Chemiluminescence of *N*-Methylacridone Induced by Potassium Superoxide

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Summary The chemical reaction between *N*-methylacridone and potassium superoxide is chemiluminescent and appears to involve the generation of the excited *N*-methylacridone radical anion.

The chemical reactions which generate *N*-methylacridone (NMA) in the excited state have been widely investigated. Thus, the chemiluminescence produced in the reactions of *NN'*-dimethyl-9,9'-biacridinium salts with hydrogen peroxide in basic solution[1] or with electrochemically generated superoxide ion,[2] the addition of singlet oxygen to 10,10'-dimethyl-9,9'-biacridylidene,[3] the one-electron oxidation of *N*-methylacridone ketyl radical anion ($NMA^{\cdot-}$),[4] and other chemical reactions of the acridine system,[5] has been shown to result primarily from the decay of excited NMA to its electronic ground state.

We observed that the chemical reaction between NMA and potassium superoxide, KO_2, is also accompanied by a visible light emission. The recorded emission spectrum resulting from the mixing of saturated dry Me_2SO solutions of NMA and KO_2 in a fast flow system, exhibited a broad emission band with three peak maxima at 470, 494, and 532 nm of the relative intensities 1·5:2·5:1, respectively. In contrast, the fluorescence spectrum of NMA in Me_2SO solution, had two peaks at 421 and 440 nm. Identical emission bands to those from the chemiluminescent reaction, in addition to the bands of NMA fluorescence, were recorded in the fluorescence spectrum obtained by reflection from the already mixed reagents, using incident light of wavelength 365 nm. Addition of water modified the emission recorded, to that of pure NMA. The work-up of the reaction mixture resulted in the recovery of starting NMA.

These results can be explained by the following mechanism for the chemiluminescence observed:

$$\mathrm{NMA} + \mathrm{O_2^-} \longrightarrow [\mathrm{NMA}^{\cdot-}]^* + \mathrm{O_2}$$

$$[\mathrm{NMA}^{\cdot-}]^* \longrightarrow \mathrm{NMA}^{\cdot-} + h\nu$$

This scheme is supported by the fact that the fluorescence spectrum of *N*-methylacridone radical anion generated by alternative methods, such as sodium reduction of NMA in dimethoxyethane[4] or photolytic reduction in Me_2SO solution containing KOH[6] was found to exhibit the same bands as the chemiluminescence spectrum of the reaction between KO_2 and NMA. The primary step of the suggested mechanism, the one-electron transfer from the superoxide radical anion to NMA, is confirmed by e.s.r. data. Since the redox potential of O_2–O_2^- is 0·56 V in basic solution,[7] an expected feature of this superoxide anion is the ability to act as a reductant in the presence of electron acceptors. Thus, we have shown that the intermolecular interaction between superoxide and quinones spontaneously generates semiquinone anion radicals.[8] The radical expected from the reaction of superoxide ion, O_2^-, with NMA, *N*-methylacridone ketyl, was detected in a continuous fast flow system by mixing the separate Me_2SO solutions of KO_2 and NMA in the immediate vicinity of the e.s.r. spectrometer cavity. Under our detection conditions, a spectrum composed of five broad lines was observed which is characteristic of ketyls with this type of structure.[6] In the stationary mixture, no signal was obtained. However, by u.v. irradiation of this mixture, the signal could be regenerated.

The reaction between KO_2 and NMA can be explained in terms of a chemiluminescent electron-transfer process.[4] Assuming that this reaction involves only the transfer of an electron from O_2^- to the acceptor, it is possible that such a large amount of energy is released in such a short time that it cannot be converted into vibrational energy quickly enough. Consequently it causes the electron to occupy an excited level rather than a ground state one.

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