On the Mechanism of Enone Photoannelation: Activation Energies and the Role of Exciplexes[1][†]

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Abstract: The mechanism of enone photocycloaddition has been reexamined. It has been found that: (a) the triplet exciplex previously postulated is formed essentially irreversibly; (b) the triplet exciplex is very short-lived, since it is not quenched by dienes; and (c) the effect of temperature on the quantum yield of product formation was found to be related to the activation energy difference between biradical closure and fission.

Since its initial reporting, the photochemical cycloaddition of α,β-unsaturated carbonyl compounds to olefins has received much attention.[3] Early work showed that the reactive state in the case of cyclopentenone and cyclohexenone was a triplet[4] and that the triplet yield was equal to unity.[5,6] It was shown that at least one intermediate was formed, by combination in some way with the olefin, and that this intermediate(s) was able to decay to ground state starting materials as well as give product. Its formation was thus one of the deactivation processes available to the excited enone. Similar conclusions were reached, with regard to cyclopentenone dimerization, by Wagner.[7]

With the purpose of revealing more detail on the reaction energy surface we were concerned to ascertain whether, after generation of the excited enone, significant energy barriers had to be traversed by this species on its way to product. Few studies concerning the effect of temperature on excited state reactions had and indeed have been made (for examples see ref 8). The present contribution will describe our findings, which represent the first report of the thermodynamic parameters of photocycloaddition.[9]

Experimental Section

All solvents used for photoaddition reactions were Fisher spectral grade. Cyclopentenone (Aldrich), cyclohexene (Phillips), *cis*-dichloroethylene (Eastman), cyclohexenone, *trans*-3-hexene, and 2,5-dimethyl-2,4-hexadiene (Aldrich) were purified as previously described.[6] The method of Liu[10] was used in preparing bicyclo[4.2.0]-oct-7-ene (bp 132 °C). *cis*-Piperylene (K and K Laboratories) and *trans*-piperylene (Aldrich) were purified by distillation over sodium wire and then passed over neutral alumina. The calibrating compounds in GLC analysis were naphthalene, 2-methylnaphthalene, acenaphthene, and biphenyl. All were crystallized from 95% ethanol and then sublimed.

Infrared spectra were recorded with a Beckman IR-7, using CCl_4 (Fisher spectral grade) as solvent. Nuclear magnetic resonance spectra were run on a Varian A-60 instrument, in CCl_4, using Me_4Si as internal standard. Chemical shifts are given in parts per million.

Photolysis and Preparation of Adducts. The cycloadducts from the photoaddition of cyclopentenone to cyclohexene, *cis*-dichloroethylene, *trans*-3-hexene, and cyclopentene and cyclohexenone to cyclohexene, cyclopentene, and *trans*-3-hexene were prepared and separated following the procedure previously described.[5,6] A typical preparation was as follows.

Cyclopentenone and Bicyclo[4.2.0]oct-7-ene. Irradiation of cyclopentenone (0.5 g) and bicyclooctene (3 mL) in cyclohexane (10 mL), with a Hanovia 450-W medium-pressure mercury vapor lamp (Pyrex filter) for 2 h, resulted in the disappearance of the enone carbonyl band at 1710 cm^{-1} and the formation of only one adduct, tetracyclo[6.5.0.$0^{2,7}$.$0^{9,13}$]tridecan-10-one (**1**) (GLC). The product was chromatographed on silica gel (BDH 60–120 mesh) using ethyl acetate–hexane (1:9). The oily product obtained, ν_{max} 1735 cm^{-1}, showed a molecular ion at *m/e* 190, indicating that it was a 1:1 adduct of the enone and bicyclooctene.

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 81.75; H, 9.88.

The structure of the adduct (**1**) followed from its mode of formation, its composition and molecular weight, and from the following sequence of chemical transformations.

Baeyer-Villiger Oxidation of 1. To the adduct (**1**) (108 mg) in 1 mL of acetic acid was added 52 mg of sodium acetate followed by the dropwise addition of 0.8 mL of peracetic acid (Aldrich). The slurry was allowed to stand at room temperature overnight, the reaction then being complete as indicated by thin layer chromatography (TLC) (silica gel; ether–benzene 1:3). R_f values of 0.86 and 0.72 were observed for **1** and δ-lactone **2**, respectively. After isolation the lactone (**2**) was obtained as a colorless liquid in 75% yield: ν_{max} 1745 cm^{-1}; *m/e* 206.12.

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.79; H, 8.95.

The methine proton on carbon bearing oxygen appeared at δ 4.85. The crude δ-lactone (**2**) (224 mg) with alcoholic potassium hydroxide (10 mL; 0.5 N) was refluxed for 1.5 h, the acidic material isolated in the usual way, and esterified with diazomethane to give the hydroxy ester **3**: ν_{max} 3610, 3470, 1740 cm^{-1}; *m/e* 220 (M − 18); δ 3.05 (1 H), 4.4 (1 H), 3.7 (s, 3 H).

Oxidation to Keto Ester 4. The hydroxy ester **3** (50 mg) in dry acetone (3 mL) was titrated with Jones reagent (0.7 g of chromium trioxide in 5 mL of water and 0.6 mL of concentrated sulfuric acid) until a permanent pink color was obtained. Isolation of the product in the usual way gave, after TLC (ether–benzene, 1:3), 35 mg of the tricyclo keto ester **4** as an oil: ν_{max} 1790, 1745 cm^{-1}, *m/e* 236. The high frequency absorption clearly indicated the presence of a cyclobutanone, and hence the absence of rearrangement in the cycloaddition to form **1**.

Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.54. Found: C, 71.71; H, 8.83.

Low-Temperature Quantum Yields. The optical bench system has been described previously.[6] The samples were irradiated in a quartz apparatus, which allowed liquid at low temperature to be circulated around a 2 × 3 cm oval sample cell (1-cm path length and 5 mL capacity). The sample cell was situated in a quartz envelope equipped with two windows parallel to that of the cell. This was evacuated to prevent condensation forming on the surface of the cell. The sample was cooled by circulating an acetone–ether mixture, which was held at the required temperature by means of a thermostated bath (Lauda constant temperature and circulator Model K2, connected to a solid carbon dioxide heat exchanger Model KS). Temperatures below −60 °C were obtained by circulating the mixture through a copper coil placed in one of the following slurries: −70 °C, CO_2-acetone; −90 °C, methylene dichloride–liquid nitrogen; −102 °C, carbon disulfide–liquid nitrogen. The sample temperature was measured using an iron constantan thermocouple. Solutions were degassed by the freeze–pump–thaw cycle to a residual pressure of 5×10^{-5} mmHg, and conversions were carried to between 3 and 5% (ca. 1 h).

Analysis of the products were performed with an Aerograph Hy-Fi-600C gas chromatograph equipped with a flame ionization detector. A column of 5% FFAP on Diatoport S (8 ft × ⅛ in.) was used with a helium flow rate of 40 ml/min. The results are listed in Table I. Values are averages of three to four determinations. Plots of log (ϕ^{-1}

[†] Dedicated to Professor R. B. Woodward on the occasion of his 60th birthday.

Table I. Quantum Yields for Cycloaddition[a]

Ketone	Olefin[b]	$\Phi_{27^\circ C}$	$\Phi_{-5^\circ C}$	$\Phi_{-10^\circ C}$	$\Phi_{-41^\circ C}$	$\Phi_{-71^\circ C}$	$\Phi_{-90^\circ C}$	$\Phi_{-102^\circ C}$
Cyclopentenone	Cyclohexene[c]	0.46 (0.48)[d]		0.51	0.55	0.62 (0.72)[d]	0.684	0.72
	Cyclopentene	0.23[e]		0.31		0.61		
	trans-3-Hexene	0.22				0.19		
	cis-Dichloroethylene	0.35[f]				0.49		
	Bicyclo[4.2.0]-oct-7-ene	0.23	0.25					
	3-Hexyne	0.49[g]				0.31		
Cyclohexenone	Cyclohexene	0.48				0.43	0.41	
	Cyclopentene	0.36	0.39			0.45		
	trans-3-Hexene	0.063	0.060			0.052		
Tricyclo[3.3.2.0]-dec-3-en-2-one (**5**)	Cyclohexene	0.19				0.21		

[a] All irradiations were performed on an optical bench using 313-nm light. Error ±3%. [b] Olefins were used as solvent (neat). [c] 3.66 M in ether, the Φ was 0.52 in diglyme. [d] The values in parentheses are for neat olefin. [e] The values reported earlier were 0.32 and 0.27. Indeed the later value was obtained if impure cyclopentene (from exposure to air) was used, and another peak appeared under that of the adduct on changing the GLC condition. [f] The value reported previously was 0.24 based on the observation of three adducts only. The value given here was based on all four adducts. [g] Determined by Dr. M. C. Usselman.

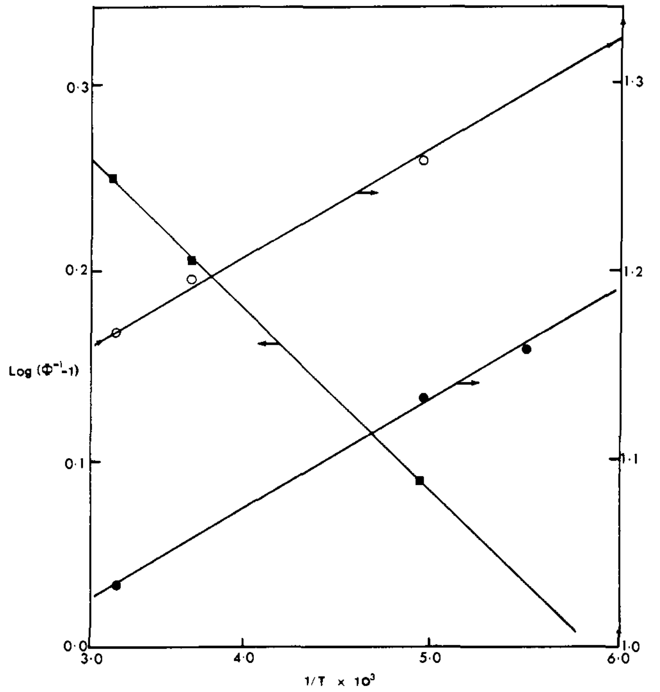


Figure 1. Arrhenius plots for the photocycloaddition of 2-cyclohexenone to (■) cyclopentene, (●) cyclohexene, and (○) *trans*-3-hexene (right scale).

— 1) vs. reciprocal temperature for cyclopentenone additions to cyclohexene, cyclopentene, and *trans*-3-hexene, were given in ref 9. A similar plot for cyclohexenone addition to the same hydrocarbons appears in Figure 1. Insufficient points were determined for the other substrates to draw other than qualitative conclusions.

Quantum Yields of Cyclopentenone and Cyclohexenone Triplets at −70 °C. The quantum yield of sensitized isomerization of piperylene by benzophenone was determined in the usual way,[11] but using methyl acetate as solvent instead of benzene (for benzene $\phi_{c\to t} = 0.55$; $\phi_{t\to c} = 0.44$ at 25 °C). The values found in methyl acetate were $\phi_{c\to t} = 0.53$, $\phi_{t\to c} = 0.47$ at 25 °C. Similar determinations at −71 °C in methyl acetate gave 0.51 and 0.49, respectively.

Cyclopentenone (190 mg) and the appropriate weights of *cis*-piperylene were dissolved in 10 mL of methyl acetate. The solution (5 mL) was degassed and irradiated (optical bench) at −71 °C at 313 nm (3-5% conversion). The ratio of cis to trans isomers was determined using a 20% β,β-oxydipropionitrile on diatoport S column (25 ft × ⅛ in.) at 20 °C. The quantum yield, $\phi_{c\to t}$, was determined using the method of Lamola and Hammond.[11]

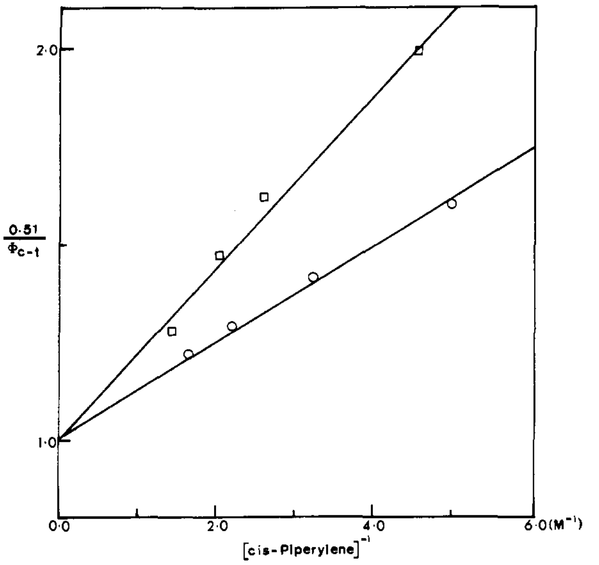


Figure 2. Variation in quantum yield of sensitized c → t isomerization of piperylene as a reciprocal function of diene concentration. Sensitiser: 0.2 M *cyclopentenone* (○); 0.2 *M cyclohexenone* (□).

A similar determination was made for cyclohexenone, also at −71 °C. A plot of $0.51/\phi_{c\to t}$ vs. the reciprocal *cis*-piperylene concentration is shown in Figure 2 for both enones. The concentrations were corrected for contraction of the solutions on cooling.

Rate Measurements and Temperature Dependence. a. Variation of Quantum Yield with Substrate Concentration. The quantum yields were measured on the optical bench at 313 nm for degassed solutions containing 0.1 M cyclopentenone in diethyl ether containing various concentrations of cyclohexene and *cis*-dichloroethylene both at room temperature and at −71 °C. Product analysis was carried out with a 5% FFAP column on Diatoport S (5 ft × ⅛ in.) at 130 °C for the cyclopentenone-cyclohexene system (calibrating compound: acenaphthene). For the cyclopentenone-*cis*-dichloroethylene system a 10% SE-30 column on Diatoport S (6 ft × ⅛ in.) at 125 °C was used (calibrating compound: dibenzyl). A plot of ϕ^{-1} vs. (olefin)$^{-1}$ is shown in Figure 3 and the derived slopes and intercepts listed in Table II. For the system cyclohexenone-cyclohexene a FFAP (5%) on Diatoport S column (9 ft × ⅛ in.) at 146 °C was used. Low-temperature irradiations were performed on the optical bench. Room temperature (20 °C) additions (diethyl ether and *n*-hexane as solvents) were performed in a merry-go-round[12] by a procedure already described and single points determined on the optical bench.[6] A plot of ϕ^{-1} vs. (cyclohexene)$^{-1}$ is shown in Figure 4 and the derived slopes and intercepts listed in Table II.

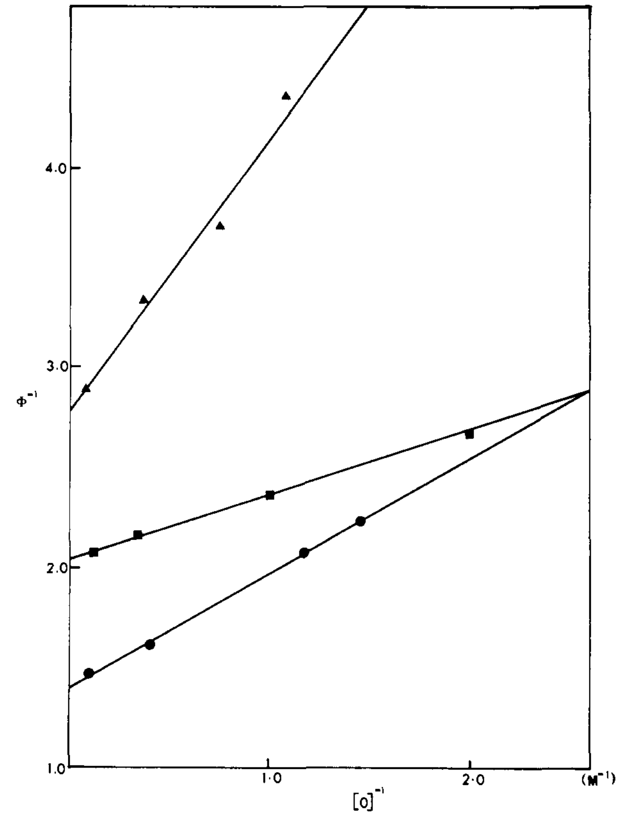


Figure 3. Reciprocal quantum yield of addition of cyclopentenone to olefin as a function of reciprocal olefin concentration: cyclohexene at −71 °C (■) in ether; cyclohexene at 25 °C (●) in ether; *cis*-dichloroethylene at 25 °C (▲) in ether.

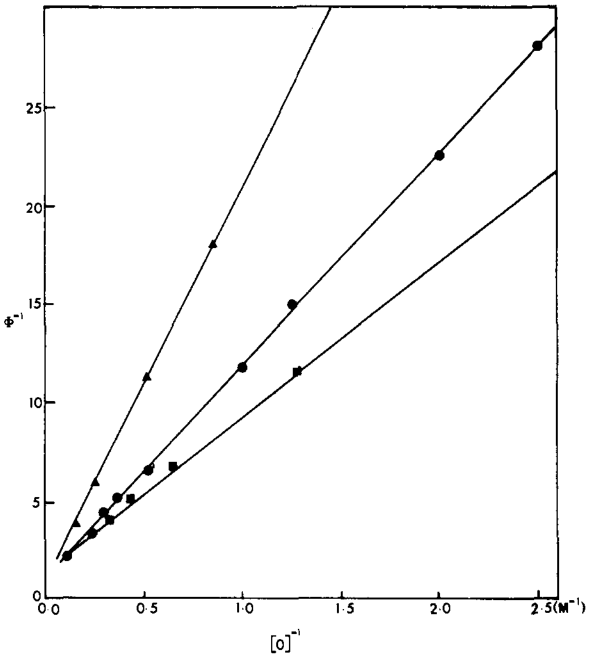


Figure 4. Reciprocal quantum yield of addition of cyclohexenone to olefin as a function of reciprocal olefin concentration: cyclohexene at 20 °C (■) in ether; cyclohexene at −71 °C (●) in ether; cyclohexene at 20 °C (▲) in *n*-hexane.

b. Stern–Volmer Plots. The quantum yields of cyclopentenone (0.2 M) addition to cyclohexene (1.67 M) and to *cis*-dichloroethylene (2.66 M) in diethyl ether containing 2,5-dimethyl-2,4-hexadiene were determined on the merry-go-round with some points being repeated on the optical bench. A plot of ϕ_0/ϕ vs. (Q) appears in Figure 5, the values for k_q and the slopes for cyclohexene at 20 and −71 °C and dichloroethylene at 20 °C are listed in Table II. The Stern–Volmer plots for addition of cyclohexenone to cyclohexene in ether at 20 and −71 °C and in *n*-hexane appear in Figure 6; the values for k_q and the slopes are given in Table II.

Results and Discussion

The most striking observation made in this study is that the quantum yields for cycloaddition of enones to olefins may be markedly temperature dependent, and that this dependence is related both to enone and to olefin structures.[9] Both increases

Table II. Addition and Decay Rate Constants

Enone	Quencher (solvent)	Plot of ϕ^{-1} vs. $[O]^{-1}$ Intercept	Slope	Slope/intercept	$k_q\tau$, M^{-1}	Olefin, M	k_q,20 $M^{-1}\,s^{-1}$ (10^{10})	$1/\tau$ (10^8)	k_r, $M^{-1}\,s^{-1}$ (10^8)	$k_d[1 + C]$ (10^7)
[Cyclopentenone]	Cyclopentenone (acetonitrile)	2.78	0.17	0.06	26.5	0.5	1.0	3.77	6.73	4.04
[0.10]	Cyclohexene (ether)	2.07	0.32	0.15	8.72	1.66	1.3	14.91	8.24	12.35
[0.10]	Cyclohexene (ether, −71 °C)	1.41	0.57	0.41	3.60	2.88	0.36[a]	10.0	3.04	12.46
[0.10]	Cyclopentene (hexane)	3.8	0.43	0.113	11.6	1.0	1.3	11.21	10.07	11.38
[0.17]	*cis*-Dichloroethylene (ether)	2.79	1.37	0.49	18.8	2.66	1.3	6.91	2.2	10.75
[0.05]	*trans*-3-Hexene (hexane)	4.7	0.89	0.189	64.6	0.75	1.3	2.01	2.14	4.05
Cyclohexenone	Cyclohexenone (acetonitrile)	1.35	3.65	2.72	13.7	1.0	0.6	4.38	1.17	32.0
[0.14]	Cyclohexene (ether)	0.98	10.67	10.88	23.7	1.87	1.0	4.42	0.33	36.0
[0.14]	Cyclohexene (hexane)	1.00	7.73	7.73	23.8	1.83	1.0	4.20	0.44	34.0
[0.14]	Cyclohexene (cyclohexane)	0.99	7.5	7.5	31.0	0.98	1.0	3.22	0.38	28.5
[0.14]	Cyclohexene (ether, −71 °C)	0.96	19.87	20.66	13.9	2.09	0.50*	3.6	0.158	32.66

[a] Experiment was carried out at −71 °C, k_q was estimated from the Debye equation using the experimentally measured solution viscosity at −71 °C.

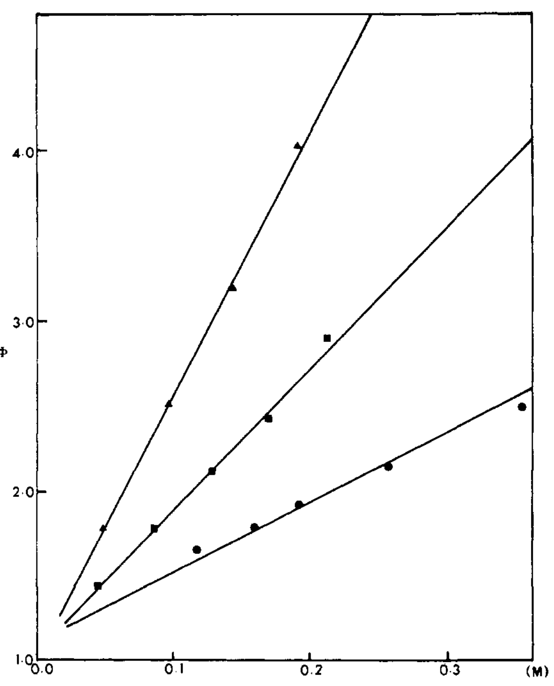
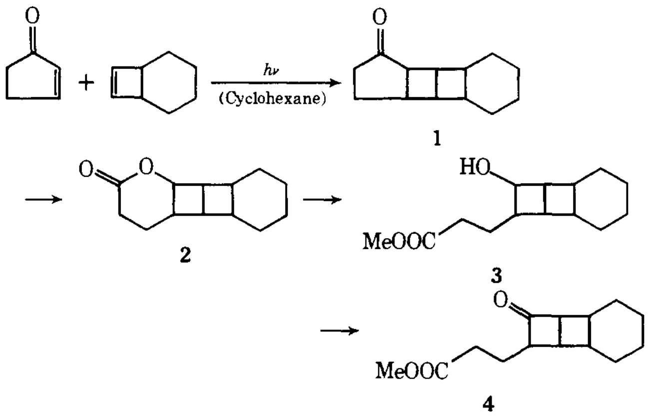
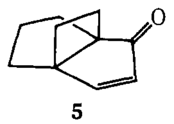


Figure 5. Stern–Volmer quenching of cyclopentenone–olefin addition with dimethylhexadiene: cyclohexene (2.88 M) at −71 °C (●); cyclohexene (1.66 M) at 27 °C (■); *cis*-dichloroethylene (2.66 M) at 20 °C (▲).

and decreases were noted with simple enones (Table I), and the effect was observed to extend to the addition to the acetylene, 3-hexyne. It was noted also in the addition of cyclopentenone to the strained double bond in bicyclo[4.2.0]oct-7-ene (the product, **1**, was partially degraded to ensure rearrangement had not occurred during the addition) and to a smaller extent to the addition of the rigid enone **5**[13] to cyclohexene. The most remarkable change was noted in the addition of cyclopentenone to cyclopentene: the quantum yield increased by a factor of 2.6 between 27 and −71 °C.





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We were first concerned that the temperature effects might be related to viscosity changes with the lowering of the temperature. That this was not so was shown by the observation that the cyclopentenone–cyclohexene addition in diglyme at 22 °C (η = 1.01 cP, twofold more viscous than diethyl ether at −100 °C) was close (ϕ = 0.52) in quantum yield to that (ϕ = 0.48) in the fourfold less viscous diethyl ether (η = 0.23 cP at 22 °C).

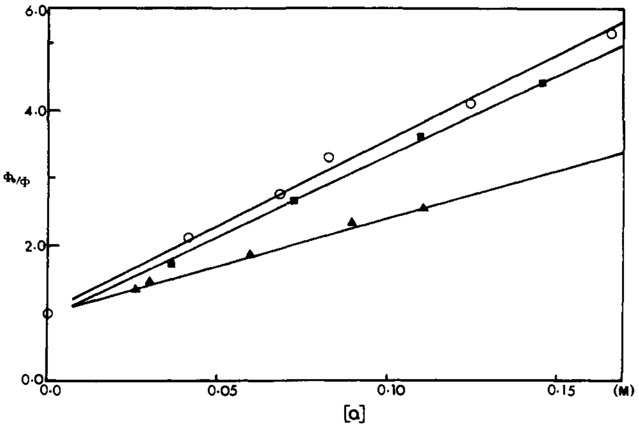
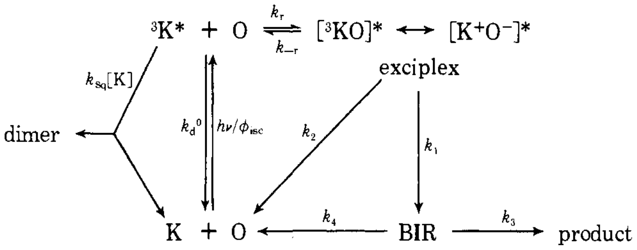


Figure 6. Stern–Volmer quenching of cyclohexenone–cyclohexene addition with dimethylhexadiene: 2.09 M at −71 °C in ether (▲); 1.86 M at 20 °C in ether (■); 1.82 M at 20 °C in *n*-hexane (○).

Scheme I



A generalized mechanistic scheme is presented below (Scheme I), where K, O, and BIR are the enone, olefin, and biradical, respectively. This scheme differs from that proposed earlier[3,14] in that it includes a bimolecular self-quenching step, rate constant k_{sq},[15] which, as will be seen, is important in determining the lifetime of the cyclopentenone triplet, but is less so for cyclohexenone. In this scheme is also included a step for the potential reversal of the exciplex to the olefin and triplet (k_{-r}).[16] Under these circumstances the rate constants evaluated in the earlier studies[3,7,14,15] require a modified interpretation. In addition, as earlier recognized, there remains the question of whether the exciplex as well as the triplet is quenched in the rate measurements.

The actual decay rate of enone triplets (k_d) will, of course, be dependent on the ketone concentration [K];

$$k_d = k_{sq}[K] + k_d{}^0 \qquad (1)$$

The values of k_{sq} have been reported, from dimerization studies of cyclopentenone and cyclohexenone in acetonitrile, by Wagner and Bucheck.[15] They are 6.74 × 10^8 and 1.14 × 10^8 M^{-1} s^{-1}, respectively. The values for the unimolecular decay constant at infinite dilution are 4.05 × 10^7 and 3.1 × 10^8 s^{-1} for cyclopentenone and cyclohexenone, respectively.[15]

With this scheme and the usual steady state assumption we obtain

$$\phi = \phi_{isc}\left(\frac{k_3}{k_3 + k_4}\right) \times \left[\left(\frac{k_1 + k_2}{k_1}\right)\left(\frac{k_d + k_r[O]}{k_r[O]}\right) + \frac{k_d k_{-r}}{k_1 k_r[O]}\right]^{-1} \qquad (2)$$

where k_r is the rate constant for formation of the triplet exciplex. This, rather than biradical formation, was originally postulated as the initial quenching step to explain the very fast rates of reaction. The rate constant, k_{-r}, will depend essentially on $-\Delta G°$ (where $\Delta G° = E_{ex} - E_{3_K}$), the difference in energy between the exciplex and the enone triplet. Reversibility at least in singlet exciplexes is well established.[17] Evidence with regard to triplet exciplex reversibility is more sparse and in enone cycloaddition there has been a tendency to assume, tacitly, that the exciplex formation is irreversible,[3,18] i.e., that the decay or forward reaction of the triplet exciplex dominates. In oxetane formation Caldwell has shown, by means of isotope effects, that triplet exciplex formation is, indeed, irreversible.[19] In our terms this implies $k_{-r}/(k_1 + k_2)$ is small. If we denote p as the fraction of intermediates giving products, then:

$$p = \left(\frac{k_3}{k_3 + k_4}\right)\left(\frac{k_1}{k_1 + k_2}\right)$$

and eq 2 may be rewritten:

$$\phi^{-1} = \frac{1}{p\phi_{\text{isc}}} \times \left\{1 + \frac{k_d}{k_r[\text{O}]} + \left(\frac{k_d}{k_r[\text{O}]} \cdot \frac{k_{-r}}{k_1 + k_2}\right)\right\} \tag{3}$$

In a plot of reciprocal quantum yield against reciprocal olefin concentration, the intercept is given by

$$\text{intercept} = 1/P\phi_{\text{isc}} \tag{4}$$

and the slope by

$$\text{slope} = \frac{1}{P\phi_{\text{isc}}}\frac{k_d}{k_r}\left(1 + \frac{k_{-r}}{k_1 + k_2}\right) \tag{5}$$

whence the slope/intercept = $(k_d/k_r)(1 + C)$, where $C = k_{-r}/(k_1 + k_2)$. The Stern–Volmer plot derived is then:

$$\frac{\phi_0}{\phi} = 1 + \frac{k_q[\text{Q}]}{k_d + k_r[\text{O}] + k_dk_{-r}/(k_1 + k_2)} \tag{6}$$

or, with C as defined:

$$\frac{\phi_0}{\phi} = 1 + \frac{k_q[\text{Q}]}{k_d(1 + C) + k_r[\text{O}]} \tag{7}$$

From the equation, values for k_r and $k_d(1 + C)$ may be evaluated if k_q be known. There could be an uncertainty in the value of k_d if different enone concentrations were used, but at the same enone concentration its value should not vary whether the triplet excimer reverses or not. However, there is no expectation that C should be the same for all olefins, and hence *the value of* $k_d(1 + C)$ *should, unless C be small, vary with the olefin used.* In fact, with cyclopentenone, for cyclohexene, cyclopentene, and *cis*-dichloroethylene, the values lie between 10.75 and 12.35 × 10^7 s^{-1}. This suggests that, indeed, C is small. The value of $k_d(1 + C)$ obtained is, incidentally, close to that obtained from eq 1 (10.8 × 10^7 s^{-1}) using Wagner's values of k_{sq} (6.73 × 10^8 M^{-1} s^{-1}) and $k_d{}^0$ (4.04 × 10^7 s^{-1})[15] on the assumption that k_{sq} is solvent independent.[20]

It is also significant that the value of $k_d(1 + C)$ obtained in the cyclopentenone-cyclohexene system at −71 °C (12.46 × 10^{-7} s^{-1}) is apparently the same, within experimental error, as at room temperature. It seems improbable that $k_d{}^0$ should vary much, but the value of $(1 + C)$ should, as should k_d if triplet excimer reversal be important. This also suggests that C is a small term. The same observation with regard to temperature holds for $k_d(1 + C)$ determined for the cyclohexenone-cyclohexene system.

The only olefin that shows a difference in the value of $k_d(1 + C)$ is *trans*-3-hexene. We are presently unable to account satisfactorily for the difference, a factor of 2, but it may be relevant that the enone concentration is lower here. It is also true that this reaction gives more 'ene' products, which may complicate analysis.

The above considerations necessitated a knowledge of ϕ_{isc} at low temperature. The earlier determinations[6] used the method of Lamola and Hammond[11]—the isomerization of piperylene in benzene. For the present experiments it was convenient to use methyl acetate as solvent. Calibration was again with benzophenone. A plot of $C/\phi_{c\rightarrow t}$ against the reciprocal of the piperylene concentration (where C is the quantum yield under these conditions for the formation of *trans*-piperylene from piperylene triplet (0.51)) had intercepts ($\phi_{\text{isc}}{}^{-1}$) close to unity for both ketones (Figure 2) at −77 °C.

Table III. Activation Energy Difference between Closure and Fission in Tetramethylenes

Ketone	Olefin	ΔE_a, kcal/mol	k_4/k_3 293 K	k_4/k_3 202 K	$E_3 - E_4$, kcal/mol
Cyclopentenone	Cyclohexene	−0.9	1.07	0.41	−1.24
	Cyclopentene	−2.10	3.35	0.64	−2.15
	cis-Dichloroethylene	−0.45	1.89	1.04	−0.77
	trans-3-Hexene	0.23	3.54	4.26	0.24
Cyclohexenone	Cyclopentene	−0.46	1.78	1.22	−0.49
	Cyclohexene	0.27	1.08	1.32	0.26
	trans-3-Hexene	0.25	14.87	18.23	0.26

The triplet exciplex energy, while not known, is expected to be close to, and most probably slightly lower than, that of the ketone triplet. The repulsion in the ground state is also unlikely to be large, and hence the exciplex vertical excitation energy is not expected to drop the ~20 kcal/mol necessary to bring it near that of the diene triplet. The exciplex, therefore, in principle, should be quenchable, and recently Hammond has reported the quenching of an acetophenone-olefin exciplex by piperylene.[21] The Stern–Volmer expression for the quenching of two sequential species has the general form

$$\frac{\phi_0}{\phi} = (1 + k_q[\text{Q}]\tau_1)(1 + k_q[\text{Q}]\tau_2) \tag{8}$$

where $\tau_1 = 1/(k_1 + k_2)$ and $\tau_2 = 1/(k_d + k_r[\text{O}])$.

Since k_q should be near diffusion controlled and essentially identical in both processes,[20] at high quencher concentrations the "squared" term becomes significant, and the Stern–Volmer plot should be nonlinear. We take the view, since there seems reason to doubt that quenching is other than diffusion controlled,[21] that $\tau_1 \lesssim 10^{-9}$ s.

With the first term in eq 8 neglected, the Stern–Volmer equation assumes its simplest form. The linearity spoken of above is illustrated in Figures 5 and 6.

Activation Energies. If the assumption is made, for which there is no direct evidence, that $k_1 \gg k_2$, then eq 3 may be written:

$$\left(\frac{1}{\phi} - 1\right) = \frac{k_4}{k_3}\left[1 + \frac{k_3}{k_4}\frac{k_d}{k_r[\text{O}]} + \frac{k_d}{k_r[\text{O}]}\right] \tag{9}$$

When [O] is large, then eq 9 becomes:

$$\ln\left(\frac{1}{\phi} - 1\right) = \ln\frac{k_4}{k_3} + \frac{k_3}{k_4}\left(\frac{k_d}{k_r[\text{O}]} + \frac{k_d}{k_r[\text{O}]}\right) \tag{10}$$

or:

$$\ln\left(\frac{1}{\phi} - 1\right) = \ln\frac{A_4}{A_3} + \frac{\Delta E_a}{RT} + \Delta \tag{11}$$

where Δ, while not a constant, should be small, A_4/A_3 is the ratio of preexponential terms, and ΔE_a is a difference of activation energies for the pathways for the biradical leading to cyclobutane and to starting materials.

For some systems sufficient data were obtained for plots to be made. The results of the application of eq 11 for cyclopentenone have been reported,[9] those for cyclohexenone are given in Figure 1. Values of ΔE_a are given in Table III. The linearity over the temperature range studied indicates the merit of the approximation, though it cannot be regarded as decisive.

Table IV. Activation Energy and Frequency Factors for Enone–Cyclohexene Reaction

	T(°K)	Cyclopentenone	Cyclohexenone
k_r, $M^{-1}\ s^{-1}$	293	8.24×10^8	3.3×10^7
	202	3.04×10^8	1.58×10^7
E_a, kcal/mol		1.3	0.96
log A		9.9	8.2

The intercepts derived from eq 3, with the same assumptions with regard to the value of $k_1/(k_1 + k_2)$ give $(1 + k_4/k_3)$, and are the equivalent of solutions of infinite concentration of olefin. Using values obtained at 202 and 293 K one may again obtain values of $E_3 - E_4$ and these are shown for comparison in Table III. The agreement justifies further the assumptions made in arriving at eq 11.

The effect of temperature on the reaction rate (k_r) is quite significant. As a result the term:

$$(k_r[\mathrm{O}]/(k_d + k_r[\mathrm{O}]))$$

has negligible effect on the change in quantum yield of product formation in the cyclopentenone–cyclohexene addition, but such is not the case for cyclohexenone. An interesting observation is the change in the frequency factor (Table IV), which may be a consequence of the more flexible nature of triplet cyclohexenone[22] and hence the difficulty of finding the appropriate orientation for complex formation.

The conversion of the exciplex to product, via the biradical, shows its temperature dependence not only in the changes in overall quantum yield, but also in product distribution. Thus, in the addition of cyclopentenone to cyclohexene over the range 171–293 K the three isomers, from major to minor, all decrease in ϕ except in the fractions 0.70, 0.64, and 0.42, respectively, implying a serious change in product ratios. The relative rates of closure of the biradical conformations are, unsurprisingly, differently temperature dependent and cis cyclization presumably predominates at lower temperatures.[23] It must, however, be reiterated that the ratio of products does *not* give an indication of initial bond formation unless ϕ is large, or more specifically when $k_3/(k_3 + k_4)$ is so. Since reported quantum yields at quite high olefin concentrations are frequently only of the order of 10% one may doubt that the above situation always obtains. Similar arguments apply to *any* conclusions reached on the orientation of addition, and on the formation of syn- or anti-fused adducts simply based on product ratios where not even quantum yields, quite aside from the more relevant $k_3/(k_3 + k_4)$ values are known (inter alia ref 23–26).

Recently[25] it has been proposed that the products derived from the photoaddition of enones to olefins are determined by the conformational stability of the excited state. It is assumed that the β carbon is pyramidal, or that the energy of pyramidalization in the process of the reaction of a planar center with the olefin is related to the energy of the sp^3 conformer; i.e., thus the process of configuration-selection is kinetically controlled. The specific proposal is that the cis product, derived at low temperature, is that formed on the face having the free lobe of the pyramidalized carbon. The general applicability and usefulness of the rule itself is difficult to ascertain at the moment, since the number of examples where the β position is tertiary, i.e., configuration can be determined, *and* where this bond is not already that which would, in any event, result from approach from the less hindered side, are few. Furthermore, most examples of such additions in the literature, other than those of Wiesner,[25] have been carried out at room temperature, and so are, presumably, less directly indicative because of conformational mobility.

Essentially all the additions reported[25] so far are of allenes, which require that the fusions formed be cis, and so one cannot discuss the bond formation at the β position with more significance than that at the α. The simplest interpretation is that the excited molecule is a molecule like any other: given that rotation around the double bond is the desired mode of relaxation[22] the molecule selects that conformation which permits this to occur most easily and which at the same time does not introduce severe nonbonded interactions or ring strain. Given also that the α carbon (and probably the β) is not planar,[22] then the ultimate conformation adopted may well be that discussed by Wiesner. Overlap of the β orbital with the "π system" is now undesirable. The first bond formation is probably that having the stereochemistry perpendicular to the original double bond and now, in the preferred *triplet* conformation, quasi-axial. From this conformation of the biradical adduct only cis closure is possible.[26] Conformational inversion permits trans closure. Increase in temperature, then, may have two effects: population of less-favored conformations of the triplet; and the already discussed effect on the closure (or cleavage) of the tetramethylene, which includes conformational inversion of the biradical adduct.

In summary, we believe that the presently available evidence indicates that: in enone cycloaddition, a triplet exciplex[3] is first formed, irreversibly; the exciplex is short-lived; the exciplex collapses to a 1,4-biradical (or radicals) which then cyclizes or reverts to starting material; and, this reversion represents the main source of inefficiency in the cycloaddition. It has been shown that the addition is temperature dependent, and that this is most probably related to the activation energy difference between biradical closure and fission. There is insufficient evidence at present to indicate whether, in a product, the bond α or β to the carbonyl group is formed first, or that there is a general rule: such evidence as has been reported,[3c,e] is inconclusive. It must be recognized, in view of the frequent high biradical reversion proportion, that even if established, the bond first formed in a product does not, per se, indicate the kinetically preferred bond formation overall.

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Electron Photodetachment from Negative Ions of C_{2v} Symmetry. Electron Affinities of Allyl and Cyanomethyl Radicals

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Abstract: The cross sections for electron photodetachment from allyl and cyanomethyl anions have been measured. The threshold behavior of these cross sections is shown to be in agreement with that predicted by symmetry from molecular orbital theory. The cross sections at threshold are calculated assuming molecular orbital initial states for the ions and a plane wave final state for the detached electron. The electron affinities of allyl radical (0.550 ± 0.054 eV) and cyanomethyl radical (1.507 ± 0.018 eV) are determined by fitting the calculated cross sections to the experimental data. An estimate is made of the resonance energy of the allyl anion.

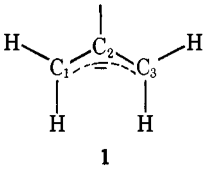
Photodetachment spectroscopy is becoming one of the most commonly employed methods for obtaining accurate electron affinities. Extracting electron affinities from photodetachment data is straightforward for atoms.[1-3] However, for diatomic and polyatomic molecules the photodetachment data become a complicated function of rotational,[4] vibrational,[5,6] and occasionally electronic transitions,[7] each transition having in general some complicated dependence on the photoelectron energy. This process is

$$A^-(J,v) + \hbar\omega \rightarrow A(J',v') + e^-(E_k) \qquad (1)$$

where J and J′ are initial and final rotational states, v and v' are initial and final vibrational states, and E_k is the energy (momentum k) of the photoelectron.

When only a single vibrational transition is involved ($v = v'$), interpretation of photodetachment data is straightforward provided the dependence of the cross section on photoelectron energy is known. This dependence is determined to first order at threshold by the symmetry of the anion and the symmetry of the orbital from which the electron is detached.[8] The photodetachment threshold behavior can thus provide information on orbitals and their symmetry in anions.[8]

In this paper we present the photodetachment spectra of two anions possessing C_{2v} symmetry: allyl anion, **1**, and cyanomethyl anion, **2**. The highest occupied molecular orbital (HOMO) of allyl anion has A_2 symmetry, while the HOMO of cyanomethyl anion has B_2 symmetry. Since the A_2 irreducible representation transforms as a d_{xy} atomic function, the allyl anion should show a $E^{3/2}$ or smoothly rising p-wave energy dependence at threshold.[9] The B_2 representation transforms as a p_y atomic function; thus the cyanomethyl anion should show a $E^{1/2}$ or discontinuous s-wave energy dependence at threshold.



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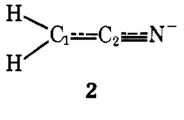

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The experimental threshold behavior of these anions is contrasted and shown to be in good qualitative agreement with the expected behavior based on both group theory and a more quantitative formulation of the threshold law.[8] We then fit the experimentally measured cross sections to the calculated cross sections in the threshold region. From this treatment we obtain the electron affinities of the allyl and cyanomethyl radicals.

Experimental Section

Both the allyl and cyanomethyl anions were generated and trapped in a modified Varian V-5900 ion cyclotron resonance spectrometer.[10] The allyl anion was generated from propene via proton abstraction by OH^-. The OH^- was formed by dissociative electron capture by H_2O at 5.5 eV. Total pressure was 1×10^{-6} to 4×10^{-6} Torr consisting of approximately equal amounts of water and propene. Cyanomethyl anion was generated from acetonitrile via proton abstraction by F^-. The F^- was formed by dissociative electron capture by NF_3 at 1.7 eV. Total pressure in this case was about 5×10^{-7} Torr and consisted of about 80% acetonitrile and 20% NF_3. At these pressures the ions could be trapped for about 0.5 s.

The light source for the photodetachment experiments was a 1000 W xenon arc lamp used in conjunction with a grating monochromator.[11] A grating blazed at 1500 nm was used to collect data above 1000 nm for allyl anion with a resolution (fwhm) of 39.6 nm. All other data were obtained using a grating blazed at 600 nm and have a resolution