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DIRECT CHEMILUMINESCENCE FROM AIR OXIDATION OF 9,10-DIISOBUTYRYLANTHRACENE AND RELATED COMPOUNDS IN ALKALINE APROTIC SOLVENTS

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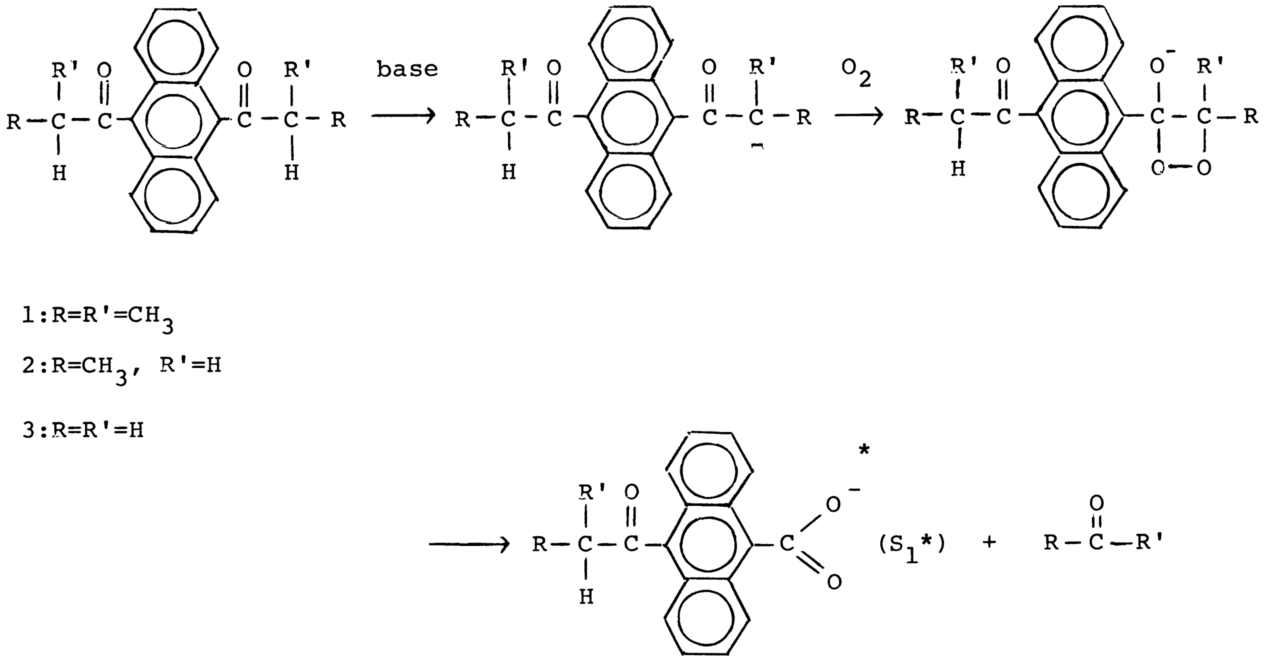
It was previously reported that excited triplet products were predominantly generated from air oxidation of various simple ketones in alkaline aprotic solvents. In the present study, we have found that excited singlet product, 9-isobutyrylanthracene-10-carboxylic acid which emits fluorescence, was generated from air oxidation of 9,10-diisobutyrylanthracene under the same experimental conditions. This finding lends strong support to the hypothesis that dioxetanes may be the critical intermediates to give excited singlet products (good emitters).

In previous studies,[1)] we reported that various simple ketones exhibited indirect chemiluminescence from air oxidation in alkaline aprotic solvents containing 9,10-diphenylanthracene or 9,10-dibromoanthracene. By summarizing the emission features observed, it was concluded that excited carbonyl compounds, predominantly in triplet rather than singlet state, were generated from those molecules with a -CO-CH- group via dioxetane intermediates, which were produced by oxygenation of the anion of the compounds formed by the loss of a proton from the α-carbon atom.

In the present study we have succeeded in observing an intense direct chemiluminescence due to the generation of an excited singlet product arising from air oxidation of such a compound having a -CO-CH- group as 9,10-diisobutyrylanthracene(1).

When a solution of potassium t-butoxide in t-butyl alcohol was added to an aerated solution of 9,10-diisobutyrylanthracene(1) in dimethyl sulfoxide or N,N-dimethylformamide (10^{-3} mol l^{-1}) there appeared an intense yellowish chemiluminescence. The emission showed a rapid rise which is followed by a relatively rapid decrease, and then a much slower decay.[3] The chemiluminescence spectrum[4] had a peak at 490 nm, and was very similar to the fluorescence spectrum[4] of 9-isobutyrylanthracene-10-carboxylic acid(4)[5] one of the reaction products from the diisobutyryl compound(1). This finding suggests that excited singlet carboxylic acid(4) is generated from air oxidation of the diisobutyryl compound(1) via a dioxetane intermediate.

Similar direct chemiluminescence was exhibited from air oxidation of 9,10-dipropionylanthracene(2) with an intensity about one tenth of that from the higher homologue(1). A feeble light was also observed from 9,10-diacetylanthracene(3) on oxidation. As shown from these results, the chemiluminescence intensity is much affected by the structure of the reactant, namely by the class of the C-H bond adjacent to the carbonyl group; it increases in the order, primary < secondary < tertiary. However, the intensities of fluorescence emissions of the reaction products from the diisobutyryl(1)-, dipropionyl(2)-, and diacetylanthracene(3) were almost equal. Thus, it would be reasonable to conclude that the chemiluminescence efficiency depends upon the tendency to loose a proton from the C-H bond.



1: $R=R'=CH_3$

2: $R=CH_3$, $R'=H$

3: $R=R'=H$

All of the results described above provide a conclusion that the diisobutyrylanthracene(1) should also follow the same reaction pathways, as those proposed for the oxidation of simple ketones,[1)] involving a dioxetane to give the carboxylic acid(4) in excited singlet state. When a concentrated solution of potassium t-butoxide was added, the carboxylic acid(4) was further decomposed. However, no appreciable light could be detected in the decomposing step.

Though numerous dioxetanes have been synthesized and all of them have been found to give excited products,[6,7)] these synthetic stable dioxetanes did not satisfy the requirement for high intensities of luminescence, as observed in some chemi- abd bioluminescent reactions, because the products derived from such dioxetanes were poor emitters being mostly in triplet state. Moreover, no one has succeeded, up to date, in isolating the hypothetical dioxetanes which would produce good fluorescers on fragmentation.[7)]

Part of the difficulties will be attributed to the fact that the dioxetanes are too unstable to isolate. Our present finding lends strong support to the hypothesis that dioxetanes may be the critical intermediates to give excited singlet products which emit fluorescence.

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References and Notes

1) I. Kamiya and T. Sugimoto, Chem. Lett., 1976, 33; Bull. Chem. Soc. Jpn., 50, 2442 (1977); I. Kamiya, ibid., 50, 2447 (1977).

2) A Friedel-Crafts condensation of anthracene and isobutyryl chloride in carbon disulfide in the presence of aluminium trichloride at 20 °C gave the diisobutyrylanthracene in 35% yield, mp 125-126 °C (from ethanol); m/e at 318 (M^+). The location of the substituent at the 9- and 10-positions was confirmed by a ^{13}C NMR spectrum. A similar condensation of anthracene with propionyl chloride or acetyl chloride gave respectively the dipropionylanthracene(2) in 30% yield, mp 171-172 °C (from benzene) and m/e at 290 (M^+), and the diacetylanthracene(3) in 30% yield, mp 216-217 °C (from ethanol) and m/e at 262 (M^+).

3) The light intensity observed as a function of time was strongly dependent upon the concentration of added potassium t-butoxide.

4) Both chemiluminescence and fluorescence spectra were measured on a Hitachi MPF-2A fluorescence spectrophotometer.

5) Isolated from the oxidation products of the diisobutyryl compound (1) by acidification with dil. hydrochloric acid, evaporation to dryness under reduced pressure, and then column chromatography on silica gel eluted by a mixture of ethyl acetate and benzene (1:4) in 2% yield, mp 177-179 °C, dec. (from benzene); m/e at 292(M^+).

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