Tetrahedron Letters No. 25, pp 2069 - 2072, 1975. Pergamon Press. Printed in Great Britain.

QUANTUM CHAIN PROCESSES. DIRECT OBSERVATION OF HIGH QUANTUM YIELDS IN THE DIRECT AND PHOTOSENSITIZED EXCITATION OF TETRAMETHYL-1,2-DIOXETANE

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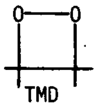
(Received in USA 7 March 1975; received in UK for publication 8 May 1975)

A quantum chain reaction is a photochemical reaction in which electronic excitation is cycled through a number of steps.[1] This concept has been employed[2,3] to explain the concentration dependent kinetics of the thermal decomposition of tetramethyl-1,2-dioxetane (TMD).[4] We report here that (a) the photochemical decomposition of TMD also involves a quantum chain reaction; (b) the experimental quantum yields for decomposition of TMD exceed 200 and approach 1000 in the limit; and (c) a kinetic analysis of the photodecomposition of TMD has been made. The irradiation of acetonitrile solutions of TMD results in an extremely rapid disappearance of TMD and formation of acetone as the only detectable product. The unusually rapid rate of disappearance suggested that a chain reaction was occuring. Our assumed mechanism for the chain decomposition of TMD is given in equations 1-4, where A = acetone, ^3A = acetone triplet, the state which is responsible for initiating and propagating

			Rate	
 TMD	$\xrightarrow{h\nu}$	$^3A + A$	βI_a	(1)
^3A + TMD	$\xrightarrow{\alpha k_c}$	$^3A + 2A$	$\alpha k_c[^3A][TMD]$	(2)
^3A + TMD	$\xrightarrow{(1-\alpha)k_c}$	chain termination	$(1-\alpha)k_c[^3A][TMD]$	(3)
^3A	$\xrightarrow{k_D}$	A	$k_D[^3A]$	(4)

the quantum chain, α = the fraction of reactions between ^3A and TMD which are successful at propagating the chain and $(1-\alpha)$ = the fraction of ^3A which are quenched by TMD to terminate the chain, and β is the efficiency of formation of ^3A by direct photolysis of TMD.

This simple mechanism predicts (Stern-Volmer kinetics) a linear relationship between the reciprocal of the quantum yield for decomposition of TMD into acetone (ϕ_D) and the reciprocal of [TMD]. Such a linear relationship was found experimentally. The intercept of such a plot corresponds to the reciprocal of the limiting quantum yield for the chain process, and was found to correspond to a value of ϕ_D in excess of 1000! Experimental values for ϕ_D were in the range of 300 for [TMD] ∿ 0.2-0.3 M (Table 1).

The quantum yield for disappearance of TMD is given by:

$$\phi_D = \phi_o + \phi_c \tag{5}$$

where ϕ_o and ϕ_c are the quantum yield for disappearance of TMD by direct excitation and by the chain process, respectively.

In turn, the chain quantum yield for disappearance of TMD is given by:

$$\phi_c = \beta \times \frac{\alpha k_c[\mathrm{TMD}]}{(1-\alpha)k_c[\mathrm{TMD}] + k_D} = \alpha\beta k_c \tau_A[\mathrm{TMD}] \tag{6}$$

where τ_A is the lifetime of acetone triplets at a given concentration of TMD. We have measured τ_A directly by single photon counting and β by direct quantum yield measurements (Table 1). Since we have also measured ϕ_c we are thus able to evaluate $\alpha\beta k_c$, and find this quantity to equal ∿ 10^9 M^{-1} sec^{-1}. By directly measuring the lifetime of acetone as a function of [TMD] we can evaluate the magnitude of $(1-\alpha)k_c$. A Stern-Volmer analysis yields a value (eq. 7)

$$\tau_A^{-1} = k_D + (1-\alpha)k_c\ [\mathrm{TMD}] \tag{7}$$

of $(1-\alpha)k_c = 4\times10^6$ M^{-1} sec^{-1}. Since β has been independently measured and found to be ∿.40 we now have sufficient information to evaluate both α and k_c, which are found to be ∿0.99 and ∿10^9 M^{-1} sec^{-1}, respectively. The latter values are in excellent agreement with α values calculated for the thermally initiated quantum chain reaction of TMD[2,3], therefore we conclude that the mechanisms of the quantum chain propagation under both conditions are identical.

In agreement with expectation from eq. 5 and the assumption that ^3A is the chain initiating and propagating species, we find that ϕ_D = 1.0 when TMD is photolyzed in the presense of selective triplet quenchers (1,3-dienes and crotononitrile) or at 77°K in a rigid matrix (EPA).

The chain decomposition of TMD can also be initiated by singlet (pyrene)[5] or triplet (1,4-dibromonaphthalene) photosensitization. In these cases very large quantum yields for disappearance of TMD are also observed (Table 1). In addition, α values for the photosensitized quantum chain are found to be $\sim$0.99 and k_c is $\sim$1-2x10^9 M^{-1} sec^{-1}.

In summary, we report that in acetonitrile solutions[6] photoexcitation of TMD results in a chain reaction causing the disappearance of TMD and formation of acetone as the only product. Acetone triplet is the reactive intermediate responsible for chain initiation and chain propagation. The chain propagation step has an efficiency of $\alpha = 0.99$ and a rate constant of $\sim 10^9$ M^{-1} sec^{-1} and the chain terminating step which depends on [TMD] occurs with a rate constant of 4×10^6 M^{-1} sec^{-1}.

Acknowledgement

The authors at Columbia University wish to thank the Air Force Office of Scientific Research (Grant AFOSR-74-2589) and the National Science Foundation (Grant NSF-GP-2660x and NSF-GP-40330x) for their generous support of this research. We thank Mr. Daniel Weiss and Dr. Hans-Christian Steinmetzer for assistance in the early phases of this work.

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6. Comparable studies of the quantum chain in benzene and freon-113 indicate that α is somewhat smaller, but quantum yields for disappearance of TMD are much greater than unity and photosensitization of the quantum chain is still observed.

TABLE I. QUANTUM CHAIN REACTION OF TETRAMETHYL-1,2-DIOXETANE$^{(a)}$

Quantity	Value	Comments
ϕ_D	260	λ_{ex} = 313 nm, 0.32 M TMD$^{(b)}$
ϕ_D	400	Pyrene singlet sensitized, $^{(b)}$ 0.25 M TMD
ϕ_D	280	1,4-Dibromonaphthalene sensitized,$^{(b)}$ 0.25 M TMD
β	$\sim$0.40	λ_{ex} = 313, 0.01 M TMD $^{(c)}$
$(1-\alpha)k_c$	$4.1 \pm 0.5 \times 10^6$ M^{-1} sec^{-1}	From eq. 7 $^{(d)}$
α	0.99 ± 0.01	From eqs. 6 and 7 $^{(e)}$
k_c	$\sim 1 \times 10^9$ M^{-1} sec^{-1}	From eqs. 6 and 7
ϕ_o	1.0	Chain quenched by 1,3-diene $^{(b)}$

a. Acetonitrile solutions. Deoxygenated by nitrogen purging for 3 minutes at -20°C.

b. The decomposition of TMD was monitored by uv-vis absorption; ± 10%. Ferrioxalate standard.

c. From direct measurement of acetone phosphorescence. Value corrected for quantum chain process.

d. Determined from a plot of τ_A^{-1} versus [TMD]; [TMD] = 10^{-1}–10^{-3} M; least squares fit. τ_A ([TMD]=0) = 3.6×10^{-5} sec; measured directly by photon counting techniques.

e. Derived from a plot of ϕ_D^{-1} versus $[\text{TMD}]^{-1}$; least squares fit.