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CONTROLLED CHEMILUMINESCENCE DURING THE OXIDATION OF TETRAARYL-$\Delta^{2,2'}$-BIIMIDAZOLIDINES BY TRIPLET OXYGEN IN THE PRESENCE OF FLUORESCERS

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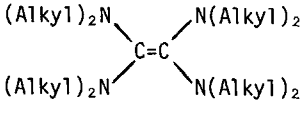
Abstract: Tetraaryl-$\Delta^{2,2'}$-biimidazolidines (3) are stable compounds in the solid state. In solution they react with triplet oxygen. In the presence of fluorescers chemiluminescence is observed. The intensity and lifetime of the chemiluminescence depends on the substituents at the aryl groups and on the solvent.

Electron-rich alkenes devoid of allylic hydrogens can generally be oxidized by singlet oxygen into dioxetanes[1]. These products decompose thermally into carbonyl compounds, and in most cases the reaction is accompanied by the emission of light[2] with a spectrum identical with the fluorescence (or phosphorescence) spectrum of the formed carbonyl compounds.

The very strongly electron-rich tetraaminoethylenes (1) are oxidized by oxygen into a number of products among which ureas predominate. This reaction too is accompanied in most cases by chemiluminescence[3,7], but the emitted light has the same spectrum as the fluorescence emission of the tetraaminoethylene used.



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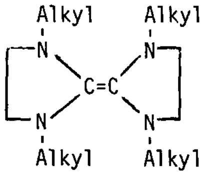

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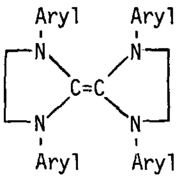

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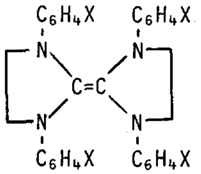
Compounds finally derived from 1 by bridging the nitrogens by an ethylene group, *viz.* 1,1',3,3'-tetraalkyl-$\Delta^{2,2'}$-biimidazolidines 2 show an analogous behaviour[8,9], but, 1,1',3,3'-tetraaryl-$\Delta^{2,2'}$-biimidazolidines[10] (3) do not show chemiluminescence though they are oxidized rapidly in solution[6,10].



3(a-h)

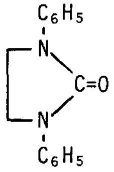
3a X=H
3b X=o-CH_3
3c X=m-CH_3
3d X=p-CH_3
3e X=o-Cl
3f X=m-Cl
3g X=p-Cl
3h X=p-CH_3O

We observed, however, that a solution of 3 (aryl=C_6H_5) in chloroform in the presence of 9,10-dibromoanthracene as a fluorescer showed a bright luminescence when shaken with air. The luminescence lasted several minutes depending on the concentration of 3.

In this paper we describe the influence of substituents in the phenyl group on the oxidation rate of 3 and on the duration of the luminescence.

The compounds 3a-h could easily be prepared from the appropriate 1,2-N,N'-diarylaminoethanes and orthoformate[10]. In contrast with the compounds 1 and 2 the tetraaminoethylenes 3 are quite stable in crystalline form; they can well be stored for months and easily handled.

The main product from the oxidation of 3a in solution appeared to be besides 1,3-diphenylimidazolidone 4[6,10c] (65%) the oxamide 5 (15%), identified by mass and IR spectroscopy. With the aid of gas-liquid chromatography combined with mass spectrometry 1,2-dianilinoethane (6) and N-formyl-1,2-dianilinoethane (7) could be identified as minor compounds (~1%) but traces of several other products were also detected. All these products were formed in the same relative amounts in three different solvents (chloroform, dichloromethane, acetonitrile) in the presence as well as in the absence of the fluorescer dibromoanthracene.



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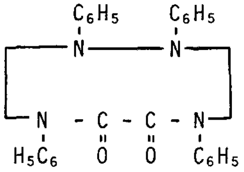

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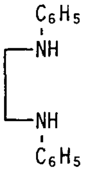

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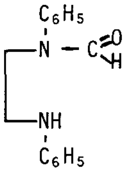

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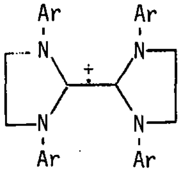
Although the mechanism of the oxidation has not yet been studied extensively, the correspondence between the oxidation products of 1[6,11] and 3a suggests that the oxidation of 3a occurs in a similar way.

The oxidation is accompanied by the occurrence of a purple colour[10]. This has been ascribed to the presence of a radical cation 8 as detected by ESR[12]. An analogous intermediate has been supposed by Urry and Sheeto[6] in the oxidation of tetrakis(dimethylamino)ethylene (1). It is, however, improbable that 8 is on the chemiluminescence reaction path as we found that the lifetime of the radical cation, as measured by ESR and by UV spectroscopy (λ_{max} = 508 nm), is much longer than the lifetime of the chemiluminescence, as measured by fluorimetry.

The concentration of the radical cation reaches its maximum after 37 min, while in this time the intensity of the luminescence has been diminished to 10% of its maximum value.



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By measuring the luminescence of derivatives of 3 it was found that the lifetime increased with decreasing electron-donating ability of the substituents in the range 3d<3c<3a<3g<3f. From measuring the increase of the carbonyl absorptions of the formed imidazolidones (4) it was found that the oxidation rate decreases in the same range. Preliminary determinations of the light yield revealed that this increases also in the same order with the exception of 3c for which the efficiency is close to that of 3f. The oxidation of 3h is so fast, that its preparation under the usual conditions gave only the oxidation product, N,N'-bis(p-methoxyphenyl)imidazolidone.

The orthosubstituted compounds 3b and 3e were oxidized very slowly, what may be due to shielding of the central olefinic bond. Chemiluminescence could not be detected with these compounds.

It was established that the chemiluminescence spectrum equals the fluorescence spectrum of the fluorescer though sometimes the 0-0-band is lacking due to the selfquenching of the fluorescer at the concentration used.

The absence of luminescence when no fluorescer is present is caused by the nonfluorescence of 3 and the very low quantum yield of fluorescence of the main oxidation product.

Using a large range of fluorescers we found chemiluminescence with 1-chloronaphthalene (energy of the S_1-state (ES = 375 kJ/mol) and 1-methylnaphthalene (ES = 376 kJ/mol) and with other fluorescers having ES<377 kJ/mol, but not with naphthalene (ES = 385 kJ/mol) or with fluorene (ES = 398 kJ/mol): so it can be concluded that the energy liberated in the oxidation step of 3 in chloroform is about 380 kJ/mol (90 Kcal/mol).

The chemiluminescence is dependent on the solvent. With dibromoanthracene as the fluorescer light emission during the oxidation of 3a was observed in chloroform, dichloromethane, 1,1,2-trichloroethane, acetonitrile and acetone, but not in methanol, several alkylhalides, dimethylsulfoxide, 1,1,1-trichloroethane, sulfolane, THF and cyclohexane. It is not yet clear whether this is caused by quenching by the solvents or by other factors. The highest oxidation rate and chemiluminescence intensity was observed in chloroform for all compounds. In dichloromethane the oxidation rate was more than ten times lower, and the lifetime of the chemiluminescence was much longer.

In view of the high intensity and long duration of light emission during the oxidation of compounds 3 in several solvents and the presence of a suitable fluorescer, they are very promising for the detection and measurements of low concentration of oxygen. They may be applied to make solutions free of oxygen, and to carry out photoreaction without light[14]. They have several advantages above the compounds 1 and 2, used until now for the determination of oxygen, because 3 can be handled much more easily and their oxidation products do not quench the light emission. With compound 1 or 2 the quenching of the light emission must be overcome by selective solvation or precipitation of the products[15,16].

We used 3a f.i. for measuring the fluorescence spectrum of 1,2-diphenylcyclopentene (9). In the presence of oxygen only the fluorescence spectrum of its photodehydrocyclisation product cyclopentano-phenanthrene can be traced. To observe the fluorescence of 9 oxygen has to be removed by several freeze-thaw cycles at 77 °K[17]. The same result was obtained by adding 1 mg of 3 to the solution of 9 in the fluorimeter cuvet. In this way all oxygen was completely consumed and only the fluorescence of 9 was observed.

REFERENCES

1. A.P. Schaap and K.A. Zaklika in 'Singlet Oxygen', H.H. Wasserman and R.W. Murray, Eds., Academic Press, New York 1979, p. 174.

2a N.J. Turro and V. Ramamurthy in 'Rearrangements in groud- and excited states', P. de Mayo, Ed., Academic Press, New York 1980, 3, p. 1;

b G.B. Schuster and S.P. Schmidt, Adv. Phys. Org. Chem. 18, 187 (1982), V. Gold and D. Berthell, Eds., Academic Press, New York.

3. A.N. Fletcher and C.A. Heller, Photochem. Photobiol. 4, 1051 (1965).

4. C.A. Heller and A.N. Fletcher, J. Phys. Chem. 69, 3313 (1965).

5. J.P. Paris, Photochem. Photobiol. 4, 1059 (1965).

6. W.H. Urry and J. Sheeto, Photochem. Photobiol. 4, 1067 (1965).

7. H.E. Winberg, J.R. Downing and D.D. Coffman, J. Am. Chem. Soc. 87, 2054 (1965).

8. R.P. Westerdahl, U.S. Technical Report AD-766-704 (1973).

9. T.M. Freeman and W.R. Seitz, Anal. Chem. 53, 98 (1981).

10a H.W. Wanzlick and E. Schikora, Chem. Ber. 94, 2389 (1961);

b H.W. Wanzlick and H.J. Kleiner, Angew. Chem. 73, 493 (1961);

c H.W. Wanzlick, F. Esser and H.J. Kleiner, Chem. Ber. 96, 1208 (1963).

11. W.R. Carpenter and E.M. Bens, Tetrahedron 26, 59 (1970).

12. D.M. Lemal and K.J. Kawano, J. Am. Chem. Soc. 84, 1761 (1962).

13. For a description of the measuring technique, see N.J. Turro and M.-F. Chow, J. Am. Chem. Soc. 102, 5058 (1980).

14. E.H. White, J.D. Miamo, C.J. Watkins and E.J. Breaux, Angew. Chem. Int. Ed. 13, 229 (1974).

15. H.E. Winberg, U.S. Patent 3, 264, 221 (1965).

16. W.R. Carpenter and E.M. Bens, U.S. Patent 3, 769, 227 (1973).

17. A.A. Lamola, G.S. Hammond and F.B. Mallory, Photochem. Photobiol. 4, 259 (1965).

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