

from levulinic acid by two steps⁷ and isolated by silica gel column chromatography (97% based on levulinic acid). The ketone IV was obtained in 97% yield by the reaction of III with *n*-hexylmagnesium bromide, and the hydrolysis of IV by our method⁸ afforded 1,4-diketone (VI) in 98% yield. Dihydrojasmane was obtained from VI according to the method of Hunsdieker⁹ in 84% yield. Analogously, olefinic 1,4-diketone (VII) was isolated in 82% yield by the reaction of III with 3-*cis*-hexenylmagnesium bromide, followed by the hydrolysis⁸ of the ethylene dithioacetal. VII was converted to *cis*-jasmane in 81% yield by the ordinary procedure.⁹

From the above results, it was assumed that thioates having a skeleton such as RCOSC=N— would preferably form ketones by treatment with Grignard reagents through the coordination intermediate. In fact, it was found that benzophenone was obtained in 98% yield by the reaction of 2-(benzoylthio)benzothiazole with phenylmagnesium bromide.

(7) The thioate III was prepared by the reaction of 4-oxovaleric acid ethylene dithioacetal, which was obtained from levulinic acid and ethanedithiol, with 2,2'-dipyridyl disulfide and triphenylphosphine in acetonitrile at room temperature for 10 min; T. Endo, S. Ikenaga, and T. Mukaiyama, *Bull. Chem. Soc. Jap.*, **43**, 2632 (1970).

(8) K. Narasaka, T. Sakashita, and T. Mukaiyama, *Bull. Chem. Soc. Jap.*, **45**, 3724 (1972).

(9) H. Hunsdieker, *Chem. Ber.*, **75**, 460 (1942).

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"Solvent Effects" on the Chemiluminescent Decomposition of Tetramethyl-1,2-dioxetane. Competitive Dark Pathways

Sir:

The kinetic parameters of the thermal decomposition of tetramethyl-1,2-dioxetane (TMD), which generates high yields of triplet acetone and very little excited singlet,¹ have recently been reported to be solvent dependent.² Thus, ΔH^\ddagger drops from 25 kcal in benzene to 13 kcal in methanol, while ΔS^\ddagger changes from -1 to -34 eu. The greatly altered activation parameters in methanol, assumed to belong to the same luminescent mechanism as in benzene, were taken to support a unique concerted, spin-forbidden process resulting in one excited triplet and one ground-state acetone molecule. The addition of amines³ has recently been shown to catalyze, with a very similar lowering of the activation energy, the decomposition of *cis*-diethoxydioxetane⁴ via a competitive "dark" pathway, superposed on the normal chemiluminescent decomposition. We present evidence here that TMD decomposes similarly by two competitive paths in methanol and ethanol, and that the *fast* reaction in these solvents produces no excited

Table I. Activation Energy of Luminescent TMD Decomposition from Temperature Drop^a

Solvent	Fluorescer	E_{chl} , kcal M^{-1b}	E_a , kcal M^{-1b}
Benzene	None added	27	27
	DBA	22	26
Ethanol	None added	23	23
	DBA	22	26
Methanol	DBA	24	28

^a Air present; temperature range, 50–70°; [TMD], 0.04 or 0.08 M; $E_a = E_{\text{chl}} - E_{\Phi F}$. ^b ± 2 kcal.

acetone, for (a) the faster the reaction, the lower the net luminescence yield, (b) the activation energy of the luminescent pathway is unchanged in the hydroxylic solvents, (c) the yield of reaction products from intercepted triplet acetone runs parallel to the chemiluminescence yield, and (d) exclusion of oxygen converts the benzene reaction from one of first order to one of second order in dioxetane, as predicted by a previous treatment,⁵ but has no effect on the order of the alcohol reaction. In addition, we show that the very rapid dark reaction is not due to the alcohols themselves, but to a powerful catalyst present in traces even after careful distillation.

In the chemiluminescent decomposition of TMD,⁶ the initial luminescence intensity (acetone fluorescence; no fluorescer added) is proportional to the initial concentration of dioxetane multiplied by the rate constant for chemiluminescent cleavage, while the rate of decline of this intensity is proportional to the total decomposition rate of the TMD by all mechanisms. Thus it is possible to study a dark reaction by observing the intensity and decay rate of the competitive chemiluminescent reaction. Although the rates of decay of luminescence from TMD at 57° can be 100 times greater in methanol or ethanol than in benzene, the initial intensities are not larger and therefore the overall quantum yields are significantly smaller in the alcohols. When 9,10-dibromoanthracene (DBA) is added to the benzene or alcohol solution of TMD, the luminescence yields in both solvents are considerably increased (because DBA receives its excitation energy from triplet acetone, much the more abundant donor here), but again the yields are much higher in benzene (by two to three orders of magnitude over the yields in methanol). Thus, unless ethanol and methanol were effective quenchers of singlet and triplet acetone, which is not the case,⁷ these results mean that fewer molecules of acetone are generated in excited states in these solvents.

The activation energy of the luminescent process is measured by quickly cooling,⁸ from T_1 to T_2 , a dioxetane solution undergoing chemiluminescent decomposition and measuring the light intensities immediately before, I_1 , and after, I_2 , the temperature drop.^{3,4b} Because the

(5) P. Lechten, A. Yekta, and N. J. Turro, *J. Amer. Chem. Soc.*, **95**, 3027 (1973). We thank Dr. Turro for a prepublication copy of this manuscript.

(6) All chemiluminescence procedures as in ref 4. TMD was prepared according to Dr. K. R. Kopecky's procedure (private communication). All solvents were Mallinckrodt, AR, used without further purification unless indicated otherwise.

(7) R. F. Borkman and D. R. Kearns, *J. Amer. Chem. Soc.*, **88**, 3467 (1966).

(8) ~ 30 sec, so that the concentration of dioxetane can be considered constant throughout this interval.

(1) N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, **94**, 2886 (1972).
(2) (a) N. J. Turro and P. Lechtken, *ibid.*, **95**, 264 (1973); (b) *Pure Appl. Chem.*, **33**, 363 (1973).

(3) D. C.-S. Lee and T. Wilson, presented at the International Conference on Chemiluminescence, Athens, Ga., Oct 1972; in "Chemiluminescence and Bioluminescence," M. J. Cormier, D. M. Hercules, and J. Lee, Ed., Plenum Press, New York, N. Y., 1973, p 265.

(4) (a) This reaction, when uncatalyzed, also generates high yields of triplet carbonyl fragments; (b) see T. Wilson and A. P. Schaap, *J. Amer. Chem. Soc.*, **93**, 4126 (1971).

Table II. Yields of Products from Reaction of Triplet Acetone, Generated by TMD Thermolysis, with Solvent^a

Solvent ^b	Reaction time, hr	Temp, °C	A Acetone, ^c %	B Benzene, ^c %	C 2-Propanol ^c + radical coupling products, ^c %
1,4-Cyclohexadiene ^d	2	70	90	7.5 ± 0.5	10 ± 1 ^e
1,4-Cyclohexadiene-CH ₂ Cl ₂ (3:2)	2.5	55	96	2 ± 1	3.5 ± 1
1,4-Cyclohexadiene-CH ₂ Cl ₂ (4:1)	2.5	55	93	6.5 ± 1	7.5 ± 1
1,4-Cyclohexadiene-methanol (4:1)	2	55	100	None observable <0.5	None observable <1

^a All reactions were carried out in sealed, degassed, nmr tubes. ^b Concentration of TMD in neat 1,4-cyclohexadiene is 0.25 M; in all other experiments, [TMD] is 0.2 M. ^c Analysis of solution on Varian T-60 nmr: 1,4-cyclohexadiene, δ 2.7, 5.7; acetone, δ 2.1; benzene, δ 7.3; 2-propanol, δ 1.1, 1.2; 2-(2,4-cyclohexadienyl)-2-propanol, δ 1.18; pinacol, δ 1.2. A + C taken as 100%. ^d The 1,4-cyclohexadiene (Eastman) was purified by vpc and was benzene free. ^e 2-Propanol: 7.5 ± 0.5%

fluorescence of DBA has an activation energy of -4 kcal, E_a , the activation energy of the luminescent decomposition of TMD, is equal to 4 + E_{ChI} , the activation energy derived from the luminescence intensities at the two temperatures. From the figures in Table I it can be seen that the activation energies of the *chemiluminescent* decomposition path are reproducible, are the same with and without fluorescer added, and are not significantly different in the alcohols from their values in benzene. This is in contrast with the reported much lower values for the *overall* activation energies in alcohols from an Arrhenius treatment.² The latter, of course, are based on total decomposition rates of the dioxetane.

A striking characteristic of the rates in methanol and ethanol is their irreproducibility. In discussing this point with Professor W. H. Richardson⁹ of San Diego State University, we learned of the observation in his laboratory that ethylenediaminetetraacetic acid (EDTA) strongly retards certain dioxetane decompositions. We have subsequently found that various treatments can lower the rate of dioxetane decomposition in methanol by the following factors: standing over Chelex 100 for 1 day, ~10; passing through a Chelex 100 column, or distilling from disodium EDTA, ~20; standing with a large amount of Chelex 100 for 4 days, ~100; reacting solution made 5×10^{-4} M in disodium EDTA, ~250. The ratio of extreme rates was 116 for ethanol and 1.6 for benzene. The lowest rate constants thus far observed were the same within 15% in these three solvents ($3.9 \pm 0.6 \times 10^{-5}$ sec⁻¹ at 57°);¹⁰ the luminescence intensities and therefore the quantum yields were also the same.

The effectiveness of disodium EDTA and the sequestering resin Chelex 100 in lowering the catalyzed rates indicates that these accelerations are due not to the alcohols but to trace impurities, probably of transition metal compounds. This catalytic effect explains a previously observed rapid decomposition of the dioxetane in the metal cavity of a microwave spectrometer.¹¹ The addition of cupric chloride in a concentration of 10^{-5} M increased by a factor of ~100 the rate of TMD decomposition in methanol distilled from disodium EDTA. Even dipping a copper wire in benzene increased the TMD decomposition in that solvent tenfold!

A dark catalytic pathway is also supported by the

(9) W. H. Richardson, personal communication.

(10) Benzene untreated, ethanol with 10^{-4} M disodium EDTA, and methanol with 5×10^{-4} M disodium EDTA.

(11) W. E. Steinmetz, private communication.

following results. When TMD is thermolyzed in degassed 1,4-cyclohexadiene as solvent, products attributable to hydrogen abstraction by triplet acetone are found (Table II). In mixed, degassed cyclohexadiene and untreated methanol (4:1, v/v), the yield of H-abstraction products is sharply decreased relative to that in mixed, degassed cyclohexadiene-methylene chloride (4:1, v/v). This indicated that the catalyzed decomposition reduced the overall yield of excited acetone from TMD by a mechanism other than dilution of the diene.

Because excited acetone rapidly attacks TMD, the reaction in degassed benzene free of H donors acquires chain character and, at high dioxetane concentration, follows second-order kinetics, though having been of first order in the presence of oxygen. The rapid reaction of 1 M TMD in untreated methanol is not appreciably affected in rate nor in order by removal of oxygen. This is independent evidence that no excited acetone is produced by the catalytic decomposition of TMD in untreated alcohol.

Further work on the nature of this catalysis is actively in progress.

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A Computer-Assisted Analysis of the Camphor-¹⁴C Sulfuric Acid Reaction.¹ Is 3,2-Endo Hydroxyl Shift Necessary?

Sir:

We have devised a computer program² which allows

(1) This research was sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

(2) The method is based on permutations of the 11 letters A-K which describe specific positions on the 2-bicyclo[2.2.1]heptyl cation as follows: 1 = A; 2 = B; endo 3 = C; exo 3 = D; 4 = E; endo 5 = F; exo 5 = G; endo 6 = H; exo 6 = I; syn 7 = J; anti 7 = K. An abbreviated notation containing $n + 1$ characters represents any