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SINGLET SENSITIZED FORMATION OF TRIPLET ACETONE FROM TETRAMETHYL-1,2-DIOXETANE

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The multiplicities of the excited states resulting from the thermal[1] and photochemical[2] decomposition of tetramethyl-1,2-dioxetane have recently been shown to result in the selective and high yield production of the (n,π^*) triplet state of acetone. We report in this note both chemical and spectroscopic evidence for the formation of triplet acetone from the pyrene singlet sensitized decomposition of tetramethyl-1,2-dioxetane (TMD)[3]. The observation that both 9,10-diphenylanthracene and 9,10-dibromoanthracene act as efficient singlet sensitizers of the photochemical decomposition of cis-diethoxy-1,2-dioxetane has already been made.[4] Product studies for such a process, however, have not as yet been reported.

Addition of TMD to acetonitrile solutions of pyrene resulted in the quenching of the pyrene fluorescence intensity. Stern-Volmer treatment of the data led to straight line plots of I^0/I vs [TMD] with $k_q\tau = 335 \pm 29$ (least squares analysis). Using the value of 352 ± 15 nsec for the pyrene lifetime under our conditions (measured via single photon counting), resulted in a value of $k_q = 9.52 \pm 1.44 \times 10^8$ $M^{-1}sec^{-1}$. A similar value of $k_q = 9.11 \pm 0.51 \times 10^8$ was obtained via Stern-Volmer analysis of fluorescence lifetime quenching as measured by single photon counting.

In order to establish whether excited acetone molecules are produced in a pyrene sensitized TMD decomposition, a chemical titration was designed. The substrate for the chemical titration must meet two standards. It should not quench the excited singlet of the sensitizer, but it should be a facile quencher of acetone triplets. The *cis*-*trans* isomerization of an α,β unsaturated nitrile[5,6] was utilized as the "chemical trap". Specifically crotononitrile (CN) was found to adequately fulfill both criteria (see Table). It should be pointed out that using the acetone-crotononitrile system allows counting of acetone triplets but we were not able to count the number of singlet acetones produced. The latter limitation results from the fact that oxetane formation (used to count singlets) is not feasible because of competitive olefin quenching of both singlet pyrene and singlet acetone at the high concentration required to trap acetone singlet and the fact that photochemical quantum yield for oxetane formation from acetone and CN is several hundred times less than that for acetone triplet sensitized *cis*-*trans* isomerization of CN[6].

A limiting quantum yield of 0.12 ± 0.01 was found for *cis*-*trans*-CN isomerization from the irradiation at 3130 Å of 6 x 10^{-3}M pyrene/1 x 10^{-1}M TMD solutions in acetonitrile over *cis*-CN concentration ranges of 0.097 to 1.12M, using valerphenone actinometry[7,8] (see Figure). Conversions of *cis*-CN were kept at about 1%. The percent triplets resulting from the above decomposition can be calculated with a knowledge of the decay ratio for acetone sensitized *cis*-*trans* isomerization, i.e. the limiting quantum yield for acetone sensitized isomerization (see Scheme). From the assumed reaction scheme the following relationship for the triplet acetone isomerization of *cis*-CN can be derived.

$$\frac{1}{\phi_{c-t}} = \left[\frac{k_c + k_t}{k_t}\right] \left[1 + \frac{k_d^t}{k_q^t\,[CN]}\right] \left[1 + \frac{k_q^s\,[CN]}{k_{st}} + \frac{k_f}{k_{st}}\right] \quad (1)$$

With knowledge of the fact that k_f for acetone[9] is only ~ 10^6 sec^{-1}, k_{st}[9] ~ 5 x 10^8 sec^{-1}, and the rate of complexation or quenching[6], k_q^s, is 1.5 x 10^7, the last factor in equation (1) is about unity. A simple plot of ϕ^{-1} *vs* $[CN]^{-1}$ results in a value of 0.39 ± 0.01 for the decay ratio. Thus, the percent triplets resulting from the pyrene sensitized decomposition of TMD is 30 (ϕ_{c-t} x 100/decay ratio). We note that this value is comparable with the value of 43% already reported for the direct photolysis of TMD at 366nm.[2]

Our spectroscopic evidence for triplet acetone production comes from the observation of an emitting transient by the SPC method. The transient possessed a lifetime of 12μsec at 460 nm resulting from the photochemical decomposition of a 2×10^{-2}M TMD/1×10^{-3}M pyrene solution (acetonitrile, 10°C).[10] A 300 nm excitation cut off filter was utilized to eliminate absorption by acetone. Under the same conditions, a control experiment with 2×10^{-2}M acetone/1×10^{-3}M pyrene indicated that no analogous transient was found in the absence of TMD. That acetone was the emitting species was also shown by the observation that cis-CN quenched the 12μsec lifetime in the pyrene sensitized TMD decomposition.

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8. It should be noted that we find that simple N_2 purging of the valerophenone/acetonitrile solution results in the same quantum yield for acetophenone formation as that from four freeze-pump-thaw cycles. It was the former method which was used here.
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10. The lifetimes of triplet acetone at 460 nm and 10°C in acetonitrile resulting from excitation of 10% acetone solutions are in the range of 10-20μsec, depending upon solvent purity and oxygen content.

TABLE

unsaturated nitrile	k_q (pyrene)[a]	k_q (singlet acetone)[b]	k_q (triplet acetone)[c]
t-dicyanoethylene	1.7×10^{10}	2.5×10^{9}	7.7×10^{9}
acrylonitrile	5.4×10^{6}	1.2×10^{8}	8.5×10^{8}
methacrylonitrile	---------	5.0×10^{7}	1.0×10^{9}
t-crotononitrile	1.0×10^{6}	$<2.5 \times 10^{7}$	6.5×10^{8}

a) from Stern-Volmer quenching of emission in acetonitrile, error limits ± 15%.

b) N.J. Turro, N. Schore, C.G. Lee, J.A. Barltrop, and H.A.J. Carless, *J. Amer. Chem. Soc.*, **93**, 3079 (1971).

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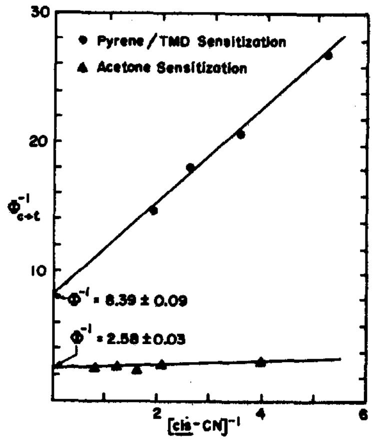
FIGURE



SCHEME

process	rate	process	rate
$A \longrightarrow A^1$	I	A^3 + cis-CN $\longrightarrow$ A + CN^3	k_q^t
$A^1 \longrightarrow A^3$	k_{st}	$CN^3 \longrightarrow$ cis-CN	k_c
A^1 + cis-CN $\longrightarrow$ complex	k_q^s	$CN^3 \longrightarrow$ trans-CN	k_t
complex $\longrightarrow$ A + CN	k_1		
complex $\longrightarrow$ oxetane	k_2		
$A^1 \longrightarrow A + h\nu$	k_f		
$A^3 \longrightarrow A$	k_d^t		

$$\text{decay ratio} = \frac{k_t}{k_t + k_c}$$