CHEMILUMINESCENCE IN THE REACTION OF SULFONYL CHLORIDES WITH TERTIARY AMINES

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Chemiluminescence was observed in the reaction of RSO_2Cl (R = $c-C_6H_{11}$ (Ia), $p-ClC_6H_4$ (Ib), $p-CH_3C_6H_4$ (Ic), and $PhCH_2$ (Id)) with tertiary amines (triethylamine (IIa), pyridine (IIb), 2,5-dimethylpyridine (IIc), and 2,4,6-trimethylpyridine (IId)) in CH_2Cl_2 (IIIa), Et_2O (IIIb), or benzene (IIIc).

A solution of $6\cdot10^{-4}$–$6\cdot10^{-2}$ mole/liter sulfonyl chloride was added rapidly with rapid stirring to a glass reactor maintained at constant 298 K containing a solution of 1–0.01 mole/liter amine. The chemiluminescence intensity (I_{CL}) was found to depend significantly on the nature of the reagents and falls in the series:
(Id) – (IIc, d) – (IIIa, b) > (Id) – (IIa) – (IIIa, b) > (Id) – (IIb) – (IIIa, b) ≫ (Id) – (IIc, d) – (IIIc) > (Ia, b, c) – (II) – (III).

The major product in the reaction of (Id) with (II) in (IIIa) and (IIIb) is stilbene (IVa), while the major product formed in (IIIc) is PhCCl=SO (IVb). The only product formed in cyclohexane is (IVb) [1]. The chemiluminescence spectrum for the reaction of (Id) with (IIc) in (IIIc) has maxima at 400 and 580 nm. The photoluminescence spectrum of the reaction products in (IIIa), (IIIb), and (IIIc) contain bands at 330, 348, 362, and 386 nm. The former three bands correspond to the fluorescence of (IVa), while the latter band likely corresponds to emission of an exciplex of (IVa) with (II). All these lines are lacking in the photoluminescence spectra of the products in isooctane (apparently, (IVb) does not luminesce).

The chemiluminescence emitter is probably (IVa) formed in accord with a scheme analogous to that proposed by Opitz et al. [2] involving $PhCH{=}SO_2$ (V):

$$PhCH_2SO_2Cl \xrightarrow{(II)} PhCH{=}SO_2 \xrightarrow{(II)} Ph\bar{C}H{-}SO_2{-}\overset{+}{N}R_3 \xrightarrow{(V)} Ph\overline{CH{-}SO_2{-}CHPh} \rightarrow$$
$$\rightarrow PhCH{=}CHPh^*$$

(Furthermore, other emitters are possible such as the exciplex of (IVa) with (II) and an intermediate emitting at 580 nm).

The I_{CL} value increases with increasing initial concentrations of (I) and (II). Linearization of the kinetic curves for chemiluminescence quenching in a plot for log I_{CL} vs. t gives the k_{exp} value. For the reaction of (Id) with (IIb), $k_{ef} = k_{exp}/[II]_0 = 10.6$ and 20.0 liters/mole·sec in (IIIb) and (IIIc), respectively. These values are similar to those obtained from the kinetics for the consumption of (Id) studied by potentiometric titration [3].

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