CHEMISTRY LETTERS, pp. 33-36, 1976. Published by the Chemical Society of Japan

EXCITED SINGLET AND TRIPLET PRODUCTS GENERATED FROM THE AIR OXIDATION OF SIMPLE KETONES AND CARBOXYLIC ACIDS IN ALKALINE APROTIC SOLVENTS

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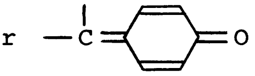
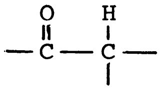
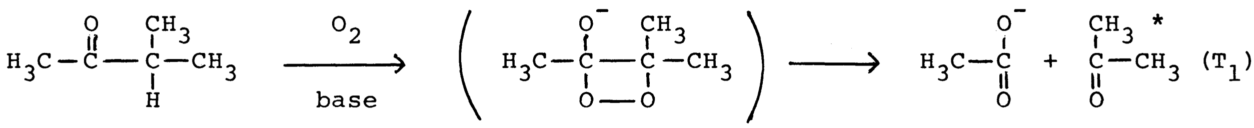
Using the indirect chemiluminescence technique, we have obtained evidences for the proposal that excited triplet acetone and benzoic acid were generated in the air oxidation of 3-methyl-2-butanone and benzoin respectively in alkaline aprotic solvents. On the other hand, it seemed that excited singlet benzaldehyde was generated from β-phenylpyruvic acid.

The reaction mechanism involving the dioxetane intermediates has been proposed for many chemiluminescent and bioluminescent reactions.[1)] A similar reaction mechanism has been suggested as the most possible mechanism for the chemiluminescent reactions of 4-hydroxy-3,5-dihalogenophenylpyruvic acid[2)] and succinylfluorescein[3)] with oxygen in the presence of tert-BuOK in an aprotic solvent such as dimethylsulfoxide(DMSO) or dimethylformamide(DMF). In these reactions, a dioxetane intermediate is formed by the oxygenation of the anion of these compounds formed by the loss of a proton from the carbon ajacent to the carbonyl or  group.

These results suggest that those molecules with a  $-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{\underset{|}{C}}}-$ group should also follow the same reaction pathways, involving a dioxetane, to yield a product in excited states. In order to test this hypothesis, we investigated the oxidation reactions of simple ketones and carboxylic acids by oxygen under the same experimental conditions.

A solution of 3-methyl-2-butanone(I) in DMSO or DMF containing tert-BuOK, as expected, absorbed an equimolar amount of oxygen. The treatments of the reaction mixture with 2,4-dinitrophenylhydrazine gave the hydrazone of acetone (mp, 128-129°C) as the main product in a 48% yield. Thus, we concluded that the main product of the oxidation of I was acetone. We then investigated the direct and indirect chemiluminescence of I in the absence and in the presence of 9,10-diphenylanthracene(DPA) or 9,10-dibromoanthracene(DBA). A solution of I (10^{-3}M in DMSO or DMF, 2.00 ml) was placed in a quartz cell, which was kept at 40°C by a thermostatically controlled cell holder. The intensity of the chemiluminescence emission was measured immediately after the addition of tert-BuOK (10^{-2}M in tert-BuOH or DMF, 0.30 ml) on a Hitachi MPF-2A type fluorescence spectrophotometer with the exciting source off.

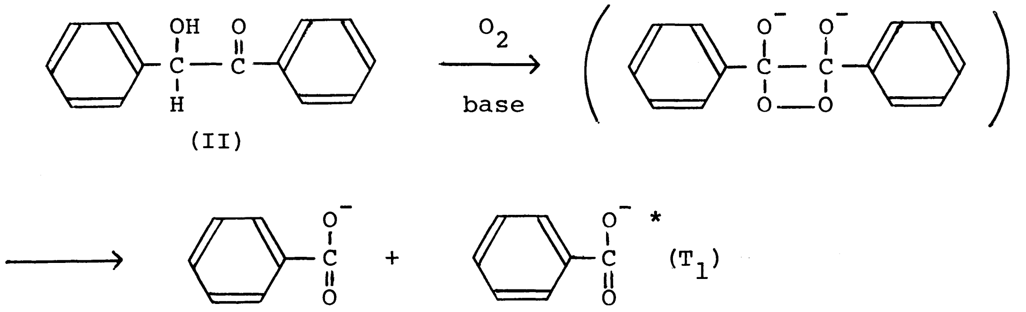
No direct chemiluminescence could be detected from the reaction solution of I. However, in the presence of DPA or DBA, a fluorescence of low intensity from the anthracene (peak at 430 nm) was observed. The intensity of the indirect chemiluminescence with DBA was markedly higher than with DPA in spite of the much higher fluorescence efficiency of the latter. These observations show clearly that the excited triplet acetone was directly formed during the reaction:4) DBA is more capable of converting the energy of the excited triplet acetone into singlet energy than is DPA, because of the increased spin-orbit coupling and mixing of singlet and triplet states due to heavy atoms, and the energy transfer step leading to the chemiluminescence is mainly of the triplet-singlet type. Turro and his co-workers also observed the formation of the excited triplet acetone in the thermal decomposition of tetramethyl-1,2-dioxetane.5) However, the direct formation of excited triplet acetone in the oxidation reaction by oxygen has not been reported. We assume that the excited triplet acetone is formed from I by the following reaction scheme, involving a dioxetane intermediate.



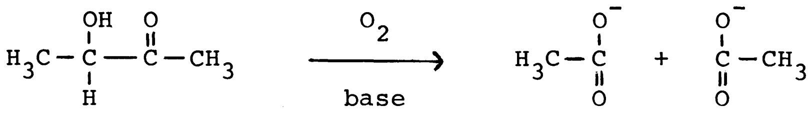
$$H_3C-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{CH_3}{C}}-CH_3 \xrightarrow[\text{base}]{O_2} \left(H_3C-\overset{O^-}{C}-\overset{CH_3}{C}-CH_3 \atop \quad\;\; O-O \right) \longrightarrow H_3C-\underset{O}{\overset{O^-}{C}} + \underset{O}{\overset{CH_3}{C}}{}^{*}-CH_3 \;(T_1)$$

(I)

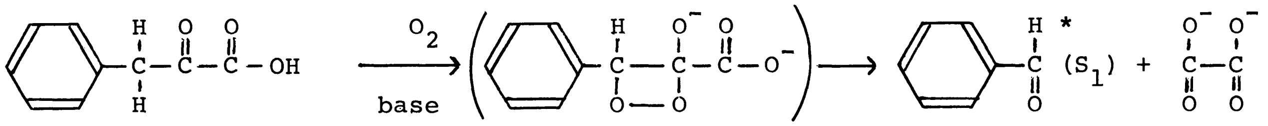
Benzoin(II) was also oxidized by oxygen under the same experimental conditions, and exhibited a very intensive indirect chemiluminescence emission in the presence of DBA. We isolated benzoic acid (mp, 122-123°C) from the reaction mixture as the main product in a 59% yield (based on two moles of benzoic acid), and thus concluded that excited triplet benzoic acid was generated by the oxidation of II, again presumably via the dioxetane intermediate.



With acetoin, however, neither direct nor indirect chemiluminescence emission could be observed. This is probably because a large amount of energy, greater than the sum of the reaction enthalpy and activation energy, is required to excite acetic acid produced.


$$H_3C-\overset{OH}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\text{base}]{O_2} H_3C-\overset{O^-}{\underset{O}{\underset{\|}{C}}} + \overset{O^-}{\underset{O}{\underset{\|}{C}}}-CH_3$$

When β-phenylpyruvic acid was oxidized under the same experimental conditions, very weak indirect chemiluminescence emissions were observed. It was confirmed spectroscopically that β-phenylpyruvic acid was almost quantitatively converted into benzaldehyde on the oxidation. It is of interest to note that the emission yield with DBA was much lower than with DPA. These results suggest that excited singlet benzaldehyde is generated, though in a low yield, by the aerial oxidation of the acid. A similar indirect chemiluminescence was exhibited on the oxidation of n(and iso)-valeric acid; the emission yield with DPA was higher than with DBA. Thus, we assume that excited singlet species are produced by the oxidation of the acids.



We are not able to account for the differences in the reaction products at the present time. It would, however, be of interest to note that the energy difference between the first excited state, $(n\pi^*)^1$, and the ground state of benzaldehyde (77 kcal/mol) is much smaller than in the cases of acetone (88 kcal/mol) and benzoic acid (120 kcal/mol).6)

Further studies with other molecules and solvents, including detailed kinetic and mechanistic studies, are in progress.

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(Received October 29, 1975)