Chemiluminescent Oxygenation of 9,10-Dicyanoanthracene Radical Anion

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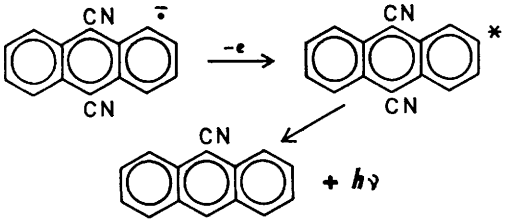
Summary The oxidation of 9,10-dicyanoanthracene radical anion with peroxides or oxygen is chemiluminescent: the former appears to be a simple electron-transfer oxidation to produce excited 9,10-dicyanoanthracene whereas the latter involves oxygenation to produce the excited 10-cyano-9-anthrolate anion.

CHEMILUMINESCENT reactions of electron-transfer oxidations of anion radicals of fluorescent aromatic compounds have been studied extensively.[1] We have found that the oxidation of 9,10-dicyanoanthracene[2] anion radical ($\mathrm{DCA}^{\overline{\cdot}}$) with benzoyl or hydrogen peroxide in deaerated dimethylformamide (DMF) is chemiluminescent. Strong but short-lived emission occurs at 445 and 460 nm. No emission is detectable at 380 and 535 nm.† The fluorescence spectrum of DCA has maxima at 445 and 470 nm (Figure). It thus appears that this reaction is another example of a chemiluminescent electron-transfer oxidation of the radical anion of a fluorescent aromatic compound analogous to 9,10-diphenylanthracene.



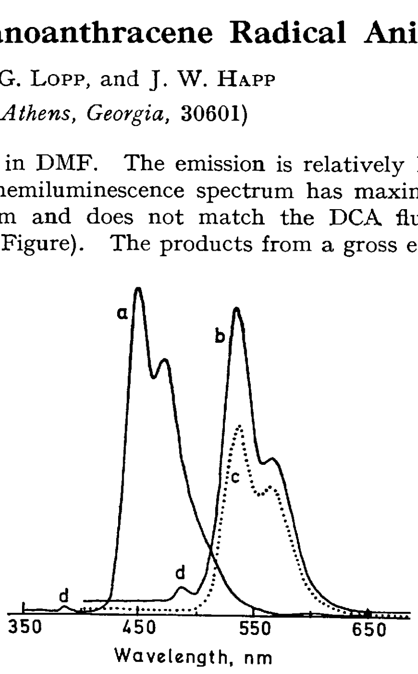


FIGURE. (A) *Fluorescence spectrum of* 9, 10-*dicyanoanthracene in DMF*; (B) *fluorescence spectrum of* 10-*cyano*-9-*anthrolate anion in DMF*; (C) *chemiluminescence spectrum of oxygenated* 9, 10-*dicyanoanthracene radical anion in DMF* (*as described in the text*); (D) *scatter peak from excitation. All experiments recorded on either a Perkin Elmer MPF-2A or Aminco Bowman spectrophotofluorometer.*

A more novel reaction occurs when $\mathrm{DCA}^{\overline{\cdot}}$ reacts with air or oxygen in DMF. The emission is relatively long lived and the chemiluminescence spectrum has maxima at 535 and 565 nm and does not match the DCA fluorescence spectrum (Figure). The products from a gross electrolysis at −1·0 volt *vs.* SCE‡ of a 0·035 M-solution of DCA in DMF containing tetraethylammonium perchlorate through which oxygen was bubbled continuously until chemiluminescence ceased (18 hr.), were separated on an alumina column. In addition to anthraquinone, unreacted DCA and other

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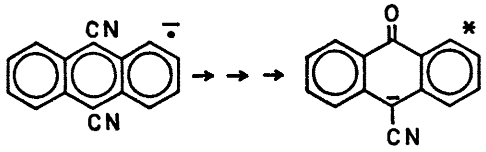
† Separate experiments were performed wherein $\mathrm{DCA}^{\overline{\cdot}}$ was electrolytically produced in deaerated DMF containing tetraethylammonium perchlorate to which either solid benzoyl peroxide or 1 drop (per 2 ml solution) 30% H_2O_2 was added.

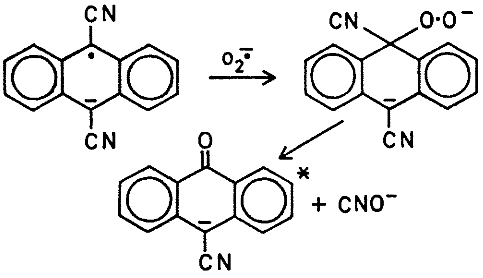
‡ $E_{\frac{1}{2}}$ = − 0·80 and − 1·58 volts *vs.* SCE for 1 mM-DCA in DMF containing 0·1M tetraethylammonium perchlorate.

unidentified products, a compound identical with 10-cyano-9-anthrol[2] was isolated The fluorescence spectrum of this compound in DMF (but not in dilute acetic acid in DMF) matches the chemiluminescence spectrum obtained from the reaction of DCA$^{\cdot-}$ with oxygen (Figure) The structure of the emittor in the oxygenation of DCA$^{\cdot-}$ is thus assigned to 10-cyano-9-anthrolate anion (CNA$^-$)



The possibility of exciting CNA$^-$ by a non-chemical route i e energy transfer from DCA* (if produced by oxidation of DCA$^{\cdot-}$ by oxygen or superoxide ion) was checked by recording the fluorescence spectrum of a DMF solution of DCA and CNA$^-$ irradiated at the absorption maximum of DCA (400 nm) A relatively weak fluorescence for CNA$^-$ was observed in addition to a strong fluoroescence of DCA Increase in concentration of CNA$^-$ decreased the fluorescence of DCA Similar results were obtained from a sample of an electrolysed solution Although these experiments show that energy transfer is possible it seems unlikely that this is the CNA$^-$ excitation mechanism in the chemiluminescent reaction at the concentration of CNA$^-$ probably present at the electrode surface

It is significant to note that the 10-cyano-9-anthrolate anion is π-isoelectronic with *N*-methylacridone which is known to be the emittor in the chemiluminescent oxygenation of *N*-methyl-9-cyanoacridan in basic solution [3,4] The same reactions for DCA are feasible



It is not known at this time whether oxygen or superoxide ion is the oxygenating agent [5]

In addition DCA$^{\cdot-}$ can be detected by e s r and the same chemiluminescence is observed in the addition of cyanide ion to air-saturated solutions of 9-cyanoanthracene in DMF [5]

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[2] Synthesized by the method of C Dufraisse and J Mathieu *Bull Soc chim France*, 1947, 302

[3] F McCapra D G Richardson, and Y C Chang, *Photochem and Photobiol* , 1965, **4** 111, F McCapra and D G. Richardson, *Tetrahedron Letters* 1964, 3167

[4] J W Happ and E G Janzen, *J Org Chem* , 1970, **35**, 96, see also K E Whitaker and H R Snyder, *ibid* , p 30, J W Happ and E G Janzen in preparation

[5] M D Malbin and H B Mark, jun , *J Phys Chem* , 1969, **73** 2786