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

Solvent	Dielectric Const.*	$k_{obs} \times 10^5$
CH_3CN	36.2	30.2 ± 0.6
EtOH	24.3	14 ± 2
THF	7.3	8 ± 1
$C_6H_5CH_3$	2.4	6 ± 1

*Measured at 25 °C.

here one would expect neutral disubstituted product $Cr(CO)_4(PR_3)_2$ to dominate. This was not the result; in fact only 20% of the disubstituted product was obtained at 65 °C. The product distribution (major $Cr(CO)_5PR_3$ and PPN^+ $Mn(CO)_5^-$; minor $Cr(CO)_4(PR_3)_2$) 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 $Mn(CO)_5^-$ on the disruption by PR_3. This result may be inconsistent with Graham's observation that negative charge resides on $Cr(CO)_5$ moiety of $CrMn(CO)_{10}^-$.[4] The observation that there was no depression in reaction rate upon adding $Mn(CO)_5^-$ (equimolar amount of $CrMn(CO)_{10}^-$) to the reaction solution may be ascribed to the result ($W(CO)_5PPh_3$ (~90%) and $WMn(CO)_{10}^-$ (~10%)) of the previous competition reaction of $Mn(CO)_5^-$ and 20 fold excess of PPh_3 with $W(CO)_5{}^\circ$ 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

1. D. A. Roberts and G. L. Geoffroy, "Comprehensive Organometallic Chemistry", Pergamon press, Oxford, **6**, 763 (1982).
2. F. W. B. Einstein, R. K. Pomeroy, P. Rushman, and A. C. Willis, *J. Chem. Commun.*, 854 (1983).
3. L. W. Arndt, Dissertation, Texas A & M Univ., (1986).
4. U. Anders and W. A. G. Graham, *J. Am. Chem. Soc.*, **89**, 539 (1967).
5. J. R. Johnson, D. M. Duggan, and W. M. Risen, Jr. *Inorg. Chem.*, **14**, 1053 (1975).
6. J. R. Johnson, R. J. Ziegler, and W. M. Risen, Jr. *Inorg. Chem.*, **12**, 2349 (1973).
7. S. Onaka, T. Sugawara, Y. Kawada, and H. Iwamura, *J. Chem. Soc. Dalton*, 257 (1982).
8. R. A. Levenson and H. B. Gray, *J. Am. Chem. Soc.*, **97**, 6042 (1975).
9. J. K. Ruff, *Inorg. Chem.*, **7**, 1818 (1968).
10. A. J. Gordon and R. A. Ford, "The Chemist's Companion", Wiley-Interscience, New York (1972).
11. L. W. Arndt and M. Y. Darensbourg, *Inorg. Syn.*, in Press.

Excitation Mechanism of Fluorescent Polycyclic Aromatic Amines and Polycyclic Aromatic Hydrocarbons in Peroxyoxalate 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 (TCPO) 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 results 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 peroxyoxalate chemiluminescence(POCL), much attention has been focused on developing efficient chemical light source as a cold light.[1,2] Recently, the excellent sensitivity of POCL as a detection of fluorescent compounds has been utilized for chemical analysis by high-performance liquid chromatography(HPLC).[3-7]

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.[8-10] Ryan *et al.* reported that fluorescers with low excitation energy appeared to give high CL efficiencies,[9] 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 McCapra[11] and Rauhut,[12] 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 peroxyoxalate systems.[13-15] Imai *et al.*[13] 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,[14] 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 peroxyoxalate 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.[5,13]

Therefore, in this report we compared the excitation mechanism of amino-PAHs with other PAHs in the peroxyoxalate 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[17] and recrystallized from nitrobenzene. They were identified with melting points, IR and NMR spectra. Hydrogen peroxide was purchased from Riedel-deHaén 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.[16] 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 0091 X-Y recorder were employed to record the cyclic voltammogram of the fluorescer from which the oxidative half-wave potentials were obtained.

Table 1. Spectroscopic and Electrochemical Data for Amino-PAHs and PAHs

Fluorescer	ϕ_f	$E_{1/2\,(ox)}{}^a$	$E_s{}^b$	$I_m{}^c$	$I_m{}^d$
1. 1-aminoanthracene	0.29	0.40	2.22	8.68	482
2. 6-aminochrysene	0.30	0.46	2.60	5.60	189
3. 3-aminofluoranthene	0.37	0.50	2.16	22.0	1062
4. 1-aminonaphthalene	0.60	0.55	2.75	2.92	19
5. 9-aminophenanthrene	0.21	0.52	2.73	2.62	15
6. 1-aminopyrene	0.78	0.38	2.57	60.0	232
7. anthracene	0.31	1.09	2.65	4.56	145
8. 9-anthracenecarbonitrile	0.89	1.45	2.45	0.17	13
9. 9-anthracenecarboxylic acid	0.69	1.29	2.47	0.46	79
10. 9,10-diphenylanthracene	1.0	1.07	2.51	46.3	1472
11. 1-(2-phenylethenyl)pyrene	0.77	0.93	2.54	44.4	687
12. 1-(2-phenylethenyl)-naphthalene	0.22	1.24	2.90	0.33	20

[a]in volts *vs.* SCE. [b]in um^{-1}. [c]TCPO. [d]DNPO.

CL Measurements. The CL reaction was carried out in a 1.0 cm fluorescence cell inserted in a thermostated housing of the spectrofluorimeter. A 1.5 m*l* solution of DNPO or TCPO and a fluorescer in 5% *t*-butylalcohol/ethylacetate was added to the cell. The solution was purged with nitrogen. The CL reaction was initiated by injecting 0.5 m*l* mixed solution of H_2O_2 and sodium salicylate. The time course of the CL intensity was monitored by the spectrofluorimeter 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 ($E_{1/2\,(ox)}$), 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 $(1/\lambda_{abs} + 1/\lambda_{em})/2$, where λ_{abs} and λ_{em} are the absorption and the fluorescence emission maximum wavelengths, respectively.[13]

As can be noted in Table 1, I_m was enhanced with the substitution of phenyl, phenylethenyl, or amino group, but diminished with cyano or carboxyl substituent. The effect of substituents on the CL intensities agrees with the previous result.[14] 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.[18] The low oxidative half-wave potential of the amino-PAHs are responsible for the very sensitive detection of the amino-PAHs over other fluorescent compounds by HPLC.[5]

All the fluorescer 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[8] 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

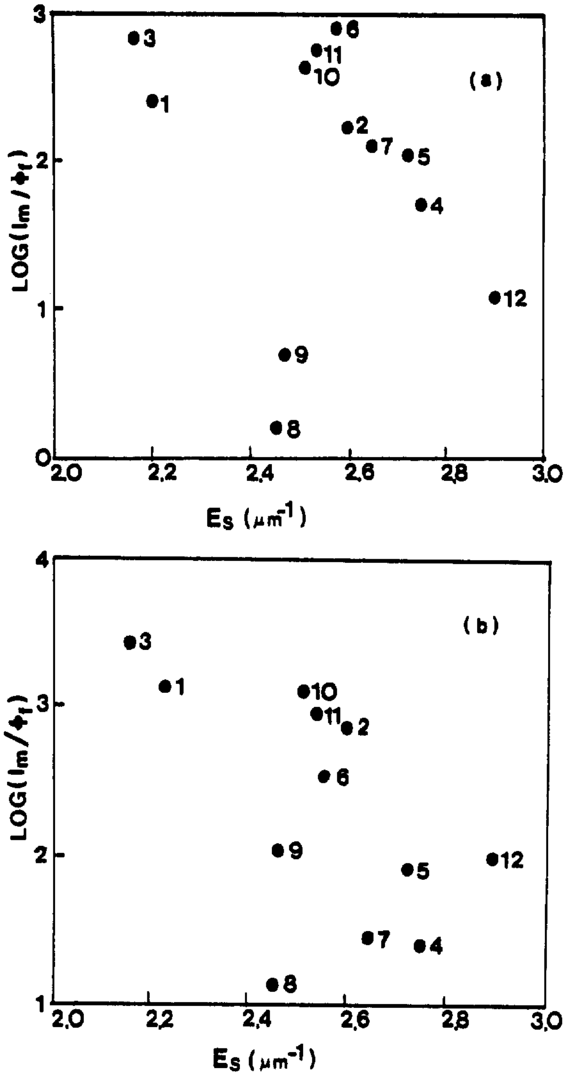

Figure 1. Plots of the log(I_m/ϕ_f) *vs.* singlet excitation energy(E_s) of amino-PAH and PAH in POCL reactions: (a) TCPO system; (b) DNPO system. Numbers refer to the list in Table 1.

excitation energy of the fluorescer increases up to approximately 105 kcal/mol (=272 nm). Their plots of log (I_m/ϕ_f) *vs.* E_s yielded a monotonically decreasing line. Using the data in Table 1, plots of log (I_m/ϕ_f) *vs.* E_s suggested by Lechtken and Turro 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 preoxyoxalate system. Imai *et al.*[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 ϕ_f and the oxidative half-wave potential. In order to observe this relationship to hold, a polt of log (I_m/ϕ_f) *vs.* $E_{½(ox)}$ is 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.

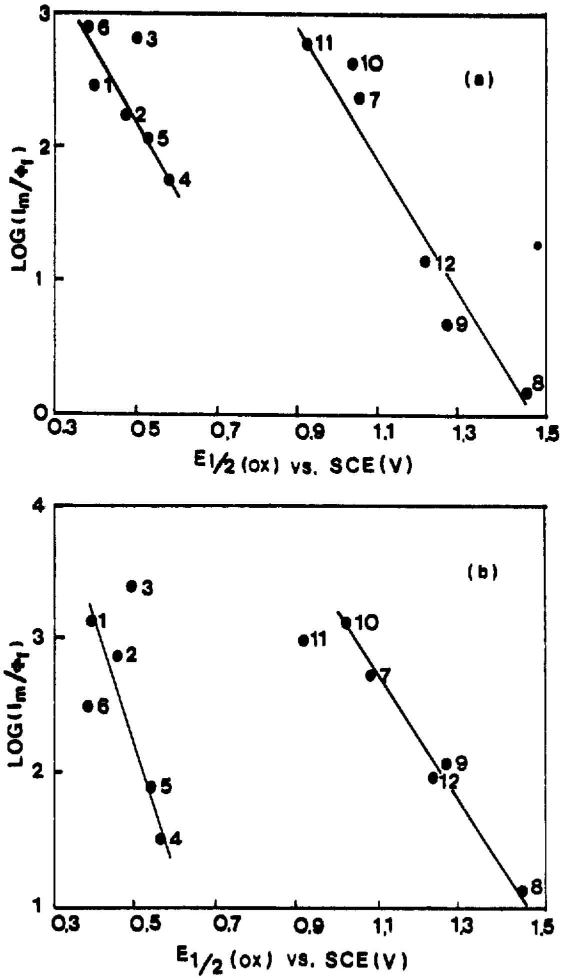

Figure 2. Plots of the log(I_m/ϕ_f) *vs.* oxidative half-wave potential $(E_{½(ox)})$ of amino-PAH and PAH in POCL reaction: (a) TCPO system: (b) DNPO system. Numbers refer to the list in Table 1.

At any rate, the experimental data demonstrate that a charge transfer mechanism is involved in the excitation step of the fluorescer. Then I_m/ϕ_f may be described as[14]

$$I_m/\phi_f \propto \exp\{-(IP-EA-\Delta S_{mol}-e^2/\epsilon r)/RT\} \quad (1)$$

where IP is the ionization potential of a fluorescer, an electron donor; EA is the electron affinity of the intermediate, an electron acceptor; ΔE_{sol} is the difference in slovation energy between the compound and its positive ion; and $-e^2/\epsilon r$ is the Coulombic energy between the positive fluorescer ion and the negative intermediate ion separated by r in a medium of dielectric constant ϵ. Previously EA, ΔS_{sol}, and $-e^2/\epsilon r$ were assumed to remain almost the same for varying only the fluorescers under given experimental conditions.[14] However, a slight modification to ΔE_{sol} appears to be necessary to account for the present results of Figure 2.

Since the linearity was enhanced for the amino-PAHs, S_{sol} may be related to an approximately linear function of IP, that is,

$$\Delta E_{sol} \propto k \cdot IP \tag{2}$$

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

$$\alpha \cdot E_{1/2(ox)} = IP - \Delta E_{sol} + \delta \tag{3}$$

where α is a constant and δ includes other minor terms.[18] Combining of Eqs. (1) through (3) gives

$$I_m/\phi_f \propto \exp\{-\frac{\alpha}{1-k}E_{1/2(ox)}\} \tag{4}$$

since EA is a constant for a given peroxyoxalate system. Variations in the Coulombic energy was assumed to be less significant than those in other terms. Eq. (4) implys that the $\log(I_m/\phi_f)$ *vs.* $E_{1/2(ox)}$ 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 π-system in the other PAHs. Since the resultant electron deficiency in PAHs may be partially supplemented by the π-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 ΔE_{sol} becomes substantial. Incidently, 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 ΔE_{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 peroxyoxalate CL reactions.

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References

1. M. M. Rauhut *et al.*, *J. Am. Chem. Soc.*, **89**, 6515 (1967); B. G. Robert, R. H. Whiteman, L. J. Bollyky, and M. M. Rauhut, *J. Am. Chem. Soc.*, **89**, 6523 (1967).
2. D. R. Maulding and B. G. Roberts, *J. Org. Chem.*, **34**, 1734 (1969).
3. V. K. Mahant, J. N. Miller, and H. Thakrar, *Anal. Chim. Acta*, **145**, 203 (1983).
4. K. Honda, J. Sekino, and K. Imai, *Anal. Chem.*, **55**, 940 (1983).
5. K. W. Sigvardson, J. M. Kennish, and J. W. Birks, *Anal. Chem.*, **56**, 1096 (1984); K. W. Sigvardson and J. W. Birks, *Anal. Chem.*, **55**, 432 (1983).
6. M. L. Grayeski and W. R. Seitz, *Anal. Biochem.*, **136**, 277 (1984).
7. G. J. de Jong *et al.*, *Anal. Chem.*, **59**, 1458 (1987).
8. P. Lechtken and N. J. Turro, *Mol. Photochem.*, **6**, 95 (1974),
9. P. A. Sherman, J. Holtzbecher, and D. E. Ryan, *Anal. Chim. Acta*, **97**, 21 (1978).
10. P. J. Hanhela and D. B. Paul, *Aust. J. Chem.*, **34**, 1669 (1981).
11. F. McCapra, *Prog. Org. Chem.*, **8**, 258 (1973).
12. M. M. Rauhut, *Acc. Chem. Res.*, **2**, 80 (1969).
13. K. Honda, K. Miyaguchi, and K. Imai, *Anal. Chim. Acta*, **177**, 111 (1985).
14. H. S. Song, H. S. Shin, and K. J. Kim, *Bull. Korean Chem. Soc.*, **8**, 454 (1987).
15. C. L. R. Catherall, T. F. Palmer, and R. B. Cundall, *J. Chem. Soc. Faraday Trans 2*, **80**, 837 (1984).
16. D. D. Cowan, and R. L. Drisko, "Elements of Organic Photochemistry", Plenum Press, New York, 1976.
17. A. G. Mohan and N. J. Turro, *J. Chem. Educ.*, **51**, 528 (1974).
18. E. S. Pysh and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 2124 (1964).