The Photoinduced Isomerization of Anthrone to Anthranol

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The photoinduced isomerization reaction from anthrone to anthranol was observed in several solvents, such as ethanol, ether, *n*-heptane and acetonitrile; the yield was large in the former two solvents, and very small in the latter two. Detailed experiments were done only in the case of the ether solution, on which we will report here.

By the irradiation of the degassed ether solution of anthrone by a light flash, anthrone was isomerized to anthranol. This may be clearly seen from Fig. 1, where the absorption spectrum (curve 1) of anthrone ($\sim$300 mμ) changes into that (curve 3) of anthranol ($\sim$370 mμ) after the irradiation.

The absorption spectrum immediately ($\sim$25 μ sec.) after the irradiation by the flash was photographed by the aid of the flash-spectroscopy technique; a new absorption band thus appeared at 340 mμ. This band may be expected to be due to the reaction intermediate from the facts that the 300 mμ band of anthrone disappears with the appearance of the new 340 mμ band and that, furthermore, the 370 mμ band of anthranol appears as the 340 mμ band disappears.

The 340 mμ band of the intermediate was found to be similar in position and shape to the spectrum of the benzophenone ketyl radical observed by Porter et al.[1,2] (curve 4 in Fig. 1). Therefore, the 340 mμ band may safely be assigned to the anthrone ketyl radical, whose π electron structure is very similar to that of the benzophenone ketyl radical. This shows that the abstraction of the hydrogen by the anthrone from solvent molecules occurs as the first step of the reaction. This conclusion seems to be supported also by the experimental fact that the yield of anthranol is large in ethanol and ether, solvents whose hydrogen is rather easily abstracted.

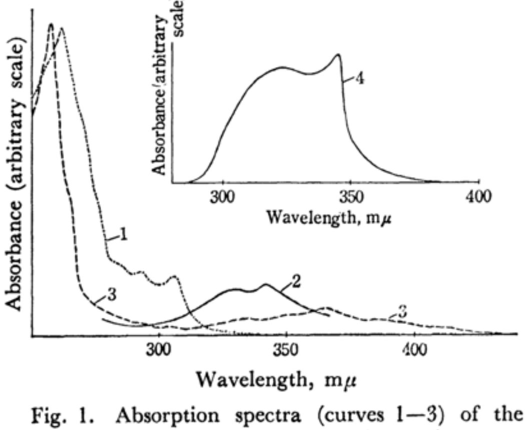
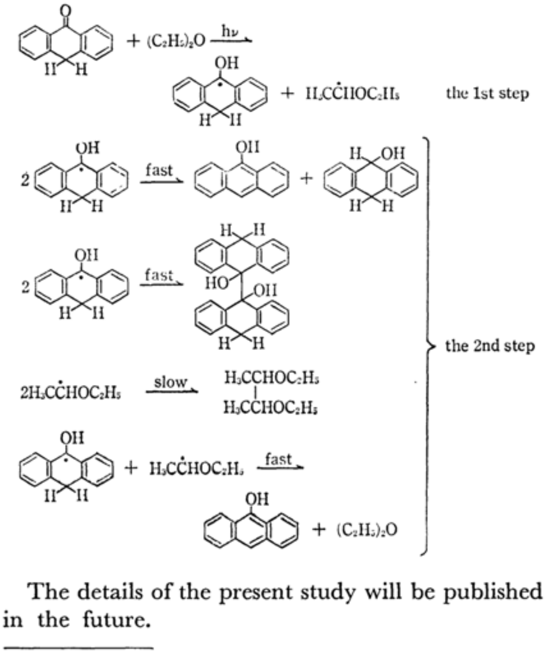


Fig. 1. Absorption spectra (curves 1—3) of the ether solution of anthrone under various conditions and the absorption spectrum (curve 4) of the benzophenone ketyl radical.

1. before irradiation
2. immediately (25 μsec.) after irradiation
3. (a few minutes) after irradiation
4. benzophenone ketyl radical[1,2]

The second step of the isomerization reaction, namely, the change of the ketyl radical to anthranol, was detected photoelectrically by measuring the absorption intensity of the 340 mμ band of the intermediate. The results show that the intermediate decays at the initial stage, following the second-order reaction formula, with the rate constant of about 10^7 mol^{-1} sec^{-1}, and at the next stage, following the first-order reaction formula.

The formation of the intermediate ketyl radical and its decay curve observed by the present authors can be explained satisfactorily in terms of the following reaction scheme:



The details of the present study will be published in the future.

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1) G. Porter and M. W. Windsor, *Proc. Roy. Soc.*, **A245** 238 (1958).

2) G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57** 1686 (1961).