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Fluorescence of the Hindered Phenoxyl Radical*

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Synopsis. Fluorescence and excitation spectra of the 2,4,6-tritertiarybutylphenoxyl radical which is stabilized by a steric hindrance have been measured in benzene at room temperature. The emitting state seems to correspond with a state visualized in the excitation spectrum.

Absorption spectra of the phenoxyl radical and its alkyl derivatives were extensively investigated by means of flash photolysis method.[1,2] The 2,4,6-tritertiarybutylphenoxyl has an almost identical spectrum with that of the phenoxyl.[1] The emissions of these free radicals have not yet been analyzed, while those of the benzyls which have the same number of conjugated π-electrons as the phenoxyls have been investigated[3-7] closely in detail. It is very interesting to study the emitting processes of these radicals comparing with that of the benzyl, in order to examine the electronic spectra of aromatic free radicals more systematically.

2,4,6-Tritertiarybutylphenol and benzene were Analytical Reagent (Aldrich Chemical) and of spectrograde, respectively. This parent material of the radical was purified by repeated recrystallizations. The 2,4,6-tritertiarybutylphenoxyl was prepared from 2,4,6-tritertiarybutylphenol dissolved in benzene at 5×10^{-2} M concentration by the addition of PbO_2 (3 g of PbO_2 in 25 ml of solution). The oxidization of the phenol was carried out under nitrogen saturated condition at room temperature. After producing the radical, the solution was transferred to a sample cell and degassed. A Farrand Mark I spectrofluorometer was used for the measurements. Bandwidth was set at 5 nm.

Fluorescence emission and excitation spectra observed are shown in Fig. 1. The radical was stable enough to be measured these spectra by the usual static method at room temperature. High stability of this radical has been reported.[8] It was suggested that tertiary-butyl substituents prevent the recombination reactions of the radicals to form quinone type products.

The excitation spectrum shows distinct peaks at 404 and 386 nm which correspond well with the reported absorption data: at 401 and 383 nm in CCl_4, and 400 and 382 nm in hexane.[2] Therefore, the emission spectrum observed by the excitation at 390 nm shown in Fig. 1 can reasonably be assigned to be the fluorescence from the 2,4,6-tritertiarybutylphenoxyl radical. The fluorescence spectrum shows a peak at 425 nm and has no distinct vibrational structure.

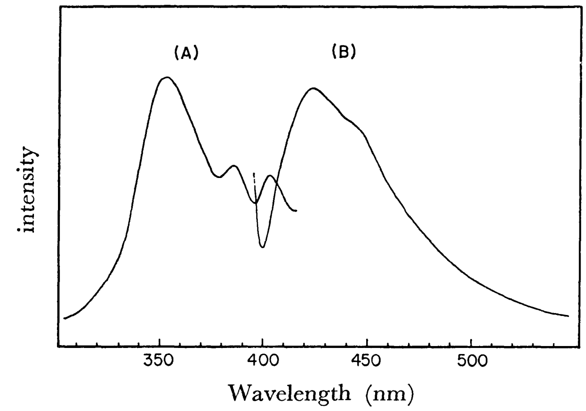

Fig. 1. Fluorescence emission and excitation spectra of 2,4,6-tritertiarybutylphenoxyl radical in benzene at room temperature.
(A) and (B) are the excitation spectrum monitored at 430 nm and the fluorescence spectrum excited at 390 nm, respectively.

The first absorption bands of the phenoxyl radicals are substantially blue-shifted and stronger compared with those of the benzyl radical, and fluorescence spectra of the benzyl radicals in rigid glass are more structured than that of the radical observed. The essential difference between these two types of radicals is that the phenoxyl has a heteroatom bearing two lone pairs which may decrease electron repulsion. This repulsion is possibly considered to lower the energy of the first electronic transition. Furthermore, the lone pairs on the oxygen atom of the phenoxyl give rise to $n\rightarrow\pi^*$ transitions in the electronic spectra. Calculations of the doublet states of the phenoxyl by P-P-P[9] and CNDO/S[10] methods were reported. In both calculations, one or two low energy states in visible region which carry low or no oscillator strength were predicted, other than the observed states in near ultraviolet region. Considering these theoretical results also, one may expect the presence of a hidden emitting state in the visible region. However, the fluorescence spectrum measured in this work indicates that the emitting state possibly corresponds to a state visualized in the absorption and excitation spectra around 400 nm, because a fluorescence peak in the observed spectrum is not much separated from the absorption one. It is also possible that there exists unknown emitting state of which absorption is weaker and hidden in the apparent absorption around 400 nm.

The above results represent one of the few reported fluorescence from a free radical at ambient temperature in solution.

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