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CHEMILUMINESCENCE IN THE OXIDATION OF PHENYL-SUBSTITUTED SILOLE RADICAL ANIONS AND DIANIONS

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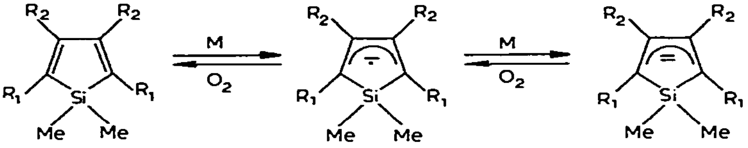
SUMMARY

The emittor in the chemiluminescent electron transfer oxidation of the radical anions and dianions of 1,1-dimethyl-2,5-diphenyl- and 1,1-dimethyl-2,3,4,5-tetraphenylsilole is shown to be the parent compound. Chemiluminescence is reported in the oxidation of the radical anions of 1,2,5-triphenylphosphole, 2,3,4,5-tetraphenylthiophene-5-dioxide and 1,1-diphenyldibenzosilole.

INTRODUCTION

In a previous communication from this laboratory[1] the alkali metal reduction of phenyl-substituted siloles was shown to produce the corresponding radical anions and dianions:



(I) $R_1 = C_6H_5$; $R_2 = H$; M = Li, Na, K, Rb
(II) $R_1 = C_6H_5$; $R_2 = C_6H_5$

The chemiluminescent electron transfer oxidation of these and a number of other closely related ions is reported in this paper.

Chemiluminescence in the oxidation of the radical ions of (I) and (II) was expected because the parent molecules are fluorescent[*,2]. A preliminary study[3] showed that a weak light emission results when these ions are exposed to air. In this paper we describe experiments which allow the assignment of the structure of the emittor. The quantum yields of the electron transfer oxidations have not been determined, however.

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[*] The quantum yields of fluorescence of (I) and (II) were found to be 0.48 and 0.05 respectively when measured relative to anthracene ($\Phi_{fl} = 0.26$)[11]; the extinction coefficients of (I) and (II) are 19326 and 8726, respectively.

EXPERIMENTAL

Solutions of the organometallic ions were prepared under vacuum with rigorous exclusion of oxygen using vacuum line techniques (pressures less than 10^{-3} mmHg). The alkali metal was distilled under vacuum into a side arm separated from the solvent chamber by a medium porosity glass frit (to prevent particles of potassium from interacting with the oxidant). The solvent chamber consisted of a cell appropriate for use in either a UV-visible spectrophotometer or in the light emission photometer. An ESR cell was also attached if desired. The organosilane was dissolved in an etheral solvent [1,2-dimethoxyethane (DME) or tetrahydrofuran (THF)] transferred from a reservoir on the vacuum rack by liquid nitrogen distillation. The sample cell was removed by sealing under vacuum and calmly agitated so that the solution came in contact with the potassium metal surface. The surface area of the alkali metal mirror and hence the reduction rate could be greatly increased if the side arm containing the alkali metal was as large in volume as the solution chamber and if the walls were indented somewhat like a Vigreux distillation column.

For the detection of light emission, a "Firefly" photometer incorporationg an IP21 phototube in an instrument manufactured by the Hruska Radio Company previously described in these laboratories was used[4]. Fluorescence spectra were obtained on the Aminco–Bowman recording spectrophotofluorometer Model 4-8202 and the Turner Associates Model 210. Standard 1 cm cells were used in both of these instruments. For recording the spectra of the chemiluminescent light emission an image intensifier spectrograph constructed by Ness and Hercules[5] was used. A Tektronix oscilloscope camera was used to focus on the P-11 phosphor screen of the image intensifier. Polaroid Type 107 film was used to rapidly obtain the results produced on the screen. The exposure was calibrated by mercury lines from a discharge lamp on the same film and was either evaluated as such by inspection or transferred to chart paper by means of a densitometer from a negative. The mercury lines used were 365, 404, 435 and 546 nm.

The procedure for obtaining light emission data involved either pouring the solution of the organosilane dianion through a "break-seal" from one arm of the cell to another containing solid benzoyl peroxide all under vacuum, or breaking the cell open to air and immediately vigorously introducing the solution of the oxidant under the surface of the organosilane solution by means of a long needle attached to a large syringe. The latter method gave the same results as the former and was more convenient when the sample cell had to be fixed in a specific location for detection of light emission. In the experiments with the image intensifier spectrograph the sample cell was positioned in front of the vertical slits of the aperture. For experiments with "moist" oxygen, a stream of oxygen was saturated with water vapor by prior bubbling through water. Benzoyl peroxide or potassium permanganate solutions in DME or THF were used immediately after being prepared.

All the organosilicon compounds used were a gift of Dr. W. H. Atwell, Dow Corning Company, Midland, Michigan. The 1,2,5-triphenylphosphole was obtained from Prof. T. J. Barton, Iowa State University, Ames, Iowa, and the 1,2,3,4-tetraphenylthiophene-*S*-dioxide was obtained from Prof. M. M. Bursey, University of North Carolina, Chapel Hill, N.C. The 1,1-diphenyldibenzo-1-stannol was obtained from Dr. Francis Johnson, Dow Chemical Company, Wayland, Mass. Benzoyl peroxide was an Eastman Organic Chemical and was used without further purification. 1,2-Dimethoxyethane (Matheson, Coleman and Bell) and tetrahydrofuran (Fischer) were distilled over calcium hydride and stored under vacuum over sodium–potassium benzophenone ketyl on the vacuum system.

RESULTS AND DISCUSSION

Initial exposure of the organosilanes (I) and (II) to the alkali metal produces a blue solution due to the radical anion[1]. Eventually on continued reduction a red solution results which is due to the dianion[1]. The dianion of the diphenyl derivative (I) is quite stable to further reduction with potassium although the tetraphenyl derivative (II) is not[1]. The parent compounds are produced essentially quantitatively when the dianions are exposed to air (by comparison of the NMR peak of the dianion with the peak of the parent after oxidation). A blue flash of light of short duration (6–15 sec) can be observed in a dark room with the dark-adapted eye on opening in air a sample cell containing the dianion. The dianions of (I) and (II) give qualitatively about the same amount of light under the same conditions which was estimated to be approximately 0.05% of the light emission observed in the reaction of 2.5×10^{-4} M luminol in aqueous solution containing 1.00×10^{-2} M potassium peroxydisulfate at pH 11.9 [4]. Oxidations of the dianions with benzoyl peroxide solutions gave higher yields of light (approximately 1000 times greater). Essentially the same amounts of light were detected with the radical anions of (I) and (II) although this question was not pursued quantitatively.

It was of primary interest to obtain the emission spectrum of the emittor in the chemiluminescent reaction. The recording spectrophotofluorometer was useless for this purpose because of the short duration of the light emission. A simple gravity-flow two-bulb continuous mix-and-flow system did not give uniform concentrations of the emitting species partly because the concentration of the dianion was being depleted due to incomplete degassing. Although a better flow-system adequate for this purpose could have been constructed, the existence of an image intensifier spectrograph in these laboratories designed for the purpose of displaying the emission spectrum of a short-lived light source[5] made this unnecessary.

Fig. 1 shows the emission spectrum obtained in the reaction of the anion radical or dianion of (I) with benzoyl peroxide in a mixed DME/THF solvent consisting mainly of DME*. The same spectrum was obtained with moist oxygen** or a solution of potassium permanganate in THF, freshly prepared. Also in Fig. 1 the fluorescence spectrum of (I) is shown in DME. The match with the chemiluminescence spectrum is very good on the low wavelength side. The mismatch on the high wavelength side is due in part to a solvent effect on the fluorescence spectrum of (I) [the fluorescence spectrum of (I) is shifted by 30 nm to longer wavelengths from DME to THF] and is not considered serious.

The light emission spectrum of the oxidation of the radical anion or dianion

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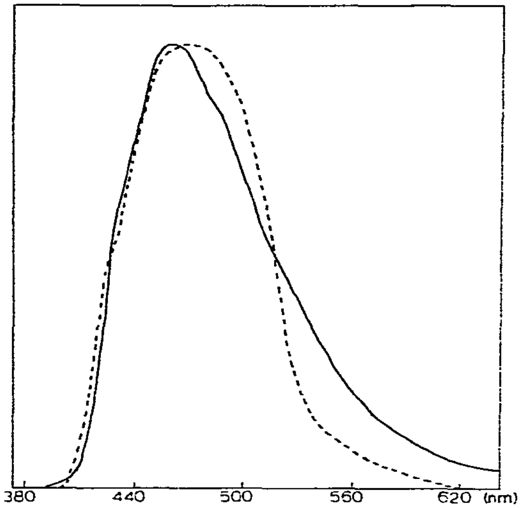
* Through an oversight a solution of benzoyl peroxide in THF was added to a solution of the dianion of (I) in DME. Practical reasons prevented redoing this experiment.

** "Moist" oxygen was found to give "brighter" chemiluminescence (*i.e.* more light) than dry oxygen (see Experimental).



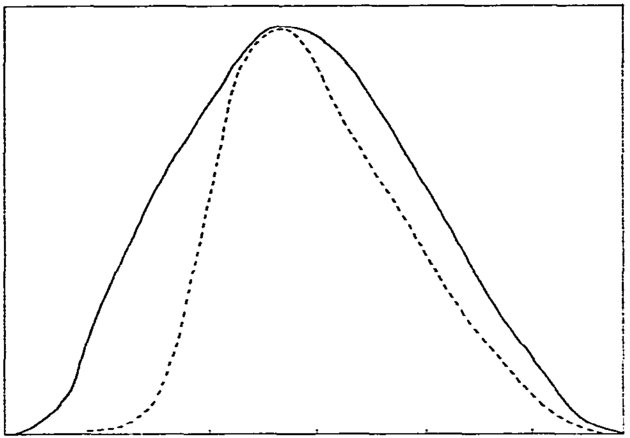


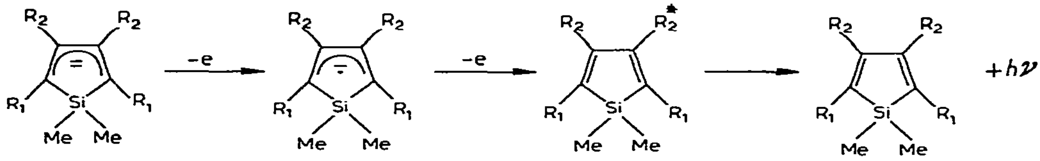
Fig. 1. ------Chemiluminescence of approx. 10^{-4} *M* 1,1-dimethyl-2,5-diphenylsilole dianion in DME/THF oxidized with benzoyl peroxide; —— fluorescence of the above compound in DME.

Fig. 2. ------ Chemiluminescence of approx. 10^{-4} *M* 1,1-dimethyl-2,3,4,5-tetraphenylsilole dianion in DME oxidized by benzoyl peroxide; —— fluorescence spectrum of above compound in DME.

of (II) with benzoyl peroxide or moist oxygen all in DME is shown in Fig. 2. The fluorescence spectrum in DME is also given for comparison. The chemiluminescence spectrum is somewhat broader than the fluorescence spectrum. Since this may be due to an artifact in the method of transcribing the data from the film it is not considered serious.

Control experiments wherein the solvent was exposed to the alkali metal mirror for varying lengths of time and subsequently allowed to react with air gave no chemiluminescence.

Our results lead to the conclusion that the emittor in the electron transfer oxidation of the radical anion and dianion of (I) and (II) is the parent organosilane. We have no evidence supporting a novel chemiluminescent reaction of the dianion and we assume it is first oxidized to the radical anion whose oxidation is chemiluminescent:



Partial results on a number of compounds of similar structure but having the same number of π-electrons as (I) and (II) can be reported. 1,2,5-Triphenylphosphole can be reduced to the blue radical anion with potassium in THF which is only stable at −75°. The ESR spectrum shows two broad lines separated by 28.7 gauss undoubtedly due to the phosphorus splitting in the radical anion*. Further exposure to potas-

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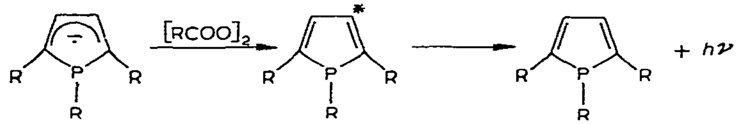
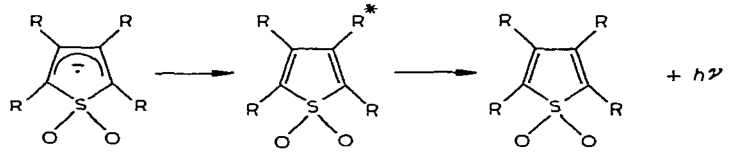
* Phosphorus splitting has been reported with sodium in DME, see ref. 7.

sium destroys the signal and a brown solution results (after 8 h). The exposure of the blue solution of the radical ion to air does not produce chemiluminescence. However oxidation with benzoyl peroxide gives a blue chemiluminescence which resembles the fluorescence color ($\lambda_{max}=510$ nm) of the parent solution. We are at present unable to use the image intensifier spectrograph to verify these observations. We tentatively assign the emittor to the parent phosphole by analogy to the silacyclopentadiene system:



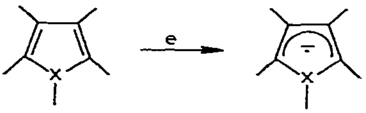
R = phenyl

1,2,3,4-Tetraphenylthiophene-*S*-dioxide can be reduced with potassium in THF to a blue anion radical. The ESR signal consists of a broad singlet. No resolution of the signal could be accomplished. The blue solution becomes purple upon further reduction(2 days) perhaps due to the formation of a dianion. The exposure to air of the purple solution produces chemiluminescence but the maximum for the light emission as determined with the image intensifier spectrograph occurs at a longer wavelength (540±10 nm) than the maximum for the fluorescence spectrum (499 nm in THF). Practical reasons have prevented us from investigating this system in further detail. However, the most likely chemiluminescence mechanism would be analogous to the above:

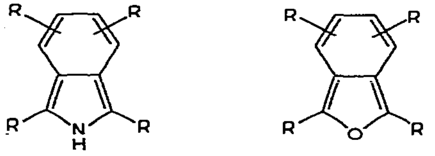


R= phenyl

In summary it can be concluded that radical anions of the general structure,

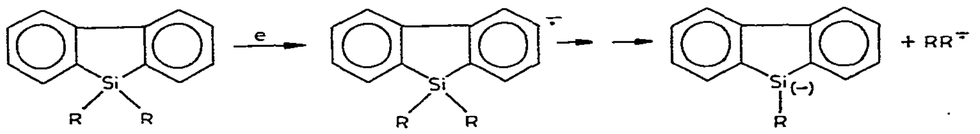


where X is a valence saturated second-row element (silicon, phosphorus, sulfur) produce chemiluminescence in the electron transfer oxidation to the parent compound. Probably in all cases the parent compound is the emittor. It is of interest to note that no example of a chemiluminescent electron transfer oxidation involving a radical anion of an analogous structure where X is a first-row element (boron, carbon, nitrogen, oxygen) has been reported. We have found no light emission in the air or benzoyl peroxide oxidation of the radical anion and (probable) dianion of 2,3,4,5-tetraphenylcyclopentadienone. However polycyclic compounds having a first-row heteroatom incorporated in the same 5-membered ring structure have been shown to produce chemiluminescence when the electrolytically produced anions are oxidized[8]:



R = phenyl

A polycyclic organosilane of previous interest in our laboratory is 1,1-diphenyldibenzosilole (III)[3,9]. Upon reduction the radical anion of (III) is produced[9] which upon further reduction appears to lose a phenyl group to form biphenyl radical anion and presumably the corresponding silyl anion:



(III)
R = phenyl

The exposure of solutions of reduced (III) to air or benzoyl peroxide gives extremely bright light emission [approximately 100 × the amount observed from radical anions of (I) and (II)] which persists over time periods of several minutes [5–10 ml of 0.01 *M* (III) in DME or THF]. The chemiluminescence emission spectra obtained from the image intensifier spectrograph however differ depending on the oxidant used (moist

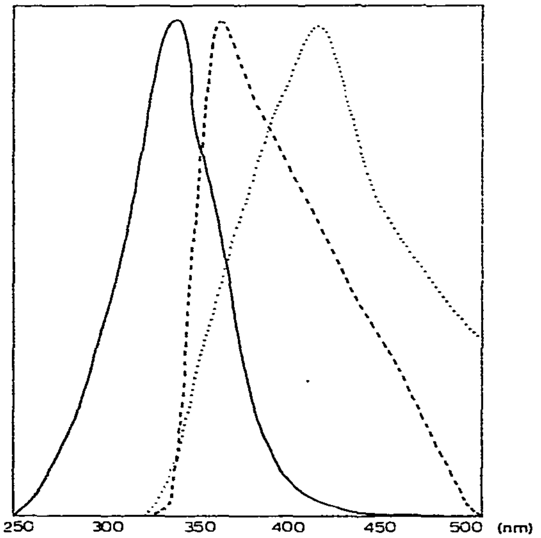


Fig. 3. —— Chemiluminescence of the reduction product of 1,1-diphenyldibenzosilole in DME oxidized by benzoyl peroxide; ······ chemiluminescence of above compound when oxidized with moist oxygen; —— fluorescence of 1,1-diphenyldibenzosilole in DME.

oxygen or benzoyl peroxide) and do not match the fluorescence spectrum of (III) (Fig. 3). Biphenyl radical anion does not give detectable chemiluminescence under comparable conditions. The reduction product of 9,9-diphenylfluorene, 9-phenylfluorene dianion radical[10], also gives no chemiluminescence under these conditions. It is apparent that the chemiluminescent oxidation of the reduction product of (III) does not simply involve the electron transfer oxidation of the radical anion but rather that some other reaction, possibly an oxygenation of the organosilanide anion or radical is causing light emission. As was noted previously[3] (triphenylsilyl)lithium also gives light emission with oxygen although of weaker intensity than the reduction product of (III).

The potassium reduction of 1,1-diphenyldibenzostannol in DME produces a red solution but no radical anion was detected. The oxidation with benzoyl peroxide was chemiluminescent but the light emission was only one hundredth as bright as that observed from the reduction product of (III).

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REFERENCES

1 (a) E. G. Janzen, J. B. Pickett and W. H. Atwell, *J. Organometal. Chem.*, 10 (1967) P6; (b) J. B. Pickett, *An ESR, NMR and Visible U.V. Spectroscopic Investigation of Unsaturated Organosilicon Radical Anions and Dianions*, Ph.D. thesis, The University of Georgia, 1970.
2 E. H. Braye, W. Hübel and I. Caplier, *J. Amer. Chem. Soc.*, 83 (1961) 4406; W. H. Atwell, D. R. Weyenberg and H. Gilman, *J. Org. Chem.*, 32 (1967) 885.
3 E. G. Janzen, W. B. Harrison and J. B. Pickett, *J. Organometal. Chem.*, 20 (1969) P13; W. B. Harrison, *Studies into the Chemistry of the Group IV Organometallic Radicals and Ions*, Ph.D., The University of Georgia, 1971.
4 G. E. Philbrook, J. B. Ayers, J. F. Garst and J. R. Totter, *Photochem. Photobiol.*, 4 (1965) 869.
5 S. Ness and D. M. Hercules, *Anal. Chem.*, 41 (1969) 1467.
6 R. E. Dessy and R. L. Pohl, *J. Amer. Chem. Soc.*, 90 (1968) 1995.
7 C. Thompson and D. Kilcast, *Chem. Commun.*, (1971) 214.
8 A. Zweig, *Advan. Photochem.*, 6 (1968) 425; A. Zweig, A. K. Hoffman, D. L. Maricle and A. H. Maurer, *J. Amer. Chem. Soc.*, 90 (1968) 261.
9 E. G. Janzen, W. B. Harrison and J. B. Pickett, *J. Organometal. Chem.*, 16 (1969) P48.
10 E. G. Janzen and J. L. Gerlock, *J. Organometal. Chem.*, 8 (1967) 354.
11 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley, London, 1970, p. 88.