pulses of various energies (100–500 J) were used. Absorbance vs. time data were obtained using a high-stability analyzing light beam (from a 75-W Xenon Corp. source powered by a PEK Model 401 power supply) passed through appropriate light baffles, filters, and monochromators. The data were collected with an EMI 6256B photomultiplier tube and recorded with either a Tektronix Model 564 storage oscilloscope or a Biomation 805 transient waveform recorder coupled with a Hewlett-Packard 7035B XY recorder. Instrumental dead time was approximately 35 μs under typical conditions. Sample cells were concentric jacketed quartz cells 1 cm in diameter and either 12 or 20 cm in length. Cutoff filter solutions were placed in an outer jacket for wavelength selection of flash irradiation. All ruthenium(II) substrate solutions (10^{-5} M in substrate, 0.2 M NaCl/HCl) were

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