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Preliminary communication

Chemiluminescence in the oxygenation of potassium organosilanides

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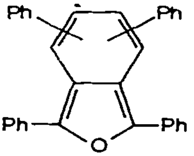
The emission of light in the reactions of certain organic compounds with oxygen[1,2] may be caused by peroxide decompositions[3], electron transfer reactions[4] or formation of excited oxygen[5]. In the first two cases the emitter is normally a fluorescent molecule produced in the reaction or present in the system as an impurity. In a continuation of our previous studies on the chemistry of cyclic unsaturated organosilane radical anions and dianions[6-9], we have searched for chemiluminescence in the reaction of these compounds with air. Since we are not aware of previous reports of observed chemiluminescence from organometallic anions under these conditions our preliminary results of this study are reported here.

The compounds studied are listed in Table 1. In a standard procedure (see experimental section) each organosilane was reduced with potassium in dimethoxyethane at room temperature for a period of many days until no further color change in the solution was observed. The cell was opened to air and light emission monitored. In most cases a short burst of blue-violet light was observed which died away quickly but at a variable rate depending on the compound used. The chemiluminescence from solutions of reduced II and V was readily discernable with the eye in a darkened room. Moist air gave the brightest light emission whereas pure oxygen and pure carbon dioxide gave lower yields of light than dry air.

Although only partial data are available at this time, the mechanism of light emission is clearly of interest. Questions for immediate consideration are: what is (1) the structure of the reduced organosilane, (2) the oxygenation mechanism and (3) the light emitter.

The alkali metal reduction products of the silacyclopentadiene derivatives (I) are the radical anions and dianions[6]. The oxidation of these ions by electron transfer potentially could give the excited state of the parent organosilanes since these compounds are fluorescent[10]. Fluorescent compounds with somewhat analogous structures have shown chemiluminescence if the reduced species is electrolytically oxidized[4,11]:



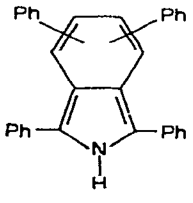
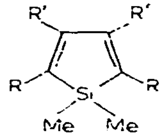
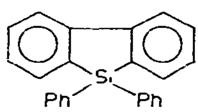
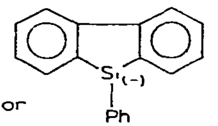
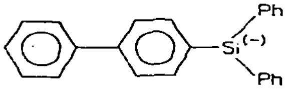
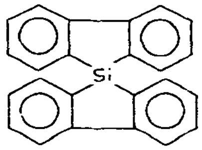
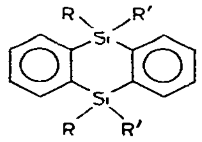
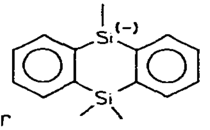
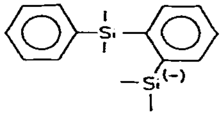


TABLE 1

	Starting organosilane		Probable reduced organosilane	Relative maximum light emission
I		Ia, R = R' = C_6H_5 Ib, R = C_6H_5, R' = H	$Ia^{-\cdot}$, Ia^{2-} $Ib^{-\cdot}$, Ib^{2-}	3.4 1.5
II			 and/or 	100
III			$III^{-\cdot}$, III^{2-}	0.5
IV		IVa, R = R' = Me IVb, R = Me, R' = C_6H_5 IVc, R = R' = C_6H_5	$IVa^{-\cdot}$  and/or 	0.0 2.0 2.8
V	$(C_6H_5)_3SiX$	Va, X = Cl Vb, X = $Si(C_6H_5)_3$	$(C_6H_5)_3Si^{(-)}$	2.1 20.0

The relatively low yield of light was disappointing but further experiments with other oxidizing agents are needed.

The reduction of IVa is known to give the radical anion[7] which appears to be quite stable to further reduction. The reductions of IVb, IVc and II at room temperature lead to unstable radical anions. In the case of II[9] and phenyl- and diphenylsilane derivatives[13] the reduction products apparently decompose by a phenyl— or aryl—silicon bond cleavage since biphenyl radical anion is an ESR detectable product of the decomposition. Probably an organosilanide anion is produced simultaneously. Because of the similarity in structure, triphenylsilanide produced by the reduction of hexaphenyldisilane or triphenylchlorosilane was investigated as well. The aryl-silanides as a group thus react with oxygen with significant light emission.

George and Gilman[14] have shown that the products of the oxygenation of triphenylsilyllithium in tetrahydrofuran or tetrahydropyran at room temperature are triphenylsilanol, triphenylsilane and hexaphenyldisilane (in order of decreasing yield). Probably triphenylsilyl radicals and hydroperoxide anions[15] are intermediate molecules produced in a chain autooxidation as in the case of carbanions[16]. Although chemiluminescence has been detected in the oxygenation of certain carbanions[17] there is no obvious light emission mechanism apparent in this study. Recently the chemiluminescence of phenylmagnesium bromide in oxygen has been attributed to the formation and emission of a small amount of *p*-terphenyl during the oxidation[18]. A similar chemiluminescence mechanism might be operative in the oxygenation of the organosilanides★. Further investigations are underway.

EXPERIMENTAL

Initial experiments were run on samples prepared for ESR studies using standard vacuum line techniques. However, such solutions were in contact with alkali metal and contained metal particles when air was admitted. To eliminate the possibility that the observed chemiluminescence was connected with metal oxidation★★ a cell was constructed wherein the alkali metal mirror was separated from the cell used in the light detector by a fine glass frit. Under these conditions a solution of tetrahydrofuran or dimethoxyethane saturated with potassium metal (up to 60 days) did not emit light upon introduction of air.

The procedure was to make up a solution of the organosilane in dimethoxyethane (approx. 10^{-3} *M*) on a vacuum line in a cell to which a side arm containing freshly distilled potassium separated by a glass frit was attached. The solution was poured onto the potassium and reduction continued with occasional shaking until no further color change was observed (7–22 days). The colors of the radical anions and/or dianions were observed for Ib, III and IVa while for Ia, II, IVb and IVc these colors were replaced by a brown coloration apparently due to decomposition products. The pale yellow of the triphenylsilanide anion was observed before oxygenation for Va and Vb. The cells were opened to air inside a dark housing for the light detector in a dark room. Since the cells were under the partial pressure of solvent vapor, air rapidly saturated the system. The maximum light emission was very rapid (within 5 seconds) and of short duration (approx. 1 minute). The emission is reported as maximum relative intensity obtained from a IP21 phototube incorporated into a "Firefly" photometer manufactured by the Hruska Radio Company previously used in these laboratories[19].

★A referee has suggested consideration of biphenyl radical anion or phenyl potassium as chemiluminescence sources. Although the former might be a possibility in cases where biphenyl anion radical is detected (*e.g.* II) the latter would not appear to be likely since protonation of phenylpotassium in tetrahydrofuran or dimethoxyethane is known to be fast.

★★Freshly cut potassium exposed to humid air will emit a glow of light readily visible in a darkened room (observation first made by J.L. Gerlock in our laboratories).

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