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The Chemiluminescence of Indole Accompanying Oxidation by Perbenzoic Acid

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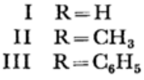
Previously we[1] investigated the chemiluminescence of indoles using two types of reaction: *A*, the indoles in alkaline ethanol, to which a mixture of 3% hydrogen peroxide and 3% potassium ferricyanide has been added, and *B*, the indoles in DMSO, to which a 5 N potassium hydroxide aqueous solution has been added. We[2] also proposed the mechanism of chemiluminescence in the system B, a mechanism which is in accord with the report by McCapra *et al.*[3]

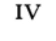
The previous papers[1-5] on the chemiluminescence of indoles have dealt almost exclusively with the reaction in a basic solution. Now we have found a chemiluminescent reaction of indoles which proceeds in a chloroform solution by means of perbenzoic acid. This is a new chemiluminescence of indoles in that it takes place in the absence of a base.

Results and Discussion

Indole (I), 3-methylindole (II), and 3-phenylindole (III) were chosen as typical indole compounds. The compound II is suitable for the investigation of the inductive effect of a 3-substituent on the indole nucleus, and compound III, for a study of the mesomeric effect.



I R=H
II $R=CH_3$
III $R=C_6H_5$



IV

Witkop and Fielder[6] reported that II gave *o*-formamidoacetophenone (IV) by perbenzoic acid oxidation. We observed the emission of light in this reaction. Thus we measured the chemiluminescence of indoles which accompanied the oxidation reaction caused by perbenzoic acid in chloroform. The relative intensities of the chemiluminescence of I, II, and III are summarized in Table 1. As a comparison, the relative intensities in the two systems, A and B, are also quoted from our previous report.[1]

TABLE 1. RELATIVE INTENSITIES OF CHEMILUMINESCENCE OF INDOLES

Indoles (10^{-2} mol/*l*)	Perbenzoic acid		A	B
	(10^{-2})	(10^{-1})		
Indole (I)	0.6	9.6	1	1
3-Methylindole (II)	8.2	71	0.5	13
3-Phenylindole (III)	0.1	1.5	90	0

A: $EtOH-KOH-H_2O_2-K_3Fe(CN)_6$
B: $DMSO-KOH-O_2$

The intensity of chemiluminescence by perbenzoic acid decreases in the order: II>I>III, while that in the system A decreases in the order: III>I>II, and that in the system B: II>I>III. The order in each system is considered to depend on the substituents on the 3-position. The change in the order between the reaction systems suggests a difference in the reaction mechanism. It is probable that the mechanism of chemiluminescence in the system A involves the formation of a hydroperoxy radical, a process which can be expressed by the equation: $H_2O_2+Fe^{3+}\rightarrow HOO\cdot+Fe^{2+}+H^+$. The system B involves a cyclic peroxide intermediate.[2,3] As the order in the perbenzoic acid oxidation system is similar to that in the system B rather than to that in the system A, the mechanism of the chemiluminescence of oxidation by perbenzoic acid seems to be analogous to that of the chemiluminescence with a base and oxygen in DMSO.

After the chemiluminescent reaction of II by perbenzoic acid, the ultraviolet absorption maxima of II at 275 and 291 nm change to 260 and 320 nm and the fluorescence maximum, 465 nm,

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[1] N. Sugiyama, M. Akutagawa, T. Gasha, Y. Saiga and H. Yamamoto, This Bulletin, **40**, 347 (1967).

[2] N. Sugiyama and M. Akutagawa, *ibid.*, **40**, 240 (1967); N. Sugiyama, M. Akutagawa and H. Yamamoto, *ibid.*, **41**, 936 (1968); N. Sugiyama, H. Yamamoto, Y. Omote and M. Akutagawa, *ibid.*, **41**, 1917 (1968).

[3] F. McCapra and Y. C. Chang, *Chem. Commun.*, **1966**, 522.

[4] G. E. Philbrook, J. B. Ayer, J. F. Garst and J. R. Totter, *Photochem. Photobiol.*, **4**, 869 (1965).

[5] A. W. Berger, J. N. Driscoll and J. A. Pirog, *ibid.*, **4**, 1123 (1965).

[6] B. Witkop and H. Fielder, *Ann.*, **558**, 91 (1947).

changes to 497 nm. These facts shown that the indole chromophore changes into another one. The spectral data of II are summarized in Table 2.

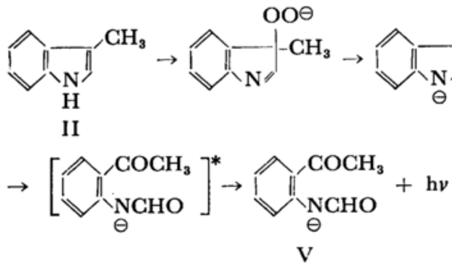
Table 2. Fluorescence and chemiluminescence maxima of 3-methylindole (nm) in $CHCl_3$

	Fluorescence	Chemiluminescence
3-Methylindole(II)	465 (497) (495)*	weak 495*
o-Formamidoacetophenone (IV)	525 495*	
Perbenzoic acid	470	
Benzoic acid	no	

* in DMSO-alkali condition
( ) fluorescence after chemiluminescent reaction

The presence of benzoic acid or perbenzoic acid was not proved to have any influence upon the chemiluminescence. The chemiluminescent spectrum of II by perbenzoic acid in chloroform could not be measured because of the weakness of the emission and the short life-time of the emitter. However, it was proved that 40% of the IV was produced from the chemiluminescent reaction in chloroform by perbenzoic acid. The product was identified with an authentic sample by TLC and by a study of the spectral data.

The spectrum of the chemiluminescence of II in DMSO in the presence of oxygen and a base (type B) was also measured (Table 2); from its reaction mixture, 15% of the IV was obtained, along with some unreacted II. From the facts that the chemiluminescence maximum is in accord with the fluorescence maximum after the chemiluminescent reaction in the DMSO-oxygen-base system, we propose the following reaction mechanism for the chemiluminescence of II in a basic solution.



Scheme

It is clear that the emitter in a basic solution is the singlet excited state of the *o*-formamidoacetophenone anion (V). However, the excited state of V cannot be the emitter in the chemiluminescence by perbenzoic acid because the fluorescence maximum of IV in chloroform is different from that after the chemiluminescent reaction of II. Therefore, we tentatively suggest that the emitter of this chemiluminescence is different from the anion of IV, but it might be IV itself. The difference in the fluorescence maxima might result from the fluorescence of the unreacted indole or the peracid.

Experimental

Materials. The commercial indole (I) was recrystallized from ligroin and sublimed *in vacuo*. Mp 52°C. The commercial 3-methylindole (II) was also purified in the same way; mp 95°C. The 3-phenylindole (III) was synthesized by a modification of the procedure of Fischer;[7] mp 88.8°C. The *o*-formamidoacetophenone (IV)[8] was prepared from *o*-aminoacetophenone;[9] mp 78.2—78.5°C. The perbenzoic acid[10] was freshly prepared before the oxidation experiment.

Chemiluminescence Intensity. One milliliter of a indole chloroform solution (10^{-2} mol/*l*) was mixed with 1 m*l* of a perbenzoic acid chloroform solution (10^{-1} mol/*l*) in a glass tube (10 mm × 70 mm). Moreover, the light intensity was measured by a modified Model 139 Hitachi Photometer.

Spectra. The chemiluminescent spectrum was measured by means of a EPS-2 Hitachi Spectrophotometer into which 5 m*l* of a 3-methylindole DMSO solution (10^{-1} mol/*l*) and 2 g of solid potassium hydroxide were bubbled by an oxygen stream. The fluorescence spectrum was measured by the same photometer equipped with a high-pressure mercury lamp (365 nm line for excitation).

Separation and Identification of Products. Ten milliliters of a 3-methylindole solution (10^{-2} mol/*l*) were mixed with 10 m*l* of a perbenzoic acid chloroform solution (10^{-2} mol/*l*). The evaporation residue showed a main spot with R_f 0.60 (Wakogel B-5) upon TLC with a benzene-ether (1 : 1 v/v) mixture. The product was purified by means of a silica-gel column (Wakogel C-200) with benzene. The ultraviolet absorption spectrum of this product was identical with that of *o*-formamidoacetophenone.

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7) E. Fisher and T. Schmidt, *Ber.*, **21**, 1811 (1887).

8) R. Camps, *ibid.*, **34**, 2703 (1901).

9) H. G. Walker and C. R. Hauser, *J. Am. Chem. Soc.*, **68**, 1386 (1946).

10) G. Brown, C. R. Noller and P. Liang, "Organic Synthesis," Coll. Vol. I, p. 431 (1956).