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REDOX-PHOTOSENSITIZED CHAIN MONOMERIZATION OF cis,syn-DIMER OF DIMETHYLTHYMINE; UNUSUAL EFFECT OF MOLECULAR OXYGEN[1]

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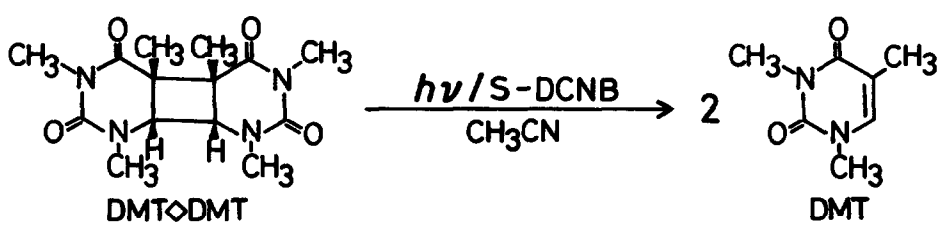
Summary: cis,syn-Dimer of dimethylthymine was monomerized by means of a chain reaction upon the selective photoexcitation of phenanthrene in aerated acetonitrile in the presence of p-dicyanobenzene. It was found that the dimer forms a CT-complex with O_2.

Photosensitized monomerization of thymine dimers is of biological interest with regard to enzymatic photoreactivation (PR) of damaged DNA and has been investigated for understanding of unknown molecular mechanisms of PR.[2-4] Even in typical photosensitized reactions, however, quantum yields for the monomerization are usually low,[2,3] 0.5 at best.[4] Since PR is thought to be very efficient,[5] model reactions should meet, at least, the requirement that efficiencies be high. We have found that cis,syn-dimethylthymine cyclobutane dimer (DMT◇DMT) is efficiently monomerized by the redox-photosensitization using aromatic hydrocarbon (S)-p-dicyanobenzene(DCNB)-acetonitrile systems[6,7] and that oxygen molecules remarkably enhance efficiencies of the photosensitized monomerization.



DMT◇DMT DMT

Irradiation of an air-saturated dry acetonitrile solution containing phenanthrene, DCNB, and DMT◇DMT at 313 nm gave N,N'-dimethylthymine (DMT) in nearly

quantitative yield (>97%) even at 100% conversion, whereas both phenanthrene and DCNB were completely recovered. Table 1 lists quantum yields for the formation of DMT (Φ_{DMT}) and oxidation potentials ($E^{ox}_{1/2}$) of S and DMT◇DMT. As is shown in Table 2, quantum yields remarkably depend on concentration of dissolved O_2. Surprisingly, the limiting quantum yield for air-saturated solution is 205! This clearly demonstrates the occurrence of a chain reaction.

Table 1. Quantum Yields for Redox-photosensitized Monomerization of DMT◇DMT and Oxidation Potentials of S and DMT◇DMT

	S					
	Triphenylene	Naphthalene	Phenanthrene	Chrysene	Pyrene	DMT◇DMT
Φ_{DMT} [a]	10.68	8.83	8.36	0.11	0.00	-
$E^{ox}_{1/2}$ /V [b]	1.29	1.22	1.17	1.05	0.78	1.45

a) Values at 313 nm for air-saturated dry acetonitrile solutions containing S (0.01 M), DCNB (0.1 M), and DMT◇DMT (0.01 M). b) Determined vs. Ag/Ag^+ in acetonitrile by cyclic voltammetry.

Table 2. Effect of Molecular Oxygen on Redox-photosensitized Monomerization of DMT◇DMT[a]

		Gas-saturated[c]		
	Degassed[b]	N_2	Air	O_2
Φ_{DMT} [d]	0.14	3.1	30.1	6.6
Φ^{∞}_{DMT} [e]	1.20	-	205	38

a) In all the runs, 0.01 M of phenanthrene and 0.1 M of DCNB were used. b) By five freeze-pump-thaw cycles under high vacuum ($<10^{-5}$ mmHg). c) Each gas-saturated solution was obtained by bubbling with the corresponding gas for 20 minutes. d) Values at 0.04 M of DMT◇DMT. e) Limiting quantum yields obtained from the intercepts of linear plots of Φ^{-1}_{DMT} vs. $[DMT◇DMT]^{-1}$.

The end absorption of DMT◇DMT was found to be correspondingly shifted, when a thoroughly degassed solution was in turn saturated with air, argon, and air (Figure). This indicates the formation of a CT-complex between O_2 and DMT◇DMT. Since the spectrum of O_2-saturated solution is identical to that of air-satu-

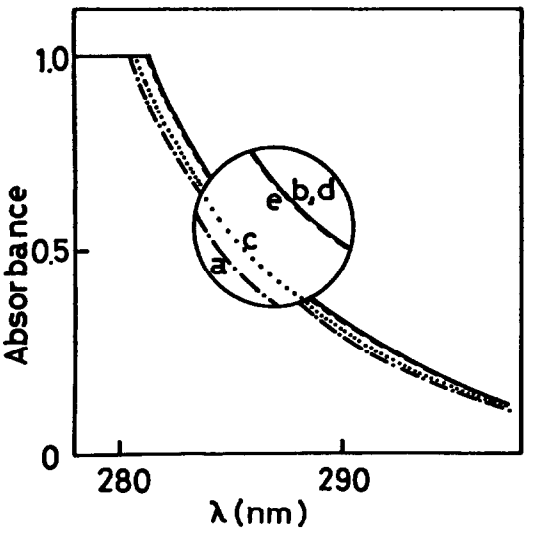


Figure. UV-spectra of DMT◇DMT (0.01 M) (a) in a thoroughly degassed acetonitrile solution (—·—) and after bubbling for 20 min in turn (b) with air (——), (c) with argon (·····), (d) with air (——), and then (e) with pure O_2 (----)

rated solution, air saturation can provide enough amounts of O_2 for the maximum formation of the CT-complex. Thus, the spectral changes are in line with the results in Table 2. The remarkable enhancement of ϕ_{DMT} by air saturation is clearly due to the formation of the CT-complex. On the other hand, saturation with pure O_2 results only in an increase of uncomplexed O_2, thus giving rise to a lower ϕ_{DMT} than air saturation, since the uncomplexed O_2 perhaps deactivates reaction intermediates such as excited species and ion radicals. It is of interest to note that the CT-complex still exists in part even after bubbling with argon.

$$S \xrightarrow{h\nu} {}^1S^*$$

$${}^1S^* + DCNB \longrightarrow S^{+\cdot} + DCNB^{-\cdot}$$

$$DMT\diamond DMT + O_2 \rightleftharpoons DMT\diamond DMT\cdot O_2$$

$$S^{+\cdot} + DMT\diamond DMT\cdot O_2 \xrightarrow{fast} S^{+\cdot} + 2\ DMT + O_2$$

$$S^{+\cdot} + DMT\diamond DMT \xrightarrow{slow} S^{+\cdot} + 2\ DMT$$

$$S^{+\cdot} + X \longrightarrow S \text{ and/or others}$$

(X = $DCNB^{-\cdot}$, O_2, H_2O, and inpurities)

The mechanism involving the catalytic monomerization by the cation radical of S ($S^{+\cdot}$) without the intervention of $DMT\diamond DMT^{+\cdot}$ is suggested from the following reasons: (1) DMT◇DMT did neither quench the fluorescence of S nor form any CT-

complexes with S and DCNB, (2) the photosensitized monomerization did not occur in ethyl acetate, (3) ϕ_{DMT} depends on $E^{ox}_{1/2}$ of S, (4) $E^{ox}_{1/2}$ of S is considerably lower than that of DMT◇DMT, and (5) a similar mechanism has been demonstrated for the redox-photosensitized cycloreversion of indene cyclobutane dimers.[7] According to this mechanism, the cation radical of phenanthrene can monomerize more than one hundred molecules of the dimer complexed with O_2. However, it can not be reasonably interpreted at the present time why the complexation with O_2 makes the dimer much more susceptible of the catalytic monomerization by the cation radical of S.

At any rate, the redox-photosensitized monomerization of DMT◇DMT *via* the CT-complex with O_2 is extremely efficient, thus providing a possible model reaction for PR. Finally, it should be noted that the *cis,anti*-dimer was not monomerized at all by the redox-photosensitization. We are now intending to apply this reaction to the *trans,syn*-dimer.

References

1) Part 4 of Redox-photosensitized Reactions. Part 3; T. Majima, C. Pac, and H. Sakurai, Chem. Lett., 1133 (1979).
2) G. J. Fisher and H. E. John, "Photochemistry and Photobiology of Nucleic Acids," S. Y. Wang, Ed., Academic Press, New York, N.Y., 1976, Vol. 1, p. 226.
3) C. Hélène and M. Charlier, Photochem. & Photobiol., 25, 429 (1977).
4) A. A. Lamola, Mol. Photochem., 107 (1972).
5) H. Harm, "Photochemistry and Photobiology of Nucleic Acids," S. Y. Wang, Ed., Academic Press, New York, N.Y., 1976, Vol. 2, p. 219.
6) C. Pac, A. Nakasone, and H. Sakurai, J. Am. Chem. Soc., 99, 5806 (1977).
7) T. Majima, C. Pac, A. Nakasone, and H. Sakurai, J. Chem. Soc., Chem. Commun., 490 (1978).

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