CHEMISTRY OF SINGLET OXYGEN. XX.
MECHANISM OF THE SENSITIZED PHOTOOXIDATION
OF ENAMINES[1]

Christopher S. Foote*, Alice A. Dzakpasu[+] and John W.-P. Lin
Contribution No. 3425 from the Department of Chemistry,
University of California, Los Angeles, California 90024

Enamines undergo photosensitized oxygenation at room temperature to give carbonyl and amide fragments.[2,3] At low temperatures, chemical and spectroscopic studies gave evidence for an intermediate at the oxidation state of dioxetane 1, but the nmr spectra of the intermediates had more lines than would be consistent with monomeric dioxetanes, and it was believed that non-monomeric material was also present.[2] We now report the identification and partial character-ization of dioxetane intermediates in the photooxygenation of two enamines, and additional evidence for the mechanism of the reaction.


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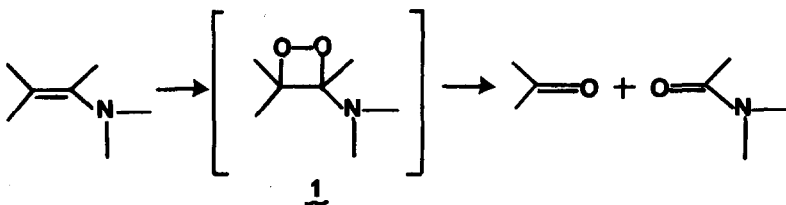
That the reaction is a singlet oxygen reaction and not a Type I reaction[4] (i.e., involving sensitizer-substrate interaction) was demonstrated by the fact that competition[5] reactions using tetramethylethylene (TME) gave reproducible results over a wide range of ratios of N,N-dimethylisobutenylamine (2) to TME (0.089 - 2.01:1), demonstrating inhibition of photooxygen-ation of 2 by the singlet oxygen acceptor TME. Competition runs were carried out using 2 (0.05 - 0.146 $\underline{M}$) and TME (0.0492 - 1.63 $\underline{M}$) in benzene with zinc tetraphenylporphine (ZTP) as sensitizer. The solutions were reduced by adding trimethyl phosphite or $NaBH_4/CH_3OH$ and analyzed by glc (internal standard). The value of k_2/k_{TME} (ratio of reaction rates of singlet oxygen with 2 and TME) was 10.3 ± 1.0 (seven runs). Using the value 4.8 x 10^7 $\underline{M}^{-1}s^{-1}$ for k_{TME}[6], gives k_2 the very high value of 4.9 x 10^8 $\underline{M}^{-1}s^{-1}$, in keeping with its very high electron density.

In order to characterize the intermediate more completely, careful photooxygenation at low temperature and low concentration was carried out. A 2 x 10^{-2} $\underline{M}$ solution of 2 in a mixture of


[+]AFGRAD Fellow, 1969-71.

90% Freon 12 and 10% deuterochloroform containing 2 mg of ZTP was completely photooxygenated at -78° using visible light.[7] A portion of the reaction mixture was stripped of solvents under vacuum at -78° to give a thick residue which could not be crystallized from cold pentane or pentane-chloroform mixture. The nmr spectrum at -58° of a second portion of the reaction mixture had resonances (δ, TMS, 60 MHz) at 1.20, 1.56, 2.53, and 4.90, all sharp singlets, in the ratio 3:3:6:1. A third portion of the reaction mixture was warmed and shown by glc and spectral analyses to give only acetone and N,N-Dimethylformamide. The nmr signals are in accord with a monomeric dioxetane, and are much simpler than those previously reported[2] which were of solutions photooxygenated with less careful temperature control and worked up at somewhat higher temperatures.

$$(CH_3)_2C\!\!=\!\!CHN(CH_3)_2 \xrightarrow{\,{}^1O_2\,}$$

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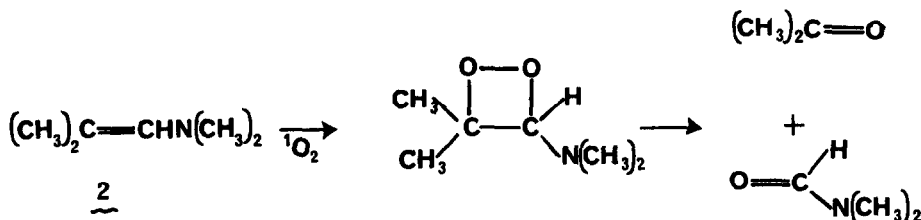
Although the intermediate could not be isolated at room temperature, its molecular weight was determined as follows. The freezing point depression constants (K_f) for CH_3NO_2 and $CHCl_3$ were determined, using 2 as a solute. Found: $K_f^{CH_3NO_2}$ = 3.7 ± 0.1° $\underline{M}^{-1}$, $K_f^{CHCl_3}$ = 5.04 ± 0.25° $\underline{M}^{-1}$ (reported[8] 4.7 - 4.9° $\underline{M}^{-1}$). A 0.127 $\underline{M}$ solution of 2 in 10 ml Freon 12 and 0.3 ml CH_2Cl_2 was completely photooxygenated at -78° using ZTP. The residue left after stripping solvents at -78° under vacuum was dissolved in CH_3NO_2 kept at about -30°. Product and starting material analyses were carried out at -30° by nmr using $CHCl_3$ as internal standard. This technique showed the extent of decomposition of the intermediate to be less than 5%. The freezing point depression was corrected for residual CH_2Cl_2 and decomposition products, as determined by nmr. The weight of the intermediate was taken to be the sum of the weights of decomposition products after warming to room temperature less decomposition products at -30°. The molecular weight of the intermediate found using the above procedure was 120 ± 15. When $CHCl_3$ was used as the cryoscopic solvent, a more precise melting point of the solution was determined from cooling curves. In these cases, CH_2Cl_2 was the internal standard for nmr analyses. The molecular weight found using 0.83 molal solutions of 2 was 140 ± 24. The molecular weight of a monomeric dioxetane is 131.2.

Photooxygenation of 1,2 Diphenyl-1-morpholinoethylene (3) was also carried out at -78° in dimethylether (ZTP). A solid product precipitated after 30 min. After stripping solvents at -78°, the intermediate, a pale yellow crystalline solid which exploded at -6° ± 0.5°, was isolated. The decomposition products from this intermediate were identified by glc, ir, and nmr analysis as N-benzoylmorpholine and benzaldehyde. Unfortunately, the nmr spectrum of the intermediate itself at low temperature was not very informative, because the unique resonance

of the proton on the dioxetane ring (which would be expected to be at least 1 ppm downfield from the corresponding proton in the dioxetane from 2 (which absorbs near 5 ppm)) appears to be obscured by the phenyl absorptions.
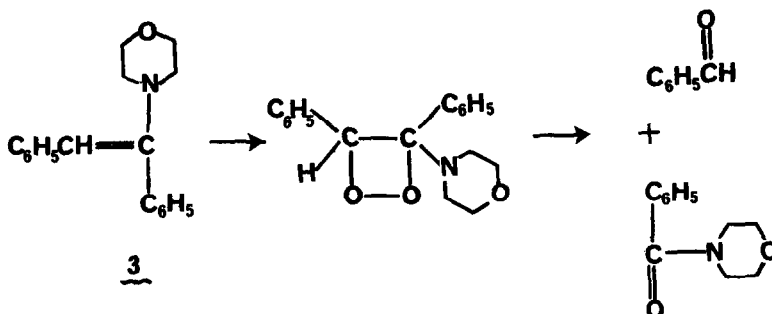
Cryoscopic molecular weight determination was carried out on this intermediate in CH_3NO_2; the weight of intermediate was determined using gas chromatographic analysis of decomposition products to determine intermediate concentration. The molecular weight so determined was 302 ± 18 (calc. 297 for monomeric dioxetane). Thus the intermediates formed from both 2 and 3 are unequivocally monomeric dioxetanes; these dioxetanes are less stable than alkyl[9] and alkoxydioxetanes,[10] and cannot be further characterized, as they break down below room temperature.

In order to determine the solvent effect of the reaction between 2 and $^1O_2$, competitive rates were measured with 2 and TME in a variety of solvents in the same way as previously. The rate of reaction of TME is probably essentially independent of solvent, as are the rates for 2-methyl-2-pentene[11] and several aromatic hydrocarbons.[12] The results are shown in the table (some benzene was used in all solvents in order to use ZTP in each case).

Table. Effect of Solvent on Relative Rate of Reaction of Enamine 2 and TME

Solvent	k_2/k_{TME}
Benzene	10.3 ± 1.0
20% DMSO - Benzene	10.8 ± 0.05
40% DMSO - Benzene	7.6 ± 0.10
80% DMSO - Benzene	9.1 ± 0.03
20% CH_3CN - Benzene	7.8 ± 0.12
95% CH_3CN - Benzene	9.4 ± 0.20
95% Pentane - Benzene	7.1 ± 0.20
70% CH_3OH - Benzene	2.9 ± 0.10
95% CH_3OH - Benzene	2.2 ± 0.15

It will be seen that there is extremely little solvent effect over the range 95% pentane - 95% CH_3CN. We conclude that the rate k_2 is essentially invariant over this range. Only in methanol is the rate somewhat lower. This may be due to hydrogen bonding to the enamine, which

makes the electrons less available.

   Unfortunately, because of the high rate of reaction of enamine 2, no conclusions can be drawn from the lack of solvent effect. If the reaction of 2 is like that of other substrates of comparable reactivity,[4b,13] it has an activation enthalpy of 1 kcal or less; it does not seem likely that solvent effects would have a major effect on a reaction with this low an activation enthalpy even if the transition state were fairly polar. We have reason to suspect that reactions of singlet oxygen with electron-rich olefins leading to dioxetanes may proceed by way of an electron-transfer or charge-transfer mechanism,[14] and have experiments in progress to test this hypothesis.
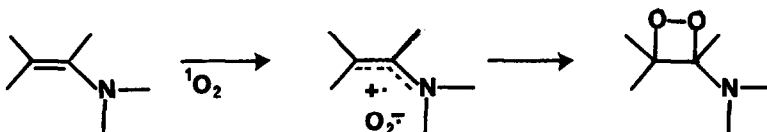
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