CHEMISTRY LETTERS, pp. 401-404, 1975. Published by the Chemical Society of Japan

A NEW TYPE OF PHOTOSENSITIZED REACTION INDUCED BY VISIBLE LIGHT ON THE SOLID SURFACE: THE PHOTOCHEMICAL REACTION OF HETEROCYCLIC N-OXIDE BY GREEN LIGHT IRRADIATION

Norisuke HATA
Department of Chemistry, College of Science and Engineering,
Aoyama Gakuin University, Chitosedai, Setagaya-ku, Tokyo 157

When the alumina powder dyed with eosin suspended in a benzene solution of isoquinoline- or acridine-N-oxide was illuminated with green light (~540 nm), there occured reactions originated from the T_1 state of isoquinoline N-oxide or from both the S_1 and T_1 states of acridine N-oxide. The results appear to be accounted for by assuming as a primary act the transfer of an electron from the excited singlet eosin to the alumina conduction band and/or the T-T transfer between the triplet eosin and the N-oxide on the alumina surface.

It is of quite importance in photochemistry to develop a means for utilizing visible light longer than 500 nm in relation to the conversion of sunlight-energy into useful forms of chemical energy. In this connection, photosensitization has been widely applied to populate triplet states of molecules where direct photoexcitation is usually not feasible. We report here a new type of photosensitized reaction taking place on the surface of the alumina powder dyed with eosin.

It is well known that the ultraviolet irradiation of heterocyclic N-oxides in solution leads to isomerizations through the lowest excited singlet state (S_1), whereas the deoxygenation reaction occurs from the lowest triplet state (T_1) in a predissociative manner.1-5) Thus, the triplet sensitization of aromatic amine N-oxides by an appropriate sensitizer can induce the dissociation of the N-O bond to give rise to the parent amines5); that is, as seen from Fig.1, the eosin-sensitization of acridine N-oxide results in the formation of acridine, but that of isoquinoline N-oxide does not cause any reactions because of the endothermic T-T transfer.

The present author carried out the green light (~540 nm) illumination of a benzene solution of isoquinoline- or acridine-N-oxide, in which the alumina powder dyed with eosin was suspended. The alumina powder used as an adsorbent was as follows; No.1: "Activated alumina (300 mesh)" for column chromatography (Wako Pure Chemical Industries), No.2: "Aluminiumoxid 150 neutral (Type T)" for TLC (Merck & Co.), No.3: "Aluminiumoxid sauer (Type T)" for TLC (Merck & Co.), and No.4: "Aluminiumoxid basisch (Type T)" for TLC (Merck & Co.). The eosin used as a sensitizer was a JIS specific grade "Eosin Y" of Wako Pure Chemical Industries. The light source was a 250W high-pressure mercury lamp (Ushio-250) equipped with a Toshiba filter V-052 for the irradiation of visible light longer than 520 nm. The general procedure of the photolytic experiment was as follows. A benzene solution (115 ml) containing 1.0~1.4 X 10^{-3}M of the N-oxide, in which ca. 2 g of the alumina powder dyed with eosin$^{6)}$ was suspended, in a Pyrex reaction vessel was irradiated for 40 or 50 hr at 20°C under bubbling in of nitrogen while the solution was being vigorously stirred with a magnetic stirrer. The amounts of the products and unreacted N-oxides were measured by means of a chromatographic separations (column: alumina, eluent: diethyl ether and also chloroform-ethanol (20 : 1)) combined with a spectrophotometric determination. All the experiments were undertaken in the dark.

The experimental results are shown in Table 1. In the case of isoquinoline N-oxide 1, interestingly the deoxygenation reaction characteristic of the T_1 state was induced to yield the isoquinoline 1a in ca. 10% yield. Further interesting finding was that, in the case of acridine N-oxide 2, besides the formation of acridine 2a (ca. 20% yield) from the T_1 state the isomerization product 2b originated from the S_1 state was obtained in ca. 10% yield. In either case, no chemical change of eosin was entirely detected. Moreover, in view of the facts that both the eosin being the sole light-absorbing species in the system and more than 80% of the N-oxide dissolved originally in benzene were strongly adsorbed on the surface of alumina powder, the reaction was regarded as initiated by the absorption of ~540 nm light by the eosin on the alumina surface.

Such a photochemical phenomenon taking place in the system consisting of eosin, N-oxide and alumina suspended in benzene appears to be interpreted qualitatively by assuming the spectral sensitization of alumina by eosin as follows, although the structure of the energy band of alumina and the ionization potential of eosin are

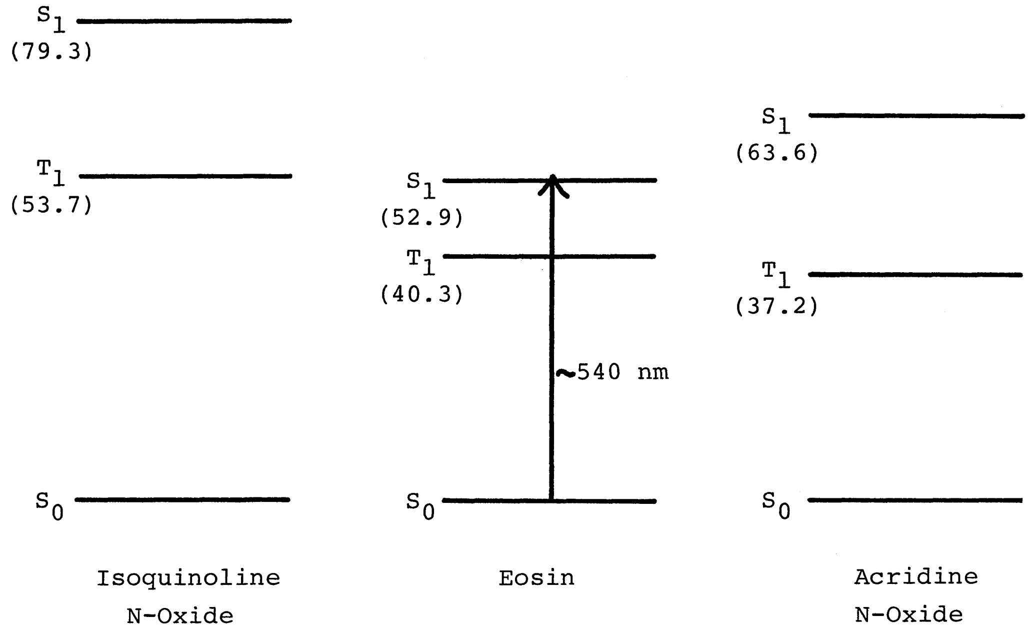


Fig.1 Excitation Energies (kcal.mol^{-1}) of the Lowest Excited Singlet and Triplet States of Eosin, Isoquinoline N-Oxide, and Acridine N-Oxide.

ambiguous. The effect of the excited singlet eosin (E^{*S}) is presumed to make available photoelectrons in the alumina conduction band; the transfer of an electron from the excited singlet eosin to the alumina results in the formation of both eosin cation-radical ($E^{\dot{+}}$) on the solid surface and mobile conducting electrons (e) in the alumina conduction band (Eq.(2)). The cation-radical of eosin owing to its great electron affinity would accept an electron from the isoquinoline N-oxide (N) to give its cation-radical ($N^{\dot{+}}$) (Eq.(3)). The conducting electron could be finally trapped to the cation-radical of N-oxide on the surface, giving rise to the triplet N-oxide (N^{*T}) responsible for the deoxygenation reactions (Eqs.(4) and (5)). The formation of the triplet state of isoquinoline N-oxide by such a recombination mechanism (Eq.(4)) is energetically feasible, because the excitation energy of the S_1 state of eosin is approximately equal to that of the T_1 state of isoquinoline N-oxide (Fig.1). However, an alternative mechanism may be also assumed for the formation of the triplet N-oxide; that is, the N-oxide anion-radical ($N^{\dot{-}}$), if it is formed by reaction between the ground state N-oxide and conducting electron (Eq.(6)), would interact with the eosin cation-radical to give rise to the triplet N-oxide (Eq.(7)).

$$E + h\nu\ (540\ \mathrm{nm}) \longrightarrow E^{*S} \qquad (1)$$

$$E^{*S} \longrightarrow E^{\dot{+}} + e \qquad (2)$$

$$E^{\dot{+}} + N \longrightarrow E + N^{\dot{+}} \qquad (3)$$

$$N^{\dot{+}} + e \longrightarrow N^{*T} \qquad (4)$$

$$N^{*T} \longrightarrow \text{Deoxygenation} \qquad (5)$$

$$N + e \longrightarrow N^{\dot{-}} \qquad (6)$$

$$E^{\dot{+}} + N^{\dot{-}} \longrightarrow E + N^{*T} \qquad (7)$$

Adding the processes described above, in the case of acridine N-oxide its triplet state is considered to be efficiently formed by the energy transfer from the triplet eosin (E^{*T}) to the N-oxide (N) (Eq.(9)). The triplet N-oxide (N^{*T}) is therefore anticipated to be densely populated on the surface of the alumina powder, which probably makes it possible to cause the triplet-triplet annihilation (Eq.(10)) besides the deoxygenation reaction (Eq.(5)), generating the excited singlet acridine N-oxide (N^{*S}) responsible for the isomerization reaction (Eq.(11)).

$$E^{*S} \longrightarrow E^{*T} \qquad (8)$$

$$E^{*T} + N \longrightarrow E + N^{*T} \qquad (9)$$

$$N^{*T} + N^{*T} \longrightarrow N + N^{*S} \qquad (10)$$

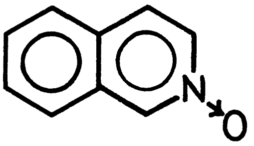
$$N^{*S} \longrightarrow \text{Isomerization} \qquad (11)$$

Such a new type of photosensitized reaction found in the present investigation, although the mechanism is still in a speculative stage, seems to be applicable in photochemistry as a means for utilizing effectively the visible light longer than 500 nm which is the most abundance in sunlight. Further detailed studies are now in progress.

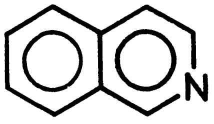
The author wishes to thank Miss Kayoko Kuroda for her assistance.

Table 1. Photochemical Reactions of Isoquinoline- or Acridine-N-Oxide on the Surface of the Alumina Powder Dyed with Eosin in Benzene on 540 nm Irradiation.

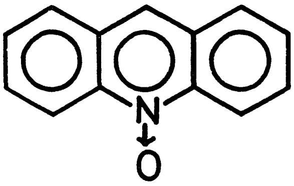
N-Oxide	Alumina	Irradiation Time (hr)	Conversion (%)	Product (Yield,%)
1	No.1	50	27	1a (9)
1	No.2	50	23	1a (11)
1	No.3	50	20	1a (10)
1	No.4	50	24	1a (10)
2	No.1	40	17	2a (21), 2b (11)
2	No.2	40	21	2a (21), 2b (8)
2	No.3	40	16	2a (22), 2b (9)
2	No.4	40	17	2a (18), 2b (13)



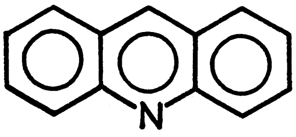
1



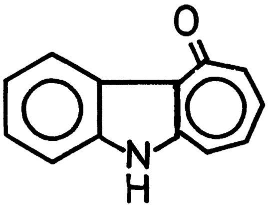
1a



2



2a



2b

References

1) G.G.Spence, E.C.Taylor, and O.Buchardt, Chem.Rev., 70, 231 (1970).
2) C.Lohse, J.Chem.Soc. Perkin II, 229 (1972).
3) K.B.Tomer, N.Harrit, I.Rosenthal, O.Buchardt, P.J.Kumler, and D.Creed, J.Am.Chem.Soc., 95, 7402 (1973).
4) I.Ono and N.Hata, Bull.Chem.Soc.Japan, 46, 3658 (1973).
5) N.Hata, I.Ono, and M.Kawasaki, Chem.Lett., 25 (1975).
6) The adsorption of eosin on the alumina surface was accomplished by adding 21 g of alumina powder into 100 ml of an ethanol solution containing 5.7 X 10^{-2}M of eosin.

(Received February 26, 1975)