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CHEMILUMINESCENT INTENSITIES FROM SUBSTITUTED LOPHINES

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Hayashi and Maeda have proposed a preliminary mechanism for the chemiluminescent emission of lophine.[1,2,3] It is proposed that the anion of lophine is oxidized to the dimer, 1,1'-bi-(2,4,5-triphenylimidazolyl). They show that this compound dissociates into a pair of 2,4,5-triphenylimidazolyl radicals. The free radicals are then presumed to react with molecular oxygen to form a peroxide which decomposes immediately with the emission of light.

We have prepared a series of 14 compounds which are derivatives of lophine bearing substituent groups in the 3 and/or 4 positions of the 2-phenyl group. Eight of these compounds are apparently unreported in the literature and two more have not been described. All of these compounds gave satisfactory elemental analyses and satisfactory infrared and ultraviolet absorption spectra, as well as satisfactory chemiluminescence data. The intensities were determined using a 1P21 photo tube coupled to a sensitive amplifier and a pen recorder. The chemiluminescent intensities were determined in a medium consisting of 70 % dimethylsulfoxide - 30 % water, 1 N. in NaOH. The concentration of lophine derivatives is 1.5 x 10^{-3} M. Oxygen was bubbled through the solutions continuously. The

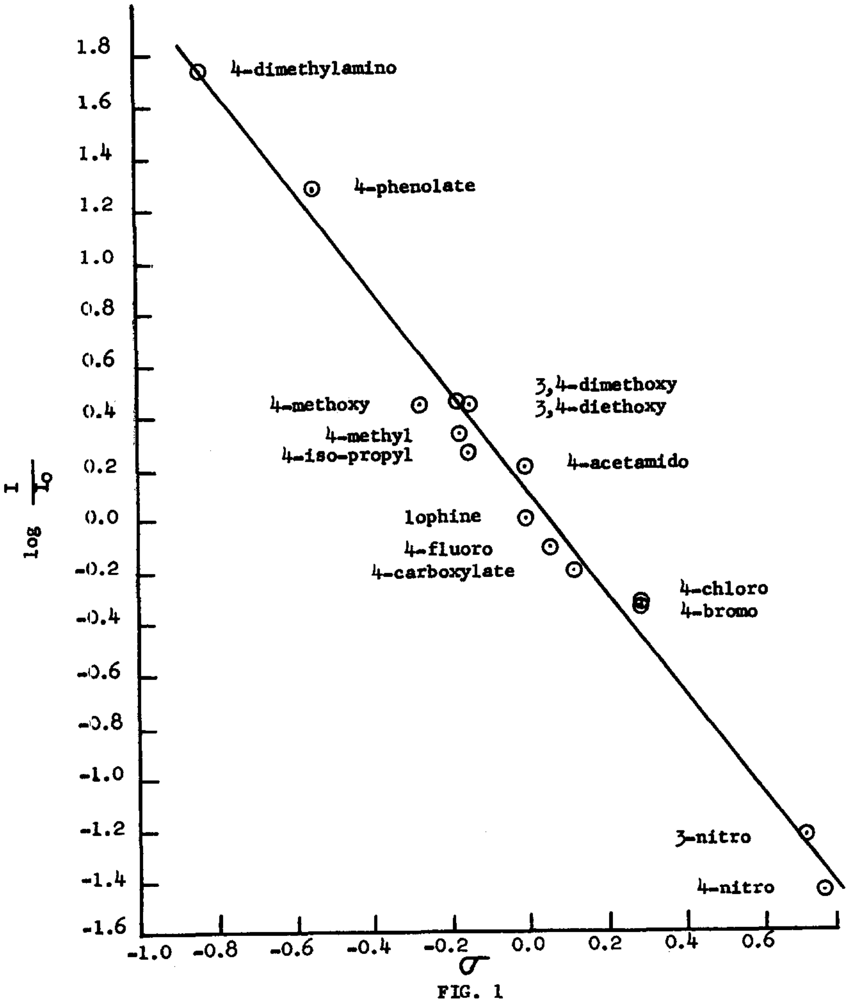

FIG. 1

Plot of log $\frac{I}{I_0}$ vs. σ for lophine derivatives with substituents in the 2-phenyl group. I at maximum emission.

intensity rose to a maximum in 1-2 minutes and then fell over a 10-20 minute period to a nearly constant value lasting from 2-12 hours, depending on the compound. The 2-(p-hydroxyphenyl) derivative gave no plateau. This compound apparently undergoes degradation to give dark-colored products.

Figure 1 presents a Hammett plot of log $\frac{I}{I_o}$ against values of σ taken from Hine.[4] I is the chemiluminescent intensity yielded by the compound at the peak of the emission curve. I_o is the intensity of lophine which is taken as the reference substance. The value of ρ determined by least squares is -1.96 ± 0.06. When a similar plot is constructed for the chemiluminescent intensity on the plateau portion of the light emission curve, the value of ρ obtained by a least squares solution is -1.87 ± 0.06. We have, at the present time, no explanation for the occurence of the peak in the early portion of the emission curves, but the values of ρ and the error of 3.1 % obtained in both cases indicates that these two portions of the curve are closely related and probably dependent on identical factors.

Similar plots were constructed using σ^+ values taken from Brown and Okamoto.[5] At the maximum of the emission curve the slope was -1.18 ± 0.08 and on the plateau the slope was -1.16 ± 0.06. In these cases the errors are 6.5 % and 4.9 % respectively. As Bartlett[6] points out, differences between the values of σ and σ^+ are, in general, small except for the case in which a methoxy group delocalizes a positive charge into the benzene ring. The data reported here do not justify a selection of either σ or σ^+ as being the most significant factor. Swain, Stockmayer and Clarke[7] have studied spontaneous thermal decomposition of substituted benzoyl peroxides. The anion derived from the lophine compounds is formally similar to the benzoate ion on which values of σ are based. The dissociation of the dimer proposed by Hayashi and Maeda[2] is analogous to the dissociation of the peroxide into two free radicals as proposed by Swain, Stockmayer and Clarke. They obtained a value of ρ of -0.38 for the thermal decomposition of the benzoyl peroxides. The much larger negative value of ρ obtained in the lophine series may be due to the destruction of the negative charge in the lophine anion by a one electron oxidation. Solutions of lophine in 70 % dimethylsulfoxide have been examined with varying concentrations of NaOH. The spectral shifts observed indicate that the anion of lophine is present in significant concentrations when the base concentration is 1N. It is not clear from this data whether the rate is being controlled by the anion oxidation, by the homolytic dissociation of the N-N bond, or by some other factor.

Due to limitations imposed by our photometer, sample holder, and accessories, it has not been possible to determine the total light output from these compounds with sufficient accuracy for sound interpretation. It appears that compounds showing a high intensity have short plateau emissions compared to those of low intensity. This may indicate comparable total light outputs for these compounds.

The emission intensities for lophine and the 4-carboxy, 4-methoxy, 3,4-dimethoxy, and 4-chloro compounds have been determined as a function of concentration over the range 3×10^{-3} to 3×10^{-5} M. The emission intensity is linear in the lophine concentration, and no evidence has been found for self quenching. Self absorption is absent, since none of these compounds absorb in this range.

The chemiluminescent intensity of these compounds has been increased by the addition of hydrogen peroxide to the system. The chemiluminescent maximum for all of the compounds, except the nitro derivatives, falls at 5300 angstroms. The nitro compounds would not give sufficient intensity for measurement. This wavelength agrees with that found for the 4-dimethylamino and 4-phenolate derivatives in the absence of peroxide and also agrees with the wavelength reported by Cottman et. al.[8] for lophine. It appears that the data obtained are best explained on the assumption that the chemiluminescent processes in all of the cases examined is yielding the same molecular fragment, and that probably the substituent present in the original lophine is not present in this fragment. The observed intensity is probably controlled by a steady state concentration of the emitting species.

Hammett's rho-sigma relationship has been found by Ziffer and Sharpless[9] to apply to a photochemical reaction. These reactions are, formally, the reverse of the chemiluminescence reaction.

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