Experimental Section

The collisional activation (CA)[3,11,13] spectra were obtained using a Varian MAT 311A double-focusing mass spectrometer, in which ions pass through the magnetic field before entering the electric field. The collision cell was differentially pumped and situated in front of the energy resolving slit. Samples were introduced via the gas inlet system and run at an accelerating voltage of 3 kV, with a nominal electron beam energy of 70 eV and a source temperature of 170 °C. The magnetic and electric fields were adjusted to transmit $C_3H_5^+$ ions (*m/e* 41); air was then introduced into the collision cell via a variable leak until the precursor ion abundance decreased to $\frac{1}{3}$ of its original value. CA spectra were then obtained by scanning the electric field, recorded on an *XY* recorder and normalized to the total ion current due to all fragment ions. Only peak heights were measured and the abundances were not corrected for reduced multiplier response. The reported CA spectra are the means of at least four independent measurements.

The kinetic energy release measurements were obtained using an AEI MS 902 double-focusing mass spectrometer. Ions decomposing in the second field-free region were detected in normal mode operation, with an accelerating voltage of 8 kV and a nominal electron beam energy of 70 eV. Ions dissociating in the first field-free region were observed by increasing the accelerating voltage, from an initial value of 2 kV, at constant electric and magnetic field strengths.[14] Samples were introduced via the all glass heated inlet system (AGHIS) and run consecutively under identical operating conditions. The reported kinetic energy releases are the means of the results from at least four scans; no correction was applied for the width of the main beam.

All compounds were commercially available or synthesized by unexceptional procedures; samples were purified by preparative GLC.

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Excited-State Energy Distribution between Dissimilar Carbonyl Molecules Produced from 1,2-Dioxetanes

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Abstract: The distribution of excitation energy between dissimilar carbonyl products, obtained from the thermolysis of unsymmetrically substituted 1,2-dioxetanes, is reported. The excited-state carbonyl products were trapped with olefins to give oxetanes. From the yield of oxetane and the quantum yield for the oxetane-olefin reaction, specific efficiencies (α_{T_1}) of the excited-state carbonyl products were calculated. With 3-phenyl-3-methyl-1,2-dioxetane (PMD), triplet acetophenone was produced with 2.3% efficiency. By difference from the total triplet efficiency (15%), formaldehyde was produced with 12.7% efficiency. Within our detectability limits, no excited-state acetone was produced from 3,3-dimethyl-1,2-dioxetane (DMD) and thus all of the excitation energy (α_{T_1} = 13%) was associated with formaldehyde. To confirm the olefin trapping procedure with DMD, a similar experiment was performed with tetramethyl-1,2-dioxetane. Here, acetone was produced with 40% efficiency, which is in excellent agreement with the efficiency obtained by the emission method with 9,10-dibromoanthracene (DBA) (α_{T_1} = 36%). The ratio of specific efficiencies of benzophenone/benzaldehyde, produced from triphenyl-1,2-dioxetane (TPD), was found to be 92 by the olefin trapping procedure. For the three simply substituted dioxetanes (PMD, DMD, and TPD), the distribution of excited-state triplet energy can be rationalized in terms of a Boltzmann distribution of carbonyl triplet energies. Precise adherence to a Boltzmann distribution is uncertain due to error limits in the triplet carbonyl energies and the efficiency values. The approach to a Boltzmann distribution pertains to simply substituted dioxetanes, where a stepwise biradical mechanism appears to be operative. With certain substituted dioxetanes, where this mechanism does not appear to be applicable, there is a clear deviation from the Boltzmann distribution. From a consideration of other data, it appears that the Boltzmann distribution with simply substituted dioxetanes pertains to the birth of the carbonyl species from the dioxetane rather than to energy transfer in the solvent cage. An alternative vibrational model for excited-state energy distribution appears unlikely, based on the results with PMD and DMD.

A considerable body of data now suggests that simply substituted 1,2-dioxetanes undergo thermolysis to give electronically excited state carbonyl products, where typically high triplet to singlet (S_1) ratios are observed.[1] Recently, it has been reported that 1,2-dioxetanes with amino substituents produce predominantly singlets (S_1) rather than high triplet yields.[2] This change in the T_1/S_1 carbonyl product ratio appears to be associated in a change in the mechanism of thermolysis of simply substituted dioxetanes vs. dioxetanes bearing an amino substituent.

Unsymmetrically substituted dioxetanes will undergo thermolysis, where the excitation energy is distributed between

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Table I. Efficiency of Excited-State Acetophenone (AP) Formation from 3-Phenyl-3-methyl-1,2-dioxetane (PMD) with Trimethylethylene (TME) in Carbon Tetrachloride at 50 °C

[PMD] $\times 10^2$, M	[TME], M	[**1**] $\times 10^5$, M	$10^3\Phi_{App}$ (AP)	% α_{AP}[a]
3.02	1.41	7.17	2.37	2.37
3.02	1.41	6.29	2.08	2.08
2.95	1.35	7.40	2.51	2.51
2.95	1.35	5.63	1.91	1.91
2.95	1.35	7.40	2.51	2.51
				av 2.28 ± 0.22

[a] With $\Phi_{ox}(\mathbf{1}) = 0.10$.[7]

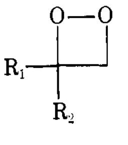
the two dissimilar carbonyl products in some manner. It would be of interest to be able to predict how this excitation energy is distributed and to have some theoretical insight into the mode of energy distribution. For this study we have selected a series of simply substituted dioxetanes, where a stepwise biradical mechanism best accommodates the thermolysis process,[3] and high triplet to singlet (S_1) ratios are expected.[1g]

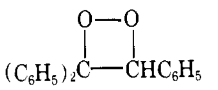
It is convenient to have working models in order to evaluate this problem. Two such models are the Boltzmann model and the vibrational model. According to the Boltzmann model, the excitation energy will be distributed between two dissimilar carbonyl products by a Boltzmann distribution of the carbonyl triplet of singlet (S_1) energies. The vibrational model would predict that the excitation energy is distributed according to the number of vibrational modes in the two dissimilar carbonyl products. Previously, we found that 3,3-diphenyl-1,2-dioxetane (DPD) gave primarily benzophenone in the excited state.[4] This result is, of course, consistent with either of the two working models. Recently, Koo and Schuster[5] reported that *trans*-3,4-diphenyl-1,2-dioxetane-*3*-d_1 gave equal amounts of excited-state protio- and deuteriobenzaldehyde, which is inconsistent with the vibrational model. The vibrational model is also called into question from the work of Bogan.[6]

We now report the specific efficiencies of carbonyl products that result from the thermolysis of a series of simply substituted dioxetanes, where these two models can be evaluated. The data are obtained by trapping the excited-state carbonyl products with olefins to give oxetanes.[7]

Results

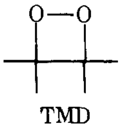
The dioxetanes that were studied by this method are shown below. The symmetrically substituted dioxetane TMD was





TBD

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



TMD

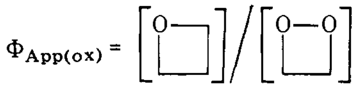
used in a control experiment with DMD and this will be discussed later. Benzene or carbon tetrachloride solutions of the dioxetanes and olefins were degassed and thermolyzed in sealed tubes for at least 10 half-lives of the dioxetane. GLC analysis was employed to determine the oxetane concentration in the resulting solution.

The efficiency (α) for producing the excited-state carbonyl from the dioxetane can be evaluated by the following two equations. The apparent quantum yield ($\Phi_{App(ox)}$) for the production of oxetane is obtained from the experimental concentration ratio in eq 1. With this value of $\Phi_{App(ox)}$, one can calculate α from eq 2 with a literature value of Φ_{ox}. Olefin

Table II. Efficiency of Excited-State Acetone (AC) Formation from Tetramethyl-1,2-dioxetane (TMD) with Tetramethylethylene (TME) in Carbon Tetrachloride at 70 °C[a]

10^4[**2**], M	$10^2\Phi_{App}$ (AC)	% α_{AC}[b]
6.46	1.78	40.5
6.46	1.78	40.5
6.03	1.66	37.7
		av 39.6 ± 1.2

[a] With [TMD] = 3.63×10^{-2} M, [TME] = 1.25 M. [b] With $\Phi_{ox}(\mathbf{2}) = 0.044$.[9]

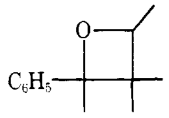


(1)

$$\Phi_{App(ox)} = \alpha\Phi_{ox} \qquad (2)$$

concentrations employed in the trapping experiments were comparable to those used in the determination of the quantum yield of oxetane formation (Φ_{ox}) by photoexcitation of the carbonyl species.

3-Phenyl-3-methyl-1,2-dioxetane (PMD) was thermolyzed in the presence of trimethylethylene in carbon tetrachloride solution at 50 °C. GLC analysis was made for oxetane **1** in



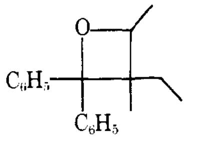
1

comparison to an authentic sample of **1**, which was prepared by photoexcitation of acetophenone (AP) in the presence of trimethylethylene. The results of these trapping experiments are presented in Table I, where the efficiency of excited-state acetophenone production (α_{AP}) from PMD was obtained with $\Phi_{ox}(\mathbf{1}) = 0.10$.[8]

3,3-Dimethyl-1,2-dioxetane (DMD) (3.10×10^{-2} to 7.30×10^{-2} M) was thermolyzed in the presence of tetramethylethylene (1.10 M) in carbon tetrachloride solution at 50 °C. GLC analysis for oxetane **2** was made by comparison to an authentic sample of **2**, which was prepared by photolysis of acetone in the presence of tetramethylethylene. Oxetane **2** was not detected in the thermolyzed reaction mixture, where detectability limits were estimated to be 5×10^{-6} M for **2**.

In order to verify the lack of oxetane **2** formation with DMD and tetramethylethylene, the thermolysis of tetramethyl-1,2-dioxetane (TMD) with this olefin was carried out. Since acetone is the sole product from TMD and since it is produced in high efficiency (α_{T_1} = 36%),[1g] there should be no problem in detecting **2**. The results of the thermolysis of TMD with tetramethylethylene in carbon tetrachloride solution are given in Table II. The efficiency of excited-state acetone production (α_{AC}) from TMD was calculated with $\Phi_{ox}(\mathbf{2}) = 0.044$.[9]

Triphenyl-1,2-dioxetane (TPD) was thermolyzed in the presence of *cis*-3-methyl-2-pentene in benzene solution at 59 °C. The major oxetane products formed from excited-state benzophenone and benzaldehyde with this olefin were **3** and **4**, respectively. GLC analyses for **3** and **4** in the thermolysis



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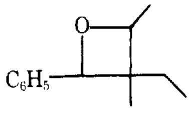

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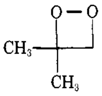
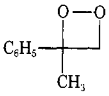
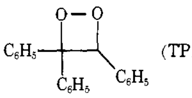
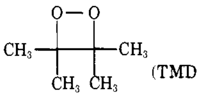
Table III. Efficiency of Excited-State Benzophenone (BP) and Benzaldehyde (BA) Production from Triphenyl-1,2-dioxetane (TPD) with *cis*-3-Methyl-2-pentene (MP) in Benzene at 59 °C[a]

$[3] \times 10^5$, M	$[4] \times 10^7$, M	$10^4\Phi_{\mathrm{App}}$ (BP)	$10^5\Phi_{\mathrm{App}}$ (BA)	% α_{BP}[b]	% $\alpha_{\mathrm{BA}} \times 10$[c]	$\alpha_{\mathrm{BP}}/\alpha_{\mathrm{BA}}$
1.45[d]	4.47	4.60	1.42	0.288	3.16	91
2.87	7.63	9.11	2.42	0.569	5.38	106
1.82	6.10	5.78	1.94	0.362	4.30	84
2.50	8.51	7.94	2.70	0.496	6.00	83
4.29	12.5	13.7	3.97	0.854	8.83	97
				av 0.51 ± 0.16	5.5 ± 1.5	92 ± 7

[a] With [TPD] = 3.15×10^{-2} M, [MP] = 0.95 M. [b] With $\Phi_{\mathrm{ox}}(3) = 0.16$.[10] [c] With $\Phi_{\mathrm{ox}}(4) = 0.45$.[10] [d] Carbon tetrachloride solution.

Table IV. Summary of Specific Efficiencies of Triplet Excited State Carbonyls from Dioxetanes

dioxetane	total % α_{T}[a]	specific % α_{T}[b]	$E_{\mathrm{T_1}}$[c]	$\Delta E_{\mathrm{calcd}}$[g]	ΔE_{obsd}[h]
 (DMD)	13	CH_3COCH_3 (~0%) CH_2O (13%)	80[14] 72.5[15]		7.5
 (PDM)	15[e]	$C_6H_5COCH_3$ (2.3%) CH_2O (12.7%)[d]	73.7[14] 72.5[15]	1.1	1.2
 (TPD)	0.52[f]	$(C_6H_5)_2CO$ (0.51%) C_6H_5CHO (0.0055%)	68.6[14] 72.0[14]	3.0	3.4
 (TMD)	36	CH_3COCH_3 (39.6%)	80[14]		

[a] Total triplet efficiency from DBA measurements. [b] Specific triplet carbonyl efficiency from oxetane formation with olefins. [c] Carbonyl triplet energies, kcal/mol. [d] By difference of total efficiency less specific efficiency. [e] Average of DBA (14%) and *trans*-stilbene (16%) data.[1g] [f] Sum of specific efficiencies by olefin trapping of excited-state carbonyls. Previously, the DBA method gave $\alpha_{\mathrm{T_1}} = 1.9\%$.[1g] [g] Difference in carbonyl triplet energies (kcal/mol), calculated from a Boltzmann distribution. [h] Difference between literature $E_{\mathrm{T_1}}$ values.

reaction solution was made by comparison to authentic samples of these oxetanes, which were prepared by photolysis of the carbonyl species with *cis*-3-methyl-2-pentene. The efficiencies of excited-state benzophenone (α_{BP}) and benzaldehyde (α_{BA}) formation from TPD were calculated with $\Phi_{\mathrm{ox}}(3) = 0.16$ and $\Phi_{\mathrm{ox}}(4) = 0.45$, respectively.[10] The results from the trapping experiments with TPD and *cis*-3-methyl-2-pentene are given in Table III.

Discussion

Before considering the data in terms of the Boltzmann and vibrational models for excited-state carbonyl production, it is worthwhile to consider the error engendered with the Boltzmann model. The difference in excited-state energies ($\Delta E = E_1 - E_2$) for two carbonyl species, with efficiencies α_1 and α_2, is given according to the Boltzmann model by

$$\Delta E = RT \ln \alpha_2/\alpha_1 \qquad (3)$$

Since the ratio of efficiencies is related exponentially to the energy difference, fairly large differences in the efficiency ratio cause rather small changes in ΔE. This means that significant errors in the efficiencies will cause only small changes in the energy difference. Thus, the error in measuring total triplet efficiencies by the 9,10-dibromoanthracene (DBA) method[1g] (estimate, 10–20% error) and the temperature effect on the quantum yield for oxetane formation[11] should not greatly affect the energy difference ΔE. The insensitivity of ΔE to differences in the efficiency ratio is also the weakness of precisely assigning a Boltzmann distribution to the excited-state carbonyl products. The values of the triplet carbonyl energies are not known with high accuracy, so that a fair range of efficiency ratios can be accommodated within the error limits of the triplet energies. This means that we can say that the distribution of excitation energy approaches a Boltzmann model, but we will be unable to say whether or not this is a precise fit. It is possible with several dioxetanes to determine whether the excitation energy distribution best fits a Boltzmann model or a vibrational model.

The specific efficiencies obtained by olefin trapping method pertain to triplets. The triplet/singlet (S_1) ratio of excited-state carbonyl products from simply substituted dioxetanes is typically high.[1] Our measured values for three of the four dioxetanes reported here confirm this observation. The triplet/singlet (S_1) ratios measured by the DBA/DPA method, for DMD, PMD, and TMD are 240, 145, and 83, respectively.[1g] Thus, the contribution of the singlet (S_1) carbonyl reaction with olefin to the oxetane yield is trivial.

Table IV summarizes the specific efficiency measurements. Considering PMD first, it is seen that the triplet excitation energy is directed primarily to formaldehyde rather than to acetophenone. This is, of course, in disagreement with the vibrational model for energy distribution. However, the distribution of excitation energy into the dissimilar carbonyl products does approach a Boltzmann distribution, subject to the error considerations discussed previously. It was previously found that the *total* efficiency of triplet carbonyl production from PMD was 16% by *trans*-stilbene isomerization and 14% by the DBA method.[1g] With the specific $\alpha_{\mathrm{T_1}}$ value for acetophenone of 2.3%, produced from PMD, this gives by difference the specific $\alpha_{\mathrm{T_1}}$ value for formaldehyde of 12.7% (= 15 − 2.3). From these specific efficiencies, the difference in triplet energies between the two carbonyl products may be calculated, based on the Boltzmann model, from eq 3. As seen from Table IV, this calculated energy difference ($\Delta E_{\mathrm{calcd}}$) is in good agreement with the reported difference in triplet energies of the carbonyl products (ΔE_{obsd}). Assuming an error of ±20%

in both the total triplet efficiency and the specific triplet efficiency of acetophenone, the ΔE_{calcd} value ranges from 0.82 to 1.35 kcal/mol, which is still in an acceptable range for a Boltzmann distribution.

With DMD, no excited-state acetone was detected with tetramethylethylene as the trap. However, under similar conditions, with TMD and this olefin, excited-state acetone was trapped (Tables II and IV). Furthermore, the efficiency (α_{T_1} = 39.6%) obtained by olefin trapping with TMD was in excellent agreement with the efficiency (α_{T_1} = 36%) obtained by the DBA method.[1g] Thus, it appears that there is no basic flaw in the attempted trapping experiment with DMD. This means that the triplet energy is diverted almost exclusively into formaldehyde rather than into acetone in the thermolysis of DMD. This observation is again in conflict with a vibrational model for energy distribution.

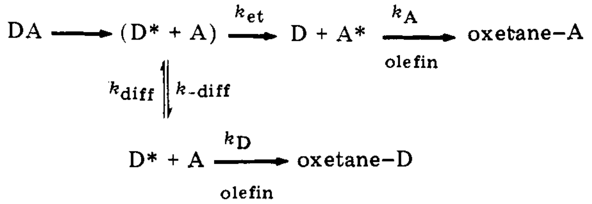
The lack of detectable trapping of triplet acetone from DMD with tetramethylethylene is reasonable in terms of the Boltzmann model. The reported E_{T_1} values for acetone and formaldehyde are 80[14] and 72.5[15] kcal/mol, respectively. This gives $\alpha_{T_1}(CH_2O)/\alpha_{T_1}(CH_3COCH_3) = 1.2 \times 10^5$ at 50 °C from eq 3. Our previous measurement of the *total* triplet efficiency of DMD by *trans*-stilbene isomerization gave α_{T_1} (total) = 13%.[1g] With this value and the above ratio of $\alpha_{T_1}(CH_2O)/\alpha_{T_1}(CH_3COCH_3)$, one obtains $\alpha_{T_1}(CH_3COCH_3) = 10^{-4}\%$. With the aid of eq 1 and 2, where $\Phi_{ox}(CH_3COCH_3) = 0.44$,[9] and the maximum DMD concentration (7.30×10^{-2} M) employed in these studies, the expected yield of oxetane is 6.0×10^{-7} M. This concentration of oxetane **2** is below our estimated detectability limits (5×10^{-6} M).

As seen from Tables III and IV, the majority of the excitation energy from the thermolysis of TPD is directed to benzophenone. Although this result is in qualitative agreement with the vibrational model, the distribution of excitation energy does approach that expected from the Boltzmann model. The average value for α(benzophenone)/α(benzaldehyde) of 92 (Table III) gives as the difference between triplet energies of these products ΔE = 3.0 kcal/mol with eq 3. The difference between the reported triplet energies for benzaldehyde (72.0 kcal/mol)[14] and benzophenone (68.6 kcal/mol)[14] gives ΔE = 3.4 kcal/mol.

These results, with simply substituted dioxetanes, suggest that the distribution of triplet energy in dissimilar carbonyl products is approximated by a Boltzmann distribution based on the carbonyl triplet energies. Although this observation has value in its practical application, a critical theoretical question remains. Namely, are the triplet carbonyl species initially produced according to the Boltzmann model or is the Boltzmann distribution the result of energy transfer within the solvent cage before diffusion apart? This problem is illustrated in Scheme I, where DA is the dioxetane, D is the carbonyl species with higher triplet energy, and A is the carbonyl species with lower triplet energy. In this scheme, only the formation of the higher energy triplet carbonyl (D*) frrom the dioxetane is considered, since only exothermic energy transfer will occur to potentially disturb an original Boltzmann distribution of excited-state carbonyl species.

From the data reported here, there is no way to differentiate between a Boltzmann distribution based on the birth of the carbonyl species vs. a Boltzmann distribution that results from energy transfer within the solvent cage. However, studies from other laboratories shed some light on this question. Turro and co-workers have analyzed the quantum chain decomposition of TMD with quenchers.[16] They conclude that "triplet acetone, quencher cage partners are capable of diffusing apart faster than exothermic triplet-triplet transfer can take place". This conclusion is consistent with an earlier report by Wagner and Kochevar,[17] where it was demonstrated that triplet energy transfer is not totally diffusion controlled in solvents of low viscosity such as benzene. From this latter paper,[17] estimates of pertinent rate coefficients can be made in order to evaluate the importance of energy transfer in the solvent cage. With the reasonable assumptions that $k_A \simeq k_D$ and at high olefin concentration with low dioxetane concentration $k_D[\text{olefin}] \gg k_{\text{diff}}[A]$, one obtains $[D^*]/[A^*] = k_{-\text{diff}}/k_{\text{et}}$ from a steady-state treatment of Scheme I. With $k_{-\text{diff}} \simeq 7.8 \times 10^{10}\ s^{-1}$ and $k_{\text{et}} \geq 9 \times 10^{10}\ s^{-1}$ in benzene, derived from the work of Wagner and Kochevar,[17] one obtains $[D^*]/[A^*] \leq 0.87$. This is the correction factor which can be applied for exothermic energy transfer within the solvent cage. The corrected efficiency ratios related to PMD and TPD are $(\alpha_T{}^{CH_2O}/\alpha_T{}^{PhCOCH_3})_{\text{cor}} \leq 0.87(\alpha_T{}^{CH_2O}/\alpha_T{}^{PhCOCH_3})_{\text{uncor}} = 0.87(12.7/2.3) = 4.80$ and $(\alpha_T{}^{Ph_2CO}/\alpha_T{}^{PhCHO})_{\text{cor}} \leq 0.87(0.51/0.0055) = 80.7$, respectively. From eq 3, the corrected energy difference between triplet acetophenone and formaldehyde, derived from PMD, is $E_{\text{calcd}} \leq 1.0$ kcal/mol. Similarly, TPD gives $E_{\text{calcd}} \leq 2.9$ kcal/mol for the energy difference between benzaldehyde and benzophenone, when the correction is made for energy transfer within the solvent cage. This energy differences, corrected for energy transfer in the solvent cage, are not significantly different from the uncorrected values, which compare favorably with a Boltzmann distribution (ΔE_{obsd}, Table IV). This suggests that a near-Boltzmann distribution applies to the birth of the triplet carbonyl species and is not the result of subsequent energy transfer within the solvent cage.

Scheme I



Conclusions

The triplet energy distribution between dissimilar carbonyl products, produced from simply substituted dioxetanes, appears to be approximated by a Boltzmann distribution based on triplet energies of the carbonyl products. The present data also indicate that a vibrational model for energy distribution is unlikely for solution-phase thermolyses of dioxetanes. In fact, our results with DMD and PMD are in direct conflict with the vibrational model.

Furthermore, it appears that the near-Boltzmann distribution of excited-state carbonyl products relates to their initial formation and is not the result of energy transfer within the solvent cage. Although this result is reasonable in terms of thermochemistry, the energy distribution is actually determined by the relative activation energies for the biradical proceeding to the triplet carbonyl products. Such a relationship between activation energy and the energy of the products is well-known (Bell-Evan-Polanyi principle).[18]

Finally, it should be emphasized that the Boltzmann model may be only applicable to simply substituted dioxetanes, which undergo decomposition by a stepwise process. There are clearly deviations from this model when the dioxetane is not simply substituted, and a change in mechanism is suspected. Furthermore, a strict adherence to the Boltzmann model cannot be certain owing to error primarily in the reported triplet carbonyl energies. Even with this problem, the Boltzmann model for triplet carbonyl product distribution serves as a useful guideline for predicting the distribution and noting deviations, which may be indicative of mechanistic changes in the thermolysis of dioxetanes.

Experimental Section[19]

Materials. The preparation of the dioxetanes was previously reported.[3b,e,20] Spectroquality (MCB) benzene was further purified by washing with concentrated sulfuric acid and then water. After drying over calcium chloride, the benzene was distilled from phosphorus pentoxide. DBA (Aldrich) was recrystallized from xylene and DPA (K & K) was used as supplied. The olefins (MCB or Aldrich) were distilled prior to use.

2-Phenyl-2,3,3,4-tetramethyloxetane (1). This oxetane was prepared by the method of Büchi and co-workers.[21] A quartz 12-mm ₸ tube containing 2.7 mL (23.3 mmol) of acetophenone (MCB, distilled) and 3.3 mL (31.4 mmol) of trimethylethylene (Aldrich) was purged with nitrogen and irradiated in a Rayonet photoreactor at 253.6 nm for 13 days. Oxetane **1** was isolated by distillation (bp 109–112 °C (10 mm), lit.[21] bp 80–84 °C (3.5 mm)), 19% yield; NMR 4-CH_3 (1.04, d (J = 6.5 Hz), 3), Z-3-CH_3 (1.11, s, 3), E-3-CH_3 (0.52, s, 3), 2-CH_3 (1.50, s, 3), 4-H (4.45, q (J = 6.5 Hz), 1), and C_6H_5 (7.10, s, 5).

Hexamethyloxetane (2). This oxetane was prepared by a previously reported method.[9] A solution of 0.5 mL (4.2 mmol) of tetramethylethylene and 2.5 mL (35 mmol) of distilled acetone was purged with nitrogen and irradiated in a Rayonet photoreactor at 253.6 nm for 33 h. The product was isolated in approximately 4% yield by distillation (bp 60 °C (37 mm), lit[9] bp 50–56 °C (28 mm)); NMR 2- and 4-CH_3 (1.20, s, 2) and 3-CH_3 (1.05, s, 1).

2,2-Diphenyl-3-ethyl-3,4-dimethyloxetane (3).[10] A solution of 0.299 g (1.64 mmol) of benzophenone (MCB, recrystallized from ethanol–water) and 0.60 mL (5.7 nmol) of *cis*-3-methyl-2-pentene (MCB) in 3 mL of benzene was purged with nitrogen and irradiated in a 12-mm ₸ stoppered Pyrex tube in a Rayonet photoreactor at 350 nm for 10 days. The solvent and the olefin were removed by rotoevaporation and the residue was recrystallized from methanol at low temperature to give white needles of **3**, mp 89.0–90.5 °C, 15% yield; NMR C_6H_5 (6.9–7.5, m, 10), 4-H (4.4, q (J = 6.5 Hz), 1), CH_2 (1.4, q (J = 6.5 Hz), 2), 4-CH_3 (1.3, d (J = 6.5 Hz), 3), 3-CH_3 and CH_3CH_2 (1.3, m, 6); IR 3090, 3060, 3030, 2960, 2930, 2870, 1610, 1500, 1455, 1390, 1072, and 988 cm^{-1}.

2-Phenyl-3-ethyl-3,4-dimethyloxetane (4).[10] A solution of 0.21 g (2.0 mmol) of benzaldehyde (MCB, distilled at 176–178 °C) and 0.60 ml (5.7 mmol) of *cis*-3-methyl-2-pentene (MCB) in 3 mL of benzene was purged with nitrogen and irradiated in a 12-mm ₸ stoppered Pyrex tube in a Rayonet photoreactor at 350 nm for 6 days. The benzene and olefin was removed by rotoevaporation and the residue was distilled to give **4** as a colorless, viscous liquid (bp 82–84 °C (9 mm)), 75% yield. The NMR was complex owing to the presence of two isomers ((E)- and (Z)-2-phenyl-3-ethyl): C_6H_5 (7.2, s, 5), 2-H (5.30, 5.25, s, s, 1), 4-H (4.6, two skewed q (J = 6.5 Hz), 1), 2CH_3 and CH_3CH_2 (1.5–0.6, m, 11); IR 3085, 3060, 3025, 2960, 2925, 2875, 1600, 1490, 1450, 1380, 1060, and 985 cm^{-1}.

Thermolysis of 3-Phenyl-3-methyl-1,2-dioxetane (PMD) with Trimethylethylene. Solutions of PMD and trimethylethylene in carbon tetrachloride solution were degassed at 10^{-4} mm by three freeze–thaw cycles. The samples were protected from mercury vapor by liquid nitrogen traps. The tubes were wrapped with aluminum foil and the room was darkened. The tubes were sealed under vacuum and heated at 50 °C in a constant-temperature oil bath for 7.5 h. GLC analysis of the reaction solution was carried out with *o*-dichlorobenzene as the internal standard vs. a standard mixture of *o*-dichlorobenzene and oxetane **1**. The GLC analysis was made with a 5 ft × 1/8 in. 5% OV-210 on Chromosorb W column with a column temperature of 115 °C, flow rate 17 mL/min, t_r(**1**) = 15.8 min, t_r(*o*-dichlorobenzene) = 4.0 min.

Thermolysis of 3,3-Dimethyl-1,2-dioxetane (DMD) and Tetramethyl-1,2-dioxetane (TMD) with Tetramethylethylene. Carbon tetrachloride solutions of DMD and TMD with tetramethylethylene were degassed and sealed in tubes as described above. Thermolyses of the DMD and TMD solutions were carried out at 50 °C for 3.3 h and at 70 °C for 6 h, respectively. Again, *o*-dichlorobenzene was added to the solutions at the completion of photolysis as the internal standard and the GLC analyses were made relative to a standard mixture of *o*-dichlorobenzene and oxetane **2**. GLC analyses were made on a 6 ft × 1/8 in. 11% Carbowax 20M on Varaport 30 column with programmed column temperatures of 70 °C (8 min) and then 150 °C with a heating rate of 30 °C/min, flow rate 18 mL/min, t_r(**2**) = 7.2 min, t_r(*o*-dichlorobenzene) = 12 min.

Thermolysis of Triphenyl-1,2-dioxetane (TPD) with *cis*-3-Methyl-2-pentene. Solutions of TPD and *cis*-3-methyl-2-pentene in benzene or carbon tetrachloride were degassed as described above. Thermolysis of the solutions was carried out at 59 °C for 20 h. Again, *o*-dichlorobenzene was added to the reaction mixture as the internal standard and the GLC analysis was made relative to a standard mixture of *o*-dichlorobenzene, **3**, and **4**. GLC analyses were made of a 5 ft × 1/8 in. 5% methyl vinyl silicone on Chromosorb W column with programmed column temperatures of 110 (6 min), 170 (20 min), and then 210 °C (20 min) with heating rates of 30 °C/min, flow rate 20 mL/min, t_r(*o*-dichlorobenzene) = 5.2 min, t_r(**3**) = 27.1 min, and t_r(**4**) = 11.7 min.

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