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Quenching of the ¹n,π* of Alkanones by Unsaturated Compounds[1]

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Abstract: Structure-reactivity profiles of a number of unsaturated compounds toward quenching of alkanone fluorescence were investigated. These studies reveal that the rate constant for fluorescence quenching is sensitive to the electron-donating ability of the dienes and olefins used and to steric effects of the alkanone. The efficiencies of quenching of alkanone fluorescence by a number of unsaturated compounds increase relative to the rates of diffusion in solution as temperature decreases. These results together with other reports in the literature concerning oxetane formation and fluorescence quenching indicate that exciplexes are intermediate in these processes.

I. Introduction

In 1961, Hammond and co-workers reported that the photosensitized cis–trans isomerization of 1,3-pentadienes was a potential probe for understanding many photochemical mechanisms.[3] Evidence was soon forthcoming that the 1,3-diene system was a convenient and well-behaved diffusion controlled quencher of many triplet states ($E_T > 60$ kcal).[4] It was generally assumed that (a) singlet quenching of the sensitizer by 1,3-diene was negligible and (b) irreversible sensitizer–diene chemistry was unimportant.[5] Subsequent careful studies by Hammond[6] and by Schenk[7] showed that neither a nor b was general. However, it was thought that the original generalizations held for alkanones and aryl ketones. In the latter case, singlet quenching by dienes is insignificant because of the normally rapid rate of intersystem crossing ($k_{st} > 10^{10}$ s⁻¹).[8] One expects, however, that the rule of no singlet quenching may break down when k_{st} drops to values less than 10^{10} s⁻¹. It is interesting to note that Barltrop has shown that aryl ketone triplets do form adducts with 1,3-dienes but in very low quantum efficiencies.[9]

1,3-Dienes have been used extensively as quenchers in the study of the mechanisms of alkanone photochemistry.[10] It was supposed that 1,3-dienes were not effective quenchers of alkanone singlets in solution, possibly on the basis of gas-phase measurements which indicated that alkanone fluorescence is not decreased significantly by 1,3-dienes.[11] The elegant use

of this idea by Hammond and Wagner[12] to separate singlet and triplet efficiencies and to determine triplet reactivity stimulated considerable use of 1,3-dienes as "triplet specific" quenchers of alkanones.

More recently, however, the quantitative measurements of quenching of alkanone fluorescence by 1,3-dienes left no doubt that significant deactivation of singlet alkanones can be induced by 1,3-dienes.[13] Although many of the qualitative conclusions reached earlier, with the assumption of negligible singlet quenching, are valid, recent quantitative studies suggest that both alkanone and diene structures will determine the rate constant for singlet quenching. We report here a study of the structure-reactivity relationship for quenching of alkanone singlets by 1,3-dienes and olefins, a temperature dependence investigation of the quenching efficiencies of both electron-rich and electron-deficient olefins on alkanone fluorescence, as well as an investigation of the oxetane formation from photoexcited acetone and 1,3-dienes. Results indicate that exciplexes are intermediate in these processes.

II. Results

Table I summarizes our results from the measurement of the rate constants for quenching of alkanone fluorescence by 1,3-dienes. The rate constants for fluorescence quenching, k_q^f, were determined by measuring the decrease in fluorescence intensity or lifetime of the alkanones as a function of diene

Table I. Quenching of the Fluorescence of Ketones by Various Quenchers[a]

| Ketone | τ_s, ns | $k_q^f \times 10^7$, M^{-1} s^{-1} | | | | | |
		cis-1,3-Pentadiene	2,5-Dimethyl-2,4-hexadiene	1,3-Cyclohexadiene	t-DCE[d]	c-DEE[e]	Biacetyl
Acetone	1.7	9.5,[b] 11.0	130	100	250	200	940[f]
2-Butanone	2.3[c]	4.8[c]					
2-Pentanone	1.8	4.8,[b] 4.3		44[b]			
Diisopropyl ketone	3.5[c]	0.26[c]					
Methyl tert-butyl ketone	4.2	1.0,[b] 1.2		150[b]			752[g]
Di-tert-butyl ketone	5.6	0.25,[b] 0.1[c]					795[g]
Norcamphor (1)	5.7	3.2	37	24	520	130	840[f]
2	6.1	3.3			560	130	800[f]
3	5.0	2.8			100	140	760[f]
4	6.0	1.8			230	85	
Camphor (5)	4.6	1.4	12		120	57	
6	3.1	<0.5	1.8		170	13	610[f]

[a] Unless noted, values apply to benzene solution, analysis of data by the method of eq 1. [b] Values apply to n-hexane solution, analysis of data by the method of eq 1. [c] S. Wettack, unpublished results. [d] Values calculated from $k_q\tau_f$ values of ref 14 and measured τ_fs. [e] Values calculated from $k_q\tau_f$ values of ref 15 and measured τ_fs. [f] Values calculated from $k_q\tau_f$ values of ref 16 and measured τ_fs. [g] M. H. Hui, Ph.D. Thesis, University of Chicago, 1973.

concentration. The data were analyzed in terms of the Stern-Volmer equations 1 or 2 in which ϕ_f^0 is the intensity of fluorescence in the absence of diene or olefin, ϕ_f is the intensity of fluorescence in the presence of diene or olefin, τ_f^0 is the fluorescence lifetime of the alkanone in the absence of diene or olefin, and τ_f is the fluorescence lifetime in the presence of diene or olefin. The fluorescence lifetimes were measured by the singlet photon counting technique.

$$\phi_f^0/\phi_f = 1 + k_q^f \tau_f^0 \text{ [olefin]} \tag{1}$$

$$\tau_f^0/\tau_f = 1 + k_q^f \tau_f^0 \text{ [olefin]} \tag{2}$$

The methods were applied to two series of ketones, (1) acetone and acyclic ketones and (2) norcamphor and its derivatives (compounds **1–6**). The values reported in Table I were
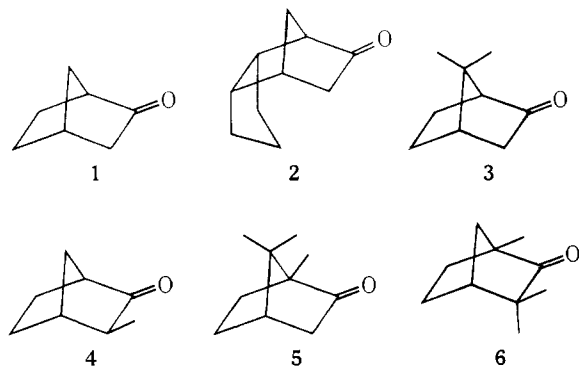
extracted from the linear slopes of the plots of eq 1 or 2. In several cases both methods were used and were found to agree with the experimental error of ±10%. Data on the quenching of alkanone fluorescence by trans-1,2-dicyanoethylene (t-DCE),[14] cis-1,2-diethoxyethylene (c-DEE),[15] and biacetyl are included in the table for comparison. The latter quencher provides an example of quenching by energy transfer resulting in the quantitative production of the excited singlet state of biacetyl.[16]

Our results for the quenching of acetone and norcamphor fluorescence by a series of dienes and olefins are summarized in Table II, and results from the laboratory of Barltrop and Carless are included for comparison.[17] The calculated quenching rate constants of these dienes and olefins and their ionization potentials (IP) are listed in Table III.

We have suggested previously that quenching of acetone fluorescence by DCE and by 1,3-cyclohexadiene may involve the intermediacy of a molecular complex of singlet excited acetone and the ground state olefin, i.e., an exciplex.[18,19] All efforts to detect the fluorescence of these exciplexes have been unsuccessful. However, the effect of variation in temperature on the efficiency of quenching of excited molecules has been used in other systems to demonstrate the presence of nonfluorescent exciplexes;[20-22] therefore, this approach was used to investigate the quenching of alkanone fluorescence by both electron-rich and electron-deficient olefins. Two alkanones were selected for this study, acetone, for its possible correlation between exciplex and oxetane formation, and adamantanone, for its relatively high fluorescence quantum efficiency ($\phi_f = 0.0052$ vs. 0.00094 for acetone[23]). The results are listed in Tables IV and V.

Oxetane formation is a chemical consequence of the interaction of alkanone singlets with unsaturated compounds. We have studied the reactions of acetone with trans-2-methyl-2,4-hexadiene (t-MHD) and 1,3-cyclohexadiene in some depth. The quantum yields for oxetane formation (ϕ_{ox}) are dependent on the concentration of diene used (Tables VI and VII). Limiting quantum yields extrapolated to high diene concentrations (ϕ_{ox-lim}) are instructive to compare and are summarized in Table VIII for these and other reported examples. Since the competitive process for the interception of alkanone singlets by unsaturated compounds is the intersystem crossing to alkanone triplets, the alkanone triplets may transfer their energy to 1,3-dienes via collisions. The 1,3-diene triplets thus formed may undergo dimerization (1,3-cyclohexadiene)[24] or isomerization (t-MHD). The experimental results for the quantum yields of formation of 1,3-cyclohexadiene dimer at various concentrations of the diene are shown in Table IX.

III. Discussion

There are several relevent aspects to the mechanisms of quenching of alkanone singlets by unsaturated compounds. These are (a) the detailed description on the deactivation of the alkanone singlet by unsaturated compounds, (b) the relationship between the formation of oxetanes and quenching of alkanone fluorescence, and (c) the kinetic analysis.

A. The Detailed Description on the Deactivation of Alkanone Singlet by Unsaturated Compounds. The deactivation of alkanone singlets by unsaturated compounds is analyzed by three approaches: (1) dependence on the structure of alkanones or the steric hindrance toward quenching, (2) dependence on temperature, and (3) dependence on the IP (ionization po-

Table II. Quenching of Acetone and Norcamphor Fluorescence by Olefinic Compounds

Olefin	$k_q^f \tau_f$	
	Acetone, M^{-1} [a]	Norcamphor, M^{-1} [b]
2,5-Dimethyl-2,4-hexadiene	2.07, 2.1,[c] 1.91,[e,f] 2.1[f]	2.1,[c] 2.1[d]
1-Methoxy-1,3-butadiene		2.2[c]
1,3-Cyclohexadiene	1.45, 1.8,[b,d] 1.52,[e] 1.52[g]	1.3[c]
trans-2-Methyl-2,4-hexadiene	0.58,[c] 0.47[e]	0.74[c]
2-Ethoxy-1,3-butadiene		0.73[d]
2-Chloro-1,3-butadiene		0.63,[c] 0.63[d]
cis-1,3-Pentadiene	0.19	
trans-1,3-Pentadiene	0.16	0.18,[c] 0.19[d]
1-Chloro-1,3-butadiene		0.18[d]
2-Methyl-1,3-butadiene	0.13[f]	0.17[c]
1-Isopropyl-1,3-butadiene		0.16[d]
cis,cis-1,3-Cyclooctadiene	0.082, 0.12[c]	0.093[c]
2,3-Dimethyl-2-butene	0.23	
2-Methyl-2-butene	0.082	
cis-3-Hexene	0.063	
1-Hexene	0.012	

[a] Measured by method of eq 1 in text with 1.0 M ketone in n-hexane. [b] Measured with 0.1 M ketone in benzene. [c] Measured by method of eq 2 in text. [d] Measured by method of eq 1 in text. [e] Measured by method of eq 21 in text. [f] J. A. Barltrop and F. A. J. Carless, J. Am. Chem. Soc., **94**, 8761 (1972). Values in cyclohexane or n-hexane. [g] Measured by methods of eq 23 in text.

Table III. Quenching Rate Constants and Ionization Potentials of Unsaturated Compounds

| Unsaturated compd	k_q^f, M^{-1} s^{-1} × 10^7		IP, eV
	Acetone	Norcamphor	
2,5-Dimethyl-2,4-hexadiene	122	36	7.91,[a] 7.84[b]
trans-2-Methyl-2,4-hexadiene	28	13	8.12[b]
trans-1,3-Pentadiene	9.4	3.2	8.68,[a] 8.59[b]
cis-1,3-Pentadiene	11.2		8.68,[a] 8.65[b]
1,3-Cyclohexadine	86	24	8.25,[a] 8.30[b]
1,3-Cyclooctadiene	4.8		8.78[c]
2-Methyl-1,3-butadiene	7.6	2.9	8.85[b]
2,3-Dimethyl-2-butene	14.1		8.53,[a] 8.42[b]
2-Methyl-2-butene	4.8		8.85[a]
cis-3-Hexene	3.8		9.14[a]
1-Hexene	0.71		9.59[a]
Acrylonitrile	17, 11[d]		10.75[a]
t-DCE[e]	63, 25[d]		11.16[f]

[a] V. I. Vedeneyev et al., "Bond Energies, Ionization Potentials and Electron Affinities", E. Arnold, London, 1966, pp 155-184. [b] G. N. Taylor, Chem. Phys. Lett., **10**, 355 (1971). [c] H. M. Hui, Ph.D. Thesis, University of Chicago, 1973. [d] N. J. Turro, C. Lee, N. E. Schore, J. A. Barltrop, and H. A. J. Carless, J. Am. Chem. Soc., **93**, 3079 (1971). [e] Values in acetonitrile. [f] B. V. Votov and V. K. Potapov, Khim. Vys. Energ., **6**, 375 (1972).

tential) and EA (electron affinity) of unsaturated compounds.

1. Dependence of Fluorescence Quenching by Unsaturated Compounds on the Structure of Alkanones, Steric Hindrance toward Quenching. As we noted in Table I, the rates of fluorescence quenching of alkanones by biacetyl do not vary more than 35%, while those by other quenchers vary extensively. Since quenching of alkanone singlets by biacetyl is known to proceed by collisional energy transfer,[16,25] different mechanisms must be operating for other quenchers. Examination of the fluorescence quenching of acyclic ketones by 1,3-pentadiene shows that the rate constants of quenching are very sensitive to increasing steric bulk of the alkanone. The rate decreases from acetone to alkanones, methyl tert-butyl ketone, diisopropyl ketone, and di-tert-butyl ketone in that order. Additional information regarding this effect is provided from a study using a series of bicyclic ketones 1-6.

Introduction of substituents to increase the hindrance to the "edge" approach of the carbonyl group decreases the rate of quenching by DEE, an electron-rich olefin, while introduction of substituents to increase the hindrance to the "face" approach of the carbonyl group decreases the rate of quenching by DCE, an electron-deficient olefin. As illustrated below, the n,π* state

| electron-rich species approach | electron-deficient species approach |
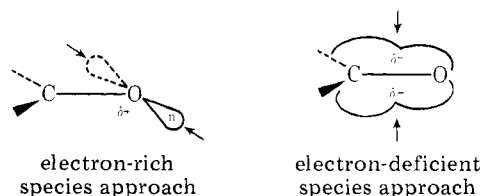
of ketones is reactive toward electron-rich species through "edge" attack on the electrophilic half-vacant n orbital whereas the excited state is reactive toward electron-deficient species through "face" attack on the nucleophilic π-orbital system. The data in Table I on the quenching of alkanone fluorescence

Table IV. Quenching of Alkanone Fluorescence in Methylcyclohexane

	Acetone[a]					Adamantanone[g]			
Temp, °C	CHD[b]	DMHD[c]	Acrylo-[d] nitrile	k_{diff}[e]		Temp, °C	TMF[b]	DMHD[b]	cis-1,3-Pentadiene[b]
−10		0.40		4.9		−32			0.025
0	0.99	0.44		6.1		−23	0.012	0.090	0.026[h]
10	0.92	0.44	0.16	7.4		−11			0.027
20	0.93[f]	0.46	0.17	8.9		0			0.029
30	0.96	0.46	0.15	11		10			0.030
40	0.91	0.46	0.14	12		18	0.015	0.085	0.031[i]
50	0.88		0.13	14					
60	0.87		0.12	17					
70			0.12	19					

[a] 0.1 or 1.0 M in methylcyclohexane. Quenching rates [calculated assuming τ = 1.7 ns, A. M. Halpern and W. R. Ware, *J. Chem. Phys.,* **54**, 1271 (1971)] are in 10^9 M^{-1} s^{-1}. [b] Determined from two points only. Estimated error ±15%. [c] Error ±0.05. [d] Error ±0.01. [e] 10^9 M^{-1} s^{-1}, calculated from $k_{diff} = 8RT/3000$. Values for viscosity from "Landolt-Börnstein Zahlenwerte und Funktionen", II Band, 5 Teil, p 159. [f] Measured at 21 °C. [g] 0.1 M in methylcyclohexane. Quenching rates [calculated assuming τ = 8 ns, J. C. Dalton, D. Pond, and N. J. Turro, *J. Am. Chem. Soc.,* **92**, 2173 (1970)] are in 10^9 M^{-1} s^{-1}. [h] Measured at −20 °C. [i] Measured at 22 °C.

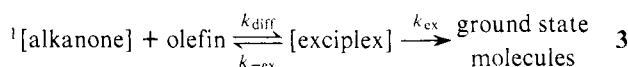**Table V.** Quenching of Acetone Fluorescence by *t*-DCE in Acetonitrile

Temp, °C	k_q[a]	$k_{diffusion}$[b]
0	6.4	14
10	6.6	16
20	6.3	18
30	6.5	20
40	6.1	23
50	5.9	26
60	5.9	29

[a] k_q, in 10^9 M^{-1} s^{-1}. Determined from two points only, assuming τ = 1.7 ns [A. M. Halpern and W. R. Ware, *J. Chem. Phys.,* **54**, 1271 (1971)]; errors estimated to be ±15%. [b] Rate of diffusion, in 10^9 M^{-1} s^{-1}, calculated from $k_{diff} = 8RT/3000$. Values for viscosity from "Landolt-Börnstein Zahlenwerte und Funktionen", II Band, 5 Teil, p 246.

Table VI. Quantum Yields of Formation of Oxetanes and *cis*-MHD[a]

trans-HMD, M	% ^{1}A[b]	7	8	9	10	*cis*-MHD
3.9	70	0.049	0.049	c	c	0.2
2.2	55	0.037	0.036	c	c	0.5
1.2	40	0.028	0.029	c	c	
0.61	30	0.018	0.020	c	c	
0.24	10	0.006	0.006	c	c	>.5

[a] In 6.8 M acetone with various concentrations of *trans*-MHD in *n*-hexane. Excitation 313 nm. Actinometer valerophenone in benzene ($\phi_{acetophenone}$ assumed to be 0.33). [b] Approximate percent of the acetone singlets trapped. Calculated from the measured τ_f and k_q values. [c] Trace amounts (<5% of **9** or **10** in all cases).

by dienes and olefins correlate closely with the results of DEE quenching indicating that there is a preference for "edge" attack of the partial vacant n orbital in the fluorescence quenching step.[26]

2. Dependence of Fluorescence Quenching on Temperature. Since the limiting quantum yield of product formation from the photochemical interaction between alkanones and unsaturated compounds is substantially less than unity (Table VIII), there must be an additional mode or modes of nonradiative decay of excited alkanones. It was suggested that such processes may occur from the exciplex between the excited alkanone and the ground state unsaturated compound.[18,19] The formation of exciplexes of aromatic compounds is usually demonstrated by their unique fluorescence.[22,27] Since alkanone fluorescence is usually weaker by two orders of magnitude than the fluorescence of aromatic hydrocarbons,[23] it is not surprising that we failed to detect any exciplex from alkanones by spectroscopic methods. The quenching rates of unsaturated compounds on alkanone fluorescence are usually slower than those of diffusion controlled processes. If exciplexes are involved as intermediates in the quenching, the reaction may be a reversible one which may be schematically represented by the following expression:[27,28]

$$^1[\text{alkanone}] + \text{olefin} \underset{k_{-ex}}{\overset{k_{diff}}{\rightleftharpoons}} [\text{exciplex}] \xrightarrow{k_{ex}} \begin{array}{c} \text{ground state} \\ \text{molecules} \end{array} \quad \textbf{3}$$

Judging from the result of the previous section that there is a steric control in the quenching process, and from the fact that

chemical consequence of quenching, the formation of oxetane, is usually regioselective (section B), we conclude that exciplex formation requires a specific orientation between the two components. Therefore, the formation of an [^{1}alkanone:olefin] exciplex will have an unfavorable entropy factor, as in the case for the formation of molecular complexes and other types of exciplexes. Furthermore, if the quenching of alkanone fluorescence by unsaturated compounds proceeds via an exciplex as the intermediate, the quenching may proceed faster relative to the rate of diffusion in solution at lower temperatures.

The results, presented in Tables IV and V, indicate that there is little change in quenching efficiency of the fluorescence of acetone and adamantanone by either electron-rich or electron-deficient olefins. The quenching of adamantanone by *cis*-1,3-pentadiene decreases slightly with decreasing temperature, as does the quenching of acetone by 2,5-dimethyl-2,4-hexadiene. In contrast, the quenching of acetone by 1,3-cyclohexadiene shows a slight increase with decreasing temperature, and the quenching by acrylonitrile shows a definite increase in efficiency (40%) as the temperature is lowered from 70 to 10 °C. The effect of temperature on the quenching efficiency of both classes of quenchers is therefore similar and modest.

An increase in quenching efficiency with reduced temperatures may also be due to an increase in the lifetime and ϕ_f of singlet excited alkanones. This possibility is excluded because the ϕ_f of acetone remains constant within experimental error as the temperature is varied between −10 and 40 °C (Table X). Since we have shown that ϕ_f of alkanones is proportional to τ_f, it follows that the lifetime of excited acetone remains constant within experimental error. Also, if the increase in

Table VII. Quantum Yield of Formation of Oxetane from the Photochemical Reaction between Acetone and 1,3-Cyclohexadiene

	[Q], M	1/[Q], M^{-1}	$\phi_{ox}{}^a$	$1/\phi_{ox}$
Run 1	2.049	0.488	0.0371	27.0
	0.967	1.034	0.0320	31.2
Run 2	2.017	0.496	0.0392	25.5
	0.920	1.087	0.0260	38.5
	0.521	1.919	0.0207	48.3
	0.339	2.950	0.0165	60.6
Run 3	1.049	0.953	0.0295	33.9
	1.259	0.794	0.0316	31.6
	1.469	0.681	0.0339	29.5
	1.678	0.596	0.0351	28.5
	2.098	0.477	0.0357	28.0

^{a} The values are derived from the average of four GC analyses. The value of individudal analysis is usually within ±2% of the average but always within ±5%. For other details, see Experimental Section.

Table VIII. Quantum Yields for Oxetane Formation

System	$\phi_{ox\text{-lim}}{}^a$	$k_q{}^f \times 10^{-7}$, M^{-1} s^{-1}
Acetone–2,5-dimethyl-2,4-hexadiene	0.1^b	130
Acetone–2-methyl-2,4-hexadiene	0.14^c	27
Acetone–1,3-cyclohexadiene	0.05^c	90
Acetone–1,3-cyclooctadiene	0.03^{d,e}	7.4

^{a} The value of ϕ as defined in eq 21 in the text. ^{b} J. A. Barltrop and H. A. J. Carless, *J. Am. Chem. Soc.*, **94**, 8761 (1972). ^{c} This work. ^{d} K. Shima, Y. Sakai, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **44**, 215 (1971). ^{e} The rate constant obtained for fluorescence quenching is incompatible with that obtained from kinetic analysis of oxetane formation in this case.

quenching efficiency were caused by an increase in lifetime, one might expect similar increases in quenching efficiency to occur with all quenchers. Since this is not the case, it is clear that a change in excited ketone lifetime is not responsible for the changes in quenching.

Since the rate of diffusion decreases as temperature decreases (Tables IV and V), it is obvious that for a single, nonreversible quenching reaction, the quenching rate must decrease at least as rapidly as the rate of diffusion. Therefore, in cases where the quenching efficiency remains approximately constant or increases as the temperature decreases, the reasonable conclusion is that the quenching occurs via the reversible formation of an intermediate, i.e., an exciplex. Therefore, although no emissions attributable to exciplexes were observed, it is clear that the quenching of acetone by acrylonitrile involves an exciplex, while the involvement of exciplexes in other [^{1}alkanone:olefin] systems is highly probable.

3. Dependence of Fluorescence Quenching on the Ionization Potentials (IP) and Electron Affinities (EA) of Unsaturated Compounds. Results from the previous section suggest that exciplexes may be involved in the fluorescence quenching of alkanones by unsaturated compounds. For two molecules, A* and B, the wave function for the exciplex may be written as[29]

$$\Psi_{ex} = \alpha\Psi_1(A^-D^+) + \beta\Psi_2(A^+D^-)$$
$$+ \gamma\Psi_3(A^*B) + \delta\Psi_4(AB^*) \quad (4)$$

Since the two molecules are not identical in an exciplex, $\alpha \neq \beta$ and $\gamma \neq \delta$. Since exciplexes may be considered to be excited charge-transfer complexes, the charge-resonance terms will be important while the exciton resonance terms will be relatively unimportant, thus $\alpha,\beta \gg \gamma,\delta$.

Table IX. Quantum Yield of Formation of Diene Dimer in the Photolysis of Acetone in the Presence of 1,3-Cyclohexadiene

	[Q], M	1/[Q], M^{-1}	$\phi_{dim}{}^a$	$1/\phi_{dim}$
Run 1	1.049	0.953	0.243	4.11
	1.259	0.794	0.220	4.55
	1.469	0.681	0.208	4.81
	1.678	0.596	0.175	5.71
	1.882	0.530	0.175	5.71
	2.098	0.477	0.154	6.49
Run 2	1.049	0.953	0.255	3.92
	1.259	0.794	0.229	4.37
	1.469	0.681	0.212	4.72
	1.678	0.596	0.183	5.46
	2.098	0.477	0.156	6.41

^{a} The values are derived from the average of four GC analyses. The value of individual analysis is usually within ±2% of the average but always within ±5%. For other details, see Experimental Section.

Table X. Effect of Temperature on Acetone^a Fluorescence

Temp, °C	Rel intensity	Temp, °C	Rel intensity
−10	0.98	21	1.01
0	1.01	32	1.00
10	1.00	40	1.01

^{a} 1.4 M acetone in methylcyclohexane.

Since IPs of olefins and vinyl ethers are less than those of alkanones (9.3–9.7 eV),[30] these compounds can be expected to form exciplexes by electron transfer to the excited alkanone, i.e., the important term in the wave equation will be [alkanone$^-$:olefin$^+$·]. Following the reasoning by Evans,[28] the scheme leads to the equations

$$\phi_0/\phi = 1 + [k_{diff}k_{ex}/(k_{-ex} + k_{ex})]\tau_s[\text{olefin}] \quad (5)$$

$$k_q = k_{diff}k_{ex}/(k_{-ex} + k_{ex}) \quad (6)$$

$$k_{ex}/k_{-ex} = k_q/(k_{diff} - k_q) \quad (7)$$

If we assume that k_{-ex} is the rate constant for diffusion out of the solvent cavity, it will be to the first approximation determined by the properties of the solvent only. Then

$$\ln(k_{ex}/k_{-ex}) = \ln[k_q/(k_{diff} - k_q)] \propto \Delta G^{\ddagger} \quad (8)$$

where $\Delta G^{\ddagger}$ is the free energy of activation for the exciplex formation. For a constant fluorescer and a series of related quenchers, $\Delta G^{\ddagger}$ will be related to electron-donating ability of the quencher. Since the IP of the quencher is a measure for the electron-donating ability, $\Delta G^{\ddagger}$ will be proportional to IP + C, where C is comprised of a series of terms related to the interaction between the exciplex and its environment. In other words, the charge-transfer interaction between ^{1}[alkanone] and olefins will lead to the expression

$$\ln[k_q/(k_{diff} - k_q)] = A(\text{IP}) + C \quad (9)$$

where A and C are constants.

By plotting values of $\ln[k_q/(k_{diff} - k_q)]$ from the fluorescence quenching of acetone by a series of olefins against their IP, using 1.7 ns for τ_s of acetone (Table I) and 1.0×10^{10} M^{-1} s^{-1} as k_{diff} for *n*-hexane, the data on acetone may be expressed by

$$\ln[k_q/(k_{diff} - k_q)] = (-3.01 \pm 0.19)\text{IP} + (21.5 \pm 1.6)$$

and using 2.0×10^{10} M^{-1} s^{-1} as k_{diff} for *n*-hexane

$$\ln[k_q/(k_{diff} - k_q)] = (-3.00 \pm 0.19)\text{IP} + (21.4 \pm 1.6)$$

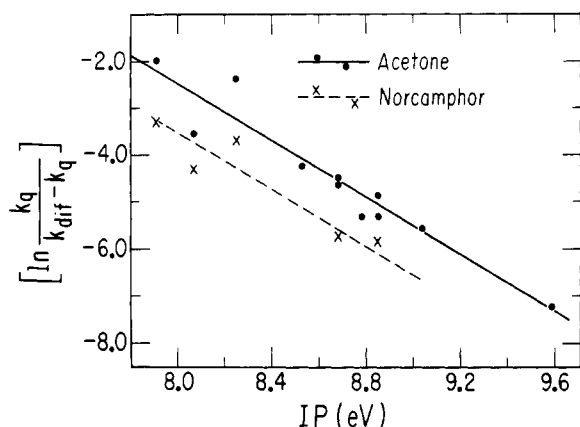Using 5.7 ns for τ_s of norcamphor (Table I) and 1.0×10^{10}

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Figure 1. Dependence of rates of alkanone fluorescence quenching of unsaturated compounds on their ionization potentials.

M^{-1} s^{-1} as k_{diff} for benzene, the data for norcamphor may be expressed by

$$\ln [k_q/(k_{diff} - k_q)] = (-3.00 \pm 0.30)IP + (20.8 \pm 2.0)$$

On the basis of these correlations, we conclude that the nature of interaction between [1][alkanone] and olefins may involve the charge-transfer interaction with the olefin as donor and the [1][alkanone] as acceptor. It is interesting to note also that the plots on fluorescence quenching of acetone and of norcamphor by olefins (Figure 1) exhibit virtually identical slope indicating similar nature of interaction between the components in the exciplex but different intercepts suggesting a difference in the environment of interaction. This difference in the environment may be attributed to the difference in the stereochemistry in the "edge" approach of olefins to these two alkanones, as we have discussed in section A-1.

Originally Evans had analyzed the quenching of excited 2,3-diazabicyclo[2.2.2]oct-2-ene, an aliphatic azo compound, and naphthalene by unsaturated compounds similar to those used in this investigation and concluded that exciplexes were intermediates in these reactions.[28] Linear correlations were obtained by plotting the values of $\ln [k_q/(k_{diff} - k_q)]$ vs. IP of unsaturated compounds. The slopes of these plot are -4.91 eV^{-1} for diazabicylooctene and -6.13 eV^{-1} for naphthalene, both of which are considerably larger than -3.0 eV^{-1} for alkanones found in this investigation. The results indicate that the deactivation of excited alkanones by unsaturated compounds is less dependent on their IPs, and suggest that the $^1n,\pi^*$ of alkanones is more reactive with unsaturated compounds in general than excited aliphatic azo compounds or excited aromatic compounds.

However, the IP of acrylonitrile and t-DCE (10.75^{30} and 11.16 eV^{31}, respectively) are appreciably higher than those of alkanones, indicating that α,β-unsaturated nitriles are unlikely to function as donors to the excited alkanones in exciplex formation. Accordingly, there is a lack of correlation between the k_q of alkanone fluorescence and the IP of these compounds. Instead, we[32] as well as Barltrop and Carless[33] have suggested that in this type of system the excited ketone may function as a donor, transferring charge from the half-filled π^* orbital to the LUMO of the unsaturated nitrile. Such a transfer of charge is reasonable on energetic grounds, since the electron affinities of unsaturated nitriles are larger than those of alkanones. For example, the polarographic reduction potential of acrylonitrile, which is a measure of EA of the ground state, is -2.01 V vs. a saturated calomel electrode,[34] while the reduction potential of acetone, determined under the same conditions, is -2.61 V.[35] Furthermore, calculations by Barltrop and Carless[33] indicate that interaction between the π^* orbital of acetone and Ψ_3 of crotonitrile will cause the energy of Ψ_3 to decrease, re-

sulting in increased stabilization for this type of charge transfer. Therefore the direction of charge transfer in exciplexes between alkanones and electron-deficient olefins is predicted to be the opposite of that in exciplexes involving electron-rich olefins, i.e.,

$$^1[alkanone] + YCH\!=\!CHCN$$
$$\rightleftharpoons [alkanone^+\!\cdot\!:YCH\!=\!CHCN^-\!\cdot] \quad (10)$$
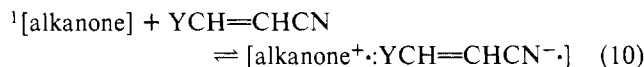
Since t-DCE is expected to have a higher EA than acrylonitrile, the higher quenching efficiency of t-DCE on acetone fluorescence may be attributed to this difference (Tables IV and V).
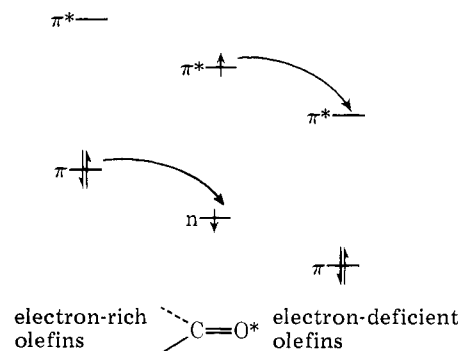
B. The Relationship between Quenching of Alkanone Fluorescence, Oxetane Formation, and Other Deactivation Processes of Excited Alkanones. Oxetane formation from photoexcited carbonyl compounds and unsaturated compounds may occur from either the singlet excited state or the triplet state of carbonyl compounds.[36] The reaction may proceed via a biradical intermediate, particularly when the reactive state of carbonyl compounds is the triplet state. Since [^{1}alkanone: olefin] exciplex is an intermediate in the deactivation of singlet alkanone by olefins, there are four possible pathways in the formation of oxetane from singlet alkanones, i.e., directly via a concerted $[2\pi_s + 2\pi_s]$photocycloaddition, via a singlet biradical intermediate, via an exciplex followed by a concerted cycloaddition, and via an exciplex followed by a single biradical intermediate.
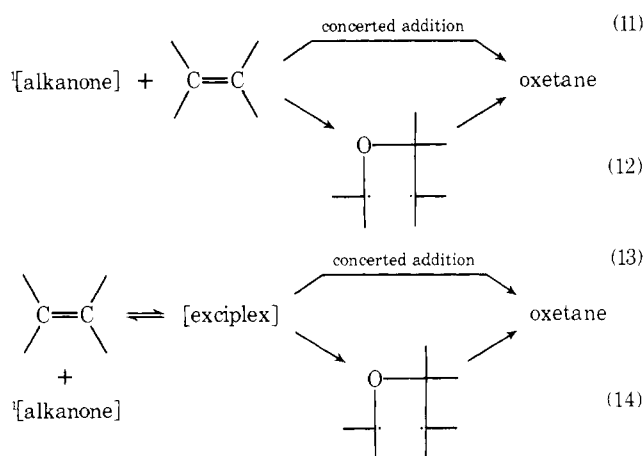

We have shown that singlet acetone exhibits marked difference in its reactivity with 2,3-dimethyl-2-butene and 2-methyl-2-butene as well as with 1,3-cyclohexadiene and 1,3-cyclooctadiene (Table III). Since singlet acetone would react with both members of each pair of these unsaturated compounds to give biradicals of similar stability, the biradical formation cannot be involved in the rate-determining step in the deactivation of singlet acetone by these compounds.

The role of an exciplex derived from [1][alkanone] and a simple olefin was suggested by Morrison in the efficient in-

tramolecular deactivation by photoexcited 5-hepten-2-one to give an oxetane in low efficiency.[37] Oxetane formation from aromatic carbonyl compounds, the Paterno–Büchi reaction, proceeds via a biradical intermediate;[36,38] however, Caldwell and co-workers demonstrated elegantly that exciplexes may be the precursor of these biradicals.[39] Caldwell and Smith had also shown that photocycloaddition of β-methylstyrene to cyanophenanthrene occurs via the exciplex since both the exciplex fluorescence and photocycloaddition are quenched by another quencher, dimethyl acetylenedicarboxylate.[40] We have shown recently that the photocycloaddition of 1,3-dienes to anthracene proceeds via the exciplex since both the anthracene fluorescence quenching by the diene and photocycloaddition exhibit the same negative temperature dependence.[22]

Since [¹acetone:olefin] exciplexes are nonfluorescent and the exciplex formation (as measured by fluorescence quenching) has a negative temperature dependence which is small relative to the experimental error of quantum yield determinations of oxetane formation, neither of the above methods is applicable to demonstrate the role of the exciplex in oxetane formation. However, the intermediacy of exciplexes in the related photocycloadditions mentioned above does provide indirect support for our scheme that exciplex is the intermediate in oxetane formation. The inefficiency of oxetane formation from singlet excited alkanones (Table VIII) is then due to the competing nonradiative decay of the exciplex to ground state alkanones and olefins.

1. Oxetane Formation from Acetone and Electron-Rich Olefins. We studied the oxetane formation from acetone and *trans*-2-methyl-2,4-hexadiene (*t*-MHD) in order to examine its stereoselectivity and regioselectivity. Among the eight possible vinyloxetanes which could result, only two are formed in approximately equal amounts under conditions of low conversion, **7** and **8**. Extended irradiation results in the appearance of oxetanes **9** and **10**. This is due to the eventual production of

(15)
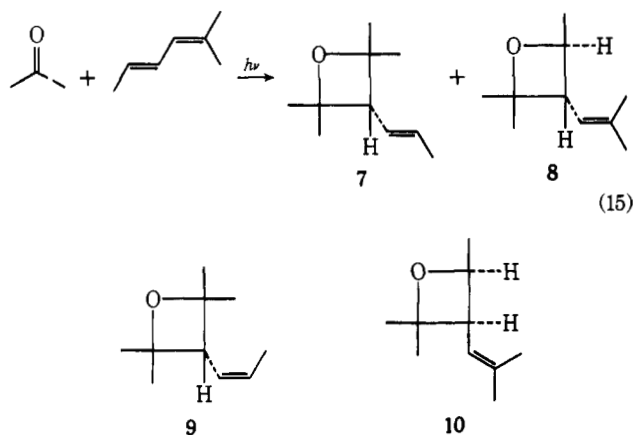
cis-2-methyl-2,4-hexadiene (*c*-MHD) arising from triplet sensitized isomerization of *t*-MHD. Since the trans stereochemistry of the diene is retained in oxetanes **7** and **8**, oxetane formation from 1,3-dienes is highly stereoselective if not stereospecific.

It should be noted also that excited acetone may react with simple olefins and methoxypropenes via both ¹n,π* and ³n,π* states.[41,42] Although the triplet state reaction is nonstereoselective, the singlet reaction is stereoselective.

On the other hand, the oxetane formation is only partially regioselective. As reported by Barltrop and Carless,[17] acetone reacts with 1,3-dienes regioselectively to give 3-vinyloxetanes. The only exception is 1,3-butadiene which gives a mixture of 2,2-dimethyl-3-vinyloxetane (**11**) and 2,2-dimethyl-4-vinyloxetane (**12**) in a 4:1 ratio. A possible explanation for the formation of **12** is that 1,3-butadiene may behave as an electron-rich as well as an electron-deficient olefin (see section
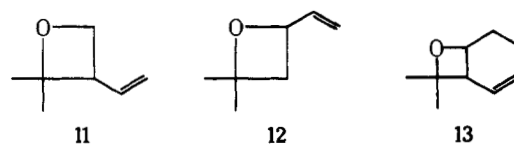
B-2). We have found that 3-vinyloxetanes are the only oxetanes formed in the addition of acetone to *t*-MHD (**7** and **8**) and to 1,3-cyclohexadiene (**13**). However, there is no selectivity in the formation of **7** and **8** from *t*-MHD.

The lack of specificity in $[2\pi_s + 2\pi_s]$ additions between photoexcited compounds and unsymmetrical 1,3-dienes has been noted by Lewis in the addition of stilbene to 1,3-dienes, which occurs preferentially to the more substituted double bond.[43] A similar preference has been reported by Barltrop and Carless on the addition of acetone to isoprene.[17]

The formation of exciplex intermediate involves interaction between the π system of the olefin (donor) and the partially vacant n orbital of the excited alkanone (acceptor). This conclusion is reached by considering the correlation between the fluorescence quenching efficiency and the IPs of various olefins and dienes, and the relationship between quenching efficiency and the stereochemistry of the alkanone. Since the olefin will approach the excited alkanone from the "edge" (section A-1), the stereochemistry is not favored for concerted $[2\pi_s + 2\pi_s]$ cycloaddition. Therefore, the formation of a singlet biradical intermediate from the exciplex cannot be excluded. The formation of 3-vinyloxetane rather than 4-vinyloxetane may be then justified by assuming that the precursor of 3-vinyloxetane is an allylic biradical (**14**) while that of 4-vinyloxetane (**15**) is not.

Since the 1,3-diene is the donor component in the exciplex and the more substituted double bond is electron richer, the initial association between singlet excited acetone with a 1,3-diene to form the exciplex may be more favorable at the more substituted double bond. The formation of oxetane is controlled initially by the formation of exciplex, which will determine the position of interaction between the carbonyl and the diene, and subsequently by the decay of exciplex via the biradical, which leads to the formation of 3-vinyloxetane selectively. The ratio of two oxetanes formed, such as **7** and **8**

(16)

(17)
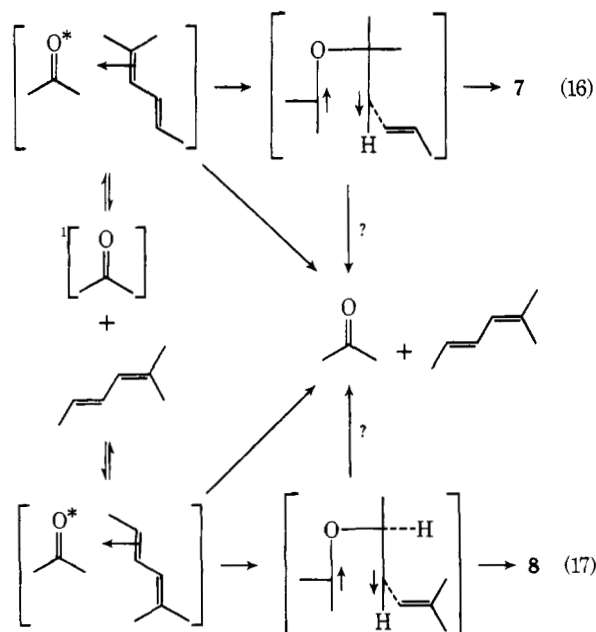
from t-MHD, will be determined not only by the equilibria in the formation of exciplexes but also by the rate and proportion of each exciplex which will decay to give oxetane.

2. Oxetane Formation from Acetone and Electron-Deficient Olefins.
Since singlet acetone reacts with t-DCE to give only trans-2,3-dicyano-4,4-dimethyloxetane and with acrylonitrile and methacrylonitrile to give only 2-cyanooxetanes (eq 19), oxetane formation from singlet acetone and electron-deficient olefins is both highly stereoselective and regioselective.

It should be noted that the dipole moment of ground state acetone is 2.84 D while that of the $^1n,\pi^*$ state is reported to be about 1.0 D, which is reduced from that of the ground state but is still oriented in the same direction.[44] If we treat the C=O double bond as composed of a σ bond and a π bond then the overall dipole moment will be a composite of a σ component and a π component. By using the dipole moment of 2-propanol (1.69 D)[45] as a model for the σ contribution to the dipole moment of acetone and assuming that the σ component of acetone is not appreciably altered by the excitation, one finds that the π component of the dipole moment of acetone has been changed from 1.15 D in the ground state to approximately -0.5 D in the $^1n,\pi^*$ state. Therefore, there is a localization of π^*-electron density on carbonyl carbon causing a reversal in the dipole orientation of the π system of acetone.

Since an exciplex has been demonstrated as the intermediate in the quenching of acetone fluorescence by α,β-unsaturated nitriles, the orientation between the $^1n,\pi^*$ state of acetone and the unsaturated nitrile in the exciplex may be schematically represented by **16**. The regioselectivity in the formation of 2-cyanooxetanes may be accounted for by two alternative explanations, (a) by the orientation between the two components in the exciplex followed by a concerted addition, and (b) by the formation of a biradical intermediate.
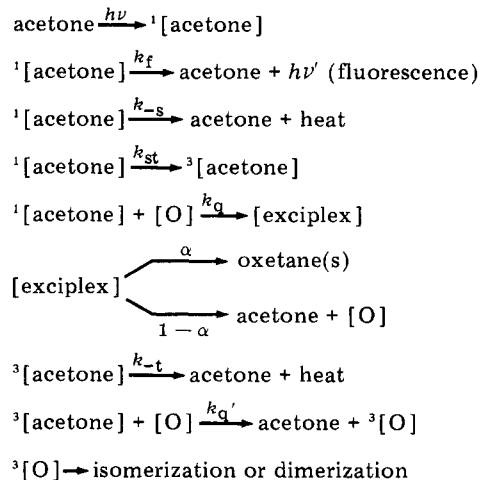
(a) The stereochemistry of exciplex formation from singlet acetone and electron-deficient olefins involves the face to face approach of the π systems of the two components (section A-1) which is identical with that of the $[2\pi_s + 2\pi_s]$ cycloaddition. If a biradical is the intermediate in the 2-cyanooxetane formation, it will be either **17** or **18**. Both of these will be less stable than **19**, the precursor of 3-cyanooxetane which are not detected in the reaction mixtures. Therefore, the formation of 2-cyanooxetane may not be justified through the most stable biradical intermediate, implying rather a concerted $[2\pi_s + 2\pi_s]$ cycloaddition, in which the regioselectivity is controlled by the favorable dipole–dipole orientation between the two components in exciplex **16**. This view is favored by the group at the University of Chicago.

(19)

R = H or CH₃   R = H or CH₃

16

17   **18**   **19**
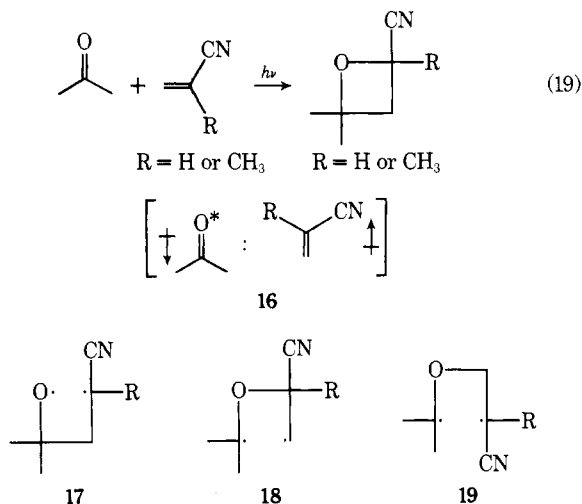
(b) An alternative view is favored by the group at the Columbia University. Since there is a localization of electron density of π^* electron at the carbonyl carbon of the $^1n,\pi^*$ of

acetone, the formation of 2-cyanooxetanes from exciplex **16** may proceed via a kinetically controlled nucleophilic attack of the carbonyl carbon on the unsaturated nitrile to give the singlet biradical **17** which subsequently cyclizes to give 2-cyanooxetanes.

C. Kinetic Analysis.
Although we have shown previously that the exciplex formation is a reversible process and the apparent quenching constant k_q is a composite of several rates, for the sake of simplicity, we shall use k_q in this kinetic analysis by assuming the exciplex formation to be nonreversible. The behavior of a singlet excited alkanone, acetone, in the presence of an unsaturated compound, [O], may thus be represented by the following scheme:

acetone $\xrightarrow{h\nu}$ ^{1}[acetone]

^{1}[acetone] $\xrightarrow{k_f}$ acetone + $h\nu'$ (fluorescence)

^{1}[acetone] $\xrightarrow{k_{-s}}$ acetone + heat

^{1}[acetone] $\xrightarrow{k_{st}}$ ^{3}[acetone]

^{1}[acetone] + [O] $\xrightarrow{k_q}$ [exciplex]

[exciplex] $\begin{cases} \xrightarrow{\alpha} \text{oxetane(s)} \\ \xrightarrow{1-\alpha} \text{acetone} + \text{[O]} \end{cases}$

^{3}[acetone] $\xrightarrow{k_{-t}}$ acetone + heat

^{3}[acetone] + [O] $\xrightarrow{k_q'}$ acetone + ^{3}[O]

^{3}[O] $\rightarrow$ isomerization or dimerization

$$\tau_s = (k_f + k_{-s} + k_{st})^{-1} \qquad (20)$$

In this scheme the quantum yield of oxetane formation (ϕ_{ox}) may be given as

$$\phi_{ox} = \frac{\alpha k_q[O]}{\tau_s^{-1} + k_q[O]}$$

or

$$\phi_{ox}^{-1} = \alpha^{-1} + (\alpha k_q \tau_s[O])^{-1} \qquad (21)$$

Therefore, there will be a linear relationship when values of ϕ_{ox}^{-1} are plotted against $[O]^{-1}$ with an intercept of α^{-1} and a slope of $(\alpha k_q \tau_s)^{-1}$. The value of α^{-1} gives the limiting quantum yield of oxetane formation at infinite [O], or ϕ_{lim}. The value of $k_q \tau_s$ thus obtained should be the same within experimental error as that obtained from the fluorescence quenching studies of acetone by [O].

The relationship between deactivation of alkanone singlet by 1,3-dienes and oxetane formation has been dealt with previously by Barltrop and Carless.[17] They demonstrated that the kinetics of oxetane formation are consistent with the interaction of 1,3-dienes with alkanone singlet and not the triplet. In order to examine the relationship between quenching of acetone fluorescence, oxetane formation, and other deactivation processes, two systems were analyzed in some depth, [acetone-1,3-cyclohexadiene] and [acetone-trans-2-methyl-2,4-hexadiene] (or acetone-t-MHD).

As stated in the previous section, we studied the [acetone-t-MHD] system in order to examine the stereoselectivity and the regioselectivity of oxetane formation. The quantum yields for oxetane formation and for cis–trans isomerization of the diene were measured as a function of diene concentration (Table VI). A plot of ϕ_{ox}^{-1} vs $[t\text{-MHD}]^{-1}$ is linear with a slope of 16.0 ± 4.0 M and an intercept of 7.4 ± 1.8. Interpretation of the slope and intercept in terms of a Stern–Volmer analysis yields a limiting total ϕ_{ox} of 0.14 and a value of $k_q\tau_s$ of 0.46 ± 0.11 M^{-1}, in good agreement with the value of $k_q\tau_s$ of $0.58 \pm$
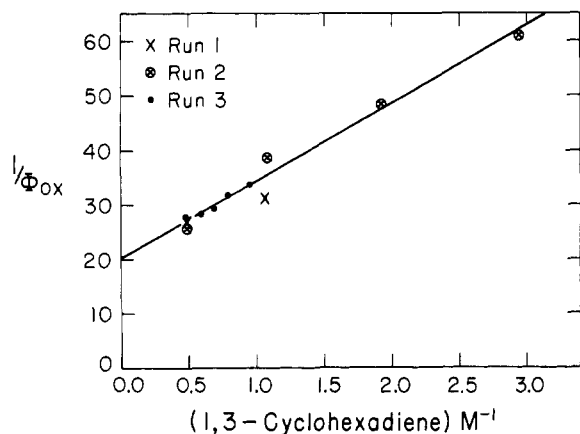
Figure 2. Oxetane formation from the photoreaction between acetone and 1,3-cyclohexadiene.

Figure 3. Formation of 1,3-cyclohexadiene dimer from the photoreaction between acetone and 1,3-cyclohexadiene.

0.06 M^{-1} obtained from the fluorescence quenching of acetone by t-MHD.

We chose the [acetone-1,3-cyclohexadiene] system in order to examine not only the relationship between the fluorescence quenching of acetone by the diene and the oxetane formation but also the relationship between these processes with the intersystem crossing. Since acetone triplet will sensitize the dimerization of 1,3-cyclohexadiene,[24] we shall be able to measure the formation of acetone triplet quantitatively by measuring the amount of diene dimer formed in the reaction. According to the scheme proposed above, the quantum yield for the diene dimer formation, ϕ_{dimer}, may be expressed as

$$\phi_{dimer} = \left(\frac{k_{st}}{\tau_s^{-1} + k_q[0]}\right)\left(\frac{\beta k_{q'}[0]}{k_{q'}[0] + k_{-t}}\right) \qquad (22)$$

where β is the fraction of 1,3-cyclohexadiene triplet that dimerizes.

Since $k_q[0] \gg k_{-t}$ and the quantum efficiency of intersystem crossing of acetone ($\phi_{st} = k_{st}\tau_s$) has been estimated at 0.9,[46] the expression may be simplified,

$$\phi_{dimer} = 0.9\beta(1 + k_q\tau_s[0])^{-1}$$

or

$$\phi_{dimer}^{-1} = 1/0.9\beta(1 + k_q\tau_s[0]) \qquad (23)$$

In other words, a plot of the reciprocal of ϕ_{dimer} vs. 1,3-cyclohexadiene concentration will be linear with a slope of $(1/0.9\beta)k_q\tau_s$ and an intercept of $1/0.9\beta$ which will provide a third independent measure of $k_q\tau_s$.

The main product from the irradiation of acetone in the presence of cyclohexadiene is the oxetane **13** together with variable amounts of cyclohexadiene dimer and traces of 2-propanol, 1,4-cyclohexadiene, and benzene. The kinetic analysis of the oxetane formation at various concentrations of the diene (Table VII and Figure 2) may be expressed by the equation

$$\phi_{ox}^{-1} = (14.2 \pm 1.2)[0]^{-1} + (19.7 \pm 1.9)$$

According to eq 21, the limiting quantum yield of oxetane formation is 0.05 and the value of $k_q\tau_s$ is 1.52 ± 0.10 M^{-1}, in excellent agreement with the value of $k_q\tau_s$ obtained from the fluorescence quenching, 1.45 ± 0.03 M^{-1}.

Subsequently, the quantum yields of acetone sensitized dimerization of 1,3-cyclohexadiene were measured at various concentrations of the diene, and the results are given in Table IX. The quantum yield actually decreases with increasing diene concentration as predicted by the above mechanism, since increasing proportion of acetone singlet will be intercepted by the diene resulting in a lower yield of acetone triplet. When
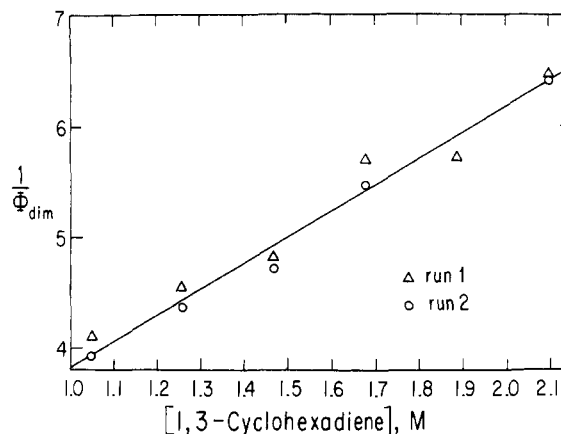
reciprocals of ϕ_{dimer} were plotted against [0], a straight line resulted (Figure 3) and the result may be represented by

$$\phi_{dimer}^{-1} = (2.32 \pm 0.13)[0] + (1.53 \pm 0.21)$$

From this expression, we found that $\beta = (0.9 \times 1.53)^{-1} = 0.73 \pm 0.11$ and $k_q\tau_s = (2.32 \pm 0.13) \times 0.9\beta = 1.52 \pm 0.15$ M^{-1}.

Therefore, the values of $k_q\tau_s$ have been obtained from three independent sources, namely, fluorescence quenching, oxetane formation, and sensitized dimerization of the diene. The respective values are 1.45 ± 0.03, 1.52 ± 0.22, and 1.52 ± 0.15 M^{-1}. The consistency of these three values lends excellent support to the proposed scheme.

IV. Conclusion

On the bases of (1) relationship between the quenching efficiency of alkanone fluorescence by a given olefin and the stereochemistry of alkanones, (2) temperature dependence on the quenching of alkanone fluorescence by olefins, (3) relationship between the IP of electron-rich olefins and EA of electron-deficient olefins and their quenching efficiencies, and (4) stereoselectivity and regioselectivity of oxetane formation, we conclude that exciplexes are intermediates in the deactivation of singlet excited alkanones by olefins and dienes. There are two types of [1alkanone:olefin] exciplexes, those with electron-rich olefins and 1,3-dienes involving the charge transfer interaction from the olefin or diene to excited alkanone and those with electron-deficient olefins involving charge transfer interaction from excited alkanone to the olefin.

V. Experimental Section

General. NMR spectra were taken on a Varian HA-100 or A-60A spectrometer. Fluorescence spectra were recorded on a Perkin-Elmer MPF-2A or MPF-4 spectrofluorimeter with corrected spectrum assembly and thermostatic cell cmpartment. Fluorescent lifetimes were measured using the single-photon counting technique as described previously.[47]

Solvents. n-Hexane (Philips Petroleum Co., pure grade, 99 mol % minimum) was purified by successive washings with concentrated sulfuric acid until the acid layer was almost colorless, 20% fumic sulfuric acid, concentrated sulfuric acid again until the acid was colorless, acidic potassium permagnate solution, water, 10% NaOH solution, and finally water. Each washing included periodic shaking until no further change could be discerned in the nonhexane layer. The hexane was then dried with sodium sulfate and distilled from sodium through a Podbelniak Heligrid column rated at 50 theoretical plates, and stored over sodium.

Benzene (Mallinckrodt Spectrar grade) was purified by washing with concentrated sulfuric acid, twice with water, twice with saturated $NaHCO_3$, and twice again with water. After drying overnight over P_2O_5, the benzene was decanted onto fresh P_2O_5 and was distilled

through a 43-cm Vigreux column. The middle 80% of the distillate was collected and stored in airtight amber bottles under nitrogen.

Methylcyclohexane (Eastman Spectro grade) was refluxed for 1 h over sodium and distilled through a 40-cm glass helices column under nitrogen, the middle portion being collected. In some cases, passage through a column of activated alumina aided in the removal of remaining impurities.

Acetonitrile (Aldrich, spectral grade) was distilled under argon from molecular sieve 3A, and then passed through silica gel.

Dienes and Unsaturated Compounds. 1-Hexene, cis-3-hexene, 2-methyl-2-butene, trans-1,3-pentadiene, cis-1,3-pentadiene, 2,3-dimethyl-2-butene, 1,3-cyclohexadiene, and 2,5-dimethyl-2,4-hexadiene were all purchased from Chemical Samples Co. at 99% grade except 2-methyl-2-butene, which was at 99.9% grade. However, nearly all of them contain traces of impurities which increased UV absorption and fluoresced appreciably. All these compounds met the standard of the manufacturer according to GC analysis and distillation over sodium was not effective to remove the impurities. In most cases, passing these olefins through a short column of activated alumina was good enough to eliminate the impurities. In case this failed, the process was repeated until it reached the satisfactory purity.

trans-Dicyanoethylene (fumaronitrile, Aldrich Co.) was recrystallized from petroleum ether before use, mp 95–96 °C.

1,3-Cyclooctadiene (Aldrich, 95%) was first passed through a column of activated alumina to remove the yellow color. It was then fractionally distilled through a spinning band column rated at 125 theoretical plates under nitrogen, and finally passed through another alumina column.

trans-2-Methyl-2,4-hexadiene. trans-2-Methyl-4-hexen-3-ol (Chemical Samples Co.) was percolated through a hot (220 °C) alumina column to afford trans-2-methyl-2,4-hexadiene (25%) along with 2-methyl-3,5-hexadiene (74%) and cis-2-methyl-2,4-hexadiene (1%). The desired compound was purified by preparative gas chromatography followed by distillation from lithium aluminum hydride, bp 110 °C.

Ketones. Acetone (Merck, analytical reagent, or MCB, spectroquality) was distilled before use. Adamantanone (Aldrich, lot 100617) was used as received.

Bicyclic ketones **1, 2, 5,** and **6** were commercially available and were purified by preparative gas chromatography followed by flash vacuum distillation (**2** and **6**) or by sublimation (**1** and **5**) immediately prior to use. Ketones **3** and **4** were available from previous studies.[26] Pure **4** was obtained by preparative gas chromatography (20-ft FFAP column at 170 °C) followed by flash vacuum distillation. Pure samples of **3** were sublimed prior to use.

General Procedure for Measuring Fluorescence Quenching. Since the fluorescence of alkanones and cycloalkanones is relatively weak, the sepctra were recorded with both the excitation and emission slits of the spectrofluorimeter set at 5-nm band pass. Since the background emission from the solvent may be significant in some of the samples, a blank of the solvent or the solvent containing the quencher was invariably run for comparison. The intensity of the background emission was determined by comparing the heights of the solvent Raman band in the presence and absence of ketone; the Raman band provided a convenient internal standard whereby the background emission intensity could be normalized. The background emission, which does not exceed 10% of the total emission at 400 nm, was subtracted from the total emission at 400 nm. This correction was applied whenever necessary.

No shifts in fluorescence maxima were observed upon increase in quencher concentration, and *no new fluorescence bands were discernible in all of the measurements.*

Acetone. For the quenching of acetone fluorescence, the concentration used was 1 mL in 10 mL of n-hexane solution containing the quencher. This relatively high concentration was used to ensure that absorption by the quencher olefin was negligible. Owing to the relatively short lifetime of its singlet, degassing was found to be unnecessary.

Adamantanone. Owing to the longer lifetime of singlet excited adamantanone, the solution was degassed by three freeze–thaw cycles with an apparatus described elsewhere.[48]

Bicyclic Ketones 1–6. Nondegassed solutions of 0.1 M ketone in benzene containing varying amounts of quencher were prepared in stoppered quartz fluorescence cuvettes. Competitive absorption by the dienes was found to be insignificant except in the case of 2,5-dimethyl-2,4-hexadiene. In this case the observed intensities were

corrected according to the relationship

$$I_f^{corr} = \frac{I_f(1 - 10^{-\epsilon_K C_K})(\epsilon_K C_K + \epsilon_D C_D)}{\epsilon_K C_K(1 - 10^{-\epsilon_K C_K - \epsilon_D C_D})}$$

where ϵ_K, C_K, ϵ_D, and C_D refer to the molar extinction coefficients and concentrations of the ketone and diene, respectively. After such a correlation the Stern–Volmer slope $(k_q^f \tau_0^f)$ according to eq 1 agreed well with that obtained from eq 2.

Photoreaction between Acetone and 1,3-Cyclohexadiene. A solution of 15 mL of 1,3-cyclohexadiene and 85 mL of acetone was irradiated with a Hanovia 450-W Hg immersion lamp through a Pyrex filter for 48 h and then fractionally distilled. The low-boiling fractions (60 mL) when subjected to gas chromatography analysis with 20 ft × 0.375 in. Carbowax 20M (30%) on Chromosorb P column at 150 °C showed, in addition to predominant amounts of unreacted acetone (retention time 6 min), traces of 2-propanol (8 min), 1,3-cyclohexadiene (9.5 min), 1,4-cyclohexadiene (12 min), and benzene (13 min). The later fractions were analyzed with a 5 ft × 0.25 in. SE-30 (20%) on Chromosorb P column. Three main peaks were detected. The later two (8 and 9 min) were cyclohexadiene dimers. The compound corresponding to the first peak (3 min) was collected. It is a colorless, sweet-smelling liquid: bp 75 °C (10 mm); IR (neat) 920 cm^{-1} (C–O); NMR (CCl$_4$) δ 1.10 (s, 3 H), 1.10–1.30 (m, 1), 1.60 (s, 3 H), 1.70–1.90 (m, 1 H), 2.00–2.40 (m, 2 H), 2.70–3.05 (doublet of doublets, 1 H, J = 5.8 Hz), 4.90–5.15 (doublet of triplet, 1 H, J = 2.5 and 6.4 Hz), 5.38 (m, 1 H), and 6.15 ppm (m, 1 H). Anal. Calcd for C$_9$H$_{14}$O: C, 78.21; H, 10.21. Found: C, 78.05; H, 10.32.

About 20 mL of viscous residue was left after the distillation.

The kinetic data were obtained by irradiating samples of acetone (1.36 M in n-hexane) with various concentrations of the diene in a "merry-go-round" apparatus at 313 nm.[49] The formation of oxetane and cyclohexadiene dimers were followed by gas chromatography using the SE-30 column. 2-Hexanone in n-hexane was used as the secondary actinometer.[50] The results were summarized in Tables VII and IX.

Photoreaction of Acetone and trans-2-Methyl-2,4-hexadiene. A solution containing 2.0 mL of acetone and 0.25 g (1.3 M) of trans-2-methyl-2,4-hexadiene was irradiated in a Pyrex test tube to high conversion to give a mixture of vinyloxetanes **7, 8, 9,** and **10** in a relative ratio of 27:39:10:24, respectively. The vinyloxetanes were separated by preparative gas chromatography on a Carbowax 20M on KOH washed Chromosorb P column and characterized by NMR. Oxetane **7** exhibits δ 1.22 (s, 6 H), 1.32 (s, 6 H), 1.69 (doublet of doublets, 3 H, J = 6 and 1.2 Hz), 2.78 (d, 1 H, J = 9.5 Hz), 5.37 (doublet of quartets, 1 H, J = 14.3 and 6 Hz), and 5.68 ppm (16 lines, 1 H, J = 14.3, 9.5, and 1.2 Hz). Oxetane **8** exhibits δ 1.22 (s, 3 H), 1.31 (s, 3 H), 1.31 (d, 3 H, J = 6 Hz), 1.59 (d, 3 H, J = 1.5 Hz), 1.72 (d, 3 H, J = 0.5 Hz), 2.82 (doublet of doublets, 1 H, J = 9.5 and 6.1 Hz), 4.29 (doublet of doublets, 1 H, J = 6 and 6.1 Hz), and 5.28 ppm (d, 1 H, J = 9.5 Hz). Oxetane **9** exhibits δ 1.20 (s, 6 H), 1.35 (s, 6 H), 1.59 (doublet of doublets, 3 H, J = 6.1 and 2 Hz), 3.21 (d, 1 H, J = 8.5 Hz, and 5.54 ppm (m, 2 H). Oxetane **10** exhibits δ 1.19 (s, 3 H), 1.20 (d, 3 H, J = 6 Hz), 1.40 (s, 3 H), 1.56 (d, 3 H, J = 1.5 Hz), 1.78 (s, 3 H), 3.37 (doublet of doublets 1 H, J = 8.1 and 9.5 Hz), 4.75 (doublet of doublets, 1 H, J = 6 and 8.1 Hz), and 5.48 ppm (d, 1 H, J = 9.5 Hz). Authentic samples of **8** and **10** were prepared by the irradiation of a 1:1 mixture of acetaldehyde and 2,4-dimethyl-2,5-hexadiene.

For kinetic results, solutions of acetone (6.8 M) and various concentrations of trans-2-methyl-2,4-hexadiene in n-hexane were irradiated simultaneously in base-washed Pyrex test tubes on a "merry-go-round" apparatus with 313-nm light.[49] Samples were withdrawn periodically and analyzed by gas chromatography with the Carbowax 20M on KOH washed Chromosorb P column for the vinyloxetanes and cis-2-methyl-2,4-hexadiene formed. The conversion of valerophenone to acetophenone in benzene (ϕ = 0.33) was used as the secondary actinometer.[51] Quantum efficiencies for the product formation were extrapolated to zero conversion and are summarized in Table VI.

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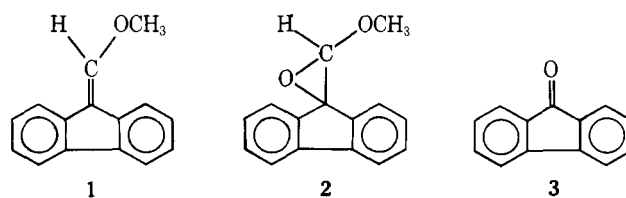# Photooxidation of 9-(Methoxymethylene)fluorene

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Abstract: The unsensitized photooxidation of 9-(methoxymethylene)fluorene (**1**) in carbon tetrachloride yields mixtures of epoxide (**2**) and fluorenone (**3**) in ratios from 0.04 at −20 °C to 2.6 at 75 °C. The efficiency of the oxidation depends on the chain character ($\phi = 12$) imparted by even small concentrations of carbon tetrachloride or tetrabromide. The reaction can be initiated thermally by generating the bromoperoxy radical **5** in the dark in the presence of **1** and oxygen. Mixtures of **1** and 2,3-dimethyl-2-butene show little change in the hydrocarbon without added sensitizer but rapid formation of allylic hydroperoxide when tetraphenylporphin is added. This evidence shows that singlet oxygen is not involved in the photooxidation of **1**. A chain mechanism is proposed.

Photooxidation of alkenes has been accomplished by (1) sensitized oxidation generating singlet oxygen[1] as the oxidizing agent; (2) self-sensitized oxidation[2] (probably involving singlet oxygen); and (3) sensitized oxidation, especially with α-diketones, not involving singlet oxygen.[3] Of particular interest has been the mechanism by which certain photooxidations[3,4] lead to epoxides as products. Recent reports of epoxides accompanying the reaction of singlet oxygen with biadamantylidene,[4c] norbornene,[4d] and binorbornylidene[4a,b] have been interpreted as indicating deoxygenation of intermediate peroxiranes by pinacolone[4c] or singlet oxygen[4b,e] (yielding ozone). Recent results in this laboratory[3,5] indicate that the photooxidation of alkenes to epoxides, sensitized by biacetyl or benzil, does not involve singlet oxygen. We now report unsensitized

photooxidation of 9-(methoxymethylene)fluorene (**1**) to ep-

oxide (**2**) and fluorenone (**3**) under conditions where singlet oxygen is not generated.

Results

Irradiation of 9-(methoxymethylene)fluorene (**1**) in carbon