A Chemiluminescent Iminehydroperoxide

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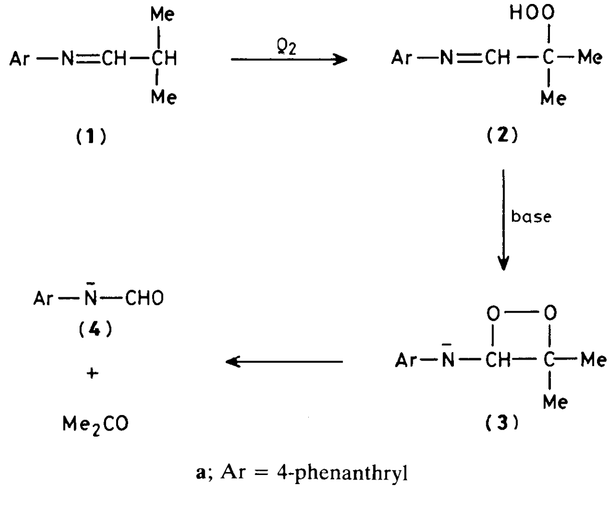
Autoxidation of the imine prepared from 4-phenanthrylamine and isobutyraldehyde gave a chemiluminescent hydroperoxide; comparison of the chemiluminescence of the imine with that of the peroxide gave strong evidence for the formerly postulated mechanism of the chemiluminescent reaction of imines.

The chemiluminescence of Schiff's bases (imines) is of interest in relation to Latia[1] and bacterial bioluminescence.[2] Imines from isobutyraldehyde and aromatic amines have been studied extensively since they exhibit strong chemiluminescence,[3] although isolation of the imines is usually difficult. The chemiluminescent reaction of the imines (1) has been presumed to proceed *via* the hydroperoxide (2) and the dioxetane (3). The same intermediates, (2) and (3), have also been postulated for the chemiluminescence of aminotrioxanes.[4,5] However, the two intermediates have been neither isolated nor detected.[6] In this communication, we report the isolation of a chemiluminescent imine and the corresponding hydroperoxide. Direct comparison of the chemiluminescence of the two compounds provides strong evidence for intermediacy of the hydroperoxide (2) in the chemiluminescence of the imine (1).

N-(2-Methylpropylidene)-4-phenanthrylamine (**1a**) was prepared from 4-phenanthrylamine and isobutyraldehyde in 64% yield. The hydroperoxide (**2a**) was obtained in 12% yield when a solution of (**1a**) in hexane and isobutyraldehyde was left at room temperature in the presence of air. The structures of (**1a**) and (**2a**) were determined by elemental analyses and spectral data [*e.g.* (**2a**): m.p. 124—125 °C; i.r. (KBr) 3140 and 1640 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 1.64 (6H, s, Me), 6.89 (1H, m, Ar), 7.91 (1H, s, N=CH), 7.21—8.00 (7H, m, ArH), 9.18 (1H, s, OOH, exchangable with D_2O), and 9.43 (1H, m, ArH); ^{13}C n.m.r. ($CDCl_3$) δ 22.0 (q, Me), 83.8 (s, C–O), 117.8 (d, ArC), 126.1—133.7 (ArC), 150.2 (d, ArC), and 166.7 (d, C=N); M^+, *m/z* 279]. Among nineteen† aromatic amines that we have examined, only 4-phenanthrylamine gave the corresponding iminehydroperoxide.

The chemiluminescence of (**1a**) was observed in dimethyl sulphoxide (DMSO) with potassium t-butoxide in the presence of oxygen. The luminescence faded when argon was passed through the mixture. The reaction of (**2a**) with Bu^tOK in DMSO led to emission of a flash of light even under argon. Both (**1a**) and (**2a**) emitted bluish green light on treatment with the base, and produced the amide corresponding to (**4a**). The chemiluminescence spectra ($\lambda_{max.}$ 483 nm) of the two compounds were in accord with the fluorescence spectrum of the corresponding amide in the same system.[3,4] The total



a; Ar = 4-phenanthryl

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† We studied aniline and its derivatives (2-, 3-, 4-Me; 2,4-, 2,5-, 2,6-, 3,4-Me_2; 2,4,6-Me_3), naphthylamines (1-, 2-), anthrylamines (1-, 2-, 9-), and phenanthrylamines (1-, 2-, 3-, 4-, 9-).

emission of (**2a**) was comparable with that of (**1a**),‡ and the chemiluminescent reaction of (**2a**) was considerably faster than that of (**1a**) as expected. These results give almost conclusive evidence for the intermediacy of the hydroperoxide in the chemiluminescent reactions of the imines and the aminotrioxanes.

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‡ The total emission of the chemiluminescence of (**2a**) was about 4% of that for 3-isopropyl-6,6-dimethyl-5-(9-anthrylamino)-1,2,4-trioxane[4,5] under the same conditions.