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Surfactant Effect on the Chemiluminescent Reaction between Bis(2, 4-dinitrophenyl)oxalate, H₂O₂ and Fluorescent Aromatic Hydrocarbons in Acetonitrile

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Due to high sensitivity, peroxyoxalate chemiluminescence (POCL) has been utilized as a detection method for fluorescent compounds by HPLC.[1-4] In particular, when a fluorescent compound is amino-substituted, the detection limit can be far lowered probably because of low oxidation potential of the fluorescer and stability of the intermediate form of the fluorescer and a key intermediate of the CL reaction.[3b]

The present study has been conducted to improve the sensitivity by utilizing surfactant which has been proved to be useful in a variety of analytical applications.[5] Surfactants have not been utilized for POCL of polycyclic aromatic hydrocarbons (PAH) in non-aqueous solutions, although there are some reports concerning the improvements of CL of lucigenin and aqueous POCL in membrane mimetic agents.[6-8]

Experimental details are described elsewhere.[9] Imidazole was used to catalyze the reaction between bis (2, 4-dinitrophenyl) oxalate (DNPO) and H₂O₂. Figure 1 show typically that the CL decay after a maximum has apparent single exponential behavior, indicating that an intermediate is predominantly involved.[10] With increasing surfactant concentration the time to reach the maximum CL intensity becomes shorter and the decay becomes faster. An increase in maximum intensity and a decrease in half-life indicate that CL reaction is catalized by the surfactant. Further quantitative data are listed in Table 1 and 2 which summarize the effect of TX-100 (Triton X-100) and CTAB (cetyltrimethylammonium bromide) on CL intensity at $t=0$, I_0, relative integrated CL intensity, I_{CL}, time for maximum intensity to decay to half of its value, $t_{1/2}$, and relative fluorescence intensity, I_f. SDS was

not used because of its low solubility in acetonitrile.

It is noted from Table 1 and 2 that I_f is essentially invariant with respect to the concentration of surfactants, [surfactant]. In addition, the absorbances of the solutions listed in the tables were independent of the presence of surfactants. Thus the fluorescence quantum yield ϕ_f, may be assumed to be independent of [surfactant]. The value of I_0 for 1-aminoanthracene shows tremendous increase compared with anthracene with the increase of [surfactant]. That is, I_0 was increased by 66 fold with CTAB and 22 fold with TX-100, respectively, for 1-aminoanthracene whereas the increase in I_0 was at most 34% and 49% with CTAB and TX-100 for anthracene, respectively.

It is unexpected, however, to observe decrease in I_{CL} for the anthrance system upon the addition of surfactant. Under the conditions of given concentrations of DNPO and H₂O₂, and of negligible reaction between DNPO and imidazole, I_{CL} can be expressed as[11]

$$I_{CL} \propto \phi_f \cdot \phi_{ex} \frac{k_c[F]}{k_c[F]+k_d} \qquad (1)$$

where ϕ_{ex} is the fraction of complex (XF) which leads to the formation of excited states of F, F^*. F stands for a fluorescer, and k_c and k_d are the rate constants for the reactions of the key intermediate, X, as follows,[11]

$$X+F \xrightarrow{\ k_c\ } XF \qquad (2)$$

$$X \xrightarrow{\ k_d\ } non\text{-}CL \ decay \qquad (3)$$
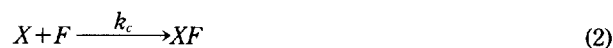
To obtain the k_c/k_d ratio, I_0 was measured by varying the fluorescer concentration over 2.0×10^{-4} M to 1.0×10^{-3} M at a given 1.0×10^{-5} M CTAB. The ratio is then available[11] as the quotient of intercept/slope from a plot of I_0^{-1} vs. $[F]^{-1}$.

The plot showed a linear dependence and the results are summarized in Table 3. The ratios for both fluorescers are enhanced upon the addition of CTAB. Similar enhancement was observed with TX-100. Therefore, the reaction leading to the formation of complex (Eq. (2)) is enhanced compared with the non-CL decay process (Eq. (3)) in the presence of surfactants.

According to Eq. (1), if $\phi_f \cdot \phi_{ex}$ remain constant upon the addition of surfactants, the enhancement in the k_c/k_d ratio
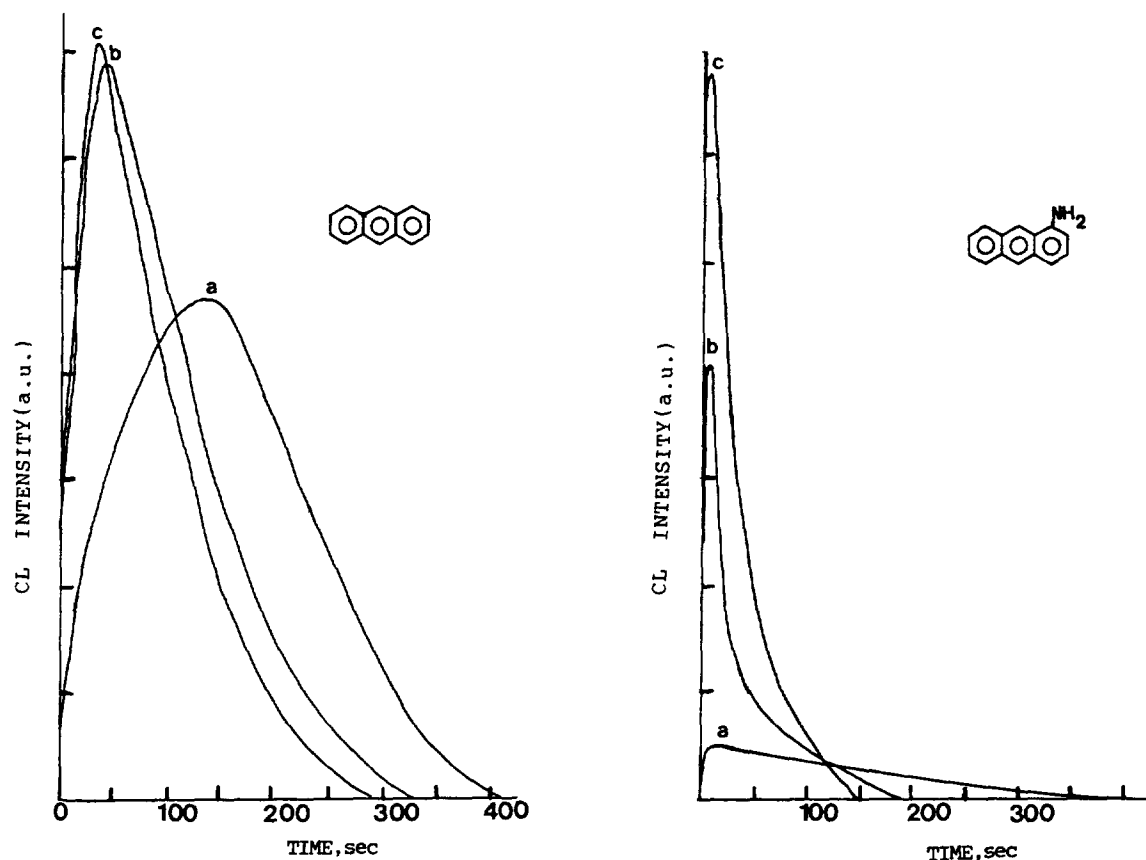
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Figure 1. Typical relative CL intensity *vs.* time profiles for the DNPO-H_2O_2 reactions of anthrance and 1-aminoanthracene in acetonitrile with a, no surfactant; b, 3.0×10^{-3} M TX-100; c, 3.0×10^{-5} M CTAB.

Table 1. Effect of Triton X-100 Concentration on the POCL Reactions

[TX-100], 10^{-4} M	Anthracene				1-Aminoanthracene			
	I_0	I_{CL}	$t_{1/2}{}^a$	I_f	I_0	I_{CL}	$t_{1/2}{}^a$	I_f
0	41	1.0	255	447	9	1.0	465	109
1	43	1.0	255	444	10	1.0	465	108
5	46	0.96	210	441	12	1.4	375	106
10	49	0.92	180	448	18	1.7	300	103
30	57	0.80	150	448	59	1.9	180	106
50	61	0.70	105	451	83	2.0	60	114
70	55	0.62	100	447	98	2.1	60	113
100	50	0.46	90	439	128	2.2	50	114
200	28	0.42	70	442	204	1.8	45	114
400	11	0.31	60	443	199	1.7	37	112
500	4	0.02	60	446	143	1.5	30	111

Conditions:3.0×10^{-3} M DNPO, 2.0×10^{-2} M H_2O_2, 1.2×10^{-4} M imidazole, 1.0×10^{-4} M fluorescer in CH_3CN. $^a t_{1/2}$ in sec.

would increase I_{CL} at a given fluorescer concentration. Since ϕ_f was found to be independent of the presence of surfactant, to account for the decrease in I_{CL} of anthracene, ϕ_{ex} should be decreased on the addition of surfactant. For the k_c/k_d ratios in Table 3, for example, Eq. (1) predicts that ϕ_{ex} for anthracene in the presence of 1.0×10^{-5} M CTAB to be 1/2 of that in the absence of the surfactant whereas for 1-ami-

Table 2. Effect of CTAB Concentration on the POCL Reactions under the Same Conditions as in Table 1

[CTAB], 10^{-6} M	Anthracene				1-Aminoanthracene			
	I_0	I_{CL}	$t_{1/2}{}^a$	I_f	I_0	I_{CL}	$t_{1/2}{}^a$	I_f
0	41	1.0	255	447	9	1.0	465	109
1	43	1.0	240	446	10	1.0	465	110
5	45	0.90	156	448	33	1.5	195	111
10	45	0.84	126	450	62	1.9	45	110
30	55	0.62	100	447	143	2.3	35	108
50	36	0.35	75	442	280	2.5	21	110
70	29	0.31	70	446	400	2.2	21	108
100	22	0.25	66	440	599	1.8	20	110
200	15	0.01	60	436	476	1.8	20	109
400	8	-	52	441	345	1.7	18	108
500	2	-	45	439	300	1.6	15	109

$^a t_{1/2}$ in sec.

Table 3. Effect of CTAB on the k_c/k_d Ratios

Fluorescer	no CTAB	with 1.0×10^{-5} M CTAB
Anthracene	1.4×10^3	2.6×10^3
1-Aminoanthracene	3.5×10^4	1.0×10^5

Concentration: 3.0×10^{-3} M DNPO, 2.0×10^{-2} M H_2O_2, 1.2×10^{-4} M imidazole in CH_3CN.

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noanthracene ϕ_{ex} to be increased by 62% upon the addition of CTAB.

This means that the complex (XF) results in higher yield of excited state (F*) of 1-aminoanthracene but lower excited state yield of anthracene in the presence of surfactants than those in the absense of surfactants, respectively. The cause of this opposite trend of ϕ_{ex} in the presence of surfactants is not clear at the present, but is speculated that surfactants affect the recombination process of the radical ions which are produced *via* electron transfer described as[12]

$$X + F \longrightarrow [X^{\overline{\cdot}} \text{---} F^{\dot{+}}] \longrightarrow F^* + \text{products} \qquad (4)$$

The ϕ_{ex} of 1-aminoanthracene was enhanced since both radical ions are possibly stabilized in the polar region of the surfactants and thus the recombination that results in the excited state is apparently enhanced. The radical anion is assumed to be polar albeit its structure is still in controversy. On the other hand, the radical cation of anthracene, due to its hydrophobicity, is apparently migrated and located in the nonpolar region of the surfactants. Thus the separation between radical ions becomes so large that the excitation is interfered. In is not uncommon that radical species are stabilized in a micellar medium. Nitrobenzene radical anion, *e.g.*, is stabilized in SDS micelle when Li^+ is present.[13] Furthermore, Birks and coworkers reported earlier that the stability of the charge transfer complex or radical cation produced from electron transfer may be greater for amino-PAH than other fluorescers.[3b]

When [surfactant] becomes too high, however, I_{CL} shows a decrease. Since I_f was not varied at such high [surfactant] it appears that the reaction between X and F was probably interfered with large concentration of surfactant. At the present it is not certain which species are involved in the competing reaction that reduces I_{CL} and which species are more stabilized in the presence of surfactant. Further studies are underway to elucidate the complex nature of the energy transfer. Nevertheless, it is highly desirable from analytical viewpoint that the sensitivity of amino-PAH detection can be improved by using surfactants over other fluorescers.

References

1. S. Kobayashi and K. Imai, *Anal. Chem.*, **52**, 424 (1980).
2. V. K. Mahaut, J. N. Miller, and H. Tharkar, *Anal. Chem. Acta*, **145**, 203 (1983).
3. (a) K. W. Sigvardson and J. W. Birks, *Anal. Chem.*, **55**, 432 (1983); (b) K. W. Sigvardson, J. M. Kennish, and J. W. Birks, *Anal. Chem.*, **56**, 1096 (1984).
4. A. J. Weber and M. L. Grayeski, *Anal. Chem.*, **59**, 1452 (1987).
5. W. L. Hinze, "Solution Chemistry of Surfactants", K. Mittal, Ed., Plenum New York, Vol. 1, p. 79 (1979).
6. L. L. Klopf and T. A. Nieman, *Anal. Chem.*, **59**, 1539 (1984).
7. T. E. Riehl, C. L. Malehorn, and W. L. Hinze, *Analyst*, **111**, 931 (1986).
8. E. J. Woolf and M. L. Grayeski, *J. Lumin.*, **39**, 19 (1987).
9. S. C. Kang and K. J. Kim, *Bull. Korean Chem. Soc.*, **11**, 224 (1990).
10. F. J. Alvarez, N. J. Parekh, B. Matuszewski, R. S. Given, T. Higuchi, and R. L. Schowen, *J. Am. Chem. Soc.*, **108**, 6435 (1986).
11. C. L. R. Catherall, T. F. Palmer, and R. B. Cundal, *J. Chem. Soc. Faraday Trans 2*, **80**, 823; 837 (1984).
12. S. C. Kang, S. K. Lee, S. H. Song, and K. J. Kim, *Bull. Korean Chem. Soc.*, **10**, 408 (1989).
13. G. B. Schuster and S. P. Schmidt, *Adv. Org. Chem.*, **18**, 187 (1982).
14. G. L. McIntire, D. M. Chiappardi, R. L. Casselberry, and H. N. Blount, *J. Phys. Chem.*, **86**, 2632 (1982).

Catalytic Effects of Anion-Exchange Resins on the Methylation of 2-Methoxyphenolate Anion

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Synthetic polymers have been employed as catalysts for many organic reactions. The catalysis may arise from the increase in the effective concentrations of reactants on the surface of the polymer,[1] changes in the pH of the microenvironment on the polymer,[2] or the increased hydrophobicity of the polymer domain.[2] Ion-exchange resins catalyze some organic reactions by acting as heterogeneous sources of acids and bases.[3]

Alkylation of the carbanion derived from ethyl 2-ethylacetoacetate with ethyl bromide is catalyzed by anion-exchange resins.[4] The anion-exchange resins contain quaternary ammonium ions. When the carbanion is adsorbed on the polymer surface, the effective size of the counter-cation is increased. Due to the reduced electrostatic interaction with the counter-cation, the carbanion becomes more naked, resulting in the increase in the intrinsic reactivity. In addition, the naked carbanion of the 2-ethylacetoacetate ester appears to be partially relieved of the steric crowdedness, leading to further rate enhancement.

Addition of crown ethers also catalyzed the ethylation of the carbanion derived from ethyl 2-ethylacetoacetate.[5] This is also attributable to the increase in the effective size of the counter-cation. Whether the reduced electrostatic interaction of the counter-cation with the anionic reactant results in the rate-enhancement or rate-retardation, however, depends on the type of the reaction.[6] If the transition state possesses smaller density of negative charge compared with the ground state, the reaction would be accelerated considerably by reducing the electrostatic interaction.

In the present study, the catalytic effects of the anion-exchange resins is extended to the reaction of 2-methoxyphenolate with methyl iodide. Unlike the alkylation of the carbanion of ethyl 2-ethylacetoacetate, this reaction does not in-