THE PHOTOREDUCTION OF CYCLOHEXANONES BY 2-PROPANOL: A NEW KINETIC MODEL

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Summary

The photoreduction of 3,3,5-trimethylcyclohexanone by 2-propanol was carried out at 313 nm with benzene as a cosolvent. The quantum yield of 3,3,5-trimethylcyclohexanol was measured systematically as a function of the concentration of the various reactants. The quantum yield increased with increasing initial ketone concentration; this effect could not be accounted for by classical mechanisms for photoreduction reactions. It could be shown that this phenomenon was caused neither by the occurrence of a radical propagation reaction, nor by a change in the terminating reactions resulting from the increase in the ketone concentration. A double photoreduction process was then considered, the reducing agent being either 2-propanol or a ketone–alcohol complex. Computer calculation by an iterative method showed that this mechanism gave the best fit with the whole set of our experimental data. The rate constants of each elementary step were determined.

The photoreduction of cyclohexanones, in contrast to that of aromatic ketones, has been little investigated because of the cleavage reactions which often accompany it and sometimes predominate over it [1]. In a previous paper [2] we showed that photoreduction could give good yields if the ketones irradiated were not α substituted. The photoreduction of substituted cyclohexanones provides a simple model to approach the study of stereoselectivity in radical reduction [3]. Recently McDaniel *et al.* [4] made use of the photoreduction of cyclohexanone by alcohols to study the dynamic interactions of cyclohexanone in lipid bilayers and subsequently to gain further insight into the behaviour of biological membranes.

The use of such a model requires a better knowledge of the photoreduction processes of cycloalkanones. Therefore we set out to establish the reaction mechanism, particularly the primary and secondary steps. For this purpose we studied the influence of various experimental factors on the

quantum yield of photoreduction of 3,3,5-trimethylcyclohexanone by 2-propanol.

Experimental

Materials

3,3,5-Trimethylcyclohexanone (purum Fluka) was doubly distilled on a Büchi spinning band column (b.p.$_{760}$ = 182 °C). The 2-propanol and benzene were Fluka spectroscopic grade solvents.

Apparatus

The light source used was a Hanovia 450 W medium pressure mercury lamp placed in the centre of a rotating circular turntable (arrangement according to Moses *et al.* [5]) and equipped with HMTO interference filters (λ = 313 nm ± 20 nm). The actinometry was performed simultaneously using potassium ferrioxalate and a benzophenone–benzhydrol mixture [6]. The average intensity of the incident light was about 0.6 × 10^6 quanta s^{-1}.

Samples

The ketone solutions (4 ml) were placed in Pyrex tubes 14 mm in diameter and degassed at 10^{-6} Torr by the freeze–pump–thaw method. These tubes were then vacuum sealed and irradiated at room temperature.

Analysis

The samples were analysed by gas chromatography using a flame ionization detector. The rates of alcohol conversion, which were never greater than 20% (a range over which the progression of the reaction is linear with respect to time), were measured using a column device: 3% UCON polar and 6% KOH on Chromosorb W 60/80; t = 110 °C. The unreacted ketone was measured using a 20% DEGS column with Chromosorb P 60/80. Benzyl acetate or naphthalene were used as internal standards. The analysis of mixtures of *cis*-piperylene and *trans*-piperylene, used in the determination of Φ_{ST}, was carried out by Weiss's method [7].

A sample of 2-methyloctan-2-ol was synthesized by addition of hexylmagnesium bromide to acetone. The product was purified by preparative GLPC Carlo Erba (column: 10% UCON polar and 10% KOH on Chromosorb W 30/60; 9 m long; t = 120 °C). It was characterized as follows.

Mass spectrometry: m/e 144(m^+), 129, 126, 111, 89, 83

Nuclear magnetic resonance: (CCl$_4$) : OH = 3.18 ppm

$$CH_3 \diagdown \atop CH_3 \diagup \hspace{-0.3em} > C\!-\!O = 1.16\ ppm$$
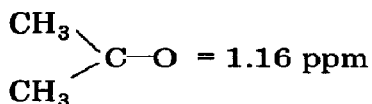
terminal CH$_3$ = 0.9 ppm

Computing techniques

The iterative method used is that due to Powell [8] : "an efficient method of finding the minimum of a function of several variables without calculating derivatives". Calculations were performed with a subprogram entitled VA 04A on a C.I.I. IRIS 80 computer. The function F to minimize was the mean quadratic error on $1/\Phi$:

$$F = \sum_{i=1}^{N=56} \left(\frac{1/\Phi_i - 1/\Phi_{exp}}{1/\Phi_i}\right)^2 \tag{I}$$

where N is the number of experimental points, $1/\Phi_i$ is the theoretical value calculated from our formula and $1/\Phi_{exp}$ is the experimental value. The accuracy of the parameter was estimated by a statistical method taking into account the fact that the experimental error was about 10%. Therefore all the experimental quantum yields were adjusted by 10% and the sign of this error was randomly distributed on the whole set of experimental values. For each distribution we have performed a new computer calculation and obtained a new set of parameters. The given error was the maximum deviation of each parameter from the optimized value.

Results

To carry out the quantitative analysis of the photoreduction process of cycloalkanones, 3,3,5-trimethylcyclohexanone was chosen as a substrate. This ketone has a very low photolysis quantum yield [1]. Its irradiation in the presence of 2-propanol (RH_2) in benzene solution leads to various products, the quantum yields of which depend on the experimental conditions, *e.g.*
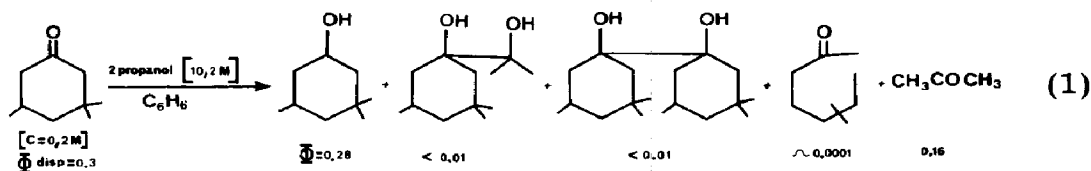
Whatever the conditions, however, low yields of the adducts or coupling products are always obtained.

We systematically investigated the variations in the quantum yield Φ of 3,3,5-trimethylcyclohexanol in benzene solution as a function of the concentrations of the various reactants. Figure 1 shows that, for a given ketone concentration, Φ depends on the concentration of the photoreducing agent. Five series of measurements, corresponding to ketone concentrations of 0.033, 0.05, 0.2, 0.68 and 1 mol l^{-1} respectively, were carried out (Table 1). In every case a linear relationship was observed between $1/\Phi$ and $1/[RH_2]$.
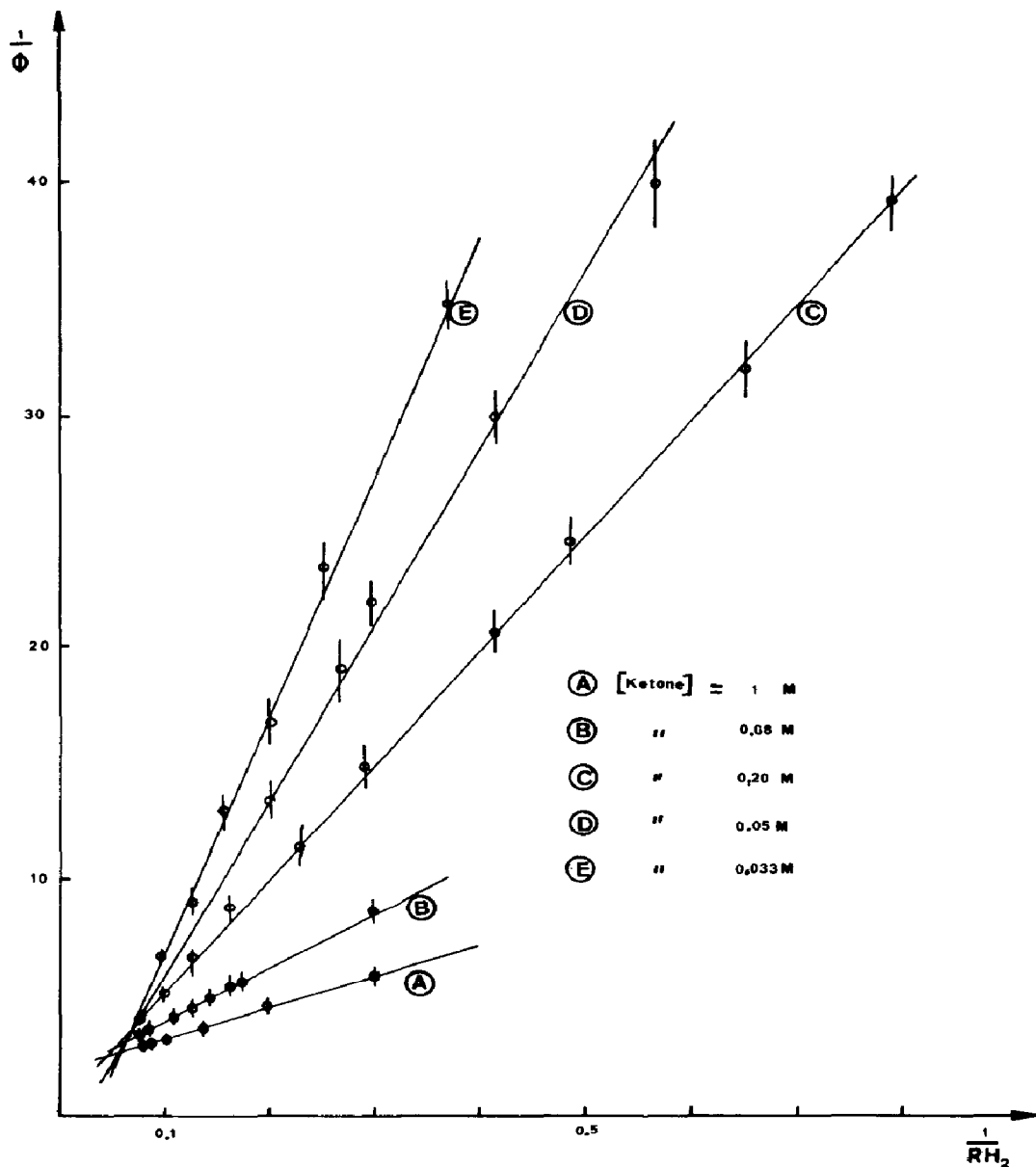
Fig. 1. The quantum yield of 3,3,5-trimethylcyclohexanol at a fixed concentration of ketone.

The correlation coefficients calculated for each of the straight lines are greater than 0.991.

Figure 2 shows the variations observed in Φ for fixed alcohol concentrations while the ketone concentration varies from 0.033 to 1 M. For sufficiently high concentrations of RH_2 there is a linear relationship between $1/\Phi$ and the reciprocal of the ketone concentration. The corresponding correlation coefficients are greater than 0.992. For lower concentrations of RH_2 (1.48 M) the variation is no longer linear.

TABLE 1

Quantum yields of photoreduction *versus* reactant concentrations

$1/\Phi_{exp}$	$1/[\text{ketone}]$	$1/[\text{RH}_2]$	$1/\Phi_{exp}$	$1/[\text{ketone}]$	$1/[\text{RH}_2]$
3.5200	1.0000	0.1300	3.1400	1.0000	0.0960
4.5200	1.0000	0.2000	3.2400	1.0000	0.1100
5.5300	1.0000	0.2860	14.0500	20.0000	0.2100
37.3600	20.0000	0.6180	19.2200	20.0000	0.2550
4.0100	0.5050	0.1530	21.7300	20.0000	0.3060
4.0000	5.0000	0.0770	31.1100	20.0000	0.4400
4.0000	5.0000	0.0790	81.8200	20.0000	1.1100
4.5400	5.0000	0.0960	5.5200	2.0000	0.1530
5.2600	5.0000	0.1120	4.5400	1.0500	0.1530
7.4000	5.0000	0.1460	4.2900	0.7600	0.1530
10.3100	5.0000	0.1940	5.0500	0.6990	0.2600
14.7000	5.0000	0.2810	6.5700	1.0030	0.2600
15.8700	5.0000	0.3060	7.5100	1.3100	0.2600
22.7200	5.0000	0.4500	10.5500	2.4210	0.2600
25.6400	5.0000	0.5150	7.2400	2.2200	0.1920
28.5700	5.0000	0.6130	5.5500	1.2800	0.1920
37.0300	5.0000	0.7630	4.7600	0.7430	0.1920
44.4400	5.0000	0.9000	4.3500	0.5480	0.1920
9.0000	1.4706	0.3320	4.5600	29.9700	0.0770
6.3700	1.4706	0.2050	5.4300	29.9700	0.0880
6.3700	1.4706	0.1940	8.4100	29.9700	0.1150
6.2500	1.4706	0.1890	8.7600	29.9700	0.1160
5.4300	1.4706	0.1690	15.3700	29.9700	0.2020
4.8500	1.4706	0.1520	28.7400	29.9700	0.3140
4.2500	1.4706	0.1260	19.6700	1.3180	0.6740
4.1100	1.4706	0.1020	32.4800	3.0500	0.6740
3.6200	1.4706	0.0890	38.6500	6.4070	0.6740
3.0400	1.0000	0.0910	43.3500	31.8200	0.6740

For a given alcohol concentration the cosolvent (benzene) concentration decreases with increasing ketone concentration. In order to study the effect of the cosolvent on the quantum yield $1/\Phi$ was plotted against $1/[\text{RH}_2]$ for various benzene concentrations (Fig. 3). Figure 3 shows that $1/\Phi$ is a decreasing function of $1/[\text{RH}_2]$ even in the absence of benzene.

Discussion

The photoreduction of cyclohexanone (A) by RH_2 was previously studied by Pitts [9] who proposed the following mechanism:
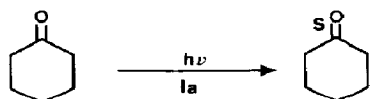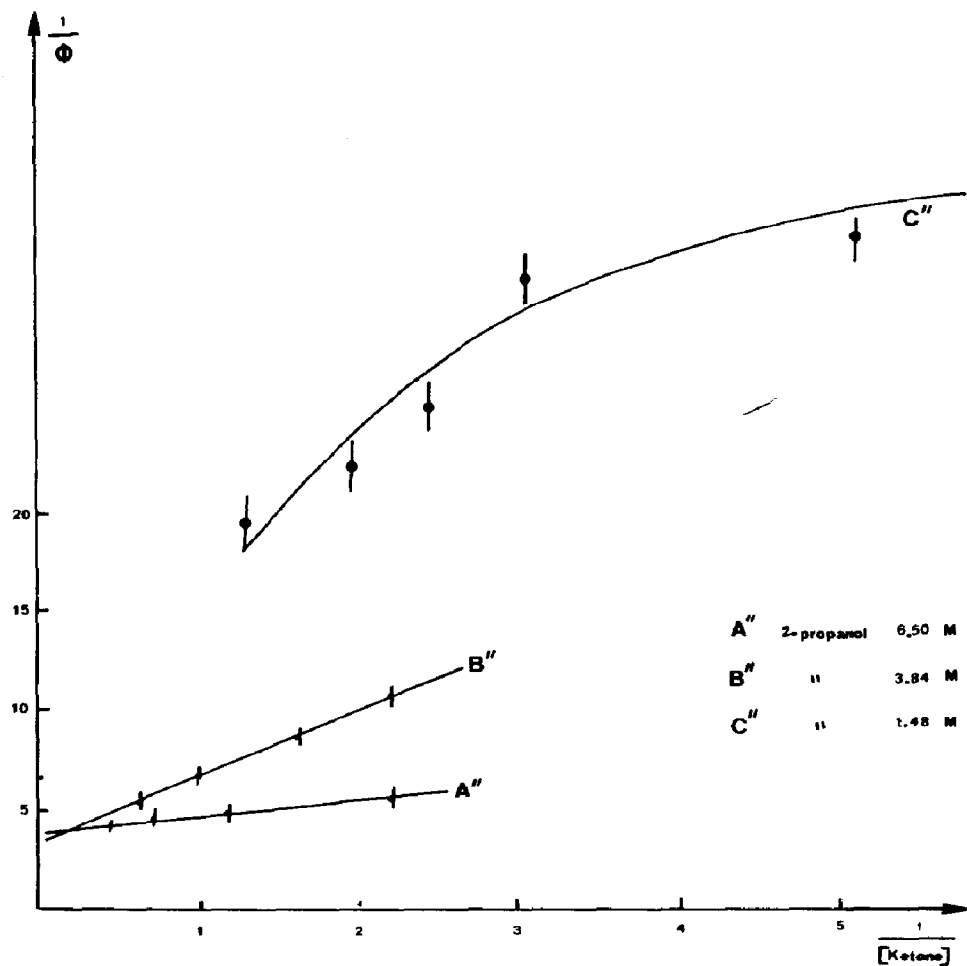

(2)

Fig. 2. The quantum yield of photoreduction at a fixed concentration of 2-propanol.
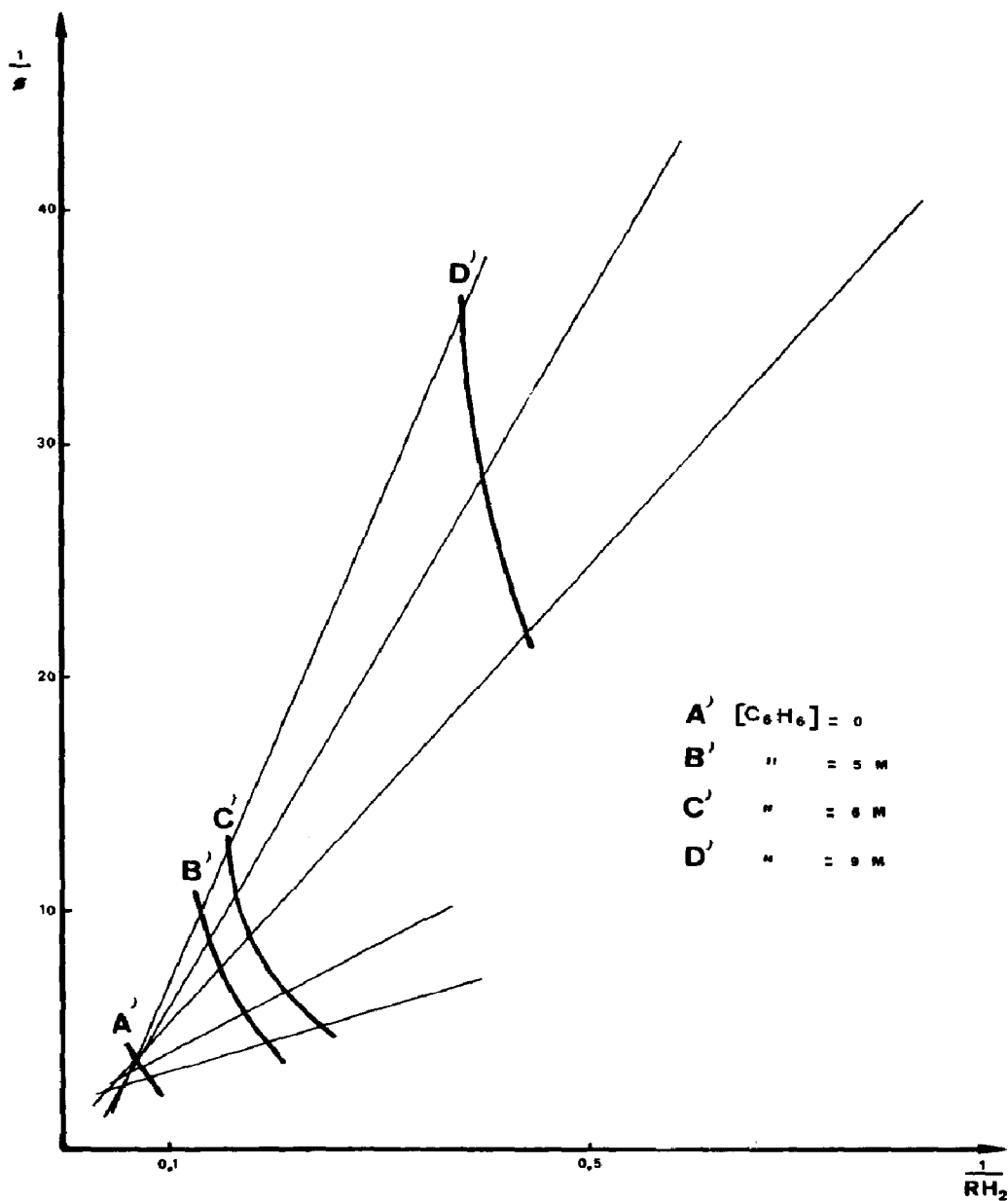

(3)

(4)

(5)

(6)

Fig. 3. The quantum yield of photoreduction at a fixed concentration of benzene.

With the usual steady state approximation the quantum yield of photoreduction is given by
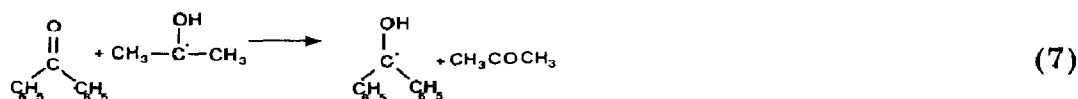
$$\frac{1}{\Phi} = \frac{1}{\Phi_{ST}}\left(1 + \frac{k_d}{k_r[RH_2]}\right)$$
(II)

This expression does not include the ketone concentration. Its lack of agreement with our experimental data does not result from the influence of the cosolvent since, even at a fixed benzene concentration or in the absence of benzene, $1/\Phi$ is not an increasing function of $1/[RH_2]$ but a decreasing one. Therefore, the increase in Φ as $[RH_2]$ decreases can only be explained by the change in the ketone concentration. It is thus obvious that the kinetics of the reaction are not zeroth order with respect to the ketone.

Several assumptions can be considered to account for the role of the ketone. We shall only examine the occurrence of a ketone interaction at the level of propagation, termination or initiation reactions.

Involvement of the ketone in a radical propagation reaction

The photoreduction of aromatic ketones has been much more thoroughly investigated than that of cycloalkanones. Quantitative studies allowed the elucidation of its mechanism. In the case of the photoreduction of benzophenone by RH_2 it was shown that the hydroxydiphenylmethyl radical resulted not only from the attack of RH_2 on the excited benzophenone, but also from the attack of the hydroxyisopropyl radical formed in the previous step on benzophenone in the ground state [10]:

$$\underset{\substack{C_6H_5 \ \ C_6H_5}}{\overset{O}{\underset{\|}{C}}} + CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 \longrightarrow \underset{\substack{C_6H_5 \ \ C_6H_5}}{\overset{OH}{\underset{|}{\overset{|}{C}\cdot}}} + CH_3COCH_3 \tag{7}$$

Evidence for the existence of a radical propagation reaction of this type was looked for in the cycloalkanone series.

The hydroxyisopropyl radical was generated in the presence of cyclohexanone (or 2-methylcyclohexanone) and RH_2 under conditions as close as possible to those of the photoreduction. The methods used were photochemical. It is known that an excited ketone (benzophenone, 3,3,5-trimethylcyclohexanone or acetone) can abstract a hydrogen atom from RH_2:

$$RR'CO \xrightarrow{\ h\nu\ } RR'CO* \tag{8}$$

$$RR'CO* + (CH_3)_2CHOH \longrightarrow RR'\dot{C}OH + (CH_3)_2\dot{C}OH \tag{9}$$
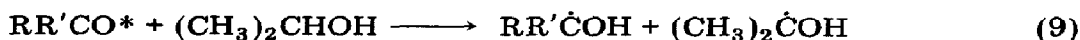
The hydroxyisopropyl radical thus formed can react with cyclohexanone or 2-methylcyclohexanone (Table 2). To avoid the direct photoreduction of these cycloalkanones, we either filtered the radiation or used a non-photoreducible substrate (2-methylcyclohexanone). Under these conditions the formation of cyclohexanols can only result from a non-photochemical radical reaction.

The photolysis of tert-butylperoxide in RH_2 [11] was also used to form the hydroxyisopropyl radical:

$$tBuOOtBu \xrightarrow{\ h\nu\ } 2tBu\dot{O} \tag{10}$$

$$tBu\dot{O} + (CH_3)_2CHOH \longrightarrow tBuOH + (CH_3)_2\dot{C}OH \tag{11}$$

TABLE 2

Results related to the efficiency of the propagation reaction

Generation of the radical	Substrates	Hydroxyisopropyl radical	Hydroxycyclohexyl radical	Alcohols
3,3,5-Trimethyl-cyclohexanone + 2-propanol 300 nm	2-Methyl-cyclohexanone (non-photo-reducible)	Yes	No	No
Benzophenone + 2-propanol 350 nm	Cyclohexanone (photoreducible)	Yes	No	No
Acetone + 2-propanol 300 nm	2-Methyl-cyclohexanone (non-photo-reducible)	Yes	No	No
tert-Butyl peroxide + 2-propanol 300 nm	2-Methyl-cyclohexanone (non-photo-reducible)	Yes	No	No

In all these experiments we could successfully show the presence of the hydroxyisopropyl radical using 1-hexene as a trap [12]. The corresponding adducts were easily detected by gas chromatography. However, neither the hydroxycyclohexyl (or 2-methylhydroxycyclohexyl) radical nor the corresponding cyclohexanol could be characterized.

These results are not due to a particular instability of the 2-methyl-1-hydroxycyclohexyl radical which could be successfully trapped by 1-hexene in other reactions [13]. It thus appears that a radical propagation reaction is not involved in the photoreduction process of cyclohexanones.

Involvement of the ketone in terminating reactions

The influence of the ketone concentration on the photoreduction quantum yield could arise from an effect of the ketone on the relative rate constants of the terminating reactions:

$$(12)$$

$$(13)$$
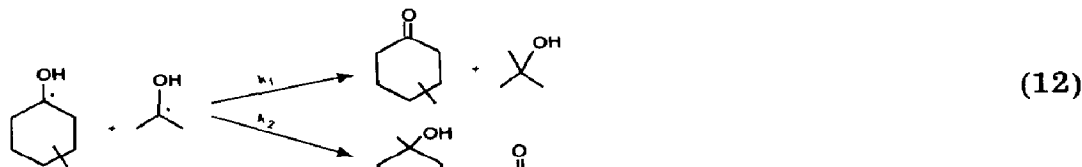
In such a case the addition of a non-photoreducible ketone (2-methylcyclo-hexanone) should have the same effect as an increase in the ketone concen-

tration and should therefore lead to an increase in the photoreduction yield. This was not observed.

Furthermore let us consider the expression formulated by Dalton and Turro [1] to describe the quantum yield of any photoreduction reaction:

$$\frac{1}{\Phi} = \frac{1}{\Phi_{ST}} \left(1 + \frac{k_d}{k_r[RH_2]}\right)\beta \tag{III}$$

where β is the reactivity of the hydroxycyclohexyl radical and its ability to yield the corresponding alcohol. It is therefore directly related to the ratio k_1/k_2. According to this assumption β should depend upon the ketone concentration. The plots of $1/\Phi$ *versus* $1/[RH_2]$ for various ketone concentrations should then be converging straight lines the focal point of which should be on the $1/[RH_2]$ axis and should have a negative abscissa. This is not observed (see Fig. 1).

*Involvement of the ketone in the primary processes of photoreduction*

Since the ketone concentration does not affect the propagation of termination reactions, a third mechanism involving the cyclohexanone in the first step of the reaction can now be considered. Figure 1 shows that the ketone concentration mainly depends on the slope of the lines $1/\Phi$ *versus* $1/[RH_2]$. This illustrates that the triplet lifetime is a function of the ketone concentration.
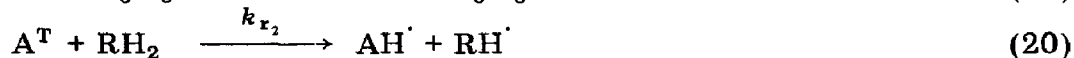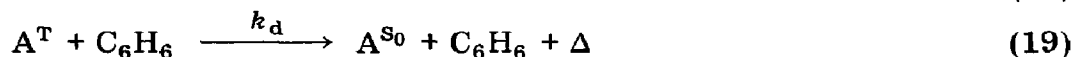
Mechanism

As was shown previously [3], the triplet state of cyclohexanone is the only excited state involved in photoreduction. It can be deactivated either directly or by interaction with benzene as in the case of benzophenone and acetone* [14] (reaction (19)). The ketone triplet can also be deactivated by interaction with any reducing agent to yield 3,3,5-trimethylcyclohexanol. This interaction may occur partly according to a model proposed by Pitts [9] since $1/\Phi$ varies linearly with $1/[RH_2]$ and partly according to another model accounting for the fact that $1/\Phi$ depends upon the product $(1/[RH_2] - a)(1/[ketone] - b)$ as shown by a comparison of the two sets of curves given in Figs. 1 and 2. In fact when the ketone concentration is sufficiently high the two families of curves $1/\Phi$ *versus* $1/[ketone]$ and $1/\Phi$ *versus* $1/[RH_2]$ can be derived from each other.

The above model suggests that the reducing agent in this case is a ketone–alcohol complex CPX such that CPX $\xrightleftharpoons{K}$ RH$_2$ + ketone.

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*This quenching effect caused by benzene was checked experimentally and it was found that Φ_0/Φ varies linearly with the benzene concentration (the ketone and alcohol concentrations are held constant).

$$(14)$$
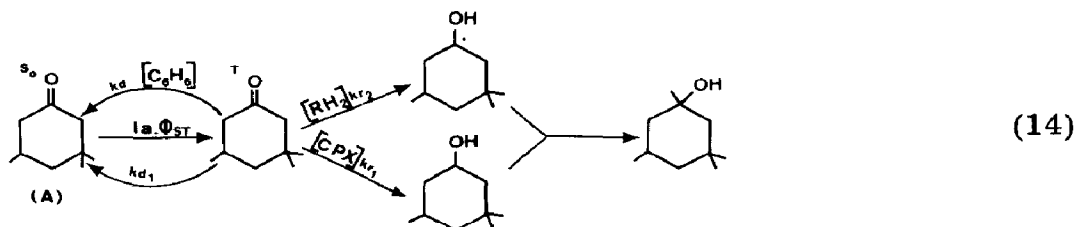
This assumption leads to the following mechanism:

$$A^{S_0} \xrightarrow{\quad I_a \quad} A^{S_1} \tag{15}$$

$$A^{S_1} \xrightarrow{\quad\quad} A^{S_0} \tag{16}$$

$$A^{S_1} \xrightarrow{\quad k_{ST} \quad} A^{T_1} \tag{17}$$

$$A^T \xrightarrow{\quad k_{d_1} \quad} A^{S_0} \tag{18}$$

$$A^T + C_6H_6 \xrightarrow{\quad k_d \quad} A^{S_0} + C_6H_6 + \Delta \tag{19}$$

$$A^T + RH_2 \xrightarrow{\quad k_{r_2} \quad} AH^{\cdot} + RH^{\cdot} \tag{20}$$

$$A^T + CPX \xrightarrow{\quad k_{r_1} \quad} AH^{\cdot} + A + RH^{\cdot} \tag{21}$$

$$AH^{\cdot} + AH^{\cdot} \xrightarrow{\quad\quad} AH_2 + A \tag{22}$$

$$AH^{\cdot} + RH^{\cdot} \left\langle \begin{array}{l} A + RH_2 \\ AH_2 + R \end{array} \right. \tag{23a}$$
$$\tag{23b}$$

$$RH^{\cdot} + RH^{\cdot} \xrightarrow{\quad\quad} RH_2 + R \tag{24}$$

and also

$$A + RH_2 \xrightarrow{\quad K \quad} CPX \tag{25}$$

Assuming a steady state we can write
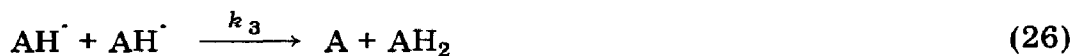
$$\frac{dT}{dt} = I_a \Phi_{ST} - k_{r_1}[T][CPX] - k_{r_2}[T][RH_2] - k_d[T][C_6H_6] - k_{d_1}[T]$$
$$= 0$$

$$\frac{d[AH_2]}{dt} = \frac{1}{2}\left(k_{r_1}[T][CPX] + k_{r_2}[T][RH_2]\right) \tag{IV}$$

whence

$$\frac{1}{\Phi} = \frac{2}{\Phi_{ST}}\left(1 + \frac{k_d[C_6H_6] + k_{d_1}}{k_{r_1}[CPX] + k_{r_2}[RH_2]}\right) \tag{V}$$

The origin of the factor 2 lies in the nature of the terminating reactions. In particular, the following terminating reactions can be considered:

$$AH^{\cdot} + AH^{\cdot} \xrightarrow{k_3} A + AH_2 \tag{26}$$

$$AH^{\cdot} + RH^{\cdot} \begin{array}{c} \xrightarrow{k_1} A + RH_2 \\ \xleftarrow{k_2} \\ \searrow AH_2 + RI \end{array} \begin{array}{c} (27a) \\ \\ (27b) \end{array}$$

$$RH^{\cdot} + RH^{\cdot} \xrightarrow{k_4} RH_2 + RI \tag{28}$$

The first of these reactions leads to the formation of one molecule of cyclohexanol from two hydroxycyclohexyl radicals. The same is true of the second reaction if it is assumed that the constants k_1 and k_2 are of the same order of magnitude.

If we assume an ideal solution, the three components of the reaction mixture are related to each other by the additivity of the molar volumes:

$$\frac{[C_6H_6]}{[C_6H_6]_{max}} + \frac{[RH_2]}{[RH_2]_{max}} + \frac{[ketone]}{[ketone]_{max}} = 1 \tag{VI}$$

where $[RH_2]_{max}$, $[C_6H_6]_{max}$ and $[ketone]_{max}$ are the concentrations of the pure components. If we introduce the following parameters

$$a = \frac{k_d}{k_{r_1}} \qquad b = \frac{k_{d_1}}{k_{r_1}} \qquad \epsilon = \frac{k_{r_2}}{k_{r_1}} \tag{VII}$$

and assume that the equilibrium constant K is low and that the concentration of the complex is negligibly small with respect to the concentration of RH_2, we can write

$$[CPX] = \frac{K[ketone][RH_2]}{1 + K[RH_2]} \tag{VIII}$$

Subsequent development (eqn. (V)) leads to the following expression for the quantum yield:

$$\frac{1}{\Phi} = \frac{2}{\Phi_{ST}} \left[1 + \left\{ \frac{1}{1 + K[RH_2]} + \frac{\epsilon/K}{[ketone]} \right\}^{-1} \left\{ \frac{a}{K} \left(\frac{1}{[ketone]} \right. \right. \right.$$
$$\left. - \frac{1}{[ketone]_{max}} \right) \left(\frac{1}{[RH_2]} - \frac{1}{[RH_2]_{max}} \right) [C_6H_6]_{max} + \frac{b/K}{[ketone][RH_2]} -$$
$$\left. \left. - \frac{a/K[C_6H_6]_{max}}{[ketone]_{max}[RH_2]_{max}} \right\} \right] \tag{IX}$$

The following values are known at 20 °C: $[ketone]_{max}$ = 6.41 M; $[RH_2]_{max}$ = 13.2 M; $[C_6H_6]_{max}$ = 11.2 M. The quantum yield for the intersystem crossing of 3,3,5-trimethylcyclohexanone, which was measured by the Lamola and Hammond method [15], was found to be Φ_{ST} = 0.89 ± 0.006. The values for the parameters a, b, ϵ and K were optimized by a computer calculation from 56 experimental points:

$$a = (0.93 \pm 0.12) \times 10^{-3}$$

$$\epsilon = (0.51 \pm 0.02) \times 10^{-3}$$

$$b = (0.86 \pm 0.08) \times 10^{-2} \text{ M}$$

$$K = (1.5 \pm 0.2) \times 10^{-3} \text{ M}^{-1}$$

Equation (IX) is therefore in very good agreement with our results since it leads to a convergent system with an error of less than 9% for the whole set of experimental points. By making use of the parameter values and the lifetime of the triplet state of 3,3,5-trimethylcyclohexanone measured in benzene [16], then

$$1/\tau(T_{C_6H_6}) = k_{d_1} + k_d [C_6H_6] = 0.25 \times 10^8 \text{ s}^{-1} \tag{X}$$

It is then possible to calculate the rate constants for the various reactions:

$$k_d = (1.25 \pm 0.1) \times 10^6 \text{ s}^{-1} \text{ M}^{-1}$$

$$k_{d_1} = (1.15 \pm 0.1) \times 10^7 \text{ s}^{-1}$$

$$k_{r_1} = (1.35 \pm 0.3) \times 10^9 \text{ s}^{-1} \text{ M}^{-1}$$

$$k_{r_2} = (0.70 \pm 0.2) \times 10^6 \text{ s}^{-1} \text{ M}^{-1}$$

It should be pointed out that the rate k_{r_1} of reduction by the complex is markedly greater than the rate k_{r_2} of reduction by RH_2.

The values of these constants can be compared with those reported in the literature: k_d is the rate constant of quenching of 3,3,5-trimethylcyclo-hexanone by benzene; its value is close to that reported by Loutfy [17] for the quenching of acetone by benzene (2.8×10^6 s^{-1} M^{-1}).

$$k_{app} = k_{r_2} + k_{r_1} K[\text{ketone}] = (1.1 \pm 0.3) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$$

represents the rate constant for the overall photoreduction of 3,3,5-trimethyl-cyclohexanone at a given concentration of 0.2 M. It is quite consistent with the value found by Pitts and Simonaitis [9] for the photoreduction of cyclohexanone:

$$k_{app} = (1.8 \pm 0.3) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$$

at a concentration of 0.2 M.

Conclusion

The mechanism involving a double reduction process by both 2-propanol and a ketone–2-propanol complex is the one which best fits the observed experimental results. The other processes considered, i.e. a radical propagation reaction or a change in the terminating reactions with increasing ketone concentration did not lead to a consistent set of parameters. Furthermore

the agreement between the values found for the rate constants by our method and those reported in the literature is further evidence that the proposed mechanism is the most likely.

The determination of the nature of the complex is presently in progress.

Acknowledgment

References

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