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PHOTOREDUCTION OF CYCLOPENTANONE AND CYCLOHEXANONE

R. Simonaitis, G. W. Cowell and J. N. Pitts, Jr.

Department of Chemistry, University of California

Riverside, California

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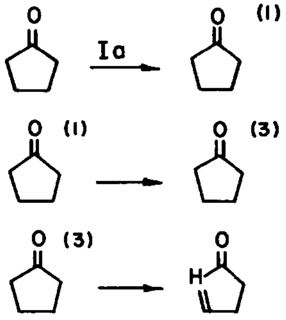
Quantitative correlations of structure and reactivity in the intermolecular and intramolecular photoreduction (Type II process) of ketones are being intensively investigated (1-3). For example, Hammond and Wagner found that the rate constant for the Type II photocycloelimination process in 2-pentanone is 75 times larger than that for butyrophenone (4). They suggest that the difference in reactivity may be due to the $^3(n,\pi^*)$ state of the aromatic ketone having some $^3(\pi,\pi^*)$ character. We wish to report a quantitative comparison of the rates of hydrogen abstraction from isopropyl alcohol (IPA) by cyclopentanone and cyclohexanone.

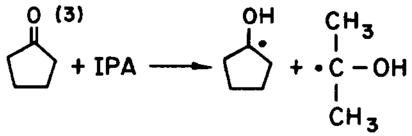
The method employed is the quenching with isopropyl alcohol of the well known isomerization to the unsaturated aldehydes (5). Dunion and Trumbore have shown that most of the isomerization occurs from the triplet state of cyclopentanone (6). Our results confirm this and further show that this is also the case for cyclohexanone (vide infra). Very recently Wagner has shown that the photoreduction of acetone by tributylstannane occurs exclusively from the triplet state (7). Since tributylstannane is a much better hydrogen donor than IPA, it is very likely that singlet abstraction need not be considered in this case. The mechanism that can be written for cyclopentanone, with an analogous one for cyclohexanone, is the following:



(1)

(2)

(3)



(4)

where the superscripts indicate singlet and triplet states respectively. From the above mechanism, the following equation can be derived:

$$\frac{\varphi^{\circ}}{\varphi} = 1 + k_r\tau\,[\mathrm{IPA}]$$

where φ° is the quantum yield of the aldehyde in the absence of IPA and φ is the quantum yield in the presence of IPA. τ is the lifetime of the excited triplet, and k_r is the rate constant for the abstraction step, reaction 4.

Degassed solutions of 0.2M cyclopentanone and cyclohexanone and various concentrations of IPA or piperylene in γ-butyrolactone as a solvent were irradiated with the 3130A line of a Hanovia 500 watt lamp (isolated with a Schott-Jena interference filter). In order to prevent attack of the unsaturated aldehydes by radicals, the solutions were made 0.2% in cyclohexene.

The photoreductive nature of the reaction is demonstrated by the products. In the case of cyclohexanone, the products characterized were cyclohexanol and acetone. In the case of cyclopentanone, the photoreduction of which apparently has not been previously reported, the products characterized were cyclopentanol and acetone. In both cases, several additional minor

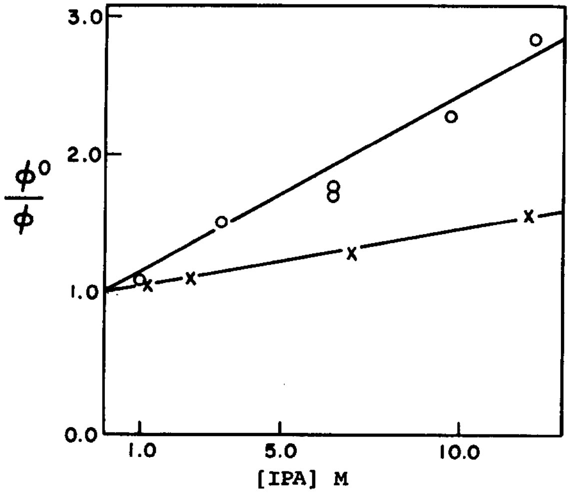


FIG. 1

Plot of $\frac{\varphi^{\circ}}{\varphi}$ for cyclopentanone (x) and cyclohexanone (o) against IPA concentration

TABLE 1

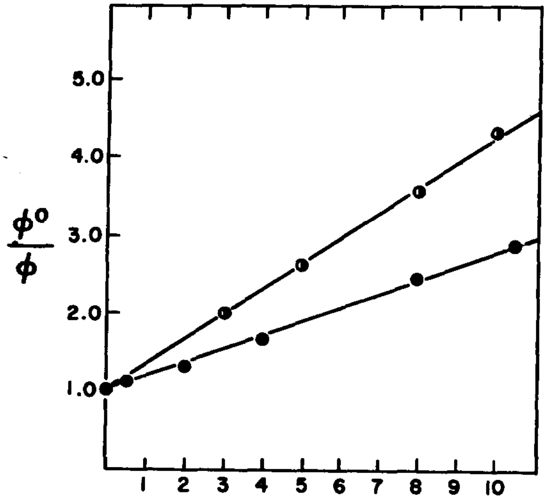
Triplet State Lifetimes and Rate Constants for Photoreduction of Ketones at 25°C

	τ (Sec) x 10^{7}	k_r x $10^{-6}M^{-1}Sec^{-1}$
Cyclohexanone	0.83	1.8 ± 0.5
Cyclopentanone	0.04	11.0 ± 3.0
Benzophenone	-	1.3 (9)

products were observed by glpc, but have not yet been characterized.

Figure 1 shows that good linear plots are obtained as predicted by equation 1. In order to obtain k_r, it is necessary to know τ. This was determined in γ-butyrolactone as solvent by quenching with piperylene (4) Stern-Volmer plots are shown in Figure 2. The quenching constant for cyclopentanone obtained from the slope of this plot is 17M. A value of 20M (neat cyclopentanone) was determined by Dunion and Trumbore (6). The excellent linearity of the plot up to $\frac{\varphi^{o}}{\varphi}$ of 4.0 shows that singlet state isomerization is also not important for cyclohexanone. The τ's, tabulated in Table 1, were calculated on the assumption of diffusion controlled quenching (k_D = 4.0 x 10^{9} liter/mole sec.) (8). Our values of k_r are also given in Table 1, and can be compared to that for benzophenone obtained by Beckett and Porter (9). The lifetime of cyclopentanone was also determined in γ-butyrolactone containing 1.5M IPA, in order to see if τ is changed on addition of IPA. The lifetime obtained under these conditions is in excellent agreement with the lifetime calculated from τ and k_r given in Table I. It appears, therefore, that a hydrogen bonding solvent has no effect on the triplet state lifetime of cyclopentanone.

Our results show that the rate constant for intermolecular hydrogen atom abstraction by cyclohexanone is close to that for benzophenone. This is consistent with Chien's results, which appeared while this work was in progress (10). His results show that diethyl ketone abstracts hydrogen from cumene only about 20% faster than does benzophenone. However, in spite of the large uncertainty in the value of k_r, the rate of abstraction by cyclopentanone appears to be appreciably greater than that for benzophenone. This enhanced reactivity of triplet cyclopentanone compared to the other ketones could be due to relief of strain on going to the transition state. That the triplet of cyclopentanone is more strained than that of cyclohexanone gains support from our lifetime data, Table I, which show that the five-membered ring opens considerably faster than the six-membered ring. Our results, and those of Chien, suggest that the lower reactivity of the aromatic ketones in the Type II process may be due to factors other than those suggested by Hammond and Wagner. Further work in this area is in progress.



[Piperylene]

FIG. 2
Stern-Volmer plots for quenching of aldehyde formation from cyclohexanone x 10^3M (half circles) and cyclopentanone x 10^2M (closed circles)

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