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"1,2-Dioxetanes. Formation, Kinetics, and Excited State Products"

Final Report

William H. Richardson

31 August 1977

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Abstract

1,2-Dioxetanes fall into a unique class of compounds that possess the ability to generate electronically excited state products on thermolysis. The production of excited state products allows for the generation of light (Chemiluminescence, CL) from these reactions. Various applications of light production by chemical means can be considered, where conventional light production would be inadvisable or impossible.

The mechanism of thermolysis of dioxetanes has been pursued by kinetic methods with a goal of better understanding the mode of generating excited state species from these cyclic peroxides. Two mechanisms have been proposed for the thermolysis of dioxetanes; a stepwise biradical mechanism and a concerted process. A kinetic analysis of our data reveals that the stepwise process is favored for simply substituted dioxetanes. We have attempted to design dioxetanes and use medium effects in order to realize a concerted decomposition, but as yet this process has not been observed. We have noted some substituent effect on the kinetics of dioxetane thermolysis, but this appears to be best interpreted in terms of the stepwise process.

The relationship between dioxetane structure, the medium, and mode of thermolysis to the efficiency of excited state carbonyl production has been pursued. Increased steric effects in the dioxetane appear to increase the efficiency. In contrast, aryl substituents, which weaken the C-C bond in the oxybiradical that is generated from the dioxetane, lower the efficiency. These results are interpreted in terms of a stepwise process, which involves both singlet and triplet oxybiradicals. A preliminary, but consistent interpretation of the kinetic and efficiency data is presented.

The thermochemistry of dioxetane thermolysis dictates that only one carbonyl product can be in an excited state. For dissimilarly substituted dioxetanes, this raises the question as to which carbonyl product is produced in an excited state. From the data that are presently available, it appears that the energy is distributed between dissimilar carbonyl products on the basis of a Boltzmann distribution of excited state energies. Several methods have been used to evaluate the energy distribution and all methods point to a Boltzmann distribution.

The kinetics of the thermolysis of a 1,2-dioxolane have been studied. These peroxides are one unit higher in the homologous series from 1,2-dioxetanes. Previous literature values of activation parameters from 1,2-dioxolane thermolysis were extremely low and could be interpreted in terms of a concerted process. Since our data with 1,2-dioxetanes have indicated a stepwise process with four-membered ring peroxides, we were interested in the apparent discontinuity of mechanism in proceeding to the five-membered ring peroxides. Our kinetic results with 1,2-dioxolanes indicate that they are extremely susceptible to induced decomposition. However, in the presence of a radical trap, activation parameters are obtained, which approach those calculated on the basis of a stepwise process. Thus, there appears to be no mechanistic discontinuity between 1,2-dioxetanes and 1,2-dioxolanes.

(20. cont'd)

We have confirmed our original findings that at sufficiently low concentrations of α-hydroperoxy ketones, the quantum yield for photolysis becomes constant. It is in this unimolecular reaction range that a Type-II process may be operative to give a dioxetane intermediate. If so, the photolysis provides for the photochemical generation of a dioxetane, from which at a later time, thermal generation of CL could result. Some detailed product studies have been made to further understand this photolysis reaction. In addition, lifetimes of excited singlet and triplet species have been determined.

Peroxide fragmentation reactions have been studied, which involve high energy peroxides. The course of these reactions has been pursued by kinetic measurements and product studies. Although the particular systems that were studied did not produce excited state species, it seems that similar systems could be designed from which this would be possible.

"1,2-Dioxetanes. Formation, Kinetics, and Excited State Products"

Final Report

Introduction

Usually photoexcitation is required to produce electronically excited state species. In a few select chemical reactions, excited state species can be produced without photoexcitation. One of the best known examples of the chemical generation of excited state species is that found with the firefly. Here, the efficiency of generating the excited state product is about 90%. With this efficiency as a goal, various synthetic systems have considerable room for improvement, where typical efficiencies range from fractions of a percent to as high as about 40%.

Various applications of these chemical excitation processes have been made. Most of the applications depend upon using the excited state product to transfer energy to an acceptor, which then fluoreses. Numerous uses of light production *via* this chemical process can be conceived, where it is either inadvisable or impossible to use electric power. Analytical applications of the chemiluminescent (CL) reaction have been made as well. Since ATP is required to produce light in the firefly luciferin reaction, an analysis for ATP is based on light production from this reaction. In general, wherever it is advantageous to produce excited state species without photoexcitation, the use of chemiexcitation processes should be attractive.

Although applications of CL reactions have been made, their utilization is still in its infancy. No doubt many important applications are still in the future. Future utilization of CL reactions depends in part on increasing the efficiency of existing CL reactions and developing new CL reactions which may be more suitable for particular applications. To accomplish these objectives, a more thorough understanding of CL reactions is required. Presently, there is a limited understanding of the relationships between structure of molecules leading to CL reactions and medium effects vs the efficiency of excited state product formation. In general, the details of how a ground state molecule undergoes reaction to produce excited state products is poorly understood.

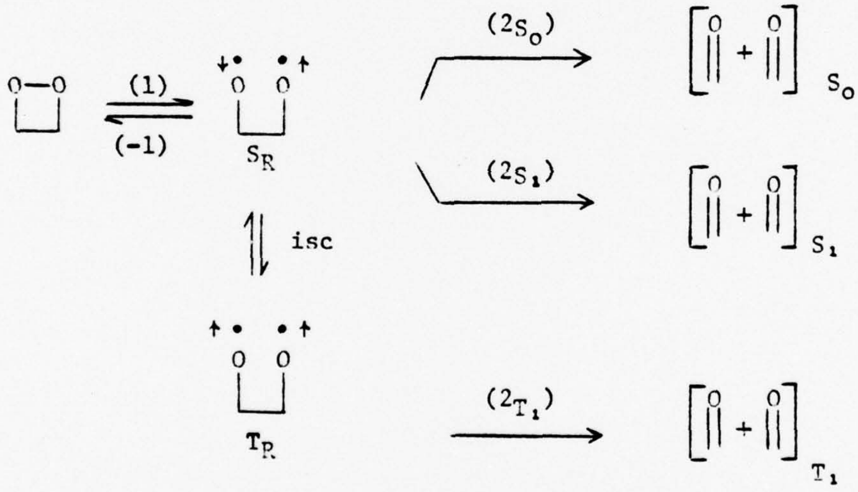
Most of our effects have been directed to the thermolyses of 1,2-dioxetanes (four-membered ring peroxides), which is one of the few classes of molecules that produces excited state species. Although light emission may not result from the thermolysis of dioxetanes, light emission can be accomplished with an acceptor which fluoreses. We have then centered our attention on the efficiency of excited state carbonyl production, since if this is high, adequate light production can be achieved with the appropriate fluorescer.

The mechanism of dioxetane thermolysis and efficiency of excited state carbonyl production may be intimately entwined. Two mechanisms can be considered, a stepwise O-O bond initiated decomposition and a concerted decomposition of the dioxetane. The efficiency and relative yields of triplet to singlet excited state carbonyls may be intimately related to the mode of decomposition. Our kinetic studies were made in an effort to determine how structural features of dioxetanes and the medium affects the mechanism of thermolysis. These kinetic studies are coupled to efficiency studies of excited state carbonyl production. The efficiency studies are directed to the measurement of triplet and singlet excited carbonyl production and also to how the excitation energy is distributed between two dissimilar carbonyl products.

We have observed that α-hydroperoxy ketones undergo photolysis to give an acid plus a ketone. Quantum yields are concentration dependent, but become constant at low peroxide concentrations. At these low peroxide concentrations, a dioxetane intermediate may be produced by a Type-II process. Thus, it may be possible to photolyze an α-hydroperoxy ketone at low concentration and then at a later time, thermally generate excited state species which could be used for light production.

Kinetics of Dioxetane Thermolysis. In this aspect of our work, we have attempted to define the mode of dioxetane thermolysis. For the dioxetanes that we have studied to date, the scheme below well accommodates our results.

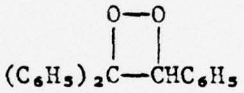
Scheme I



Here, S_0, S_1, and T_1 refer to the electronic states of the carbonyl products. The thermochemistry of the reaction dictates that only one excited state carbonyl molecule can be produced from the dioxetane. Thus, only one of the carbonyl **products in the S_1 and T_1 brackets** is in an excited state, while the other carbonyl is in the ground (S_0) state.

We have selected several dioxetanes for study in order to determine how both electronic and steric effects influence the mode of decomposition. As stated previously, the dioxetanes that we have studied to date are best accommodated by Scheme I. However, as discussed later, electronic and steric variations in the dioxetane substituents do effect the activation parameters for processes adequately defined by Scheme I. We have also been interested in preparing dioxetanes with suitable substituents so that a concerted decomposition might be realized. Furthermore, medium effects were investigated to see if this factor would influence the reaction course.

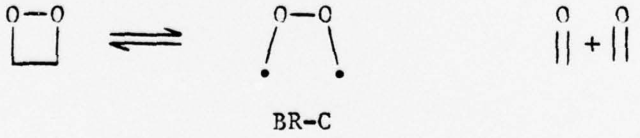
In an attempt to observe and identify a concerted dioxetane decomposition, triphenyl-1,2-dioxetane (TPD) was prepared and the kinetics of its thermolysis in benzene and methanol were studied. Three modes of decomposition can be



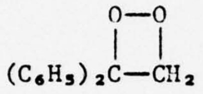
TPD

considered for TPD; an O-O initiated bond rupture (Scheme I), a C-C initiated process (Scheme II), and a concerted decomposition. Scheme II is expected to

Scheme II



become progressively more favorable relative to Scheme I as the carbon biradical (BR-C) centers are resonance stabilized by substituents such as phenyl groups. Furthermore, as the O-O and C-C bond energies become comparable, the possibility of a concerted reaction increases. One could then consider a reaction mechanism spectrum, where the two extremes are represented by O-O and C-C initiated bond rupture with the concerted process intermediately disposed. With regard to substituents, this would mean that substituents that could stabilize the potential carbon biradical (BR-C) would move the reaction type from O-O initiated rupture, to a concerted process, and finally to a C-C initiated rupture. Previously, we found that 3,3-diphenyl-1,2-dioxetane (DPD) was best charactertized as being an O-O initiated bond rupture process (Scheme I) and



$$\begin{array}{ccc} & \mathrm{O}\!-\!\!-\!\mathrm{O} & \\ & |\quad\;\; | & \\ (\mathrm{C_6H_5})_2 & \mathrm{C}\!-\!\!-\!\mathrm{CH_2} & \end{array}$$

DPD

it was hoped that TPD would progress in the reaction spectrum to a concerted process.

The results of our experimental activation parameters for TPD in benzene along with our calculated parameters based on Schemes I and II are given in Table I. It is seen from Table I that the experimental activation parameters

Table I. Experimental and Calculated Activation Parameters for Triphenyl-1,2-dioxetane (TPD)

Origin	E_a[a]	log A	$\Delta H^{\ddagger}$[a]	$\Delta S^{\ddagger}$[b]
Experimental[c]	23.3±.3	12.04±.19	22.6±.3	-5.6±.9
O-O Calcd[d]	25.1	12.8	24.4	-1.86
C-C Calcd[e]	31.6	13.9	30.9	+3.2

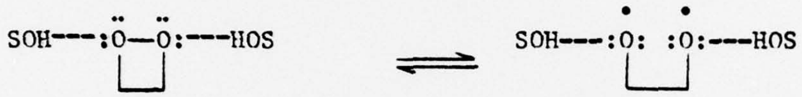
[a] kcal/mol. [b] eu. [c] In benzene. [d] Based on Scheme I. [e] Based on Scheme II.

are in best agreement with those calculated according to Scheme I (O-O bond homolysis) and differ significantly from those calculated from Scheme II (C-C bond homolysis). The experimental activation energy (E_a) is lower than that calculated according to Scheme I, which is in the direction expected for either a concerted decomposition or where steps (-1) and (2) in Scheme I become competitive. Considering the error in the calculated E_a value, a firm conclusion regarding these latter possibilities cannot be made. However, from an analysis of substituent effects in the concerted thermolyses of cyclobutenes and cyclobutenones, a concerted process appears unlikely. The results are then best interpreted in terms of Scheme I, where it may be possible that steps (-1) and (2) are competitive.

To further resolve this problem, experimental activation parameters in methanol (with EDTA) were obtained. Walling and Wagner have found that the activation energy for β-scission of _t_-butoxy radicals was lowered in proceeding from an aprotic to a protic solvent. The lower activation energy in the protic solvent is apparently due to stabilization of the developing polar carbonyl moiety by hydrogen bonding in the activated complex. This reaction provides a possible model for distinguishing between concerted and stepwise dioxetane decomposition. Since polar carbonyl moieties are generated in the rate determining step of a concerted dioxetane decomposition (eq 2), a similar response to a protic solvent would be expected as found in the β-scission process (eq 1). In contrast, if the rate determining step in Scheme I is associated with O-O bond homolysis (eq 3), little or no effect is expected upon changing from an aprotic to a protic solvent. The experimental activation parameters for TPD in methanol (with EDTA) are: $E_a = 23.3 \pm .5$ kcal/mol, $\log A = 12.07 \pm .34$, $\Delta H^{\ddagger} = 22.6 \pm .5$ kcal/mol, and $\Delta S^{\ddagger} = -5.5 \pm 1.5$ eu. Since these activation parameters are nearly identical to those in benzene, a concerted

(1)

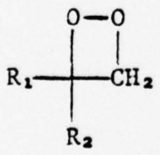
(2)



(3)

decomposition (eq 2) appears unlikely. Furthermore, if this model comparison is appropriate, Scheme I is suggested with the rate determining step associated with O-O bond homolysis.

Further use of the methanol solvent probe was used to deduce the mechanism of thermolysis of 3,3-dimethyl-1,2-dioxetane (DMD), 3-phenyl-3-methyl-1,2-dioxetane (PMD), 3,3-diphenyl-1,2-dioxetane (DPD), and 3,3-dibenzyl-1,2-dioxetane (DBD). The results of this study are presented in Table II along with the



DMD, $R_1=R_2=CH_3$

PMD, $R_1=C_6H_5$, $R_2=CH_3$

DPD, $R_1=R_2=C_6H_5$

DBD, $R_1=R_2=C_6H_5CH_2$

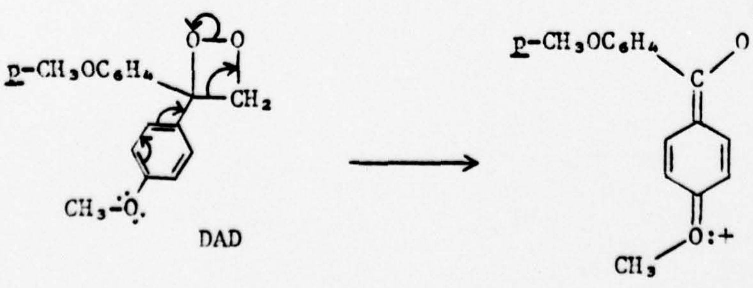
decrease in activation energy (δE_a) in proceeding from an aprotic solvent to methanol. Although some decrease in E_a is noted in proceeding from an aprotic to a protic (methanol) solvent, the decrease is small compared to that observed in the β-scission of the t-butoxy radical (6 kcal/mol, eq 1). This suggests that a concerted mechanism is not operative. However, the small decrease in E_a (ie, δE_a) could be indicative of a competition between steps (-1) and (2) in Scheme I.

Table II. Experimental Activation Parameters for the Thermal Decomposition of Substituted Dioxetanes in Methanol

Dioxetane	E_a[a]	Log A	$\Delta H^{\ddagger}$[a]	$\Delta S^{\ddagger}$[b]	δE_a[a,c]
DMD	20.7±.1	10.72	20.1±.1	-11.6±.5	2.3
PMD	21.2±.1	11.33	20.5±.1	-9.68±.38	1.7
DPD	22.2±.2	12.12	21.6±.2	-5.11±.50	0.5
DBD	22.4±.3	11.55	21.8±.3	-7.72±1.12	1.9

[a] kcal/mol. [b] eu. [c] E_a (aprotic solvent) - $E_a(CH_3OH)$.

In another attempt to observe a concerted decomposition, we have prepared and studied the kinetics of thermolysis of 3,3-(bis-p-anisyl)-1,2-dioxetane (DAD). It was thought that the "unzipping" process indicated in eq 4 might



(4)

facilitate a concerted process. Activation parameters were determined in both benzene and methanol (with EDTA) **solvent**. These data along with activation parameters for the model compound (DPD) are given in Table III. Considering the small solvent effect (benzene vs methanol) for DAD, a concerted decomposition appears unlikely. Yet, the activation energy for DAD is noticeably lower than for DPD in both benzene and methanol. In terms of relative rates at 60°C in benzene k_{DAD}/k_{DPD} is 3.65. This substituent effect can be explained in terms of Scheme I, if steps (-1) and (2) are of comparable velocities. This explanation would also be in agreement with the small decrease in E_a observed for DAD, upon changing from the aprotic to the protic solvent.

Table III. Activation Parameters for the Thermolysis of 3,3-(bis-p-Anisyl)-1,2-dioxetane (DAD) and 3,3-Diphenyl-1,2-dioxetane (DPD)

Dioxetane	Solvent	E_a[a]	log A	$\Delta H^{\ddagger}$[a]	$\Delta S^{\ddagger}$[b]
DAD	Benzene	21.4	12.07	20.7	-5.5
DAD	Methanol	20.9	11.91	20.2	-6.1
DPD	Benzene	22.7	12.36	22.0	-4.1
DPD	Methanol	22.2	12.12	21.6	-5.1

[a] kcal/mol. [b] eu.

To further delineate the possible competition between steps (-1) and (2) in Scheme I, a kinetic study of a series of para- and meta-aryl substituted dioxetanes is planned. Recently, we have synthesized 3-p-bromophenyl-3-methyl-1,2-dioxetane for this purpose. We anticipate that the kinetic studies should proceed without difficulty.

In view of the proposed biradical intermediates in the thermolyses of dioxetanes, we have been interested in the possibility of trapping these intermediates. Wagner and coworkers have successfully trapped 1,4-biradicals, produced in the Type-II photolysis of ketones, with mercaptans. This report encouraged us to attempt the trapping of 1,4-biradicals derived from dioxetanes with mercaptans. Preliminary experiments with DBD and dodecanethiol have proved interesting. At mercaptan concentrations between approximately 0.1 to 2.0 M, the rate of decomposition of DBD (3.77×10^{-4}M in benzene) is accelerated by about 40-fold and proceeds with zero-order dependence on mercaptan. The efficiency of excited state carbonyl production is also decreased in the presence of mercaptan. Although alternative explanations need to be pursued, it is attractive to interpret these results once again in terms of comparable rate coefficients for steps (-1) and (2) in Scheme I. Thus, intercepting the biradical with mercaptan and thereby preventing reclosure to the dioxetane would increase the rate of dioxetane decomposition. This would also explain the zero-order dependence on mercaptan at higher concentrations of the radical trap. Furthermore, interception of the biradical by mercaptan would divert the reaction from producing excited state carbonyls and thus lower the efficiency of this process as was observed. Further kinetic and product studies are in progress to either substantiate or reject these proposed interpretations.

Efficiency of Excited State Carbonyl Production from Dioxetanes. One of the important goals in dioxetane chemistry is to relate the efficiency of excited state carbonyl production to the structure of the dioxetane, the mode of decomposition of the dioxetane, and the medium. In order to assess the importance of these factors upon the efficiency of excited state carbonyl production, an interplay between efficiency measurements and kinetic data has been used to a considerable degree in our laboratory.

We have used two methods to determine the total triplet carbonyl efficiency production dioxetanes. In one method the isomerization of *trans*-stilbene was monitored, while in the other method light emission from 9,10-dibromoanthracene (DBA) was measured. The latter method was developed by Turro and coworkers, and was shown to specifically monitor triplet carbonyl products. By the former method, the apparent quantum yield (Φ_{App}) is given by eq 5 and 6, where α_{T_1} is the total efficiency of triplet carbonyl production,

$$\Phi_{App} = \text{mmol } \underline{\text{cis}}\text{-stilbene formed/mmol dioxetane decomposed} \qquad (5)$$

$$\Phi_{App} = \alpha_{T_1} \Phi_{ET} \Phi_{t \to c} \qquad (6)$$

Φ_{ET} is the energy transfer quantum yield, and $\Phi_{t \to c}$ is the quantum yield for *trans*- to *cis*-stilbene isomerization. With the scheme below, where K* is triplet carbonyl, *t*-S is *trans*-stilbene, and *c*-S is *cis*-stilbene, eq 7 results from eq 6. By glc analysis, the mmol of *c*-S produced is obtained, and $1/\Phi_{App}$

Scheme III

$$\longrightarrow \mathrm{K}^* + \mathrm{K}$$
$$\alpha_{T_1} \qquad (1-\alpha_{T_1})$$

$$\mathrm{K}^* \xrightarrow{k_d} \mathrm{K}$$

$$\mathrm{K}^* + \underline{t}\text{-S} \xrightarrow{k_t} \mathrm{K} + t\text{-S}^*$$

$$\underline{t}\text{-S}^* \longrightarrow \underline{t}\text{-S} + \underline{c}\text{-S}$$

$$1/\Phi_{App} = \frac{1}{\alpha_{T_1} \Phi_{t \to c}} \left[1 + \left(\frac{k_d}{k_t} \right) \frac{1}{[t\text{-S}]} \right] \qquad (7)$$

is calculated from eq 5, and then $1/\Phi_{App}$ is plotted vs $1/[\underline{t}\text{-S}]$. From the intercept, α_{T_1} is calculated with the literature value for $\Phi_{t\to c}$ (0.55).

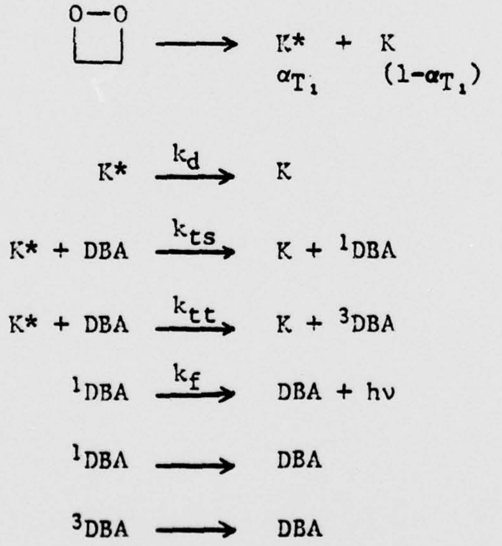
the DBA method, the apparent quantum yield is given by eq 8 and 9,

$$\Phi_{App} = \text{Photons from DBA fluorescence in Einstein's mol} \Big/ \text{dioxetane decomposed} \qquad (8)$$

$$\Phi_{App} = \alpha_{T_1}\Phi_{ET}\Phi_f^{DBA} \qquad (9)$$

where Φ_{ET} is the energy transfer quantum yield to DBA to give singlet DBA, and Φ_f^{DBA} is our measured quantum yield for DBA fluorescence. From Scheme IV, one obtains eq 10. Using a specially designed apparatus, which couples a thermostated cell to a photomultiplier tube, one can calculate $1/\Phi_{App}$ from eq 8.

Scheme IV



$$\text{O—O dioxetane} \longrightarrow \underset{\alpha_{T_1}}{K^*} + \underset{(1-\alpha_{T_1})}{K}$$

$$K^* \xrightarrow{k_d} K$$

$$K^* + DBA \xrightarrow{k_{ts}} K + {}^1DBA$$

$$K^* + DBA \xrightarrow{k_{tt}} K + {}^3DBA$$

$${}^1DBA \xrightarrow{k_f} DBA + h\nu$$

$${}^1DBA \longrightarrow DBA$$

$${}^3DBA \longrightarrow DBA$$

$$1/\Phi_{App} = \frac{1}{\alpha_{T_1}\Phi_f^{DBA}}\left[\frac{k_{ts}+k_{tt}}{k_{ts}} + \left(\frac{k_d}{k_{ts}}\right)\frac{1}{[DBA]}\right] \qquad (10)$$

The photomultiplier system was calibrated by using the α_{T_1} value for DMD as obtained by *trans*-stilbene isomerization. A plot of $1/\Phi_{App}$ *vs* $1/[DBA]$ gives an intercept of $1/\alpha_{T_1}\Phi_f^{DBA}\ [(k_{ts} + k_{tt})/k_{ts}]$. With our measured value of Φ_f^{DBA} and literature values for k_{ts} and k_{tt}, one can calculate α_{T_1}. In a similar manner, the total efficiency of excited state singlet carbonyl products (α_{S_1}) are obtained. According to this method, developed by Turro and coworkers, 9,10-diphenylanthracene (DPA) measures only the singlet (S_1) excited state carbonyl products. Here, a plot of $1/\Phi_{App}$ *vs* $1/[DPA]$ gives an intercept of $1/\alpha_{S_1}\Phi_f^{DPA}$. From this intercept and our measured value of Φ_f^{DPA}, one obtains α_{S_1}. Results of our efficiency measurements are given in Table IV. The efficiency measurement of tetramethyl-1,2-dioxetane (TMD) serves to relate our efficiency measurements to other laboratories. Our values for TMD are in good agreement with those reported by Wilson and coworkers.

Table IV. Total Triplet (α_{T_1}) and Singlet (α_{S_1}) Efficiencies of Carbonyl Products from Dioxetanes at 45°C in Benzene

Dioxetane	% α_{T_1}(*t*-S)[a]	% α_{T_1}(DBA)[b]	% α_{S_1}(DPA)[c]	α_{T_1}(DBA)/α_{S_1}(DPA)
DMD	13	≡13	4.6×10^{-2}	280
PMD	16	14	8.1×10^{-2}	170
DPD	3.5	1.2	--	--
DBD	--	22	0.65	34
TPD	--	1.9	--	--
DAD	--	0.41	--	--
DAD(MeOH)[d]	--	0.93×10^{-3}	--	--
TMD[e]	--	36	0.37	97

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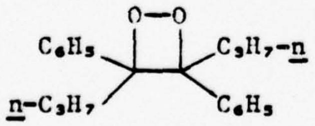
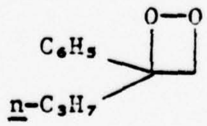
[a] By trans-stilbene isomerization. [b] By light emission from DBA. [c] By light emission from DPA. [d] In methanol solution. [e] At 70.1°C.

A comparison of the triplet efficiencies of TMD (36%) and DMD (13%) suggests that steric effects may be important in determining efficiencies. Related studies with the bromination of tetrabenzylethylene indicated large steric effects due to benzyl groups. Steric effects resulting from the benzyl groups in DBD were noted in the thermolysis of this dioxetane. In addition, a relatively high triplet efficiency was noted for DBD (22%). These steric effects are reflected in the activation energies for thermolysis of the dioxetanes. Thus, a qualitative relationship exists between larger steric effects, larger activation energies, and higher triplet efficiencies as seen in the series: TMD (E_a = 26.5 kcal/mol, α_{T_1} = 36%)> DBD (E_a = 24.3 kcal/mol, α_{T_1} = 13%). We are currently pursuing the relationship between steric effects, activation energy for thermolysis, and triplet efficiencies. We hope to prepare tetrabenzyl-1,2-dioxetane, which should be subject to considerable steric effects and thus should exhibit a high triplet efficiency. Presently, we have been able to prepare the bromohydroperoxide precursor to the dioxetane and now hope to close this intermediate to the dioxetane. We have also prepared 3,4-diphenyl-3,4-di-n-propyl-1,2-dioxetane (DPDPD) and the efficiency and activation energy of this dioxetane will be compared to those of 3-phenyl-3-n-propyl-1,2-dioxetane (PPD).



DPDPD



PPD

Lower efficiencies are observed with the more highly aryl substituted dioxetanes: DPD (α_{T_1} = 1.2%), TPD (α_{T_1} = 1.9%), and DAD (0.41% in benzene). Additional work is required before a definitive proposal can be made as to the origin of the lower efficiencies found with the more highly aryl substituted dioxetanes. However, an attractive explanation can be made in terms of a kinetic analysis based on Scheme I. Increased aryl substitution is expected to weaken the C-C bond in the oxy biradicals. This should increase the rate of decomposition of the first-formed biradical S_R to carbonyl products (S_0 and S_1) relative to the intersystem crossing of S_R to T_R (cf, Scheme I). Decomposition of S_R to carbonyl products greatly favors the formation of S_0 relative to S_1 products and low efficiencies result via this route. Since excited state carbonyls are mainly produced as triplets, increasing the ratio $(k_{2S_0} + k_{2S_1})/k_{isc}$ by aryl substitution will decrease the efficiency of excited state carbonyl production. This explanation will also accommodate the lower efficiency of DAD in methanol ($\alpha_{T_1} = 0.93 \times 10^{-3}\%$) compared to benzene ($\alpha_{T_1} = 0.41\%$). As stated previously, methanol solvent is expected to increase the rate of decomposition of the oxy biradical to carbonyl products. Thus, the rate of decomposition of the first-formed biradical S_R should be increased in methanol relative to intersystem crossing to biradical T_R. This in turn should decrease the efficiency of excited carbonyl production in methanol compared to benzene.

Previously, it was suggested that steps (-1) and (2) may be competitive in Scheme I. For dioxetanes with appropriate substitution so as to lower the activation energy of step 2, it was noted that the experimental activation energy was lower than expected. According to the preceding arguments, one would then expect lower efficiencies with lower experimental activation energies. Although the difference in efficiencies is not large, it does appear that there is a trend in this direction upon comparing DPD (E_a = 22.7 kcal/mol, $\alpha_{T_1} = 1.2\%$) and DAD (E_a = 21.4 kcal mol, $\alpha_{T_1} = 0.41\%$).

Heavy atom additives to the medium provide another potential means of modifying the efficiency of excited state carbonyl production from dioxetanes. Considering Scheme I, it can be seen that an increase in efficiency could be accomplished by "pumping" the system to the triplet biradical T_R, which produces solely T_1 carbonyl products. As stated previously, carbonyl production from the singlet biradical S_R produces excited state carbonyl products in low efficiency. Thus, addition of heavy atom additives could increase intersystem crossing from S_R to T_R and thereby increase the efficiency. This approach was tried with TMD and 0 to 2*M* *n*-butyl bromide as the heavy atom source. Unfortunately, no change in efficiency was noted. We are now proceeding to study an intramolecular heavy atom effect in the thermolysis of 3-*p*-bromophenyl-3-methyl-1,2-dioxetane.

Energy Distribution Between Dissimilar Carbonyls Produced from Dioxetanes. The data in Table IV represents total efficiencies, but does not allow one to assess the energy distribution between dissimilar carbonyl products. We have employed three methods to determine this energy distribution. By the first method, a particular excited state carbonyl product is trapped with an olefin to give an oxetane. The apparent quantum yield (Φ_{App}) for the specific excited state carbonyl product is given by eq 11, where Φ_{OX} is the quantum yield for

$$\Phi_{App} = \alpha \Phi_{OX} \qquad (11)$$

oxetane formation, obtained from the literature. By measuring the yield of oxetane by glc methods, Φ_{App} = mmol oxetane formed/mmol dioxetane decomposed) is calculated and α is determined from eq 11. By the second method, a particular excited state carbonyl product undergoes a photochemical reaction. The apparent quantum yield (Φ_{App}) for the specific excited state carbonyl product is given by eq 12, where Φ_{Photo} is the quantum yield for the production of the photolysis

$$\Phi_{App} = \alpha \Phi_{Photo} \tag{12}$$

product, obtained from the literature. By measuring the yield of photolysis product by glc methods, Φ_{App} (= mmol photolysis product/mmol dioxetane decomposed) is calculated and α is determined from eq 12. By the third method, the lifetimes of excited state carbonyl species produced from dioxetanes are measured by light emission methods in the presence of DBA and DPA.

Our working hypothesis is that energy may be distributed *via* a Boltzmann distribution based on the excited state energies of the carbonyl products. Previously, the energy distribution with DPD was qualitatively shown to be in agreement with this proposal.

Currently, we have found that thermolysis of PMD in the presence of trimethylethylene gave no oxetane derived from acetophenone. This observation is consistent with a Boltzmann model, since the triplet energies of acetophenone and formaldehyde are 74 and 72.5 kcal/mol, respectively. In contrast, the results do not fit an energy distribution based on preferential energy distribution to the carbonyl species with the greatest number of vibrational modes. Again using the first method, TPD was decomposed in the presence of 3-methyl-2-pentene to give oxetanes derived from both benzophenone and benzaldehyde. The ratio of efficiencies $\alpha_{\phi_2CO}/\alpha_{\phi CHO}$ was calculated to be 92±7, which again is in the range expected from a Boltzmann distribution of triplet energies.

We have previously employed the second method to determine the specific efficiency of excited state dibenzyl ketone production from DBD. In the future, we plan to determine the specific efficiency of excited state butyrophenone from PPD *via* the Type-II decomposition of this excited state ketone. These results will be compared to a similar process with D^{P}DPD, which we have synthesized.

According to the third method, lifetimes of excited state carbonyls, produced from dioxetanes are obtained from DBA and DPA light emission measurements. Considering Scheme IV, the rate coefficient k_d for decay of the excited state carbonyl species (K*) is given by eq 13, when $1/\Phi_{App}$ vs $1/[DBA]$ is plotted. The lifetime of the triplet species is then given by

$$k_d = \frac{\text{Slope}}{\text{Intercept}} (k_{ts} + k_{tt}) \tag{13}$$

$\tau_{T_1} = 1/k_d$. In a similar manner, the singlet lifetimes (τ_{S_1}) are calculated from k_d = (Slope/Intercept)(k_{ss}) from a plot of $1/\Phi_{App}$ vs $1/[DPA]$. The results of the lifetime measurements are given in Table V. For comparison, the reported lifetimes and energies of the excited state carbonyl species that could be produced are given in Table VI.

Table V. Lifetimes of Triplet Species Produced from the Thermolysis of Dioxetanes in Benzene

Dioxetane	τ_{T_1}(obs), sec	τ_{S_1}(obs), sec
DMD	1.2×10^{-7}	5.0×10^{-9}
PMD	3.8×10^{-7}	1.8×10^{-8}
DBD	5.3×10^{-7}	4.0×10^{-9}

Table VI. Lifetimes and Energies of Possible Excited State Carbonyl Species from Dioxetanes

Dioxetane	Carbonyl Species	τ_{T_1}[a]	τ_{S_1}[a]	E_{T_1}[b]	E_{S_1}[b]
DMD	CH_2O	4×10^{-7}	--	72.5	81
	CH_3COCH_3	9.4×10^{-7}	2.0×10^{-9}	80	88
PMD	CH_2O	4×10^{-7}	--	72.5	81
	$C_6H_5COCH_3$	3.5×10^{-6}	--	73.7	79
DBD	CH_2O	4×10^{-7}	--	72.5	81
	$(C_6H_5CH_2)_2CO$	10^{-10}	3.6×10^{-9}	~79	(~87)[c]

[a] sec. [b] kcal/mol. [c] Estimated.

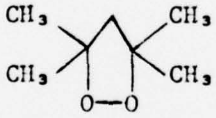
Considering the potential difficulties in obtaining accurate lifetime measurements of excited state species, the lifetimes reported in Table V are no doubt subject to considerable error. Allowing for rather wide error limits, all of the triplet lifetimes in Table V would be judged to be comparable. That is, all of the triplet lifetimes in Table V fall into the region of the reported triplet lifetime of formaldehyde (4×10^{-7} sec, Table VI). Additional support for this proposal can be found by considering the lifetime of the triplet species produced from DBD. The observed triplet lifetime (5.3×10^{-7} sec) is 5×10^{-7}-*fold* longer than that reported for dibenzyl ketone (10^{-10}sec, Table VI). This strongly suggests that the triplet energy resides predominantly in the formaldehyde rather than the dibenzyl ketone product. Similarly, the lifetime of the triplet species derived from PMD is about 10-fold shorter than that of acetophenone (3.5×10^{-6}sec, Table VI). This suggests that the triplet energy resides in formaldehyde rather than in acetophenone and this conclusion is in agreement with the oxetane results. The triplet lifetime data then again support a Boltzmann energy distribution as can be seen from Table VI.

The lifetime of the excited singlet formaldehyde species is apparently not reported. It is interesting that both DMD and DBD produce singlet species with a similar lifetime (4-5x10^{-9}sec), which may correspond to the formaldehyde excited **singlet species that is expected on the basis of a** Boltzmann energy distribution. The lifetime of the excited state singlet species produced from PMD is interesting, but at present unexplicable. First, the observed singlet lifetime is about 4-fold longer than that proposed for the formaldehyde excited singlet state. Secondly, a Boltzmann distribution would predict that the excited singlet state energy should reside in acetophenone (cf., Table VI). Thirdly, although the lifetime of excited singlet acetophenone is not reported, it is expected to be very short-lived. For example, aryl ketones such as benzophenone have singlet lifetimes of 5x10^{-12}sec. Lastly, endothermic energy transfer of singlet excited state energy from acetophenone to formaldehyde seems unlikely. Presently, we cannot rationalize all of these observations in order to assign a structure to the excited singlet species produced from PMD.

In summary, the bulk of our results can be interpreted in terms of a Boltzmann energy distribution between dissimilar carbonyl species produced from dioxetanes for both singlet (S_1) and triplet species. One can question whether or not the energy distribution pertains to the carbonyl products at their birth or after energy transfer within the solvent cage. Photolysis and quenching studies of TMD by Turro and coworkers (J. Amer. Chem. Soc., 96, 1936 (1974)) indicates that diffusion from the solvent cages is much faster than exothermic triplet-triplet quenching within the cage. Thus, it appears that the triplet species we observe represent those born directly from the dioxetane and not after energy exchange in the solvent cage.

Kinetics of the Thermolysis of 1,2-Dioxolanes. 1,2-Dioxolanes are five-membered ring peroxides, which are one carbon unit higher in the homologous series from 1,2-dioxetanes. We have advocated a stepwise decomposition path as shown in Scheme I for simply substituted 1,2-dioxetanes. The experimental activation parameters for thermolysis of the four-membered ring peroxides were in good agreement with calculated parameters based on Scheme I. We felt that if our mechanistic conclusions were correct for 1,2-dioxetanes, there should be a continuity of mechanism in proceeding to 1,2-dioxolanes. That is, a stepwise decomposition process is expected for 1,2-dioxolanes, where calculated activation parameters based on this scheme would be in agreement with experimental parameters.

To our surprise, we found that the reported activation parameters for dioxolane 1 was considerbly lower than parameters we calculated, based on a stepwise decomposition mode. This prompted us to reinvestigate the kinetics of thermolysis of 1. We have found the thermolysis of 1 in benzene solution, without a radical trap, is subject to induced decomposition. However, good first-order kinetics could be obtained in the presence of the radical trap, 2,6-di-t-butyl-p-cresol. Activation parameters were calculated by thermochemical kinetic means according to the stepwise mechanism given in Scheme V. The results of the calculations and the experimental activation parameters in benzene solution with the radical trap are given in Table VII.



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Scheme V

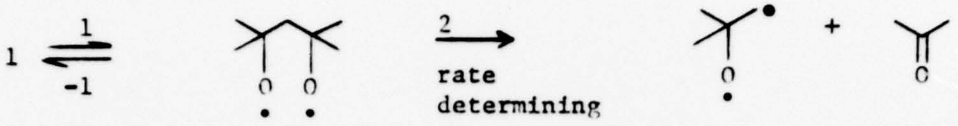


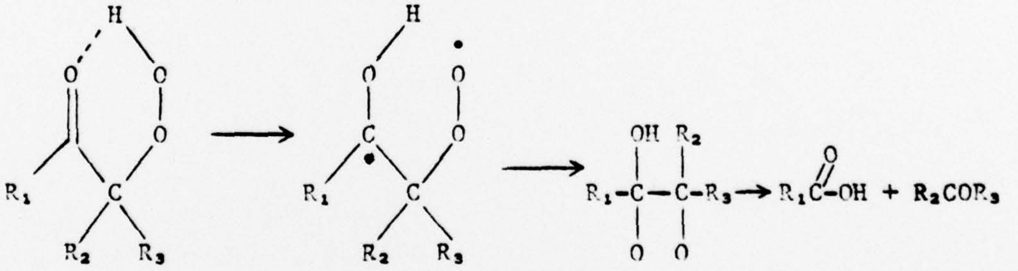
Table VII. Experimental and Calculated Activation Parameters for the Thermolysis of 3,3,5,5-Tetramethyl-1,2-dioxolane (1)[a] in Benzene Solution

Source	E_a	Log A	$\Delta H^{\ddagger}$ [b]	$\Delta S^{\ddagger}$ [c]	$\Delta G^{\ddagger}$ [b,d]
Exptl	44.4±1.1	15.76±.04	43.5±1.1	10.7±.2	38.4
Calcd	48.8	15.59	47.8	9.8	42.9

[a] [1] = 9.69×10^{-3} *M*, [2,6-di-*t*-butyl-*p*-cresol] = 7.7×10^{-3} *M*. [b] kcal/mol. [c] eu. [d] At 200°C.

It is seen from Table VII that the experimental values for both E_a and $\Delta G^{\ddagger}$ are lower than the calculated values. This is most likely the result of some residual induced decomposition of 1, even in the presence of the radical trap. The experimental activation parameters *in the presence of the radical trap* do more closely approach the calculated parameters, than the reported values in the *absence of a radical trap* ($\Delta H^{\ddagger}$ = 27.0 kcal/mol, $\Delta S^{\ddagger}$ = -24.8 eu, $\Delta G^{\ddagger}$ = 34.4 kcal/mol). Low activation parameters are characteristic of induced decomposition and the large decrease in these parameters is indicative of the great sensitivity of 1,2-dioxolanes to induced decomposition. We are presently studying the thermolysis of 1 in the gas-phase by the toluene carrier technique to avoid induced decomposition. Excluding the problem of induced decomposition, it appears that the unimolecular decomposition path for 1 is by a stepwise process as given in Scheme V. Thus, there appears to be no discontinuity between the decomposition mode of 1,2-dioxetanes and 1,2-dioxolanes. In passing, it may be noted that the decomposition mode of 1,2-dioxolanes has practical significance to the prostaglandin biosynthesis, since these peroxides are proposed intermediates.

Photolysis of α-Hydroperoxy Ketones. Previously, we found that the photolysis of α-hydroperoxy ketones yields an acid plus a carbonyl moiety. It was also found that the quantum yields were concentration dependent. However, at sufficiently low peroxide concentration, the quantum yield became constant. A reasonable interpretation of the results was made, namely, that at low peroxide concentration, a Type-II process occurred to give a dioxetane intermediate, which subsequently decomposed to give the acid and carbonyl products (eq 14).



(14)

2a, $R_1 = (CH_3)_2CH$, $R_2 = R_3 = CH_3$

b, $R_1 = R_2 = C_6H_5$, $R_3 = CH_3$

This mechanism seemed particularly attractive considering our previous observation of intramolecular hydrogen bonding of 2a at low concentrations and the propensity of hydrogen atom abstraction from hydroperoxides.

We have thoroughly investigated quantum yields for **2a** and **2b** as a function of concentration. The present results confirm our initial results where a limiting quantum yield (Φ_{lim}) is reached, which is nearly or completely independent of concentration. Our recent results with **2a** show constant quantum yields ($\Phi_{lim} = 0.50$) at 0.03*M* in carbon tetrachloride and ($\Phi_{lim} = 0.60$) at 0.003*M* in *n*-hexane. For **2b**, the quantum yield appears constant ($\Phi_{lim} = 0.61$) at about 0.002*M* in carbon tetrachloride.

The quantum yield data with **2a** indicate that the relative importance of the unimolecular reaction (*e.g.*, eq 14) and the chain process are solvent dependent. As might be expected, solvents with higher chain-transfer constants (*e.g.*, carbon tetrachloride) are more favorable for the unimolecular process than solvents with lower chain-transfer constants (*e.g.*, *n*-hexane). Furthermore, the lower concentration that is required for a constant quantum yield with **2b** *vs* **2a**, reflects the greater stability of the chain carrying $C_6H_5\dot{C}O$ radical compared to $(CH_3)_2CH\dot{C}O$. The more stable $C_6H_5\dot{C}O$ radical is then more effective in propagating the chain process.

Yields of products as a function of concentration have been made with **2b** in benzene and carbon tetrachloride. In addition to the products reported in Table VIII, benzoic acid is produced from **2b**. The chemical yield of benzoic acid is estimated to be (100% - % yield of C_6H_5CHO). The yield of phenol could be included in this equation, but it is uncertain as to whether phenol results from **2b** or the solvent. Benzaldehyde is indicative of the benzoyl radical ($C_6H_5\dot{C}O$), which is the likely chain carrying radical in the chain portion of the photolysis. As would be expected, as the chain process decreases in importance relative to the unimolecular process with decreasing peroxide concentration, the yield of benzaldehyde decreases.

Table VIII. Chemical Yields of Products from the Photolysis of **2b** to Completion in Degassed Benzene Solution

	% Yield		
[**2b**], *M*	C_6H_5CHO	C_6H_5OH	$C_6H_5COCH_3$
0.1517	5.74	2.35	95
.0983	3.26	1.92	100
.0506	3.73	2.14	99
.0253	2.09	1.81	98
.0100	1.41	0.96	106

Further evidence for benzoyl radicals, at concentrations of **2b** where the chain process is important, is seen from the photolysis of **2b** in carbon tetrachloride (Table IX). Benzoyl chloride is indicative of benzoyl radicals

Table IX. Chemical Yields of Products from the Photolysis of **2b** in Degassed Carbon Tetrachloride

	% Yield		
[**2b**], *M*	% Reaction	$C_6H_5COCH_3$[a]	C_6H_5COCl[b]
0.0498	94.2	100	49.2
.00999	100	100	39.0

[a] By glc analysis. [b] By ir analysis.

over this concentration range, where the chain process is still of importance. As with benzaldehyde, the yield of benzoyl decreases with decreased concentration of 2b, as would be expected from competing chain and unimolecular processes. Benzoic acid is also produced and it is assumed that the yield of benzoic acid is (100% - yield of benzoyl chloride).

Presently, we are making a detailed study of the products which result from the photolysis of 2a. The major products are acetone and isobutyric acid. However, minor amounts of isobutyraldehyde and carbon monoxide have been detected in hexane solvent at concentrations where the chain reaction is of importance. Radical trapping experiments with dodecanethiol are planned in order to more clearly define the mechanism of the chain process and its relative importance to the unimolecular reaction.

The lifetimes of the excited triplet state of 2b in carbon tetrachloride and benzene were measured. Also the lifetimes of the excited singlet (S_1) and triplet states of 2a were measured in carbon tetrachloride and *n*-hexane. These data are given in Tables X, XI, and XII. As seen from Table X, the triplet

Table X. Triplet (T_1) Lifetimes Obtained from Quenching Studies with Piperylene and Calculated from a Stern-Volmer Plot for 2b

[2b], *M*	Solvent	$k_q\tau_{T_1}$, M^{-1}	τ_{T_1}, sec
0.050	CCl_4	3.90	3.55×10^{-10}
.050	C_6H_6	9.5	5.9×10^{-10}

Table XI. Triplet (T_1) Lifetimes Obtained from Quenching Studies with Piperylene and Calculated from a Stern-Volmer Plot for 2a

[2a], M	Solvent	$k_q\tau_{T_1}$, M^{-1}	τ_{T_1}, sec
0.042	CCl_4	4.55	4.1×10^{-10}
0.607	CCl_4	12.0	11×10^{-10}
0.500	n-hexane	17	5.2×10^{-10}

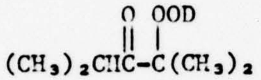
Table XII. Singlet (S_1) Lifetimes Obtained by Quenching Studies from Biacetyl Fluorescene and Calculated from a Stern-Volmer Plot for 2a[a]

Solvent	$k_q\tau_{S_1}$, M^{-1}	τ_{S_1}, sec
CCl_4	96.7	8.8×10^{-9}
n-Hexane	221	6.7×10^{-9}

[a] [2a] = 0.0940M.

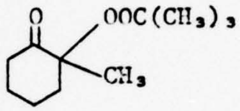
lifetimes, which are determined by per cent reaction of the peroxide with varying piperylene concentrations, are somewhat dependent on the concentration of peroxide. However, at low peroxide concentrations, it is seen that the peroxides have very short triplet lifetimes. This is indicative of a rapid photochemical reaction from the T_1 state. At low peroxide concentrations, the unimolecular Type-II process, where hydrogen atom abstraction from the hydroperoxy group occurs, would be expected to be rapid. In order to obtain the various rate coefficients for processes derived from the S_1 and T_1 states of 2a, the quantum yield of intersystem crossing needs to be measured. With this value a more detailed analysis of the photophysical and photochemical processes associated with 2a can be made.

Peroxides 3 and 4 have been prepared and photochemical processes involving hydroperoxy-hydrogen atom abstraction, such as the Type-II process, can be



$(CH_3)_2CH\overset{O}{\overset{\|}{C}}-\overset{OOD}{\overset{|}{C}}(CH_3)_2$

3



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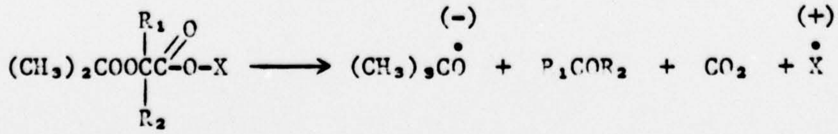
evaluated. If the Type-II process is operative at low peroxide concentrations, the triplet lifetime of 3 should show an isotope effect. With 4, one may also expect a significantly different triplet lifetime than observed for α-hydroperoxy ketones, if the latter peroxides undergo a Type-II reaction at low concentration. Furthermore, homolysis of the O-O bond in 4 should be evidenced by β-scission of the t-butoxy radical.

Peroxide Fragmentation Reactions. We have continued our study of peroxide fragmentation reactions of the type given in eq 15. Such reactions are highly exothermic and could conceivably produce the ketone product in an

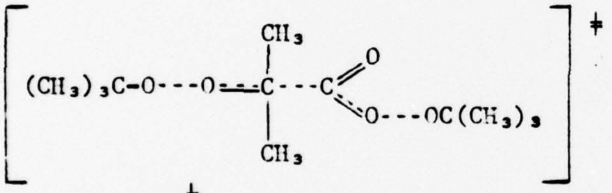


$$(CH_3)_2COO\overset{R_1}{\underset{R_2}{C}}\overset{O}{\overset{/\!/}{C}}-O-X \longrightarrow (CH_3)_3C\overset{(-)}{\dot{O}} + R_1COR_2 + CO_2 + \overset{(+)}{\dot{X}} \qquad (15)$$

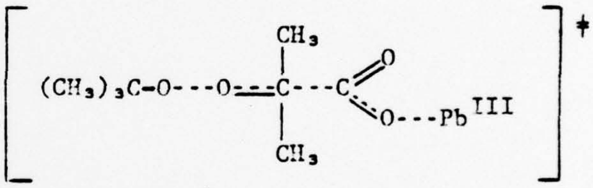
5

excited state. To date we have studied systems where $R_1=R_2=CH_3$ in **5**. In agreement with the calculated heat of reaction, no excited state acetone was observed. Nonetheless, the feasibility of this reaction is now established and one can attempt to prepare systems where the ketone product has sufficiently low excitation energy to obtain it in an excited state.

Our most recent work in this area dealt with the thermolysis of **5a** ($R_1=R_2=CH_3$, $X = OC(CH_3)_3$) and the reaction of **5b** ($R_1=R_2=CH_3$, $X= H$) with lead tetraacetate. In both instances, a homolytic decomposition occurs. A detailed product and kinetic study was made and a multi-bond homolysis process was indicated for both **5a** and **5b**. Although it was not possible to rigorously exclude a two-bond homolysis, the results were in best agreement with a three-bond homolysis (<u>cf</u>., **5a**‡ and **5b**‡). Such a concerted formation of the ketone product provides the best opportunity, in terms of thermochemistry, for the production of excited state ketone products.



5a‡



5b‡

Publications

(1) W. H. Richardson, J. H. Anderegg, M. E. Price, W. A. Tappen, and H. E. O'Neal, "Kinetics and Mechanisms of the Thermal Decomposition of Triphenyl-1,2-dioxetane," <u>J. Amer. Chem. Soc.</u>, submitted for publication.

(2) W. H. Richardson and K. W. Gunderson, "Tetrabenzylethylene. An Unusually Sterically Hindered Olefin," <u>J. Org. Chem.</u>, **41**, 2045 (1976).

(3) W. H. Richardson and W. C. Koskinen, "The Multi-bond Fragmentation of <u>t</u>-Butyl-2-Methyl-2-<u>t</u>-butylperoxyperpropanoate," <u>J. Org. Chem.</u>, **41**, 3182 (1976).

(4) W. H. Richardson and W. C. Koskinen, "The Lead Tetraacetate Oxidation of 2-Methyl-2-t-butylperoxypropanoic Acid," J. Org. Chem., **41**, 3188 (1976).

(5) W. H. Richardson, F. C. Montgomery, P. Slusser, and M. B. Yelvington, "Solvent and Substituent Effects in the Thermolysis of 1,2-Dioxetanes," J. Amer. Chem. Soc., **97**, 2819 (1975).

(6) W. H. Richardson, V. F. Hodge, D. L. Stiggall, M. B. Yelvington, and F. C. Montgomery, "1,2-Dioxetanes in the Base Catalyzed Decomposition of α-Hydroperoxy Ketones," J. Amer. Chem. Soc., **96**, 6652 (1974).

(7) W. H. Richardson, F. C. Montgomery, M. B. Yelvington, and H. E. O'Neal, "Concerted and Stepwise Decomposition of 1,2-Dioxetanes," J. Amer. Chem. Soc., **96**, 7525 (1974).

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