

substituents (possibly a heavy atom effect<sup>17</sup> on spin-orbit coupling) rather than with increasing activation energy.

In summary, we have provided evidence that if sufficient energy (as enthalpy) is available, the direct thermal population of triplet states is possible as a result of a molecular rearrangement.<sup>18</sup>

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(17) (a) It is interesting to note that benzene triplet is believed to possess  $D_{2h}$  symmetry, *i.e.*, belong to the same point group as Dewar benzene: M. S. de Groot and J. H. van der Waals, *Mol. Phys.*, **6**, 545 (1963). (b) See S. K. Lowen and M. A. El-Sayed, *Chem. Rev.*, **66**, 199 (1966), for a discussion of spin-orbit interactions in organic molecules.

(18) Nearly all reported chemiluminescent reactions involving organic molecules in solution are oxidative fragmentations or electron transfers.

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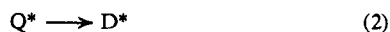
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### Tetramethyl-1,2-dioxetane. A Mechanism for an Autocatalytic Decomposition. Evidence for a Quantum Chain Reaction

Sir:

Studies directed toward an understanding of the mechanisms of chemiluminescent reactions of organic molecules in fluid solution currently provide an area of lively and expanding interest and importance. Recent breakthroughs<sup>1</sup> in the syntheses of 1,2-dioxetanes, molecules believed to be significant intermediates in many known chemiluminescent reactions,<sup>2</sup> allow a direct study of chemelectronic generation of excited states. Because of their exceptionally high energy content and unique electronic structure, 1,2-dioxetanes might well be expected to be involved in unusual and novel mechanisms. We report here evidence for such a situation, namely the occurrence of a quantum chain reaction (eq 1 and 2) in which electronic excitation energy is cycled through a number of steps.



The chemiluminescent system studied was the decomposition of tetramethyl-1,2-dioxetane (**1**). Our experiments were run by using chemiluminescence, *i.e.*, acetone fluorescence, to monitor the relative concentration of **1** (benzene solution 0.3-1.0 *M* at 72°). The decay of fluorescence was found to be experimentally indistinguishable from the disappearance of **1** as monitored by quantitative nmr analysis. The disappearance of **1** is cleanly first order for aerated solutions but shows drastic deviation from first-order kinetics when degassed solutions are analyzed (Figure 1). Indeed the half-life of a 1 *M* degassed solution of **1** (benzene) at room

(1) K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969); W. Adam and J. C. Liu, *J. Amer. Chem. Soc.*, **94**, 2894 (1972).

(2) F. McCapra, *Pure Appl. Chem.*, **24**, 611 (1970).

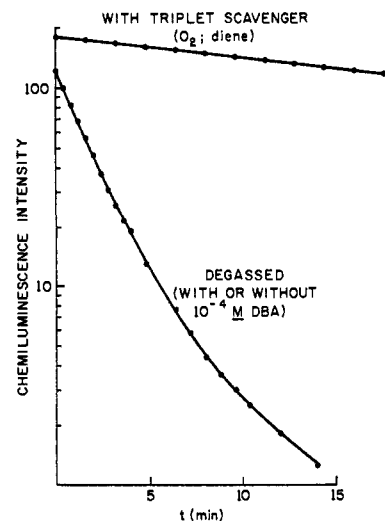
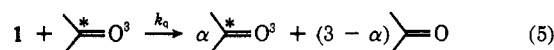
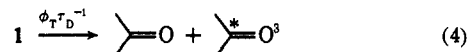
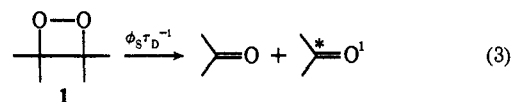


Figure 1. Typical decay of chemiluminescence intensity of **1** in aerated and degassed solution. In benzene solution at 72° the lifetime of **1** is  $\tau_D = 42$  min in the presence of oxygen or 1,3-dienes.

temperature is of the order of 1-2 min, while a 1 *M* aerated solution is of the order of  $10^3$ - $10^4$  min!

Our mechanism to explain these results is proposed in eq 3-5. In the presence of oxygen, triplet acetone is



generated<sup>3</sup> as a result of reaction 3 only by intersystem crossing ( $k_{ST} \sim 10^9 \text{ sec}^{-1}$ ) and with low efficiency ( $\phi_s \sim 0.01$ ).<sup>3</sup> Equation 4 represents the major path for production of acetone triplet. In aerated solutions the latter is deactivated by oxygen<sup>4</sup> faster than it sensitizes destruction of a molecule of **1**. Significant formation of singlet acetone in a step analogous to (5) is rendered unlikely by the observation that the initial luminescence intensity in aerated solution is *higher* than in degassed solutions; thus, when "self-sensitization," such as reaction 5, occurs fewer singlets are produced than in the thermolysis when triplets are efficiently quenched by  $\text{O}_2$  (Figure 1).

In order to calculate a rate expression for the proposed mechanism, we assume a steady state in excited acetone and thereby obtain<sup>5</sup> eq 6, which provides a

$$\exp \left[ \left( 1 + \frac{1-\alpha}{\phi_s + \phi_T} \right) \left( \ln \left( \frac{F}{F_0} \right) + \frac{t}{\tau_D} \right) \right] = \frac{1 + (1-\alpha + \phi_s + \phi_T) k_q \tau_T [1]_0 (F/F_0)}{1 + (1-\alpha + \phi_s + \phi_T) k_q \tau_T [1]_0} \quad (6)$$

measurable relationship between the fluorescence intensity  $F$  (which measures the concentration of **1**) and time. In this equation,  $F_0$  and  $[1]_0$  are the fluorescence

(3) N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, **94**, 2886 (1972).

(4) Oxygen and 1,3-pentadiene are excellent triplet scavengers; see N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1964.

(5) For a detailed derivation of eq 6, please write the senior author at Columbia University.

intensity and concentration of dioxetane at an arbitrary time  $t = 0$ ,  $\alpha =$  the number of acetone triplets in step 5,  $\phi_T$  and  $\phi_S$  are the triplet and singlet yields in steps 3 and 4,  $k_q$  is the rate constant for step 5, and  $\tau_T$  is the inherent lifetime of triplet acetone under the reaction conditions and  $\tau_D$  is the lifetime of **1** at the given temperature. By using  $(1 - \alpha)/(\phi_S + \phi_T)$  as an adjustable parameter we obtain a "best line fit" of our data for a plot of the left-hand side of eq 6 vs.  $F/F_0$ .

We find that the best line fit of eq 6 with our kinetic data for **1** in degassed solution occurs for  $(1 - \alpha)/(\phi_S + \phi_T) = 0.05 \pm 0.02$ , thereby yielding a value of  $\alpha = 0.98 \pm 0.02$ . Since the values of  $\phi_S$  and  $\phi_T$  have been measured independently<sup>3</sup> and are assumed to be independent of temperature, we calculate that  $k_q\tau_T$  (eq 6) is  $10^3 M^{-1}$  (error  $\pm 50\%$ ). These averages were determined from the linearity of plots for several runs, with the initial concentration of **1** varying from 0.3 to 1.0  $M$ .

Tests for radical induced reactions proved negative. For example, decomposition of **1** (in aerated solution) in the presence of azoisobutyronitrile showed no effects on the observed rate of decay of **1**.

Equations 3–5 predict that the decay of triplet acetone concentration should also have the same time dependence as the decay of **1** itself. To establish this relationship experimentally, we followed the triplet acetone concentration by monitoring the fluorescence of 9,10-dibromoanthracene (DBA) ( $10^{-4} M$ ), added to a degassed solution of **1** in benzene.<sup>6</sup> As predicted, the decay of emission of the DBA was the same as that of the concentration of **1** itself. It is important to note that the fluorescence of DBA results from triplet to singlet energy transfer;<sup>6</sup> however, since  $10^{-4} M$  DBA quenched less than 5% of triplet acetone, the kinetics of decomposition of **1** were not significantly altered.

As a further test of steps 3–5, we predict that the decay of **1** in degassed solutions will be the same as that of the aerated solution when a specific triplet quencher is present. Indeed, strict first-order kinetics for decay of **1** are observed in degassed solutions containing 1  $M$  1,3-pentadiene<sup>4</sup> or  $10^{-2} M$  1,3-cyclooctadiene (Figure 1).

These results contrast with those found for another dioxetane system *cis*-diethoxy-1,2-dioxetane<sup>7</sup> (**2**). Here the decay of *indirect chemiluminescence* of anthracenes, induced by decomposition of **2**, proceeds at a faster rate but with *higher* initial intensity (followed by a lower integrated intensity) in the absence of oxygen. Without anthracenes the same rates were found for aerated and degassed solutions. It was proposed<sup>7</sup> that these results could be explained on the basis of sensitization of dioxetane decomposition by triplet anthracene.

In conclusion, our results provide strong evidence for occurrence of the quantum reaction sequence involving eq 5 as the key step. To our knowledge, this represents the first example of a reaction in which the chain decomposition of a molecule occurs as the direct result of interaction with its electronically excited cleavage prod-

(6) Due to the enhancement of spin-orbit coupling by the two bromine atoms, the fluorescent  $S_1$  state of 9,10-dibromoanthracene is capable of accepting electronic energy from singlet and from triplet donors; see V. L. Ermolaev and E. B. Sveshinkova, *Opt. Spectrosc. (USSR)*, 324 (1970); V. A. Belyakou and R. F. Vassil'ev, *Photochem. Photobiol.* 11, 179 (1970).

(7) T. Wilson and A. P. Schaap, *J. Amer. Chem. Soc.*, 93, 4126 (1971).

ucts. The support for this chain resides in the good fit of our kinetic data to eq 6 (the rate expressions for mechanisms 3–5), the failure of radical initiations to affect the kinetics of decay of **1** and the identity of decay of DBA fluorescence to that of chemiluminescence of **1** in the absence of DBA, and furthermore in the ability of 1,3-pentadiene to restore first order kinetics for **1** in degassed solution.

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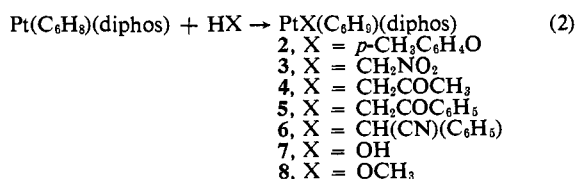
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### Formation of Platinum(II)–Oxygen and –Carbon $\sigma$ -Bonded Complexes by Protonation of Cyclohexyne–Platinum(0) Complexes with Weak Protic Acids and the Nature of the $\beta$ -Oxoalkyl–Platinum(II) Bond

Sir:

Acetylenes coordinated to platinum(0) are readily protonated by strong acids such as HCl and  $CF_3CO_2H$  to give platinum(II)–alkenyls<sup>1–3</sup> (eq 1). This property  $Pt(RC\equiv CR)[P(C_6H_5)_3]_2 + HX \rightarrow PtX(CR=CHR)[P(C_6H_5)_3]_2$  (1) is shared by the analogous complexes of cyclohexyne and cycloheptyne,<sup>4</sup> but we now report that the cyclohexyne complex  $Pt(C_6H_8)(diphos)$  (**1**)<sup>5</sup> is unique in being readily protonated by *weak* protic acids such as nitromethane, acetone, water, and methanol; the products are colorless, air-stable platinum(II) cyclohexenyls (eq 2).



The reactions are carried out either in benzene at room temperature (**2**, **3** and **8**) or in refluxing toluene (**4**, **5**, **6**, and **7**). Complexes **7** and **8** represent the first nonionic mononuclear hydroxy and methoxy complexes of platinum(II) to be isolated<sup>6</sup> and are probably formed by an initial oxidative addition of water and

(1) D. M. Barlex, R. D. W. Kemmitt, and G. W. Littlecott, *Chem. Commun.*, 613 (1969).

(2) P. B. Tripathy and D. M. Roundhill, *J. Amer. Chem. Soc.*, 92, 3825 (1970).

(3) B. E. Mann, B. L. Shaw, and N. I. Tucker, *J. Chem. Soc. A*, 2667 (1971).

(4) M. A. Bennett, G. B. Robertson, P. O. Whimp, and T. Yoshida, *J. Amer. Chem. Soc.*, 93, 3797 (1971).

(5) diphos = 1,2-bis(diphenylphosphino)ethane,  $(C_6H_5)_2PCH_2-CH_2P(C_6H_5)_2$ ;  $C_6H_8$  = cyclohexyne;  $C_6H_9$  = cyclohexenyl.

(6) The binuclear complex  $Pt_2(OH)_2[(C_6H_5)_2PO]_2[P(C_2H_5)_3]_2$ , which contains bridging phosphinato groups and terminal hydroxy groups, is known: J. Chatt and B. T. Heaton, *J. Chem. Soc. A*, 2745 (1968). The supposed hydroxy complex  $Pt(OH)[Ge(C_6H_5)_3]_2[P(C_2H_5)_3]_2$  is actually a  $\sigma$ -phenyl derivative,  $Pt(C_6H_5)[Ge(C_6H_5)_3]_2(OH)[P(C_2H_5)_3]_2$ : R. J. D. Gee and H. M. Powell, *ibid.*, 1956 (1971).