Organic and Biological Chemistry

Triplet Lifetimes of Cyclic Ketones

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Abstract: The photorearrangement of various cyclic ketones to ω-alkenals in benzene is quenched by dienes. Stern–Volmer plots furnish estimates of the rates at which the ketone triplets undergo α cleavage. For cyclopentanone, the rate constant is 1.1×10^8 sec^{-1}. Relative rates for cyclohexanone, 3-methylcyclohexanone, 3,5-dimethylcyclohexanone, 3,3,5-trimethylcyclohexanone, cyclopentanone, 2-phenylcyclohexanone, 2-methylcyclohexanone, 2,6-dimethylcyclohexanone, and 2,2-dimethylcyclohexanone are 1, 0.78, 0.76, 0.78, 3.5, 10, 15, 29, and 56, respectively. Quantum yields for alkenal formation from cyclohexanone increase with α substitution and decrease with β substitution. For all ketones studied, alkenal formation is completely quenchable and therefore is exclusively a triplet-state reaction. These results are in complete accord with the hypothesis that the primary photoprocess is simple α cleavage of the triplet ketone to yield an acylalkyl biradical. This biradical then partitions itself between disproportionation to yield alkenal, disproportionation to yield ketene, and recoupling to yield ground-state ketone in proportions which depend on the amount of substitution near the alkyl radical site.

It is now well established that the major reaction of most cyclopentanones and cyclohexanones in solution is rearrangement either to a ketene, to an alkenal, or to a mixture of both.[2,3] Although it has been suggested that the ketone-to-alkenal rearrangement may be concerted,[4] most experimental evidence is more consistent with their being a biradical intermediate involved. The facile photoepimerization of ketones assymetrically substituted at the α carbon[5] indicates efficient α cleavage to yield a biradical which can recouple. This behavior is analogous to the type I reaction of acyclic ketones. The fact that both *cis*- and *trans*-2,6-dimethylcyclohexanone yield the same mixture of *cis*- and *trans*-2-methyl-5-heptenals[6] indicates that the configurational integrity of the α-carbon is lost during the rearrangement and not merely in a side reaction.

The fact that 2-methylcyclohexanone yields only 5-heptenal and no detectable 2-methyl-5-hexenal[7,8] is consistent with α cleavage to the more stable biradical. However, the report that 3-methylcyclohexanone yields only 3-methyl-5-hexenal and no 5-methyl-5-hexenal[7] is puzzling, since α-cleavage would be expected to be equally facile in either direction.

Common triplet quenchers do quench photorearrangements of cyclopentanone and of cyclohexanone[9–11] to the alkenals. This paper presents the results of some quantitative quenching studies which provide measures of the effects of ring size and of α and β substitution on the triplet-state reactivities of cyclic ketones in benzene.

Results

Products. In dilute benzene solutions, the only isomeric photoproduct that can be detected by glpc analysis from each of the ketones (with the exception of 2-phenylcyclohexanone) is the expected alkenal. Any ketene products are undoubtedly destroyed in the hot injector block during analysis. Without exception, alkenal formation is totally quenched when 1,3-pentadiene is used as solvent. Disappearance of the ketones is not completely quenchable. Several short retention time peaks in the glpc traces suggest the occurrence of singlet-state decarbonylations in low quantum yields (<0.01). The major product from 2-phenylcyclohexanone is not 6-phenyl-5-hexenal; its structure is being investigated. Formation of this new product cannot be quenched by dienes. Consequently, it must arise from a singlet-state rearrangement.

Only one alkenal peak appared in the glpc analysis of photolyzed 3-methylcyclohexanone solutions. The product corresponding to this peak was collected by preparative glpc. Its 60-Mc nmr spectrum in carbon tetrachloride indicated that it is the reported 3-methyl-5-hexenal.[7] In particular, the methyl group appeared as a doublet at τ 9.05. There was no detectable resonance in the τ 8.0–8.5 region attributable to an allylic methyl group. Therefore little, if any, 5-methyl-5-hexenal is formed, in agreement with previous findings.[7]

Quantum Yields. Degassed benzene solutions containing approximately 0.1 *M* ketone and a known concentration of an *n*-alkane as internal standard were irradiated with the 3130-Å band of a medium-pressure mercury arc. Per cent disappearance of ketone and

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yields of alkenal were determined by glpc analysis. Light intensity was measured by parallel irradiation of pentane solutions 1.0 M in acetone and 0.2 M in *cis*-1,3-pentadiene. Formation of the *trans*-diene was determined by glpc analysis. The *cis*-to-*trans* quantum yield, corrected for back reaction, is 0.555, since acetone furnishes 100% triplets.[12,13] Table I contains values of quantum yields for product formation at relatively low conversions (5–10%) and for ketone disappearance at moderate conversions (12–20%).

Table I. Rate Data for Rearrangement of Cyclic Ketones in Benzene

Ketone	Φ_{-K}[a]	Φ_{+A}[b]	$k_q\tau$, M^{-1} [c]	$1/\tau$, 10^8 sec^{-1}
Cyclopentanone	0.28	0.24	47.0	1.1
Cyclohexanone (CH)	0.20	0.09	152.0	0.33
3-Methyl-CH	0.083	0.033	209.0	0.25
3,5-Dimethyl-CH	0.033	0.005	206.0	0.24
3,3,5-Trimethyl-CH	0.024	0.002	200.0	0.25
2-Methyl-CH	0.50	0.42	10.6	4.7
2-Phenyl-CH	0.51	0.04	15.2	3.3
2,6-Dimethyl-CH	0.55	0.40	5.4	9.3
2,2-Dimethyl-CH	0.52	0.41	2.8	18.0

[a] 12–20% disappearance of ketone. [b] 5–10% disappearance of ketone. [c] Generally the average of two separate determinations with precision ±5%.

The alkenal products have approximately the same extinction coefficients as the reactant ketones. They undergo photorearrangements back to cyclic ketones.[14] Moreover, both they and the expected ketene side products can quench the triplet states of aliphatic ketones. Consequently, quantum yields were expected to decrease appreciably at high conversions. For cyclopentanone and the 2-substituted cyclohexanones, formation of alkenal remains zero order to at least 20% conversion. With cyclohexanone, however, the decrease in quantum efficiency with increasing conversion is more serious. Srinivasan and Cremer demonstrated that the quantum efficiency of 5-hexenal formation drops significantly after 2% conversion.[7] Since their experiment was performed in neat ketone, quenching by products should have been much more serious than in our experiments because of the higher actual concentrations formed. In any event, our quantum yield values for cyclohexanone and the three 3-substituted cyclohexanones may be somewhat low, although the relative values are probably accurate.

Quenching Studies. Degassed benzene solutions containing 0.2 M ketone, a known concentration of internal standard, and various concentrations of 1,3-pentadiene were irradiated in parallel at 25° with 3130-Å radiation. Relative quantum yields of alkenal formation at 5–10% conversion were determined by glpc analysis. Stern–Volmer plots were linear out to large Φ_0/Φ values. Their slopes, together with the triplet decay rates calculated from them, are contained in Table I. A value of 5×10^9 M^{-1} sec^{-1} was assumed for k_q.[15]

Discussion

Triplet Lifetimes. The variation of triplet decay rates with ring size and with the degree of 2 and 3 substitution is entirely consistent with the primary triplet-state photoprocess for all of these cyclic ketones being α cleavage to yield a biradical. Substituents at the α-carbon which can stabilize the alkyl portion of the biradical enhance the rate of cleavage. The more strained five-membered ring opens faster than the six-membered ring. This latter effect parallels that reported for 1-alkylcycloalkoxy radicals,[16] in agreement with the idea that alkoxy radicals are good models for n,π^* ketone triplets.[17,18] The 15-fold increase in $1/\tau$ afforded by a 2-methyl group explains the formation of only 5-heptenal from 2-methylcyclohexanone.[7,8]

It is very significant that all three β-substituted cyclohexanones have triplet lifetimes identical within experimental error with that of cyclohexanone itself, even though they are markedly less efficient at rearranging to alkenals. Since all four ketones cleave to biradicals of comparable stability, it would be expected that they would do so at comparable rates. We should point out that our $1/\tau$ values for these four ketones may be somewhat high, since at the conversions studied triplet lifetimes may be shortened appreciably by product quenching. Pitts and Simonaitis have reported a $1/\tau$ value of 1.2×10^7 sec^{-1} for triplet cyclohexanone in the moderately polar solvent butyrolactone.[11]

Quantum Yields. In no case does the total quantum efficiency approach unity. Substitution at the α position increases over-all quantum yields and total chemical yields of alkenals, while similar substitution at the β positions drastically reduces both kinds of yields. Although the triplet-state lifetimes of these ketones support a biradical mechanism, they could also be consistent with a concerted rearrangement provided that the low quantum yields were due to rapid radiationless decay directly from the triplet level. The triplet lifetimes of the various β-substituted cyclohexanones would then indicate a radiationless decay rate, k_i, of 2.5×10^7 sec^{-1}. However, the value of k_i for the α-substituted ketones would then have to be much larger; *e.g.*, 10^9 sec^{-1} for 2,2-dimethylcyclohexanone. Since the rate at which triplet states of aliphatic ketones undergo radiationless decay is on the order of 10^5 sec^{-1} [19] and since much larger, varying values for k_i would have to be invoked for these cyclic ketones, we feel that the triplet lifetimes of the cyclic ketones are determined solely by the rate at which they undergo chemical reaction; *i.e.*, $k_r = 1/\tau$.

All the lifetime and quantum yield results are consistent with the biradical mechanism shown in Scheme I.

Scheme I predicts the following expressions for quantum yields of alkenal formation and of ketone disappearance. The quantum yields are determined primarily by the behavior of the biradical intermediate, as is the case for some type II photoelimination reactions.[20] Coupling of 1,5 and 1,6 biradicals to yield

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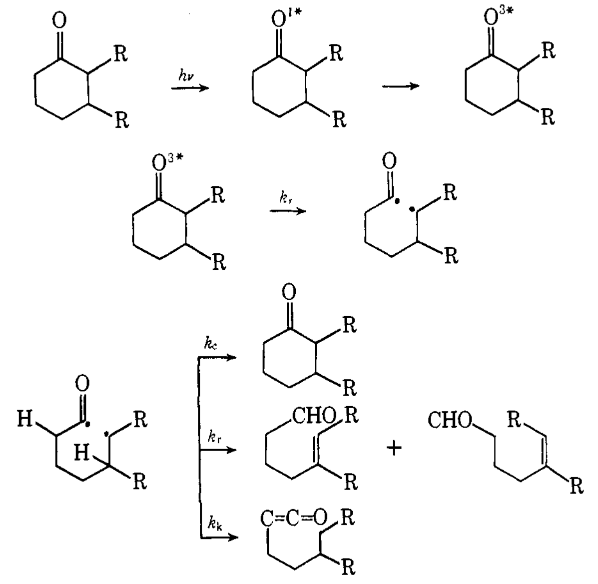
Scheme I

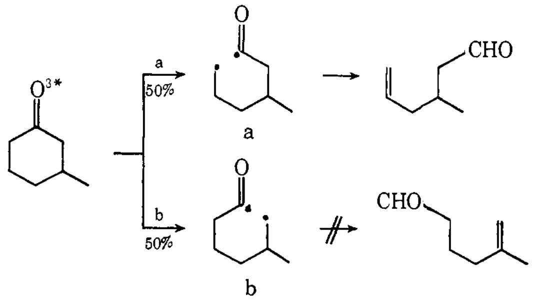


five- and six-membered rings is expected to be more favorable than coupling of the 1,4 biradicals formed in the type II process. The ketones with α substituents yield biradicals in which the alkyl radical site is secondary or tertiary. It is well established that the disproportionation/coupling ratio of alkyl radicals increases as the radicals go from primary to tertiary.[21] The increased quantum yields for the α-substituted cyclohexanones undoubtedly reflect the decreased propensity of the intermediate biradical to recouple.

$$\Phi_{+\mathrm{A}} = \frac{\Phi_{\mathrm{isc}}k_{\mathrm{a}}}{k_{\mathrm{c}} + k_{\mathrm{a}} + k_{\mathrm{k}}}$$

$$\Phi_{-\mathrm{K}} = \Phi_{\mathrm{isc}}\left(\frac{k_{\mathrm{a}} + k_{\mathrm{k}}}{k_{\mathrm{c}} + k_{\mathrm{a}} + k_{\mathrm{k}}}\right)$$

The behavior of the 3-substituted cyclohexanones is more difficult to understand fully. The decreasing availability of hydrogen atoms at the β position certainly must decrease k_a relative to k_c; but the decrease is more than statistical. For example, 3,5-dimethylcyclohexanone might be expected to be approximately 50% as efficient as cyclohexanone itself at yielding alkenal; it is only 6% as efficient. The fact that no detectable alkenal product arises from cleavage path **b** in 3-methylcyclohexanone is another manifestation of this problem. Moreover, the quantum efficiency for total ketone disappearance decreases dratistically as the number of β-methyl groups is increased. Apparently substituents in the β position not only inhibit disproportionation of biradical b, they also inhibit disproportionation of biradical a.



It is known that subtle steric factors have a marked effect on the competition between alkenal and ketene formation from cyclic ketones.[2,3] It would appear that the steric effects on the competition between the two disproportionation modes of the biradical and its recoupling are every bit as subtle. The biradical lifetime probably is so short that even the small rotational barriers introduced by methyl substitution impede hydrogen transfer.

Experimental Section

Chemicals. 2-Phenylcyclohexanone was purchased from Aldrich Chemical Co. and recrystallized from hexane. 2,2-Dimethylcyclohexanone was prepared by the method of House and Kramer[22] and was purified by preparative glpc. All the other ketones were purchased from Chemical Samples Co. and distilled before use. Benzene was washed with sulfuric acid, dried, and distilled from phosphorus pentoxide. Chemical Samples Co. *cis*-pentadiene was used as received. The various *n*-alkanes used as internal standards were purified, as was benzene.

Cyclopentanone, cyclohexanone, and 2,6-dimethylcyclohexanone were irradiated on a preparative scale in benzene solution and their product alkenals were isolated by preparative glpc. An F & M 776 Prepmaster Jr. fitted with a standard 20% Carbowax 20M column was used for the separations. The ir and nmr spectra of the products were in accord with their being the expected alkenals. These three were used to identify the glpc retention time of the alkenals. It was found to be characteristic that the alkenal has half the retention time of its parent ketone on a glpc column consisting of 4% QF-1 and 1% Carbowax 20M on 60–80 DMCS-treated Chromosorb G. 3-Methylcyclohexanone was also irradiated on a preparative scale. The product corresponding to the single glpc product peak was collected. Its nmr spectrum agreed perfectly with that reported for 3-methyl-5-hexenal[7] and showed no detectable resonance in the τ 8.0–8.5 region expected for an allylic methyl group.

Quenching Studies. For a given run, benzene solutions were prepared containing a given concentration of ketone and of internal standard and varying concentrations of pentadiene. Three milliliters of each sample was placed in a 13 × 100 Pyrex tube, degassed by three freeze–thaw cycles on a vacuum line, and sealed. All the tubes were then irradiated in parallel on a rotating turntable apparatus immersed in a 25° constant-temperature bath. The irradiation source was a 450-W Hanovia medium pressure mercury arc held in an immersion well immersed in a basic potassium chromate filter solution. Only radiation from 3000 to 3250 Å was transmitted by the filter.

After irradiation, the samples were analyzed for alkenal appearance by glpc analysis. A Varian Aerograph Model 1200 Hy-Fi III with a 10 ft × 1/8 in. column packed with the above-mentioned QF-1 and Carbowax 20M mixture was used for the analyses. An L & N Model W recorder fitted with a disk integrator was used to record the output.

Quantum Yields. Solutions 0.10 *M* in individual ketones were prepared, placed in Pyrex tubes, degassed, sealed, and irradiated at 3130 Å in parallel. They were then analyzed by glpc in order to determine the yields of alkenal produced. The area mole response of the detector for alkenal relative to internal standard was calibrated for 4-pentenal, 5-hexenal, and 2-methyl-5-heptenal, the three alkenals prepared as described above. The area mole response for the other alkenals were then interpolated from the behavior of the three. The amount of ketone disappeared was measured directly by comparing ketone/standard area ratios before and after irradiation.

Three tubes containing 1.0 *M* acetone and 0.20 *M* *cis*-1,3-pentadiene in pentane were irradiated in parallel with the above samples.

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The average yield of *trans*-diene (~10%) was measured on a 25 ft × 1/8 in. column packed with 25% tris(2-cyanoethoxy)propane on Chromosorb P. The quantum yield for the *cis*-to-*trans* isomerization, after being corrected for back reaction, is 0.555.[12] This method of actinometry was used to determine the amount of light impingent upon the ketone samples. The actual concentrations of ketones used absorb only 85–95% of 3130-Å radiation, so that a 5–15% correction in intensity was necessary in order to convert actual yields into quantum yields.

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The Reactions of Atomic Carbon with Alcohols

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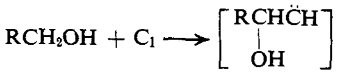
Abstract: The reactions of atomic carbon have been studied with a series of aliphatic alcohols. The reaction products have been identified and their mechanisms of reaction have been elucidated by carbon-14 and deuterium-labeling techniques. All alcohols react with C_1 to undergo deoxygenation and insertion into every OH and CH bond.

The reactions of atomic carbon with hydrocarbons,[2–4] halocarbons,[5] carbonyl compounds, and epoxides[6] have been reported; we here describe the reactions of atomic carbon with alcohols.

It could have been anticipated that carbon atoms would insert into the OH bond of alcohols to produce alkoxycarbenes; alkoxycarbenes react with alcohols by OH bond insertion;[7–10] dialkoxymethanes are major reaction products.

$$C_1 + ROH \longrightarrow [RO\ddot{C}H] \xrightarrow{ROH} (RO)_2CH_2$$

Insertion into CH bonds could also have been anticipated. Rearrangements of the expected carbene intermediates account for the observed products.



$$RCH_2OH + C_1 \longrightarrow \left[\begin{array}{c} RCH\ddot{C}H \\ | \\ OH \end{array}\right]$$

Experimental Section

The reaction system has been described.[11] Atomic carbon is produced, along with C_2, C_3, and C_4, from a 16-V (ac) carbon arc under vacuum (~1 × 10^{-4} mm). Reactions occur in condensed phase near 77°K. Products were isolated by vapor phase chromatography, and their retention times and infrared and mass spectra were compared with those of authentic compounds.

^{14}C-Enriched methanol was prepared by diluting 1.6 mg (0.1 mCi) of methanol-^{14}C to 5.0 g. ^{14}C-Enriched carbon vapor was obtained by replacing one graphite electrode with a graphite rod enriched in carbon-14 (~0.01 Ci/g). Measurements in carbon-14 experiments were carried out by passing the eluent from a gas chromatograph into an ionization chamber, thus obtaining consecutive, continuous recordings of the thermal conductivity response and the carbon-14 ionization response of each component. The integrated conductivity response was converted to a molar quantity, which was then divided into the integrated ionization response to obtain a molar activity.

Methanol-1,1,1-d_3 and ethanol-1,1,2,2,2-d_5 were obtained by distillation of the perdeuterio compounds[12] from a large excess of water (mol of H_2O:mol of ROH = 100:1).[13] Ethanol-1,1-d_2 was prepared by the lithium aluminum deuteride reduction of hexyl acetate.[14] Ethanol-2,2,2-d_3 was obtained from Merck Sharp and Dohme of Canada. The alcohols were dried by vaporization through CaH_2 at reduced pressure (~1 μ); nmr spectra confirmed the position of the deuterium label. The isotopic composition of each alcohol was determined by low-voltage mass spectrometry[15,16] on the corresponding trimethylsilyl ether derivative[17] (Table I). The deuterium analysis of each pure product was determined by low-voltage mass spectrometry.[17]

Table I. Deuterium Compositions of Alcoholic Substrates (mol %)

Deuterium content	Alcohol			
	CD_3OH	C_2D_5OH	CD_3CH_2OH	CH_3CD_2OH
d_0	1.1	0.0	3.0	5.3
d_1	0.0	0.0	0.0	0.0
d_2	1.1	6.6	1.4	94.7
d_3	97.8	0.0	95.6	
d_4		0.4		
d_5		93.0		
d_6				

Results

A. Reactions of Atomic Carbon with Methanol. The products formed by the reactions of atomic carbon with methanol are listed in Table II. These products account for 41.7% by weight of the total carbon vaporized.

B. Reactions of Atomic Carbon with ^{14}C-Enriched Methanol. The relative molar activities of the products

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