Homogeneous Oxidation of Trialkylamines by Metal Complexes and Its Impact on Electrogenerated Chemiluminescence in the Trialkylamine/Ru(bpy)$_3$$^{2+}$ System

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The oxidation of triethylamine and tripropylamine was investigated in aqueous solution by measurement of the direct oxidation at microelectrodes or by redox catalysis at ultramicroelectrodes. An effect of pH on the homogeneous or direct oxidation was observed. In the presence of an electrogenerated oxidant such as Ru(bpy)$_3$$^{3+}$, the oxidation of the amines could be achieved homogeneously. This was studied with metal complexes of different $E°$ [Ru(bpy)$_3$$^{3+}$, Fe(bpy)$_3$$^{3+}$, Mo(CN)$_8$$^{3-}$, Ru(CN)$_6$$^{3-}$]. When Ru(bpy)$_3$$^{3+}$ was the oxidant, the production of electrogenerated chemiluminescence (ECL) occurred. This homogeneous ECL generation was studied and the difference in ECL intensity was related to the ease of oxidation of the amine and of its intermediate radical.
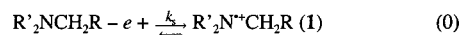
Introduction

Extensive studies on alkylamine oxidation have been published in the early 1970s.[1−5] These comprise studies of different approaches to the characterization of this oxidation, e.g., by preparative electrolysis,[2,5b] or at an analytical level, by direct cyclic voltammetric determination,[4a,5a] by homogeneous oxidation with various inorganic oxidants,[3,4] or even by enzymatic oxidants.[6] Attempts were made to extract from these data structure−activity relations to correlate the rates to available thermodynamic entities, such as the pK_a and ionization potential (IP).

These investigations tend to support a mechanism involving electron transfers and deprotonation steps according to Scheme 1 rather than hydrogen atom abstraction when oxidizing trialkylamine. In Scheme 1, **1** is the radical cation of the trialkyamine (**1P** for R = Et and R′ = Pr; **1E** for R = Me and R′ = Et) and **2** is the free radical that results from deprotonation of **1**. However, on the basis of the reported weak acidity of the trimethylamine radical anion,[7] a hydrogen atom abstraction pathway is also possible, e.g., when a geometric restriction as in the case of diazabicycloalkanes[8] is important.[9]
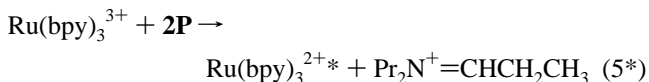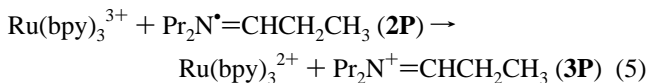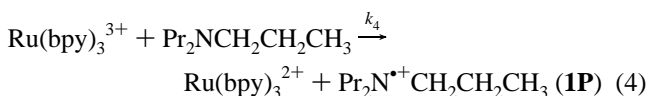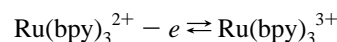
Mechanistic investigations of the trialkyamine oxidation are important because these amines are useful coreactants in electrogenerated chemiluminescence[10−13] (ECL) or chemiluminescence.[14,15] Interest in amines as coreactants date to early work in this field.[16] Currently among many coreactants used in ECL, tripropylamine (TPrA) appears to produce the highest light levels. The difference in ECL efficiency for different R$_3$N has been interpreted in terms of structure−activity relationships by differences in the coreactant IP.[15]

To explain ECL generation from the oxidation of TPrA in the presence of Ru(bpy)$_3$$^{2+}$ and such structure−activity relationships, a mechanism, based on the prevailing amine oxidation mechanism presented earlier, that takes into account the possible

SCHEME 1

$$R'_2NCH_2R - e \underset{k_{-}}{\overset{k_{+}}{\rightleftharpoons}} R'_2N^{•+}CH_2R \ (\mathbf{1}) \qquad (0)$$

$$R'_2N^{•+}CH_2R \xrightarrow{k_1} H^+ + R'_2N\text{–}C^•HR \ (\mathbf{2}) \leftrightarrow R'_2N^+\!\!=\!\!CHR \qquad (1)$$

$$\mathbf{2} - e \rightarrow R'_2N^+\!\!=\!\!CHR \qquad (2)$$

$$R'_2N^+\!\!=\!\!CHR + H_2O \rightarrow R'_2NH + RCHO + H^+ \qquad (3)$$

homogeneous electron transfers between ruthenium and the TPrA species was proposed:

$$Ru(bpy)_3^{2+} - e \rightleftharpoons Ru(bpy)_3^{3+}$$

$$Ru(bpy)_3^{3+} + Pr_2NCH_2CH_2CH_3 \xrightarrow{k_4}$$
$$Ru(bpy)_3^{2+} + Pr_2N^{•+}CH_2CH_2CH_3 \ (\mathbf{1P}) \ (4)$$

$$Ru(bpy)_3^{3+} + Pr_2N^{•}\!\!=\!\!CHCH_2CH_3 \ (\mathbf{2P}) \rightarrow$$
$$Ru(bpy)_3^{2+} + Pr_2N^+\!\!=\!\!CHCH_2CH_3 \ (\mathbf{3P}) \ (5)$$

$$Ru(bpy)_3^{3+} + \mathbf{2P} \rightarrow$$
$$Ru(bpy)_3^{2+}\!* + Pr_2N^+\!\!=\!\!CHCH_2CH_3 \ (5^*)$$

The possible structure−activity relationships seem to indicate that excited-state generation is governed by the first homogeneous electron transfer (eq 4). This type of pathway was recently confirmed and rationalized for the Ru(bpy)$_3$$^{2+}$/oxalate system.[17] In this paper, we demonstrate how the ECL alkylamine coreactant systems can be related to the dynamics of the different homogeneous electron-transfer steps (eqs 4, 5, and 5*). The purpose of the present work is to complement this study of ECL in coreactant systems for the trialkylamine family to improve our understanding of ECL generation mechanisms and to define

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possible more efficient ECL systems. We first investigated the direct oxidation of TPrA and triethylamine (TEA) in aqueous solution at an electrode. The influence of the pH on the oxidation was studied. Then we studied oxidation mediated by electro-generated oxidants and ECL generation when the oxidation occurred in the presence of Ru(bpy)$_3^{2+}$, where ECL occurs according to a catalytic mechanism.

Experimental Section

Chemicals. TPrA, TEA, and Ru(bpy)$_3$Cl$_2$ from Aldrich (Milwaukee, WI) and Na$_2$C$_2$O$_4$ from J. T. Baker (Phillipsburg, NJ) were used as received. Fe(bpy)$_3$(ClO$_4$)$_2$ was prepared as reported previously.[17]

Electrodes and Electrochemical Cells. A three-electrode configuration was employed in all experiments with a 0.2 mm Pt wire as the counter electrode, Ag/AgCl as the reference electrode, and a 2 mm diameter Pt or glassy carbon electrode or a 50 mm diameter Pt microelectrode as the working electrode. The microelectrode was prepared as previously described.[18]

Apparatus and Procedures. Cyclic voltammograms were recorded using a Bioanalytical Systems (West Lafayette, IN) Model-100A electrochemical analyzer. Cyclic voltammograms with simultaneous photon detection were recorded using a home-built potentiostat in conjunction with a photomultiplier tube (PMT, Hamamatsu R4220p or R928) installed under the electrochemical cell and connected to an operational amplifier-based current-to-voltage converter and voltage amplifier.[12c]

Results and Discussion

Direct Oxidation of TPrA and TEA. *Alkaline Medium.* To evaluate the kinetic parameters of the TPrA and TEA oxidations, we investigated their direct oxidation at a glassy carbon electrode. Savéant and co-workers have shown that it is possible to extract kinetic and thermodynamic information from the variation of the voltammetric wave characteristics with v, the potential scan rate.[19] Figure 1 shows cyclic voltammograms of 2 mM TPrA and TEA at pH 12 in a 0.1 M phosphate medium. The oxidations are characterized by an irreversible electron transfer at the first peak. Compared to Ru(bpy)$_3^{2+}$ oxidation at pH 7, the height of TEA or TPrA oxidation peaks correspond to an irreversible transfer of two electrons, as postulated in Scheme 1, if one assumes similar diffusion coefficients of 5×10^{-6} cm^2 s^{-1}. TPrA is easier to oxidize than TEA by about 50 mV at 0.1 V/s, in good agreement with previous studies.[4a] The first oxidation peak is then followed by a second irreversible oxidation attributed to the corresponding dialkylamine oxidation.[4a,5a]

For both amines, the peak potential, E_p, varied linearly with the logarithm of the scan rate with a slope of 42 mV and 65 mV per decade for TPrA and TEA, respectively. An apparent symmetry factor, α_{ap}, is deduced from the slope [$\alpha_{ap} = (2F/RT)\ \partial E_p/\partial\log v = 0.7$ for TPrA and 0.48 for TEA (where $F/RT = 38.92$ V^{-1} at 25 °C)] from these variations. Different conclusions can be drawn from these values. Since in both cases α_{ap} is greater or not too different than 0.5, the oxidation process occurs by an ECE mechanism, as was postulated in earlier studies,[1] rather than by a dissociative mechanism (for which an $\alpha_{ap} < 0.4$ would be expected[20]). The variation of the peak potential with the scan rate indicates that the process at a glassy carbon electrode is kinetically controlled by the competition between the first electron transfer (eq 0) and the chemical step (deprotonation eq 1). For pure kinetic control by this chemical step, the peak potential, E_p, varies with the scan rate, v, the chemical reaction rate constant, k_1, and the standard potential
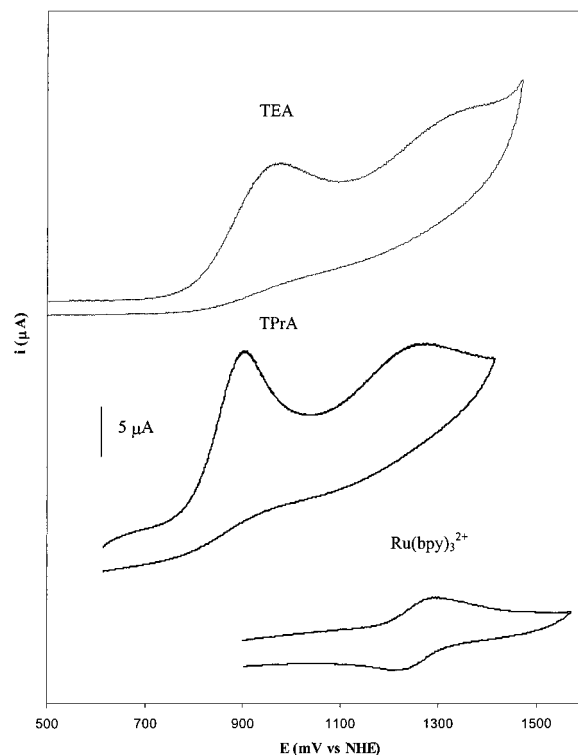

Figure 1. Cyclic voltammograms of 2 mM TEA and 2.1 mM TPrA in 0.1 M phosphate buffer (pH = 12.3) and 0.5 mM Ru(bpy)$_3^{2+}$ in 0.1 M phosphate buffer (pH = 7), at a glassy carbon electrode, 1 mm radius, scan rate $v = 0.1$ V/s.

for an oxidation reaction, $E°$, accordingly to

$$E_p = E° - (RT/2F)\ \ln(k_1\ RT/Fv) + 0.78(RT/F) \qquad (6)$$

From eq 6, pure kinetic control by the follow-up reaction implies an α_{ap} of 1. The lower values found here indicate intervention of an apparently slow first heterogeneous electron transfer (characterized by k_s, reaction 0) in the overall chemical kinetic control.[19] The competition between k_s and k_1 is depicted by a dimensionless parameter $p = [2k_1(RT/Fv)]^{1/2}k_s^2/D$, where D is the diffusion coefficient. Savéant treated the system mathematically and developed a theoretical plot of the dimensionless peak potential, $\xi'_p = (F/RT)(E_p - E°)$, as a function of p, describing the competition between these steps. The comparison of the experimental and theoretical curves depicting the variation of the peak potential and peak width, $E_p - E_{p/2}$, with v,[19] allows the extraction of two equations between the unknown $E°$, k_s, and k_1 for TPrA (Figure 2).

$$E^0_{TPrA} - (RT/2F)\ \ln k_{1,TPrA} = 0.86\ V$$

$$k_{1,TPrA}^{1/2}D^{-1}k_{s,TPrA}^2 = 2.7\ cm^{-1}\ s^{-1/2}$$

On the other hand, TEA oxidation is kinetically governed by a slow electron transfer ($\alpha \approx 0.5$) and a unique equation relating $E°$ and k_s can be obtained:

$$E^0_{TEA} - (2RT/F)\ \ln k_{s,TEA} = 1.25\ V$$

The coupling of the kinetic and thermodynamic data precludes any direct determination of the parameters ($E°$, k_s, k_1). Typically it is possible to obtain thermodynamic information from redox catalysis experiments. Before discussing these, however, we describe the amine oxidation behavior at lower pH.
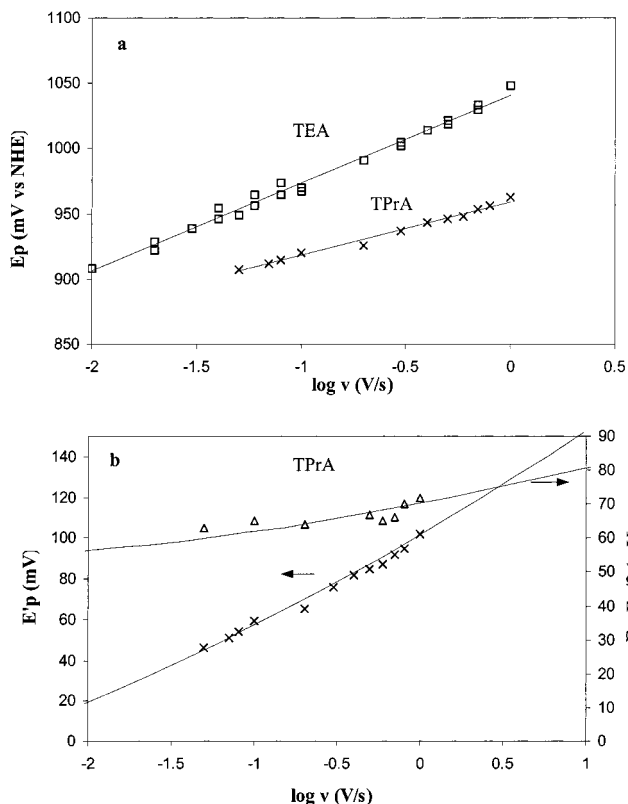
Figure 2. (a) Variation of the peak potential, E_p, with the logarithm of the scan rate, v, at a 2 mm diameter glassy carbon electrode: (solid line) TEA, (×) TPrA, pH = 11.5; 0.1 M phosphate buffer. (b) Variation of the normalized peak potential, $E_p' = E_p + (RT/2F)\ln v + C$ (×), and peak-width, $E_p - E_{p/2}$ ($\triangle$), for TPrA oxidation according to Saveant's treatment (ref 19a), (×, $\triangle$) experiment, (solid line) theory.
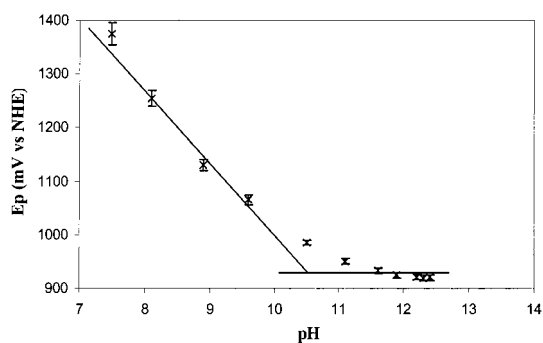

Figure 3. Variation of TPrA oxidation peak potential with pH at a 2 mm diameter glassy carbon electrode in 0.1 M phosphate buffer; $v = 0.1$ V/s.

Variation with pH. As the pH decreases, protonation of R_3N, the electroactive form, becomes important. Under these conditions the TEA or TPrA oxidation peak observed by cyclic voltammetry at a glassy carbon electrode decreases in intensity and shifts toward more positive potentials. TPrA oxidation is still observed at pH 8 for a 10 mM solution, but a peak for TEA is hardly detected at a glassy carbon electrode. The effect of pH tends to broaden the oxidation wave of the amine and this makes precise determination of the peak potential difficult. The variation of the TPrA oxidation peak potential with pH, for a range of 7.5 to 12, is presented in Figure 3. This can be interpreted as the oxidation of free TPrA (no variation from pH 11 to 12.2) followed by an increase of E_p with pH (approximately 110 mV per decade of pH). Note that in a 0.1 M TPrA solution of pH 7.5 it is still possible to observe direct TPrA oxidation at a glassy carbon electrode; so at the potential

where $Ru(bpy)_3^{2+}$ is oxidized, the current due to direct TPrA oxidation is significant.

Homogeneous Oxidation of TEA and TPrA by Electrogenerated Oxidant.

We employed redox catalysis to obtain kinetic information about these systems. We investigated the homogeneous oxidation of the amines, reactions 4, 5, and 5*, by the method described previously for oxalate oxidation at a Pt ultramicroelectrode.[17] The method consists of comparing the variation of the steady-state current measured at an ultramicroelectrode for the oxidation of a mediator P in the absence, i_{s0}, and in the presence, i_s, of the substrate. In the presence of an excess of substrate, the variation of the catalytic efficiency with the substrate concentration is given by[17,21]

$$i_s/i_{s0} = 1 + \frac{\pi a}{4}\left(\frac{2k_4[\text{amine}]^0}{D}\right)^{1/2} \tag{7}$$

where a is the electrode radius, k_4 the homogeneous first electron-transfer rate constant for reaction 4, $[\text{amine}]^0$ is the amine bulk concentration, and D is the diffusion coefficient of the redox mediator. The oxidation of TPrA and TEA were investigated by electrogenerating the oxidized form of four different inorganic redox couples that span a potential range of 0.44 V, as listed in Table 1, for solution pH ranging from 3 to 8.2. The homogeneous electron-transfer rate constant, k_4, was deduced from the variation of the catalytic efficiencies with the substrate concentration for the different couples at different pH. The rate constant is straightforwardly extracted with the knowledge of the pK_a of the investigated amine according to[17]

$$k = k_{4,\text{obs}}(1 + 10^{-\text{pH} + \text{p}Ka}) \tag{8}$$

where $k_{4,\text{obs}}$ is the observed rate constant at a given solution pH and k is the intrinsic value of the rate constant for the amine of an acidity constant, pK_a, of 10.9 and 10.4 for TEA and TPrA, respectively (as estimated by acid−base titration of a 0.1 M amine solution). These values are given in Table 1. The variations of the logarithm of the intrinsic electron-transfer rate constant with the standard potential of the redox couple is shown in Figure 4 for both TEA and TPrA.

The rate constants for the homogeneous TEA oxidation are lower by an order of magnitude compared to the values obtained by Hull et al. with different iron complexes followed spectrophotometrically and are of the same order of magnitude for those with molybdicyanide ion.[4b] However, these results are difficult to compare with ours since the pKa used in ref 4b is not given and because of possible instability of the iron complexes.

The analysis of our results according to Marcus theory is also shown in Figure 4 (solid lines). It corresponds to treatment by the following set of equations:

$$1/k = 1/k_{\text{het}} + 1/k_{\text{diff}} \tag{9}$$

where k_{diff} is the diffusion-limited rate constant taken as 3×10^9 M^{-1} s^{-1} and k_{het} is the homogeneous electron-transfer rate constant given by Marcus theory:

$$\frac{-RT}{F}\ln\left(\frac{k_{\text{het}}}{\nu_n}\right) = \Delta G_0^{\ddagger}\left[1 + \frac{E_A^0 - E_{P/Q}^0 + w_p}{4\,\Delta G_0^{\ddagger}}\right]^2 \tag{10}$$

where ν_n is a vibration frequency taken to be 10^{11} s^{-1}, E_A^0 and $E_{P/Q}^0$ represent the standard oxidation potential of the amine and the redox mediator, respectively, and w_p is the electrostatic work term (repulsive work between the two positively charged

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TABLE 1: Rate Constants for the Homogeneous Oxidation of TEA and TPrA by Several Electrogenerated Oxidants

mediator (P)[a]	$E^0_{P/Q}$[b]	w_P[c]	TEA[d]		TPA[d]	
			pH[e]	k[f]	pH[e]	k[f]
$Ru(CN)_6^{4-}$	0.82	−0.03	7.1−8.2	6.8×10^2	7.1−8.2	6×10^3
$Mo(CN)_8^{4-}$	0.87	−0.03	7.1−8.2	3×10^3	7.1−8.2	2×10^4
$Fe(bpy)_3^{2+}$	1.05	0.01	7.1	6.7×10^4	7.1	7×10^5
$Ru(bpy)_3^{2+}$	1.26	0.01	3−6	3×10^6	4.3−5.7	1.3×10^7

[a] Reduced form of the redox couple P/Q, concentration range 0.2−1.5 mM. [b] Standard potential as read by cyclic voltammetry in V vs NHE. [c] Product work function in V for 1 M ionic strength according to Eigen−Fuoss equation.[22] [d] Concentration range 0.01−0.15 M. [e] pH range investigated in 1 M phosphate buffer. [f] Average of k (standard deviation 10%), values in $M^{-1} s^{-1}$.
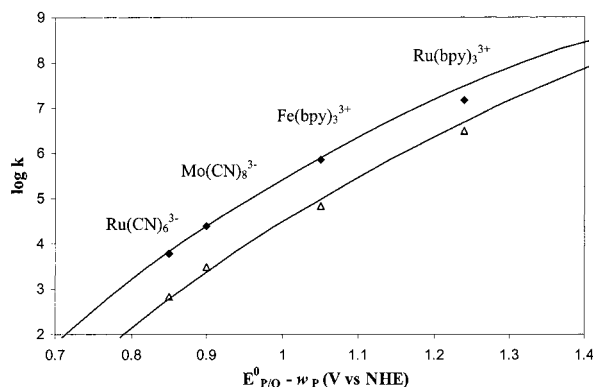

Figure 4. Variation of the logarithm of the first homogeneous electron-transfer rate constant, k, with $E^0_{P/Q} - w_P$ for (△) TEA and (♦) TPrA, (solid line) simulated variations according to Marcus theory (eq 10).

Figure 5. Variation of the apparent homogeneous electron-transfer rate constant, k_{obs}, with pH for $Ru(bpy)_3^{3+}$ and (○) TEA or (♦) TPrA. k_{obs} measured at a 25 μm radius Pt microelectrode; $[Ru(bpy)_3^{2+}] = 0.8$ mM, [TEA] or [TPrA] = 50 mM; 1 M phosphate buffer.

products) given by the Fuoss−Eigen equation.[22] The intrinsic free energy of activation, $\Delta G_0^{\ddagger} = \lambda/4$, involves a contribution from two terms: λ_i, the internal reorganization energy, and λ_0, the solvation reorganization energy. λ_0 can be evaluated from empirical equations of the form

$$\lambda_0 = A(1/a_{P/Q} + 1/a_A - 2/\sigma) \quad (11)$$

where A is a constant between 3.2 and 3.8 eV Å,[23] $a_{P/Q}$ and a_A are the mediator and amine radius, respectively, and $\sigma \approx a_{P/Q} + a_A$. To a first approximation $a_{P/Q}$ can be taken as a constant 6.8 Å and a_A is calculated with eq 12, from the amine density, ρ_a, molecular weight, M_A, and Avogadro's number, N, as 3.8 and 4.2 Å for TEA and TPrA, respectively. These values lead to average intrinsic activation energy barriers of 0.21 and 0.20 eV for TEA and TPrA, respectively.

$$a_A \text{ (in Å)} = 10^8(3M_A/4\pi N\rho_A)^{1/3} \quad (12)$$

The values of the standard oxidation potential of TEA and TPrA, E^0_{TEA} and E^0_{TPrA}, and of the intrinsic activation energies, $\Delta G_0^{\ddagger}_{TEA}$ and $\Delta G_0^{\ddagger}_{TPrA}$, were extracted from the best fit of the experimental rate constants, log k, with the variable $E^0_{P/Q} - w_P$ according to eq 10 with E^0_A and $\Delta G_0^{\ddagger}$ as adjustable parameters. The best fits are obtained in Figure 4, with the standard potentials and intrinsic barrier values of 1.19 and 1.12 V vs NHE and 0.27 and 0.26 eV for TEA and TPrA, respectively. This yields a $\lambda \approx 1$ eV for these species, a value comparable to $\lambda \approx 0.8$ eV obtained for reductive quenching of $Ru(bpy)^{2+*}$ by aromatic amines in protic solvents.[24]

From these values and the equation deduced from the direct measurement, the heterogeneous electron-transfer rate constant, k_s, is estimated to be 0.3 and 0.6 cm/s for TEA and TPrA, respectively, and the deprotonation rate constant of the TPrA radical cation, **1P**, is estimated to be approximately $k_{1,TPrA} = 5 \times 10^8 s^{-1}$. The values of the electron-transfer rate constants are close for each amine, and the fast deprotonation of **1P** is
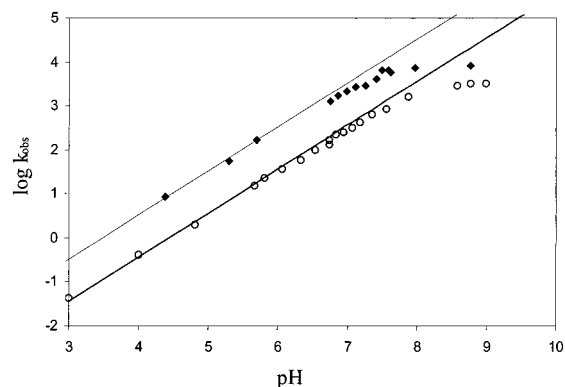
consistent with this step not being kinetically determinant in the homogeneous study. Moreover, in the case of TEA, the kinetic control by the slow electron transfer indicates a deprotonation rate of **1E** of the same order of magnitude as that of TPrA.

Ru(bpy)₃²⁺ case. For both amines, the electron-transfer rate constant for the $Ru(bpy)_3^{2+}$ mediator is slightly smaller than the values predicted by the theory (Figure 4). This disagreement can be explained by the difference in radii between $Ru(bpy)_3^{2+}$ and the less oxidizing mediators. More important is the variation of the rate of the $Ru(bpy)_3^{3+}$/amine oxidation with pH shown in Figure 5. The oxidation current is converted, by the use of eq 7, into an apparent homogeneous rate constant, k_{obs}. Figure 5 represents the variation of this apparent rate constant with the pH of the medium. These variations are useful to better understand the oxidation in the $Ru(bpy)_3^{3+}$/amine systems. The theoretical variations of the electron-transfer rate constant according to eq 8 in the case of a catalytic oxidation are indicated by the solid lines in Figure 5. A deviation from eq 8 is clearly observed for either amine at higher solution pH. This is probably due to the direct oxidation of amine at the electrode. Actually, at pH higher than 9, the wave for amine oxidation can be clearly differentiated from that for $Ru(bpy)_3^{2+}$. For pH values between 6.5 and 9, some direct amine electro-oxidation can be invoked. In this region, the observed current is then the contribution of two components describing the direct amine oxidation (eq 0) and the catalytic oxidation (eq 4). Direct oxidation of the amine at the electrode (eq 0) tends to decrease its concentration in the diffusion layer and therefore the catalytic oxidation current. The latter is then not described any longer by eq 7, but will clearly depend on both the $Ru(bpy)_3^{2+}$ and amine concentrations. Since the system response becomes more complicated in this pH range, extraction of useful kinetic data was not attempted for pH's higher than 6−7.

ECL of the Ru(bpy)₃²⁺/Amine Systems. ECL of the $Ru(bpy)_3^{2+}$/amine systems is therefore the contribution of two
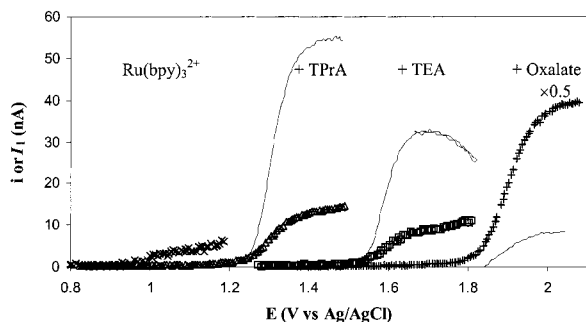
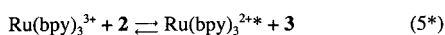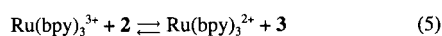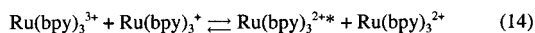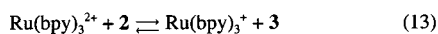**214** *J. Phys. Chem. B, Vol. 105, No. 1, 2001*

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Figure 6. Variation of the microelectrode current ($\times$, $\square$, $\triangle$, $+$) and light intensity (solid lines) with the electrode potential for Ru(bpy)$_3^{2+}$ oxidation ($\times$) in the presence of TPrA ($\triangle$) or TEA ($\square$) at pH 5.2, or in the presence of oxalate at neutral pH ($+$, current level divided by 2); [Ru(bpy)$_3^{2+}$] = 0.5 mM, [substrate] = 96 mM, 0.1 M Na$_2$SO$_4$ + 1 M phosphate buffer in the case of the amines. For clarity, the potentials are shifted by 0.3 V for each coreactant.

SCHEME 2
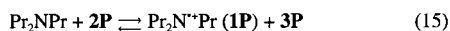
$$\text{Ru(bpy)}_3^{3+} + \mathbf{2} \rightleftarrows \text{Ru(bpy)}_3^{2+} + \mathbf{3} \quad (5)$$

$$\text{Ru(bpy)}_3^{3+} + \mathbf{2} \rightleftarrows \text{Ru(bpy)}_3^{2+*} + \mathbf{3} \quad (5^*)$$

or

$$\text{Ru(bpy)}_3^{2+} + \mathbf{2} \rightleftarrows \text{Ru(bpy)}_3^{+} + \mathbf{3} \quad (13)$$

$$\text{Ru(bpy)}_3^{3+} + \text{Ru(bpy)}_3^{+} \rightleftarrows \text{Ru(bpy)}_3^{2+*} + \text{Ru(bpy)}_3^{2+} \quad (14)$$

or in the case of TPrA

$$\text{Pr}_2\text{NPr} + \mathbf{2P} \rightleftarrows \text{Pr}_2\text{N}^{+*}\text{Pr} \ (\mathbf{1P}) + \mathbf{3P} \quad (15)$$

terms corresponding to direct amine and ruthenium oxidations at the electrode and catalytic oxidation depending on the pH range at which the ECL experiment is carried out. It is easier to understand and study the ECL phenomenon of such systems at lower pH where all ECL is due to only the homogeneous electron transfer between the ruthenium(III) and the amine species. Thus, we investigated the ECL phenomenon at pH 5.7. ECL generation in coreactant systems arises from a second electron transfer to the intermediate amino radical **2** formed upon deprotonation (eq 1) of the amino radical cation **1**. Since this **2** is easier to oxidize than the starting amine, it can be further oxidized at the electrode or more likely in solution, according to the various paths depicted in Scheme 2.

Among the different routes, only two (reaction 5* or reactions 13 and 14) generate ECL. Equation 15 accounts for the DISP mechanism and can be neglected here, since the amine radical cation, **1P**, is not stable and has a lifetime of less than 0.1 ms.[19b]

Figure 6 shows the variation of the ECL intensity, I_l, and the current with the electrode potential for similar concentrations of both amines. For comparison, the same curves for the Ru(bpy)$_3^{2+}$/oxalate system are also shown. A steady plateau current and ECL intensity were observed for both amines. We denote I_{ls} as the plateau ECL intensity. A comparison of TPrA and TEA shows that both the steady-state ECL intensity and current are almost twice as large for TPrA than for TEA, as has already been reported for the chemiluminescence intensity.[14] This tendency is clearly confirmed in Figure 7 where I_{ls} and i_s/i_{s0} for different Ru concentrations for the same amine concentration (0.1 M) are shown. As expected from eq 7, $i_s - i_{s0}$ is proportional to the Ru concentration. However, a deviation
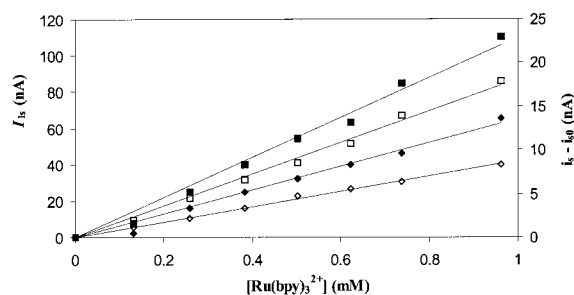

Figure 7. Variation of the steady-state light intensity, I_{ls} ($\blacksquare$,$\blacklozenge$), and catalytic enhancement, $i_s - i_{s0}$ ($\square$,$\diamond$), with the Ru(bpy)$_3^{2+}$ concentration for ($\blacksquare$,$\square$) TPrA, and ($\blacklozenge$,$\diamond$) TEA; [amine] = 0.1 M, pH = 5.7 in 1 M phosphate buffer.
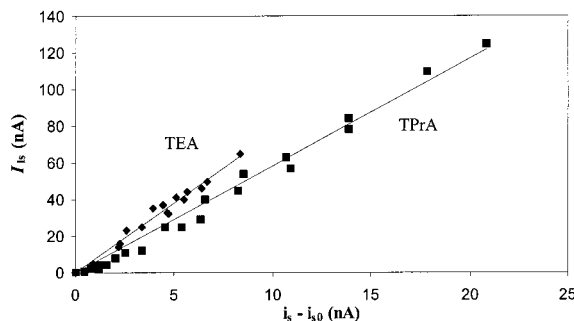

Figure 8. Variation of the steady-state light intensity, I_{ls}, with the catalytic enhancement, $i_s - i_{s0}$, for TprA ($\blacksquare$) and TEA ($\blacklozenge$); 0.1 mM < [Ru(bpy)$_3^{2+}$] < 1 mM and 40 mM < [TEA] < 100 mM or 10 mM < [TPrA] < 100 mM, pH = 5.7, 1 M phosphate buffer.

from this proportionality is observed for Ru concentrations below 0.15 mM, which can be attributed to the intervention of the direct amine oxidation. This hypothesis could also be invoked to explain the reversible decrease in light intensity when the electrode is scanned to more positive potentials. This effect, presented in Figure 6 for the case of TEA oxidation, applies to TPrA as well.

As was discussed in our previous study,[17] within the range of catalytic oxidation, the ECL intensity is proportional to the Ru concentration. We attempted to rationalize the catalytic ECL generated by homogeneous oxidation of a coreactant, and have shown that under catalytic conditions, the plateau light intensity I_{ls} should be given by the following expression:[17]

$$I_{ls} = \alpha(i_s - i_{s0}) \frac{k_{5*}[\text{Ru}^{3+}] + k_{13}[\text{Ru}^{2+}]}{(k_{5*} + k_5)[\text{Ru}^{3+}] + k_{13}[\text{Ru}^{2+}]} \quad (16)$$

This equation can be simplified according to the predominance of the various steps. Since they reflect reactions with very different driving forces, we have shown that one can neglect 5 over 5* and 13, or 13 over 5 and 5*, leading to a simpler proportionality between the steady-state light intensity and the catalytic current enhancement:

$$I_{ls} = \beta(i_s - i_{s0}) \quad (17)$$

where β depends on the photomultiplier tube efficiency, cell geometry, and the ECL efficiency of the system ($\beta = k_{5*}/(k_{5*}/k_5)$ when neglecting eq 13 or $\beta = 1$ when eq 5 is negligible). This proportionality rule is confirmed in Figure 7 for a 0.1 M amine concentration and for different Ru and amine concentrations in Figure 8. The proportionality coefficient for TEA and TPrA are different, 7.5 and 5.9, respectively, but relatively close when compared to the oxalate value of 0.11.[17] The observed

differences between oxalate and these two amines are in good agreement with previously reported work.[14,15]

From the reported estimated value of the ECL efficiency for the $Ru(bpy)_3^{2+}$/oxalate system, $\eta_{oxalate} \approx 2\%$,[25] and from the proportionality coefficient given by eq 17, we can estimate the ECL efficiency of the $Ru(bpy)_3^{2+}$/amine systems under catalytic conditions as

$$\eta_{amine} \approx \eta_{oxalate}(\beta_{amine}/\beta_{oxalate}) \qquad (18)$$

This leads to ECL efficiencies close to 100% (with considerable uncertainty, however) for both TPrA (105%) and TEA (135%). From eq 16, an efficiency of 100% is only expected if the path in eq 5 is negligible.

The low ECL efficiency in oxalate could be explained by the high reducing power of the intermediate radical anion, $CO_2^{\bullet-}$ (-1.9 V vs NHE) and more particularly by the requirement of a high reorganization and solvation energy (λ) during its oxidation. In comparison, the TEA radical, **2E**, is a strong reductant[26] but less reducing than $CO_2^{\bullet-}$. Actually its potential has been determined experimentally as -0.88 V vs NHE in MeCN[27] and can be estimated as -1.05 V vs NHE in water, if one assumes the same transfer energy from MeCN to water for **2E** as for trimethylamine radical.[28] Moreover, **2E** is a much bigger molecule and it should have a smaller λ value than the small and charged carboxylate radical anion. Therefore, for the amines studied, the second electron transfer depicted by eq 5 is highly energetic ($\Delta G^0_5 \approx -2.3$ eV) and should be located in the Marcus inverted region, and the amine radical oxidation could occur through the competitive system of eq 5* or eqs 13 and 14. In this case, and if we do not take into account the possible decay of $Ru(bpy)_3^+$ or $Ru(bpy)_3^{2+*}$ by alternative paths,[25,29,30] the observed ECL efficiency is expected to be high, as observed experimentally. Even though it is difficult to generate at a platinum electrode surface, $Ru(bpy)_3^+$ can be detected in aqueous solution when it is generated by pulse radiolysis[30] or by hot electron transfer at an oxide-covered tantalum electrode or a mercury-drop electrode[31] and is stable enough to react with the 3+ species to generate an ECL signal.

Excited-state quenching processes and ensuing reactions occurring with polypyridyl ruthenium(II) complexes in the presence of amine,[32] including triethylamine,[33] have been reported in the literature. These studies show that even in good H-atom donor solvents such as MeCN, the main oxidative paths are the electron-transfer-deprotonation steps we describe here. Moreover, it has been reported that if the quenching of excited hydrophobic and more oxidizing ruthenium complexes, RuL_3^{2+*}, (where L is an ester of the 4,4′dicarboxylic-2,2′-bipyridine acid) by TEA, depicted by eq 19, is efficient, the reduction is not irreversible, and when L = bpy, a more rapid back electron transfer (eq 20) is observed.

$$RuL_3^{2+*} + TEA \rightarrow RuL_3^+ + \mathbf{1E} \qquad (19)$$

$$RuL_3^+ + \mathbf{1E} \rightarrow RuL_3^{2+} + TEA \qquad (20)$$
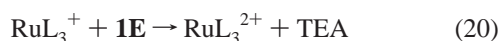
Quenching of $Ru(bpy)_3^{2+*}$ by TEA was not observed because it was too slow. This is in good agreement with the endothermic driving force ($E^0_{2+*/+} = 0.77$ V vs NHE, $\Delta G^0_{19} \approx 0.42$ eV) that can be obtained from our results. As in the case of oxalate, quenching of the excited state by the starting material thus makes a negligible contribution compared to its nonradiative and radiative decay.

TEA radical **2E** oxidation by RuL_3^{2+} in MeCN has also been discussed and is believed to be unfavorable for the less oxidizing

$Ru(bpy)_3^{2+}$.[33b] This is in good agreement with the slightly unfavorable driving force, $E^0_{2+/+} = -1.28$ V vs NHE and $\Delta G^0_{13} \approx 0.25$ eV. Therefore, formation of the less stable $Ru(bpy)_3^+$ by reaction 13 is probably negligible and the only path for ECL generation is depicted by the more favored reaction 5*, $E^0_{3+/2+*} = -0.84$ V vs NHE and $\Delta G^0_{5*} \approx -0.2$ eV. Because of the low reorganization energy needed, the highly exothermic electron transfer, eq 5 ($\Delta G^0_5 \approx -2.3$ eV), as the nonradiative equivalent of reaction 14, should be located in the Marcus inverted region and is negligible compared to 5*, leading to a high theoretical ECL efficiency.

To explain the differences in TEA and TPrA efficiencies, we could invoke possible water reduction by the amine radical **2**. This reduction was found to be efficient when carried out in the presence of $Ru(bpy)_3^{2+*}$, TEA, water, and a solid catalyst such as platinum oxide.[33b] Such catalytic effects cannot be rationalized simply, but clearly show how the ECL efficiency can depend, even in the case of homogeneously generated ECL, on the electrode surface material. This effect is currently under investigation in our group but one might expect a decrease of the ECL efficiency by competitive quenching of the ruthenium excited state at the contact of an oxidized Pt electrode.

Conclusions

The mechanisms involved in TPrA and TEA oxidation were investigated to correlate the rates and mechanisms with the behavior of amines in ECL systems. ECL generated from $Ru(bpy)_3^{2+}$/amine systems at pH lower than 6 can be interpreted by a catalytic homogeneous electron transfer between $Ru(bpy)_3^{3+}$ and the amine. At higher pH, the altered response is attributed to the intervention of the direct amine oxidation at the electrode. The effect of direct oxidation can be observed at a low $[Ru(bpy)_3^{2+}]/[free\ TPrA]$ ratio in either electrochemical detection or in light emission measurements. The differences in level of light emission in the two systems can be explained by the driving force differences: TPrA is less basic and easier to oxidize than TEA. From these arguments, at the same pH and concentration, the light emitted in the TPrA system is expected to be higher than in the TEA system, as observed experimentally. When the oxidation takes place homogeneously, the mathematical treatment developed previously for the $Ru(bpy)_3^{3+}$/oxalate system can be applied. This suggests that the ECL efficiency in the amine systems is close to 1, in good agreement with Marcus predictions on inverted-region electron transfer. The difference observed in the ECL efficiencies of the two systems might be caused by water reduction by the intermediate amine radical.

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