Table 3. Solvent Dependence of Kinetic Data for Reaction of PPN*CrMn(CO)_{10} with 20 Fold Excess of P(C_6H_5)_3 in THF at 60°C

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric Const.*</th>
<th>k_{obs} \times 10^5</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH_3CN</td>
<td>36.2</td>
<td>30.2 ± 0.6</td>
</tr>
<tr>
<td>EtOH</td>
<td>24.3</td>
<td>14 ± 2</td>
</tr>
<tr>
<td>THF</td>
<td>7.3</td>
<td>8 ± 1</td>
</tr>
<tr>
<td>C_6H_5CH_3</td>
<td>2.4</td>
<td>6 ± 4</td>
</tr>
</tbody>
</table>

*Measured at 25°C.

here one would expect neutral disubstituted product Cr(CO)_{14} (PR_2)_{12} to dominate. This was not the result; in fact only 20% of the disubstituted product was obtained at 65°C. The product distribution (major Cr(CO)_{12}PR_3 and PPN* Mn(CO)_{12}); minor Cr(CO)_{12} (PR_2)_{12} may suggest the corresponding bond strength comparisons (Cr~Mn <Cr~CO<Mn~CO). This comparison of bond strength may be related to the electron density located on each metal center. In fact, it is assumed that more electron density is located on the Mn that Cr in PPN* CrMn(CO)_{10}; therefore, the more electron density on Mn would lead to the stronger Mn–CO bond than the Cr–CO bond. The electron density on Mn moiety of PPN* CrMn(CO)_{10} eventually returns to the Mn(CO)_{12} on the disruption by PR_2. This result may be inconsistent with Graham’s observation that negative charge resides on Cr(CO)_{12} moiety of CrMn(CO)_{10}. The observation that there was no depression in reaction rate upon adding Mn(CO)_{12} (equimolar amount of CrMn(CO)_{10}) to the reaction solution may be ascribed to the result (W(CO)_{12}PPh_3 (90%) and W(CO)_{10} (10%) of the previous competition reaction of Mn(CO)_{12} and 20 fold excess of PPh_3 with W(CO)_{12} in THF at 22°C. From these results it is assumed that metal-metal bond cleavage is involved in the rate-determining step and therefore the heterolytic Cr–Mn bond dissociation energy may be approximately 27 kcal/mol.

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References


Excitation Mechanism of Fluorescent Polycyclic Aromatic Amines and Polycyclic Aromatic Hydrocarbons in Peroxyxalate Chemiluminescence Reactions

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The excitation mechanism of polycyclic aromatic amines (amino–PAHs) and polycyclic aromatic hydrocarbons (PAHs) for the chemiluminescence arising from the reaction between oxalate ester, bis(2,4,6-trichlorophenyl)oxalate (TCP) or bis(2,4-dinitrophenyl)oxalate (DNPO) and hydrogen peroxide has been studied in terms of the excitation efficiencies to singlet excitation energies and the oxidative half–wave potentials. As a result of the study, the excitations of both amino–PAHs and PAHs appear to involve the charge transfer type of energy transfer. However the chemiluminescence efficiency corrected for fluorescence quantum yield of the amino–PAHs are varied more sensitively to the oxidative half–wave potential than that of PAHs possibly due to the large difference in solvation energy between the compounds and their ions.

Introduction

During the past years after the discovery of peroxoxtalate chemiluminescence(POCL), much attention has been focused on developing efficient chemical light source as a cold light. Recently, the excellent sensitivity of POCL as a detection of fluorescent compounds has been utilized for chemical analysis by high–performance liquid chromatography(HPLC). Some researchers studied that various PAHs having emission spanning the visible–infrared spectrum could be excited by the intermediate(s) produced from a reaction between aryl oxalate ester and hydrogen peroxide. Ryan et al. reported that fluorescers with low excitation energy ap-
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Peared to give high Cl. efficiencies, however, studies on several fluorescers failed to indicate the correlation of excitation efficiency to the singlet energy of the fluorescer.

When one electron is transferred to the intermediate in the excitation step and a charge transfer complex is formed as speculated by McCaprak and Rautu, there exist linear relationships between the rate of exciting a fluorescer and the excitation efficiency of the fluorescer. The excitation efficiency is an exponential function of the oxidative half-wave potential of the fluorescer. Therefore the logarithm of excitation efficiency is a linear function of oxidative half-wave potential of the fluorescer.

There are a few reports which have evaluated the latter relationship using fluorescent PAHs in peroxoxygenate systems. Imai et al. reported that fluorescent compounds of various types showed the linear relationships. However, acetylamino-PAHs appear to deviate from the rest of PAHs.

In a previous report, we have also found that the excitation of PAH in Cl. reaction of TCPO and H_2O_2 is caused by a charge-transfer type of energy transfer.

Although there are reports which have attempted to elucidate the excitation mechanism of various types of PAH in the peroxoxygenate system, studies of amino-PAHs appear to be rare. Amino-PAHs are sensitivity detected by HPLC due to their high efficiencies in the excitation step and high fluorescence quantum yields.

Therefore, in this report we examined the excitation mechanism of amino-PAHs with other PAHs in the peroxoxygenate Cl. system as a function of singlet excitation energy and electrochemical oxidative half-wave potential.

**Experimental**

**Chemicals.** DNPO and TCPO were prepared by following the method of Mohan and Turro and recrystallized from nitrobenzene. They were identified with melting points, IR and NMR spectra. Hydrogen peroxide was purchased from Riedel-deHaen and vacuum distilled to concentrate 92% whose concentration was determined iodometrically. Solvents, ethyl acetate and acetonitrile and fluorescers were of reagent grade from Aldrich except 1-(2-phenylethenyl)pyrene and 1-(2-phenylethenyl)naphthalene which were synthesized from our laboratory. Sodium salicylate and sodium perchlorate from Junsei were used as catalyst and supporting electrolyte, respectively, without further purification.

**Fluorescence and Electrochemical Measurements.** Fluorescence quantum yield was obtained by comparing the fluorescence of a fluorescer to that of 9,10-diphenylanthracene whose fluorescence quantum yield was set to 1.0. For this, the absorbance of the compound was measured by a HP 8452A diode array spectrophotometer and the fluorescence spectrum by a Hitachi 650-60 fluorescence spectrophotometer. All absorption and fluorescence spectra were obtained in an identical solvents as the Cl. intensity measurements. A PAR Model 273 Potentiostat/Galvanostat and RE 0991 X-Y recorder were employed to record the cyclic voltammogram of the fluorescer from which the oxidative half-wave potentials were obtained.

**CL Measurements.** The CL reaction was carried out in a 1.0 cm fluorescence cell inserted in a thermostatted housing of the spectrofluorimeter. A 1.5 ml solution of DNPO or TCPO and a fluorescer in 5% t-butylalcohol/ethyelacetate was added to the cell. The solution was purged with nitrogen. The CL reaction was initiated by injecting 0.5 ml mixed solution of H_2O_2 and sodium salicylate. The time course of the CL intensity was monitored by the spectrophotometer with the lamp turned off at wavelengths such that the reabsorption of emission was negligible.

**Results and Discussion**

Table 1 summarized all the experimental data for relative maximum CL intensity (I_m), fluorescence quantum yield (φ_f), the lowest oxidative half-wave potential (E_g ( oxidative)), and singlet excitation energy (E_s) of the aromatic hydrocarbons measured under the experimental conditions. The singlet excitation energy of a fluorescer is defined as E_s = (1/λ_ab + 1/λ_em)/2, where λ_ab and λ_em are the absorption and the fluorescence emission maximum wavelengths, respectively.

As can be noted in Table 1, I_m was enhanced with the substitution of phenyl, phenylethenyl, or amino group, but diminished with cyan or carboxyl substituent. The effect of substituents on the Cl. intensities agree with the previous result, although less viscous solvent was utilized in this experiment. The oxidative half-wave potentials of amino-PAHs are much lower than those of the parent aromatic hydrocarbons. This is because the electrons corresponding to the first oxidative wave are removed from the non-bonding orbitals of the nitrogen atoms in amino-PAHs rather than from the π-system in the other PAHs. The low oxidative half-wave potential of the amino-PAHs is responsible for the very sensitive detection of the amino-PAHs over other fluorescent compounds by HPLC.

All the fluorescers were confirmed to be emitting species by matching the Cl. spectra with the fluorescence spectra, demonstrating that the singlet excited state of a fluorescer is formed by the CL intermediate produced from a reaction between an oxalic ester and H_2O_2 in the presence of a base catalyst, such as sodium salicylate.

Lechtken and Turro reported that the logarithm of I_m/φ_f, the maximum CL intensity corrected for its fluorescence quantum yield, of a fluorescer decreases as the singlet
excitation energy of the fluorescer increases up to approximately 105 kcal/mol (=272 nm). Their plots of \( \log(I_m/\phi) \) vs. \( E_0 \) yielded a monotonically decreasing line. Using the data in Table 1, plots of \( \log(I_m/\phi) \) vs. \( E_0 \) suggested by Lechtken and Turo is presented in Figure 1(a) and 1(b) for TCPO and DNPO systems, respectively. As a whole, the data points are scattered and the plots do not show the expected behavior. It may be considered that amino-PAHs roughly lie on a curve. Based on these results it appears that the singlet excitation energy alone is not sufficient enough to predict the CL intensities for a preoxyxidate system. Imai \textit{et al.}\textsuperscript{13} were also not able to produce a smooth curve from a similar CL work using a wide variety of fluorescent compounds different from those used in this study.

There are now considerable data to show that a charge transfer mechanism is operating between the CL intermediate and a fluorescer and they form a charge transfer complex. In such a reaction there is a linear relationship between the logarithm of the CL intensity at maximum corrected for \( \phi_f \) and the oxidative half-wave potential. In order to observe this relationship to hold, a plot of \( \log(I_m/\phi) \) vs. \( E_{1/2} \) for amino-PAH and PAH in POCL reaction: (a) TCPO system; (b) DNPO system. Numbers refer to the list in Table 1.

Figure 2. Plots of the \( \log(I_m/\phi) \) vs. oxidative half-wave potential \( E_{1/2} \) of amino-PAH and PAH in POCL reaction: (a) TCPO system; (b) DNPO system. Numbers refer to the list in Table 1.

shown in Figure 2(a) and 2(b) for TCPO and DNPO systems, respectively. The figures indeed show the linear relationships. Unexpectedly, however, amino-PAHs show one line and the other PAHs show another.

At any rate, the experimental data demonstrate that a charge transfer mechanism is involved in the excitation step of the fluorescer. Then \( I_m/\phi \) may be described as

\[
I_m/\phi \propto \exp\left(-\frac{(IP - EA - \Delta S_{mol} - e^2/\varepsilon r)}{RT}\right)
\]

(1)

where \( IP \) is the ionization potential of a fluorescer, an electron donor; \( EA \) is the electron affinity of the intermediate, an electron acceptor; \( \Delta S_{mol} \) is the difference in sloration energy between the compound and its positive ion; \( -e^2/\varepsilon r \) is the Coulombic energy between the positive fluorescer ion and the negative intermediate ion separated by \( r \) in a medium of dielectric constant \( \varepsilon \). Previously \( EA, \Delta S_{mol}, \) and \( -e^2/\varepsilon r \) were assumed to remain almost the same for varying only the fluorescers under given experimental conditions.\textsuperscript{14} However, a slight modification to \( \Delta E_{mol} \) appears to be necessary to account for the present results of Figure 2.

Since the linearity was enhanced for the amino-PAHs, \( S_{mol} \) may be related to an approximately linear function of \( IP \), that is.
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\[ \Delta E_{\text{sol}} \propto k \cdot IP \]  

(2)

where \( k \) is a constant depending on the group of PAHs. The oxidative half-wave potential is expressed as

\[ a \cdot E_{1/2, \text{ox}} = IP - \Delta E_{\text{sol}} + \delta \]  

(3)

where \( a \) is a constant and \( \delta \) includes other minor terms.\(^{18}\)

Combining of Eqs. (1) through (3) gives

\[ I_m/\phi_j \propto \exp \left( -\frac{a}{1 - k E_{1/2, \text{ox}}} \right) \]  

(4)

since \( EA \) is a constant for a given peroxyxalate system. Variations in the Coulombic energy was assumed to be less significant than those in other terms. Eq. (4) implies that the log(\( I_m/\phi_j \)) vs. \( E_{1/2, \text{ox}} \) will show a different slope depending on the value of \( k \). The larger the \( k \), the steeper the slope.

Figure 2 suggests that the amino–PAHs possess a larger \( k \) than the remaining PAHs and therefore experience greater change in solvation energy. This may be explained in terms of relative stabilizing of their positive ions. A radical cation is formed by the transfer of an electron from a fluorescer to the intermediate. In the amino–PAHs an electron is removed from the non-bonding orbital of the nitrogen atom, whereas the removal occurs from the \( \pi \)-system in the other PAHs. Since the resultant electron deficiency in PAHs may be partially supplemented by the \( \pi \)-system, the solvation energy change is expected to be small.

On the other hand, the amino groups in the amino–PAHs form stable hydrogen bond with the solvent, ethylacetate here, prior to the removal of an electron. After the electron removal, however, the remaining one electron in the nitrogen atom is not sufficient to form a stable hydrogen bond. Consequently the solvation of the radical cation will be quite different from the parent compound and \( \Delta E_{\text{sol}} \) becomes substantial. Incidentally, on careful inspection of the data reported by Imai et al.\(^{13}\) three acetylamino–PAHs show somewhat greater slope than the other types of aromatic compounds although the data for the acetylamino–PAHs are not well separated. Although not many acetylamino–PAHs were covered, it may be appropriate to adopt their data as a supporting evidence. Probably \( \Delta E_{\text{sol}} \) behavior of acetylamino–PAHs may be parallel with amino–PAHs. Further studies on amino–PAHs are underway to elucidate their different behavior on the excitation step of peroxyxalate CL reactions.

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References