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# STRUCTURE-REACTIVITY RELATIONSHIPS IN TRIPLET SENSITIZED PHOTOLYSIS OF AROMATIC KETONE O-ACYLOXIMES

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Structure-reactivity relationships in photoreactions are of great interest and importance.[1] Previously O-acyloximes of aromatic ketones were shown to undergo homolytic cleavage at the N-O bond on excitation to their triplet states.[2] We now wish to report on studies designed to determine structural factors responsible for reactivity of the triplet states of aromatic ketone O-acyloximes.

The mechanism of the triplet sensitized photolysis of the O-acyloximes is shown by the following kinetic scheme:

$$\begin{array}{lcl}
S \xrightarrow{h\nu} {}^{1}S^{*} \xrightarrow{\Phi_{ST}} {}^{3}S^{*} & . & {}^{3}OA^{*} \xrightarrow{k_d} OA \\
{}^{3}S^{*} \xrightarrow{k_{sd}} S & . & {}^{3}OA^{*} \xrightarrow{k_r} ArRC{=}N\cdot + \cdot OCOR' \\
{}^{3}S^{*} + OA \xrightarrow{k_t} S + {}^{3}OA^{*} & . & \text{where } S \equiv \text{sensitizer, } OA \equiv ArRC{=}NOCOR'.
\end{array}$$

Under stationary-state approximation, a linear correlation is expected between the reciprocal of the quantum yield for disappearance of a ketone O-acyloxime, $1/\Phi$, and the reciprocal of its concentration, $1/[OA]$,

$$1/\Phi = (1 + k_d/k_r)(1 + k_{sd}/k_t[OA]) \qquad (1)$$

where intersystem crossing quantum yield of a sensitizer is assumed to be unity.

We measured the quantum yields for the disappearance of O-acyloximes by irradiating their benzene solutions at different initial concentration (0.01-0.3 M) containing benzophenone or Michler's ketone as a sensitizer with 366-nm light at room temperature[3] and, according to eq. 1, estimated the values for $k_d/k_r$ which we employed as a measure of reactivity. The results are summarized in Table 1.

The $k_d/k_r$ values are very small for the O-acyloximes derived from acetophenone, benzophenone, 2-acetylnaphthalene, and 1-acetylnaphthalene, whereas the $k_d/k_r$'s for fluorenone O-acyloximes are much larger, indicating that the former acyloximes (1-4) are highly reactive on excitation to their triplet states, but

Table 1. The Values for $k_d/k_r$ Estimated from Quantum-Yield Measurements in Triplet Sensitized Photolysis of Aromatic Ketone O-Acyloximes

| Acyloxime | R' = Me | R' = Ph | R' = p-MeC$_6$H$_4$ | $E_T$ of parent ketone[5] |
|---|---|---|---|---|
| PhMeC=NOCOR' (1) | 0.3 | 0.8 | | 74 kcal/mol |
| Ph$_2$C=NOCOR' (2) | 2.2 | | 1.2 | 69 |
| 2-NpMeC=NOCOR' (3)[†] | 1.0 | | 1.0 | 59 |
| 1-NpMeC=NOCOR' (4)[†] | 0.1 | 0.2 | | 56 |
| 9-Fl=NOCOR' (5)[†] | 35 | | 20 | 53 |
| 9-AnMeC=NOCOR' (6)[†] | | ∞ | | 40-45 |

† Np = naphthyl, Fl = fluorenylidene, and An = anthryl.

the triplet states of the latter acyloximes (5) are less reactive. Furthermore, 9-acetylanthracene O-benzoyloxime (6) was found to be almost unreactive. These results show that the reactivity of the triplet acyloximes is not related to the acyl moiety but depends upon the oxime moiety, and therefore depends upon the structure of the parent ketones.

The triplet energies of the O-acyloximes are assumed to be due to the structure of the oximes and to be nearly the same as those of the parent ketones.[2b,6] Thus, the triplet energies were estimated to be in the range of 65-70 kcal/mol for acyloximes, 1 and 2, in the range of 55-60 kcal/mol for 3 and 4, in the range of 50-55 kcal/mol for 5, and lower than 50 kcal/mol for 6 on the basis of quenching experiments of phosphorescence emitted from aromatic ketones by the O-acyloximes.[2b,7]

From these considerations, it is reasonable to assume that the reactivity of the triplet states of the O-acyloximes is correlated with their triplet energies[8] and the acyloximes having the triplet energies higher than ca. 55 kcal/mol, which is in accord with the energy of the N-O bond,[9] show high reactivity.

References and Notes

1) W. G. Herkstroeter and G. S. Hammond, J. Am. Chem. Soc., 88, 4769 (1966).
2) a) H. Sakuragi, S. Ishikawa, T. Nishimura, M. Yoshida, N. Inamoto, and K. Tokumaru, Bull. Chem. Soc. Jpn., 49, 1949 (1976); H. Ohta and K. Tokumaru, ibid., 48, 2393 (1975). b) M. Yoshida, H. Sakuragi, T. Nishimura, S. Ishikawa, and K. Tokumaru, Chem. Lett., 1975, 1125.
3) The degassed solutions were irradiated on a merry-go-round apparatus using a 1 kW high pressure mercury lamp with Toshiba UV-D1B glass filters. The decrease of the substrates was determined by nmr using an internal standard. Light intensity was determined by benzophenone-benzhydrol actinometry.[4]
4) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, Inc., New York, N.Y. (1973), p. 125.
5) Ref. 4, p. 3; S. Hirayama and J. Osugi, Nippon Kagaku Zasshi, 92, 825 (1971).
6) A. Padwa and F. Albrecht, J. Am. Chem. Soc., 94, 1000 (1972).
7) Quenching rate constants of triplet benzophenone, 2-benzoylnaphthalene, and benzil by O-acyloximes were determined in carbon tetrachloride. The estimation of the triplet energies will be discussed in detail in a full paper.
8) Localization of excitation energy on the fluorenylidene and anthryl portions would in part contribute to reducing the reactivity of 5 and 6, respectively.
9) The value of 53 kcal/mol is given as the bond energy: J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N.Y. (1964), p. 77.