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# EVIDENCE FOR THE FORMATION OF OXAZIRIDINE DURING THE LIGHT IRRADIATION OF AROMATIC AMINE OXIDES[1,2]

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The wealth of information on the photochemical rearrangement reaction of aromatic amine oxides reported hitherto in literatures has been interpreted in terms of oxaziridine species as intermediates[3]. For example, in the photolysis of quinoline 1-oxides, two rearrangement pathways via the oxaziridine species have been proposed to account for the formation of benz[d]-1,3-oxazepines or carbostyrils[4] (Fig. 1).

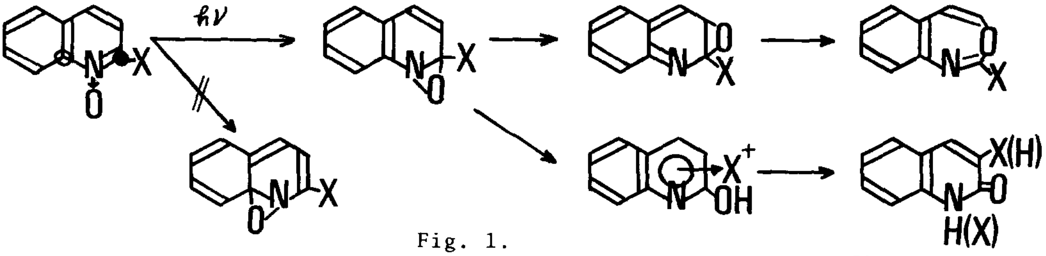
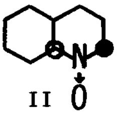
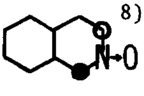
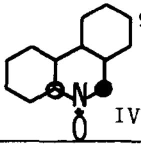
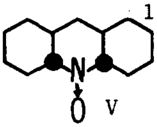


Fig. 1.

The recent trapping experiment for this reactive intermediate[5] further substantiated the adequacy of the proposed scheme. However, since the direct observation of the oxaziridine intermediate has never succeeded as yet, it seems worthy at this stage to obtain supporting evidences for the formation of this species from theoretical viewpoint. Using MO theory, we have arrived at the conclusion that the formation of this species should be preferred from the photo-excited N-oxide than from its ground state and also found a simple method predicting the structure of an oxaziridine as correct intermediate in the photolysis of a given N-oxide from which the formation of two kinds of oxaziridines can be formally expected.

Table I shows the lowest vacant MO (LVMO) of typical N-oxides obtained by HMO method6) whose photochemistry has been reported. In the formulae of the N-oxides shown in this letter, two carbon atoms adjacent to the N→O group are marked with full-circle or open-circle. It was deduced experimentally that only the former carbon atom (●) participates into the oxaziridine formation.

Table I

| Atom | MO |  I 7) |  II 4) |  III 8) |  IV 9) |  V 10) |
|---|---|---|---|---|---|---|
| oxygen | LV | +0.4047 | +0.3891 | +0.3031 | +0.3924 | +0.3915 |
| | HO | +0.7813 | +0.6807 | +0.7036 | +0.6771 | +0.6121 |
| full-circle carbon | LV | +0.3741 | +0.3845 | +0.4946 | +0.4760 | +0.1655 |
| | HO | -0.3245 | -0.3343 | -0.4271 | -0.4256 | -0.1506 |
| open-circle carbon | LV | —— | +0.0915 | -0.1115 | -0.0438 | —— |
| | HO | —— | -0.1391 | -0.1187 | -0.0587 | —— |

a) $\alpha_N=\alpha+1.6\beta$, $\alpha_O=\alpha+0.8\beta$, Ind=$(1/3)^n\times 1.6\beta$, $\beta_{NO}=1.0$ 6).

From the comparison of the sign of AO coefficients of oxygen and the full-circle-carbon atom (●), it is apparent that the positive $\pi$-overlap is possible between those two AO's in the LVMO, while in the highest occupied MO (HOMO), the corresponding partial bond order is negative. Therefore, the oxaziridine formation should be more preferable from the excited N-oxide than from its ground state. The line of this thought directly gave a conclusion that if two kinds of oxaziridine formation are possible from a given N-oxide, the C-O bond should be formed with the carbon atom, whose AO would attain more effectively a positive bond order with the oxygen AO in the LVMO. As shown in Table I, the partial bond order between full-circle carbon atom and oxygen atom is larger than that between open-circle carbon and oxygen atoms.

We found further a simple method which, without solving tedious LCAO determinant, still gives correct predictions. This technique is the application of the method of composite system and the well-known nature of nonbonding MO (NBMO) of odd alternant hydrocarbon (odd AH). Here, inductive effect due to the N-oxide group nitrogen atom on neighbouring carbon atoms was ignored for simplicity. First, an N-oxide molecule is divided into the N→O part and the resultant odd AH part. We can then calculate easily the AO coefficients of NBMO of the hydrocarbon residue. The carbon atom having a larger coefficient between the two nearrest carbons for N→O group, then, corresponds to the full-circle-carbon atom. The calculation procedure is shown in Fig. 2, taking quinoline 1-oxide as an example. The results of this calculation are shown in Table II.

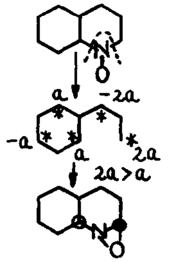
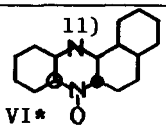
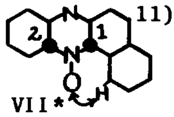
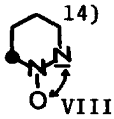


Fig. 2.

Table II

| Carbon atom | II | III | IV |  11)<br>VI* |  11)<br>VII* |
|---|---|---|---|---|---|
| full-circle | $2/\sqrt{11}$ | $1/\sqrt{2}$ | $4/\sqrt{31}$ | $4/\sqrt{107}$ | ●-1; $4/\sqrt{95}$ |
| open-circle | $1/\sqrt{11}$ | $1/\sqrt{8}$ | $1/\sqrt{31}$ | $3/\sqrt{107}$ | ●-2; $3/\sqrt{95}$ |

* Calculations of the AO coefficients are made to the corresponding benzacridine N-oxides (vide infra).



O; +0.4127
●; +0.1313
N; +0.4863

Fig. 3.

The theoretical background of this simple method is as follows. The HMO calculation of N→O part using the best set of parameters shown in Table I gives MO's $\psi^1_{N\to O}$ and $\psi^2_{N\to O}$, whose eigen-values are $\alpha + 2.277\beta$ and $\alpha + 0.123\beta$, respectively. In the LCMO concept, it is easily understood that the orbital $\psi^2_{N\to O}$ would mainly interact with and destabilize the above mentioned NBMO having the energy $\alpha$, and as a result this destabilized MO would correspond to the LVMO obtained by the whole MO calculation of the N-oxide. Since NBMO is easily obtained, this simple method seems to be quite useful for practical purposes.

The selective oxaziridine formation in the photochemical reaction of N-oxide having unsymmetrical ring system around the N-O axis was not affected by the introduction of a substituent on the ring carbon atom (quinoline 1-oxide to substituted quinoline 1-oxide$^{3)}$) or by the replacement of the carbon atom (except for the full-circle one) with a nitrogen atom (quinoline 1-oxide to quinoxaline 1-oxide$^{3,12)}$; isoquinoline 2-oxide to quinazoline 3-oxide$^{8,13)}$). These may also be expected from our calculations, since the perturbation on MO's induced by these substitutions would not be so severe as to alter the prediction.

Since in our calculations the stereochemical requirements in the step of oxaziridine formation are not considered, prediction by these methods cannot be applied to those N-oxides in which the steric effect requires the preferential bond formation between oxygen and open-circle carbon atoms. Such a steric effect seems to have a significant role in these reactions. For example, although the LVMO of pyridazine 1-oxide predicts an oxadiaziridine formation (see Fig. 3), the experimental evidences from these N-oxides[14] indicated the exclusive oxaziridine formation. The mutual repulsive interaction (⟷) between the lone-pair electrons of oxygen and nitrogen atoms in VIII may facilitate the formation of the latter species. The simultaneous formation of two oxaziridine species from VII as reported in our previous paper[11] can also be explained by the steric factors depicted in the formula, which assist in the $O\text{-}C_{\bullet-2}$ bond formation.

Finally, we would like to add the facts that the calculations by both the methods (NBMO and whole MO treatments) on benzo-[*f*]-, -[*g*]-, and -[*h*]-quinoline 1-oxides have also given the correct predictions for these photochemical reactions, the experimental detail of which will be reported soon.

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6) This parameter set for HMO calculation was recommended by one (T.K.) of the present authors to describe the electronic state (UV, dipole moment, IR etc.) of heterocyclic aromatic amine N-oxides. In diazine N-oxides, such as VIII, the coulomb integral for pyridine type-nitrogen atom was taken as $\alpha + 0.5\beta$. Using the parameter set stated above, the characteristics of the P.P.P.-type SCF-MO's were reproduced quite well from the HMO calculations. For detailed discussions, see the following paper as a leading reference. M. Yamakawa, T. Kubota and H. Akazawa, *Theoret. Chim. Acta(Berl.)*, **15**, 244(1969).

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