Chemiluminescence in the Reaction of Ozone with 10,10′-Dimethyl-9,9′-biacridylidene

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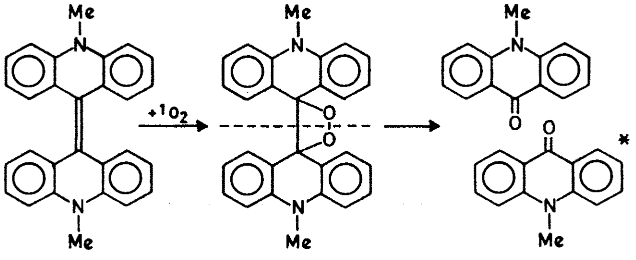
Summary A chemiluminescent reaction of ozone with 10,10′-dimethyl-9,9′-biacridylidene is described and discussed.

THE CHEMILUMINESCENT reaction of singlet oxygen with 10,10′-dimethyl-9,9′-biacridylidene (DBA) was recently described by McCapra and Hann[1] and attributed to the intermediate formation of the 9,9′-dimethylbiacridyl dioxetan.† The reaction of DBA with ozone was said to be a dark reaction although a high yield of *N*-methylacridone is obtained. No experimental conditions were given.‡



DBA

In connection with an investigation of radical formation in basic solutions of 10,10′-dimethyl-9,9′-biacridinium dinitrate (DBA^{2+})[2] the reaction of singlet oxygen with DBA was attempted. Our results were similar to those reported by McCapra and Hann[1] when NaOCl–H_2O_2 was used in EtOH or when naphthalene-photosensitized oxygen[3] was passed over solid DBA.

Our results using ozone, however, disagree with the findings reported by McCapra and Hann.[1] Light emission is observed from DBA in a variety of solvents which in some cases is even more intense than emission observed from the reaction with NaOCl–H_2O_2.§ Chemiluminescence was observed on bubbling ozone through solutions of DBA in EtOH (abs.), CH_2Cl_2, butanal, *NN*-dimethylformamide (DMF), *NN*-dimethylacetamide, benzene, and pyridine. The light yield increased in the order given over approximately a 10-fold range. A marked ozone concentration effect was observed in DMF. Whereas in EtOH light emission continues, although at a slightly lower level, when the flow of ozone is stopped (Figure), the chemiluminescence in DMF increases to *ca.* 6·5 × the previous level when the flow of ozone is stopped. This "delayed" chemiluminescence is observed in no other solvent and is not present in butanal or *NN*-dimethylacetamide. The introduction of small amounts of water to DMF enhances the delayed light emission. *N*-Methylacridone (NMA) is isolated from these reactions. The light emission matches the fluorescence spectrum of NMA. The *N*-methyl region of the n.m.r. spectrum of DBA showed no unusual absorption or emission (CIDNP) during reaction with ozone in $CDCl_3$.¶ No free radicals are detected by e.s.r. at room temperature in these experiments although the radical cation has been obtained under other conditions.[2,4] Control experiments with NMA in the same solvents gave negligible light emission.

A number of reaction pathways are consistent with mechanisms of ozonolysis of olefins. After the possible initial formation of a π[5,6] and/or charge-transfer complex the formation of a σ-complex (I),[6,7] Staudinger ozonide[8] (II), or a trioxolan (III) can be visualized. Since no e.s.r.

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† Selection rules governing the reaction of singlet ($^1\Delta$) oxygen with olefins have since been obtained by Kearns (D. R. Kearns, *J. Amer. Chem. Soc.*, 1969, **91**, 6554). Since the ease of 1,2-cycloaddition increases with decrease in π-ionization potential of the olefin, singlet oxygen 1,2-addition to DBA should be probable because of the relatively low oxidation potential of DBA (K. D. Legg and D. M. Hercules, *J. Amer. Chem. Soc.*, 1969, **91**, 1902).

‡ After the submission of this manuscript, Dr. McCapra has clarified this point in a personal communication. A solution of ozone in CH_2Cl_2 was added to DBA in $Me_2N\cdot CHO$. Under these conditions "virtually" no light was observed.

§ Dr. McCapra however, has pointed out that the light yield with ozone is low. From their experiments a quantum yield of 1×10^{-3} has been determined.

¶ We are grateful to Dr. R. H. Cox for helping with this experiment.

signal or n.m.r. CIDNP was obtained, no evidence for the existence of radicals or ion-radical pairs was found.

The intermediacy of σ-complexes in ozonization of hindered olefins has been suggested.[6,7] Products isolated from such reactions have been rationalized in terms of the formation of the epoxide and molecular oxygen resulting from the decomposition of the σ-complex. Since the oxygen produced must be singlet oxygen this mechanism provides an attractive explanation for the source of chemiluminescence in the reaction of ozone with DBA. Singlet oxygen produced from the decomposition of the σ-complex could react with DBA to form the dioxetan.

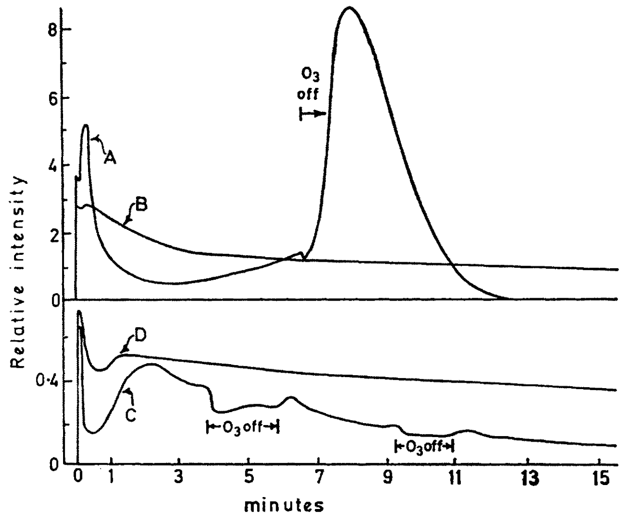
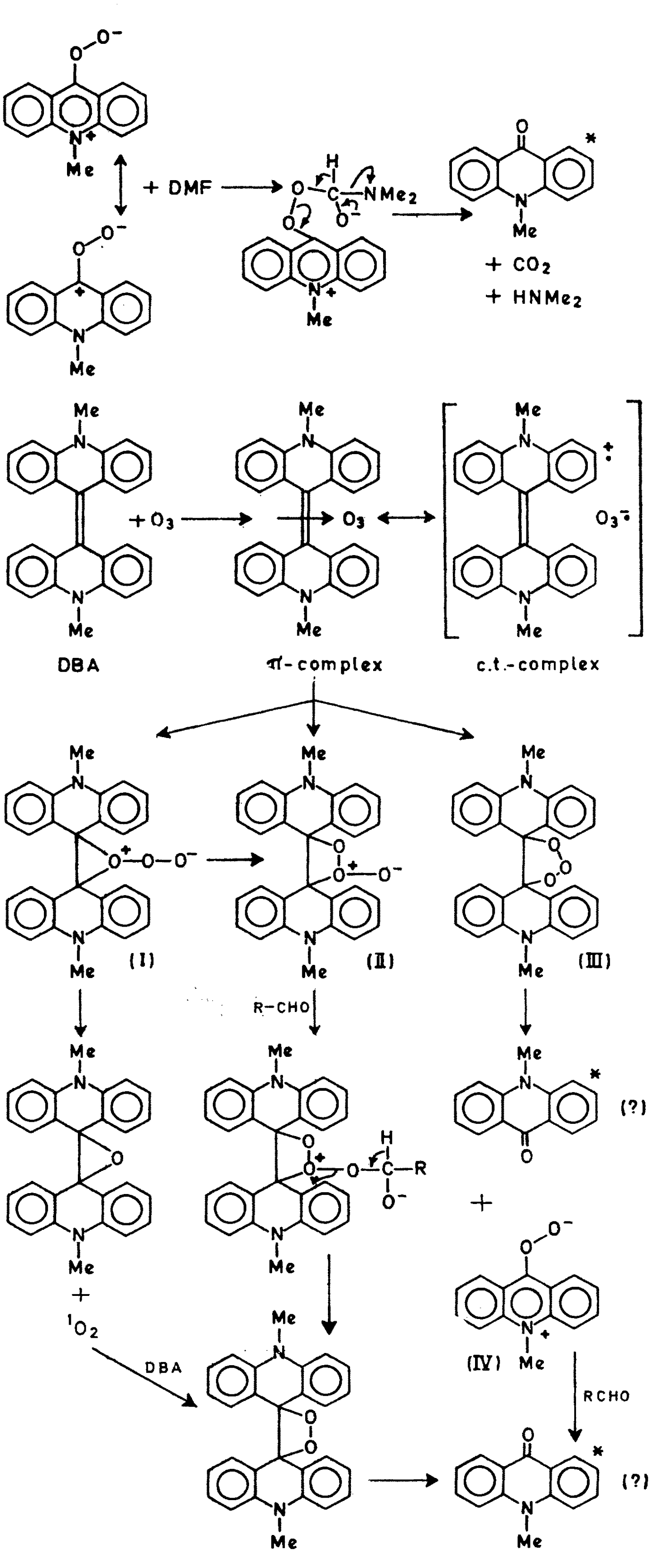


FIGURE. (A). *Relative intensity of light emission from ozone bubbled into* 5 *ml* 10^{-4} M-DBA *in* DMF *at room temperature;* (B) *light emission from sodium hypochlorite and hydrogen peroxide added to* 10^{-4} M-DBA *in* DMF*;* (C) *light emission from ozone bubbled into* 5 *ml* 10^{-5} M-DBA *in ethanol* (*note* 5× *expansion of relative intensity scale*)*;* (D) *light emission from sodium hypochlorite and hydrogen peroxide added to* 10^{-5} M-DBA *in ethanol.*

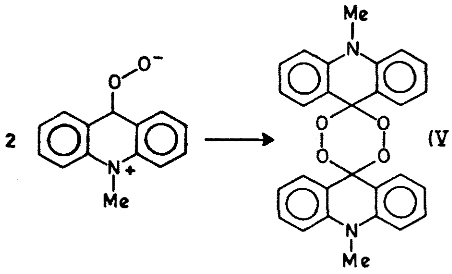
Attempts to obtain proof for the existence of molozonides of the type (II) have not been successful[9] although some results of reactions performed in the presence of certain aldehydes can best be rationalized in terms of this intermediate.[10] Although the reaction of (II) with DMF or butanal would provide an attractive route for the initial chemiluminescence *via* the formation of the dioxetan, the delayed chemiluminescence must be rationalized by some other mechanism since (II) is not expected to be long-lived.

The decomposition of the trioxolan (III), if formed, should provide *N*-methylacridone and (IV), a stabilized hydroperoxide zwitterion. It is possible that this reaction produces enough energy to excite *N*-methylacridone particularly if (III) is not a stable intermediate but rather a very short-lived high-energy species formed from ozone and DBA directly which decomposes immediately to *N*-methylacridone and (IV). The double bond in DBA is considerably strained and thermochemical data[11] indicate that the formation of initial ozonides of the type (III) is exothermic by approximately 60 kcal. In addition (IV) might react with DMF to give excited *N*-methylacridone by the mechanism shown (Scheme).



SCHEME

Some dimerization of (IV) is expected in some solvents



(V)

Although the stability of this diperoxide is unknown, temperatures of at least 150° are required, in general, for decomposition of alicyclic[12] and aryl[13,14] diperoxides. The possible chemiluminescent thermal decomposition of (V) is also of interest.[14]

Inadequate information is available at present to select a mechanism for the chemiluminescent ozonization of DBA although a route involving the σ-complex, (I), or the Staudinger ozonide (II) would appear to account for the initial burst of light observed immediately after introduction of ozone, whereas the longer-lived light emission in DMF might be the result of the chemiluminescent reaction of a more stable intermediate possibly involving a solvent molecule.

A referee has suggested consideration of a radical-induced chemiluminescent air oxidation of DBA. We have only negative evidence for free-radical intermediates. Direct e.s.r. or n.m.r. monitoring of the reaction or indirect radical detection by spin trapping using phenyl t-butyl nitrone[15] gave no results supporting free-radical intermediates. Radical intermediates, nevertheless, cannot be ruled out completely on the basis of these experiments and may be playing some role in the chemiluminescence pathway.

DBA was synthesized by the condensation of *N*-methylacridone with Zn–HCl in alcohol[16] and recrystallized from cyclohexanone or pyridine: m.p. 360° (decomp.). A small amount (*ca.* 1%) of *N*-methylacridone was the only impurity detected by column chromatography (on alumina with C_6H_6–$CHCl_3$). DBA fractions collected from the column showed the same chemiluminescence behaviour as solutions of the above material.

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