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Efficiency of Excited State Carbonyl Production from the Thermolysis of 3,3-Diphenyl-1,2-dioxetane

Sir:

The unique ability of 1,2-dioxetanes to generate electronically excited carbonyl molecules during thermal decomposition has attracted considerable interest recently in these peroxides.¹ Thermochemical calculations suggest that sufficient energy is available from the thermal decomposition of 1,2-dioxetanes to obtain one of the carbonyl products in an excited state^{1a} (efficiency = $\alpha = 1.0$). However, experimental α values range from 0.005 to about 1.0.^{11, i, j, n, o, s, z, aa, bb} It is of considerable interest to determine what factors are responsible for the efficient conversion of the available thermal energy into electronic energy.

With this longer range goal as our objective, we now report the efficiency of excited state carbonyl production from the thermolysis of 3,3-diphenyl-1,2-dioxetane (DPD). Isomerization of *trans*-stilbene was used to determine the total efficiency of excited state carbonyl formation^{1z} from DPD, while excited state benzophenone molecules were specifically monitored by cycloaddition with 2-methyl-2-butene.

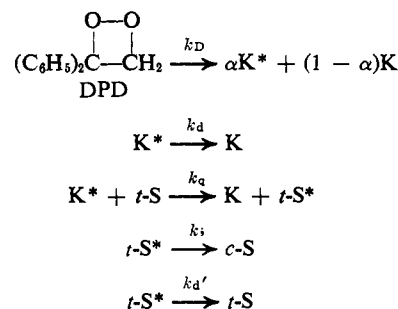
In Scheme I, the pertinent processes are shown for the decomposition of DPD in the presence of *trans*-stilbene (*t*-S) where *cis*-stilbene (*c*-S) is produced. The total excited state carbonyl molecules (benzophenone and formaldehyde) are represented by K^* and the ground state species by K . The apparent quantum yield (Φ_{App}) for isomerization of *t*-S is given by eq 1, where

$$\Phi_{App} = \alpha \Phi_{ET} \Phi_{t \rightarrow c} \quad (1)$$

$\Phi_{t \rightarrow c}$ is the quantum yield for isomerization of *t*-S and

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Scheme I



Φ_{ET} is the quantum yield for energy transfer between K^* and *t*-S (eq 2).

$$\Phi_{ET} = \frac{k_q[t\text{-S}]}{k_q[t\text{-S}] + k_d} \quad (2)$$

DPD was allowed to decompose in degassed benzene solution with *t*-S at 45° through approximately ten half-lives.² The amount of *c*-S was determined by glc (3% SE-30 on Varaport-30, 5 ft \times 1/8 in., 115°, flow 24 ml of N₂/min, FID; *t_r*(min), *c*-S (9.8), *t*-S (19)) and Φ_{App} was calculated as the ratio of millimoles of *c*-S produced/millimoles of DPD decomposed. With $\Phi_{t \rightarrow c} = 0.55^3$ and assuming Φ_{ET} is unity, α is calculated from eq 1. These data are given in Table I, where the con-

Table I. Isomerization of *trans*-Stilbene (*t*-S) from the Thermolysis of 3,3-Diphenyl-1,2-dioxetane (DPD) in Degassed Benzene at 45°

$10^3[\text{DPD}]_0$, <i>M</i>	$10^2[t\text{-S}]$, <i>M</i>	$10^2\Phi_{App}^a$	$10^2\alpha^b$
1.98	2.00	1.77	3.22
19.8	2.50	1.85	3.36
5.10	2.50	1.72	3.13
5.10	5.00	2.16	3.93
1.98	10.0	1.89	3.44
19.8	20.0	2.01	3.65
		Av 1.90 ± 0.12	Av 3.46 ± 0.23

^a Φ_{App} = millimoles of *c*-S produced/millimoles of DPD decomposed. ^b α = total efficiency of excited state carbonyl production from DPD, where $\alpha = \Phi_{App}/0.55$ and $\Phi_{t \rightarrow c} = 0.55$, $\Phi_{ET} = 1.00$.

centrations of both *t*-S and DPD are varied. The calculation of α from eq 1, with the approximation that Φ_{ET} is unity, requires that $k_q[t\text{-S}] \gg k_d$ in eq 2. This approximation appears reasonable for the data in Table I, where k_q is estimated to be $6.9 \times 10^9 M^{-1} \text{sec}^{-1}$ at 45°⁴ and at the lowest *t*-S concentration ($2.00 \times 10^{-2} M$), $k_q[t\text{-S}] = 1.4 \times 10^8 \text{sec}^{-1}$. This value is then sufficiently large, compared to $k_d \cong 10^5 \text{sec}^{-1}$ at 23°⁸ for benzophenone in benzene, to satisfy the approximation. As

(2) The preparation, characterization, products, and kinetics of DPD will be reported elsewhere.

(3) (a) D. Valentine, Jr., and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 3449 (1972); (b) H. A. Hammond, D. E. DeMeyer, and J. L. R. Williams, *ibid.*, **91**, 5180 (1969).

(4) This is obtained by correcting the reported value of $k_q = 5.0 \times 10^9 M^{-1} \text{sec}^{-1}$ at 25.5°⁸ to 45° with the Debye equation⁶ and with reported viscosities of benzene.⁷

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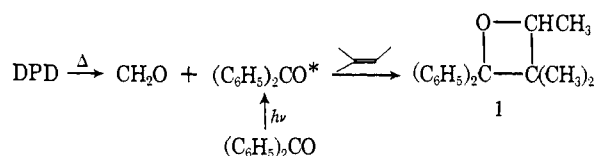
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seen from Table I, α shows little variation with a tenfold change in *t*-S concentration as would be anticipated from this approximation. Also variation in the initial concentration of DPD indicates that at these low concentrations of dioxetane, induced decomposition of DPD by excited state species^{1n,x} is unimportant.

Based on a Boltzmann distribution of excitation energy^{1d,9} between benzophenone and formaldehyde, it is expected that excited state benzophenone should be produced almost exclusively from DPD. To assess this potential model, DPD ($1.9 \times 10^{-2} M$) was decomposed with 0.946 *M* 2-methyl-2-butene in degassed benzene to give $\Phi_{A_{pp}} \cong 0.5 \times 10^{-2}$ (millimoles of **1** produced/millimoles of DPD decomposed) for **1** (Scheme II). The quantum yield for production of **1**

Scheme II



from 0.300 *M* benzophenone with 0.946 *M* 2-methyl-2-butene in degassed benzene, relative to 0.100 *M* benzophenone and 0.500 *M* benzhydrol actinometer in degassed benzene ($\Phi_{Act} = 0.91$),¹⁴ is 0.22.¹⁵ Assuming Φ_{ET} is unity, which is well approximated for stilbene isomerization, α is calculated from eq 1 to be approximately 2% for production of excited state benzophenone from DPD.

Considering experimental error, there is probably no significant difference between the total efficiency of excited state carbonyl formation and the production of excited state benzophenone, which would be in accordance with the Boltzmann distribution of excitation energy.¹⁸ Anomalous quenchers of excited state carbonyl products from DPD, to give low α values, are unlikely. The relative quantum yield for the formation of **1** from authentic reactants and from a decomposed sample of DPD with 2-methyl-2-butene is approximately unity in degassed benzene solutions. It is also unlikely that there is a "hidden" excitation of formaldehyde in the decomposition of DPD. The lifetime of triplet formaldehyde in the gas phase is estimated to be

(9) Triplet energies for benzophenone in solution and formaldehyde in the gas phase are reported to be 69¹⁰ and 72.5¹¹ kcal/mol, respectively. The corresponding singlet (S₁) energies are 74¹² and 81¹³ kcal/mol, respectively.

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(15) The minor isomer of **1**, 2,2-diphenyl-3,4,4-trimethyloxetane (**2**), is formed with a quantum yield of 0.032. Analyses for both of these isomers were performed by glc (3% SE-30 on Varaport-30, 5 ft \times 1/8 in., 130°, flow 30 ml H₂/min, FID; *t_r*(min) **1** (8.0) and **2** (6.4). Irradiations were performed with a 100-W medium-pressure Hanovia lamp on a merry-go-round¹⁶ with a potassium dichromate-carbonate filter solution to isolate the 302.5–313.0-nm region.¹⁷

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(18) Although the Boltzmann energy distribution model is consistent with the data, only the final energy distribution between the carbonyl products can be evaluated. It is possible that energy transfer between the carbonyl products in the solvent cage could occur so that the initial and final energy distribution is not the same.

10^{-8} to 10^{-9} sec.¹⁹ Considering eq 2, it should be possible to effect energy transfer from excited state formaldehyde to *t*-S at the quencher concentrations that were employed (Table I). Furthermore, when DPD was decomposed in toluene the expected "photoreduction" products of excited state formaldehyde, methanol, and ethylene glycol were not observed. Finally, the type I products from excited state formaldehyde, carbon monoxide, and hydrogen^{19,20} were not observed from the decomposition of DPD in degassed benzene. We are actively pursuing the effect of structure on α and on the distribution of excitation energy between two dissimilar carbonyl products for other substituted 1,2-dioxetanes.

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The Relationship between Metal-Donor Distance and Ring Size in Macrocyclic Complexes

Sir:

The significance of macrocyclic ligands and their metal complexes is most obvious as it relates to such natural products as the metalloporphyrins, vitamin B₁₂, and chlorophyll; however, other special aspects of such ligands have been found which will doubtless lead to a continued growth in the importance of these structurally distinctive materials.¹⁻³ The relationship between the size of the metal ion and the opening in the middle of the ring clearly must be important, because, for example, the iron porphyrins involve a 16-membered ring while the cobalt in vitamin B₁₂ occupies a 15-membered ring. Also, Pedersen's cyclic polyfunctional ethers show sharp selectivities toward alkali metal ions as a function of ring size.⁴ Early observations on complexes with substituted 14-membered tetraaza macrocyclic ligands led to the suggestion that a constrictive effect might be responsible for their surprisingly large ligand field strengths.⁵ We wish to report a quantitative assessment of the metal ion ring size relationship that is both experimental and theoretical in origin. We have demonstrated that there is an ideal ring size for any metal ion having a given metal-donor atom distance and that ring sizes slightly smaller (0.1–0.2 Å in terms of M–N distance) than the best fit ring show abnormally strong metal-donor bonds while

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