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EXCIMER INVOLVEMENT IN THE PHOTOISOMERIZATION OF AN OXIME ETHER

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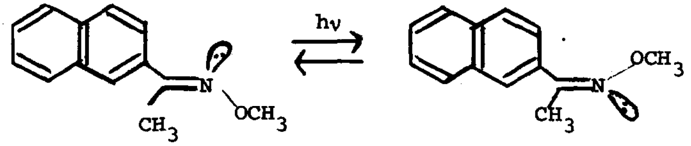
The photochemical interconversion of the *syn* and *anti*-isomers of imines is a subject of long-standing interest.[1-6] In the present communication we report on some aspects of the direct and sensitized isomerization of the 2-acetonaphthone oxime O-methyl ether system, where we note that marked discrepancies exist between predicted and measured quantum yields. This previously undiscerned phenomenon is of fundamental interest by virtue of its superficial parallels to and mechanistic differences from the corresponding situation in olefin photochemistry.

The anti-O-methyl ether of acetonaphthone oxime (2) was synthesized by treating 2-acetonaphthone with methoxylamine hydrochloride according to the procedure of Karabatsos and Hsi.[7] The corresponding *syn* isomer (1) was prepared by irradiation of (2) in pentane using 3130 Å light.



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Irradiation of degassed pentane (or benzene) solutions of *syn* (or *anti*)-oxime ethers (1 or 2) at 3130 Å, led to photostationary states whose composition varied from 64% *syn* at [oxime ether] = 0.003M to 42% *syn* at [oxime ether] = 1.35M. The data obtained indicate that the final photostationary state composition is dependent on both the temperature maintained and the concentration and solvent used during the course of the irradiation (i.e. [syn]/[anti] at 0.1M pentane = 0.92 ± 0.03 at 25° and 1.20 ± 0.05 at 80° (pentane); [syn]/-[anti] = 1.80 ± 0.06 at 0.003M (pentane, 25°), 1.11 ± 0.05 at 0.05M (pentane, 25°), and 0.72 ± 0.04 at 1.35M (benzene, 25°). The results show that high oxime ether concentrations enhance the fraction of the anti isomer in the photostationary state. High temperatures, however, tend to diminish the fraction of the thermodynamically more stable anti form.

Two possibilities come to mind in seeking an explanation for the cause of the (syn/anti) isomer variation. These are (1) association between ground-state molecules which gives rise to dimers and higher aggregates, and (2) specific interactions between ground-state and excited oxime ether molecules. Since no evidence for ground-state complexing could be found by uv, ir, or nmr spectroscopy, it would seem as though the observed variation in the photostationary state is due to interactions between excited and ground-state molecules. These interactions will be expected to be somewhat dependent on the temperature and solvent system employed.[8] The data obtained are consistent with the involvement of an excimer which is capable of inducing syn-anti isomerization and whose "decay ratio" differs from that of the excited monomer. In this connection it is worthy to note that the fluorescence of oxime ether **1** is subject to concentration quenching. Most importantly, a new component (ca λ 500 nm) became evident in the fluorescence spectrum as the concentration of the syn isomer increased. The variation of the photostationary state composition as a function of temperature can be attributed to the dissociation of the excimer with reformation of the excited monomer at higher temperatures. The equilibrium associated with excimer formation and its corresponding "decay ratio" will also be expected to be influenced by the nature of the solvent system used. Excimers have been reported to play an important role in the photoisomerization of certain olefinic systems.[9-11] In these cases it was found that a high olefin concentration also enhances the fraction of the trans isomer in the photostationary state.

In order to determine whether the concentration effects noted in the photoisomerization and fluorescence experiments were derived from a common excited intermediate, quenching experiments using 1,3-cyclohexadiene as a singlet quencher[12] (1.0-3.0M) were carried out. The quenching slopes obtained ($k_q\tau(\mathbf{1})_{isom}$ = 0.04, fluor. quenching = 0.13)) indicate that chemical quenching is only one-quarter as efficient as fluorescence quenching. One interpretation of this observation is that the photoisomerization does not proceed from a singlet state but rather involves a short-lived reactive triplet which is quenched at high quencher concentrations. That this is not the case was shown by triplet sensitization experiments in which benzophenone was used as the sensitizer (i.e. 3660 Å source, $\Phi_{A \rightarrow S} = \Phi_{S \rightarrow A} = 0.51$). The ratio of triplet quantum yields ($\Phi_{A \rightarrow S}/\Phi_{S \rightarrow A}$) is 0.73, in good agreement with the experimental value of the photostationary state (0.77). If decay from a common state is involved in both the sensitized and unsensitized experiments, the decay ratio should be the same for the two processes.[13] The difference between the two numbers (i.e. 0.73 (triplet) and 1.08 (singlet) is an indication that crossing to triplets is not the sole fate of excited oxime ether singlets. The closeness of the above values would suggest that the isomerization induced by direct irradiation is also passing, in part, through the triplet state. The triplet sensitized isomerization, however, was found to be independent of the initial oxime ether concentration.

An alternate rationale to account for the variation in fluorescence *vs* chemical quenching observed with **1** would involve the partial involvement of a short-lived unquenchable precursor to photoisomerization. This may possibly be an upper excited state or a nonquenchable upper vibrational level of the first excited state (singlet or triplet). In order to test this possibility, we examined the quantum efficiency of the oxime ether isomerization using 2537 Å light. Surprisingly, the quantum yields for isomerization at 2537 Å showed a substantial diminution in value (i.e. $\Phi_{A \rightarrow S} = 0.28$, $\Phi_{S \rightarrow A} = 0.27$) when compared to the values obtained at 3130 Å (i.e. $\Phi_{A \rightarrow S} = 0.53$, $\Phi_{S \rightarrow A} =$ 0.49). The lower quantum efficiency at 2537 Å may be related to incomplete internal energy transfer or a diminished intersystem crossing from the naphthyl

π-π^* state(s) to the imine excited state(s).[14] Alternatively, the lower efficiency may result from a radiationless decay path of the excited naphthyl state(s) which maintains geometric integrity of the oxime ether.

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13. This relationship is valid only if the rate constants for quenching sensitizer triplets by the two isomers are the same. For the case of oxime ethers 1 and 2 this should be true since energy transfer from benzophenone to naphthalene is known to be diffusion controlled.
14. For a similar situation where a diminished intersystem crossing was encountered in a bichromophoric system see W. Ferree, Jr., J. B. Grutzner, and H. Morrison, J. Amer. Chem. Soc., 93, 5502 (1971).