SELECTION OF KINETIC MODELS IN PHOTOCHEMISTRY: INVOLVEMENT OF AN ENOL SPECIES IN THE PHOTOREDUCTION OF CYCLOHEXANONES BY 2-PROPANOL

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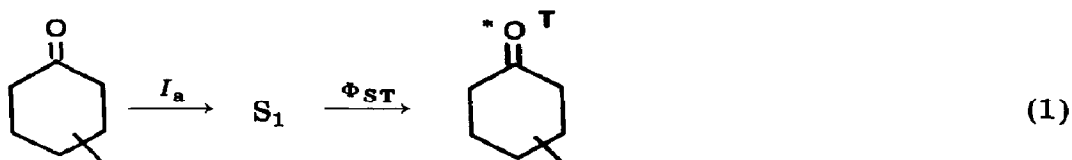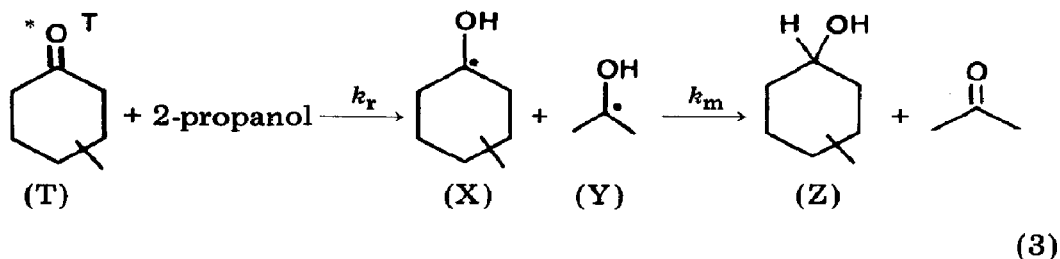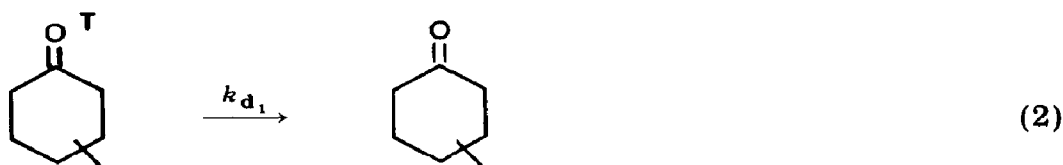(Received January 24, 1980; in revised form July 3, 1980)

Summary

The classical mechanism put forward by Pitts cannot account for the data obtained in the investigation of the photoreduction of 3,3,5-trimethylcyclohexanone in 2-propanol. The increase in the photoreduction quantum yield with increasing ketone concentration led us to consider three possible independent kinetic models involving an additional reaction step. Mathematical analysis of all the experimental data then allowed some assumptions to be ruled out. The mechanism considered involves a reducing interaction between the cyclohexanone triplet and a 1:1 cyclohexanone–2-propanol enol complex. This enol species, which is mainly generated in the course of the dismutation of the hydroxycyclohexyl radicals, has an average lifetime of about 2000 s in the photoreducing medium.

1. Introduction

The photoreduction of ketones has been extensively investigated for many years. However, most of the work pertains to aromatic ketones [1, 2], or to unsaturated aliphatic ketones [3] or to acetone [4, 5]. The photoreduction of cyclanones, particularly that of substituted cyclanones, has been investigated from a mechanistic [6] and from a stereochemical [7] standpoint.

Pitts and coworkers [8] have put forward a simple mechanism for the photoreduction of cyclohexanone:

$$
\text{(structure)} \xrightarrow{I_a} S_1 \xrightarrow{\Phi_{ST}} \text{(structure)}^{*}\;T
\tag{1}
$$

270

$$\text{(cyclohexanone, }O^T) \xrightarrow{k_{d_1}} \text{(cyclohexanone, }O) \qquad (2)$$

$$\text{(}{}^*O^T\text{)} + \text{2-propanol} \xrightarrow{k_r} \text{(X)} + \text{(Y)} \xrightarrow{k_m} \text{(Z)} + \text{(acetone)}$$

(T)   (X)   (Y)   (Z)

$$(3)$$

The kinetic analysis of this reaction scheme shows a linear dependence of $1/\Phi$ on $1/[\text{2-propanol}]$. Using the steady state approximation for the various reacting species (namely the triplet excited state of cyclohexanone (T) and the corresponding hydroxylated radical (X)), the photoreduction quantum yield can be readily calculated.

$$\frac{d[T]}{dt} = \Phi_{ST} I_a - k_{d_1}[T] - k_r[T][\text{2-propanol}] = 0$$

$$\frac{d[X]}{dt} = k_r[T][\text{2-propanol}] - k_m[X][Y] = 0$$

$$\frac{d[Z]}{dt} = k_m[X][Y] = \Phi I_a$$
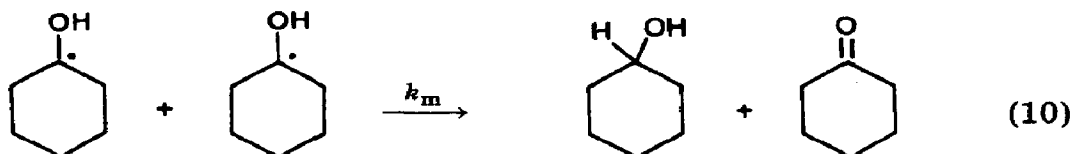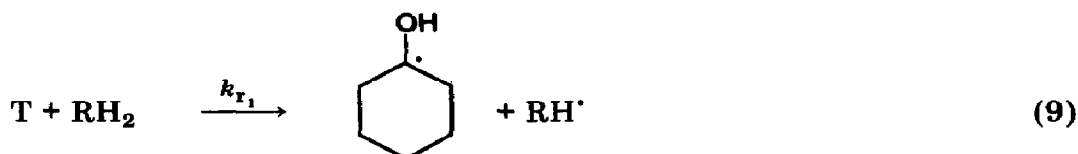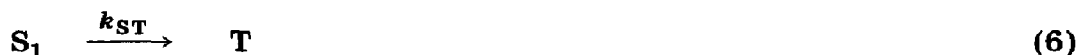
and hence

$$\frac{1}{\Phi} = \frac{1}{\Phi_{ST}}\left(1 + \frac{k_{d_1}}{k_r[\text{2-propanol}]}\right)$$

It has been shown previously [6] that the occurrence of this linear relationship can be corroborated by the systematic determination of the quantum yields of photoreduction of 3,3,5-trimethylcyclohexanone by 2-propanol in benzene (see Section 6). However, these data clearly show that the photoreduction quantum yield also depends on the initial ketone concentration, as it increases with the ketone concentration. The quantum yield variations therefore cannot be accounted for either by a simultaneous change in the cosolvent concentration or by the involvement of a radical propagation reaction analogous to that observed in the photoreduction of benzophenone in 2-propanol [6]. Other processes have to be considered.

2. Search for a reaction scheme

The following general reaction scheme involves, in addition to the classical mechanism of Pitts, a deactivation by benzene [9].

$$S_0 \xrightarrow{I_a} S_1 \tag{4}$$

$$S_1 \xrightarrow{k_f} S_0 \tag{5}$$

$$S_1 \xrightarrow{k_{ST}} T \tag{6}$$

$$T \xrightarrow{k_{d_1}} S_0 \tag{7}$$

$$T + C_6H_6 \xrightarrow{k_d} S_0 + C_6H_6 \tag{8}$$

$$T + RH_2 \xrightarrow{k_{r_1}} \quad + RH^{\cdot} \tag{9}$$

$$\tag{10}$$

$$\tag{11}$$

A further reaction step has to be considered to account for the increase in the photoreduction quantum yield with increasing ketone concentration. Such a step may be the interaction between a ketone molecule, which may be solvated (Table 1, model (3)), and an activated species which is either a radical (Table 1, model (1)) or an excited state (Table 1, models (2) and (3)).

These three reaction models must account qualitatively for the increase in the photoreduction quantum yield with increasing ketone concentration as well as for other data (electron paramagnetic resonance (EPR) spectra, products analysis). As a matter of fact, the EPR spectra of ketone–alcohol mixtures under irradiation depend on the ketone concentration. In dilute media the signal observed was that of the hydroxycyclohexyl radical [10], whereas in concentrated media the signal corresponding to the α-cyclo-

TABLE 1

Typical elementary steps of the various reaction models considered

Reaction model	Typical elementary step	Additional termination reaction
(1) Ketone–radical interaction	$\xrightarrow{k_p}$ (12)	$2 \longrightarrow$
(2) Excited cyclo-hexanone–ground state cyclohexanone interaction	$\xrightarrow{k_{r_2}}$ (13)	$2 \longrightarrow$
(3) Excited cyclo-hexanone–photoreducing complex (CPX) interaction	+ CPX $\xrightarrow{k_{r_3}}$ + products[a] (14) Ketone + 2-propanol $\underset{K_3}{\rightleftharpoons}$ CPX	[b]

[a]The nature of the other products depends on the structure of CPX.
[b]The additional termination reactions depend on the structure of CPX.

hexanonyl radical [11] prevailed. The analysis of the products corroborated these observations: the quantum yield of 2-(2-cyclohexanonyl)-cyclohexanone (I), which is generated by the dimerization of the α-cyclohexanonyl radical, increased as the initial cyclohexanone concentration increased.

The theoretical expressions of the photoreduction quantum yield for each of these three reaction models will now be considered successively.

2.1. Model (1): ketone–radical interaction (reaction (12))

In dilute solutions cyclohexanol formation proceeds through a dismutation of the corresponding hydroxylated radicals (reaction (10)). In concentrated media reaction (12), which corresponds to the interaction of these radicals with cyclohexanone, competes with reaction (10). Under these conditions only one radical (hence one photon) instead of two is sufficient for a molecule of cyclohexanol to be formed. An increase in the photoreduction quantum yield will result therefrom.

Using the steady state approximation for the various reaction species (excited states, radicals), the quantum yield can be expressed readily as a function of the concentrations of the reactants and of the various rate constants for the elementary steps considered:

$$\Phi = \frac{\Phi_{ST}}{b/[RH_2] + c[C_6H_6]/[RH_2] + 1} - a[\text{ketone}] +$$

$$+ \left(a^2[\text{ketone}]^4 + \frac{a[\text{ketone}]\Phi_{ST}}{b/[RH_2] + c[C_6H_6]/[RH_2] + 1} \right)^{1/2}$$

where the parameters a, b and c are related to the rate constants for the reaction steps as follows:

$$a = \frac{k_p^2}{8I_a k_m} \qquad\qquad b = \frac{k_{d_1}}{k_{r_1}} \qquad\qquad c = \frac{k_d}{k_{r_1}}$$

Φ_{ST} is the quantum yield for the singlet–triplet intersystem crossing of 3,3,5-trimethylcyclohexanone; I_a is the light intensity absorbed.

2.2. Model (2): ground state ketone–excited state ketone interaction (reaction (13))

In this case the additional step (reaction (13)) corresponds to a direct interaction between the cyclohexanone in the triplet state and the cyclohexanone in the ground state. Such an interaction has been suggested by Porter et al. [12] for the photolysis of acetone in solution. This reaction, which in the present case induces the formation of hydroxycyclohexyl radicals, competes with the other triplet deactivation reactions (reactions (7) and (8)). This reaction too results in an increase in the photoreduction quantum yield as the initial concentration of ketone is increased. The

quantum yield of photoreduction for this reaction scheme can be calculated as being

$$\Phi = \frac{1}{2} \Phi_{ST} \left(\frac{e + f[C_6H_6]}{[RH_2] + g[\text{ketone}]} + 1 \right)^{-1}$$

with

$$e = \frac{k_{d_1}}{k_{r_1}} \qquad\qquad f = \frac{k_d}{k_{r_1}} \qquad\qquad g = \frac{k_{r_2}}{k_{r_1}}$$

2.3. Model (3): excited state ketone–CPX interaction (reaction (14))

The interaction between the excited state of the ketone and a ketone–2-propanol complex of stoichiometry 1:1 has been proposed previously [6] from kinetic data. In this case the photoreduction quantum yield is

$$\Phi = \frac{1}{2} \Phi_{ST} \left(1 + \frac{h[C_6H_6] + i}{[CPX] + \epsilon[RH_2]} \right)^{-1}$$

and

$$[CPX] = \frac{K_3[\text{ketone}][RH_2]}{1 + K_3[RH_2]}$$

with

$$h = \frac{k_d}{k_{r_3}} \qquad\qquad i = \frac{k_{d_1}}{k_{r_3}} \qquad\qquad \epsilon = \frac{k_r}{k_{r_3}}$$

2.4. Comparison between the computed relationships and the experimental data: selection of a reaction model

For each of the three models described, the expression for the quantum yield depends on the concentrations of the various reactants. The quantum yield values Φ(calc) which were thus calculated for various concentrations of ketone and 2-propanol were compared with the values Φ(exp) found experimentally (see Section 6). A computer calculation, which has been described previously [6], showed that in these three cases the mean quadratic error between Φ(calc) and Φ(exp) could be minimized. The values of the parameters thus optimized are listed in Table 2.

In each case a set of parameters could be found which was such that the average relative error was satisfactory, i.e. of the same order of magnitude as the experimental error. The first two models do not appear to be suitable as they lead to erratic parameter values (negative rate constant or $\Phi_{ST} > 1$). Model (3) is the only model which leads to optimized parameter values that are physically satisfactory; it is also the model which best fits the experimental data. The structure and the origin of the photoreducing complex CPX involved in that reaction model will now be discussed.

TABLE 2

Values of the optimized parameters and of the mean quadratic error in the various reaction models considered

Reaction model	Optimized parameters	Average relative error (%)	Observations
(1)	Φ_{ST} = 0.705; b = 8.911; a = −0.053; c = 1.812	12	$a < 0$
(2)	Φ_{ST} = 101.116; f = 164.291; e = 2636.796; g = 7.559	15	$\Phi_{ST} > 1$
(3)	h = 0.93 × 10^{-3}; i = 0.86 × 10^{-2} ϵ = 0.51 × 10^{-3}; K_3 = 1.5 × 10^{-3}	9	The experimental value (Φ_{ST} = 0.89) was used in the calculation

3. Structure of the photoreducing complex CPX

The rate constants for each elementary step, as well as the equilibrium constant for CPX [6], could be calculated from the optimized values of the various parameters and from some literature data: K_3 = 1.5 × 10^{-3} M^{-1}; k_d = 1.25 × 10^6 s^{-1} M^{-1}; k_{d_1} = 1.15 × 10^7 s^{-1}; k_{r_3} = 1.35 × 10^9 s^{-1} M^{-1}; k_{r_1} = 0.7 × 10^6 s^{-1} M^{-1}. CPX is not a mere solvation complex between the ketone and 2-propanol. As a matter of fact, the equilibrium between the solvated and the free cyclohexanones has been quantitatively studied by various authors [13]. The value of the solvation constant of the cyclohexanone in ethanol found by Josien and Pineau [13] (2.8 ± 0.3 M^{-1}) is several orders of magnitude higher than that obtained through calculations. Therefore the most likely assumption is that CPX is a solvation complex formed between the enol species of the cyclohexanone and 2-propanol (see Fig. 1).
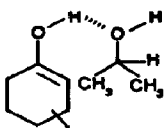

Fig. 1. The structure of the photoreducing complex CPX.

The occurrence of the α-cyclohexanonyl radical can then be accounted for by considering the abstraction of the enolic hydrogen atom by the excited cyclohexanone; this leads to the enoxy radical:

(15)

which is one of the boundary forms [14] of the α-cyclohexanonyl radical. This radical was observed for the highest ketone concentrations, *i.e.* in the solutions characterized by the highest quantum yields.

Several arguments of a chemical nature are in agreement with this assumption.

3.1. Photoreduction in the presence of phenol

In order to assess the reducing power of the hydrogen atoms of the enolic type, the reducing power of phenolic hydrogen atoms was investigated and was compared with that of 2-propanol. Small amounts of phenol were added to the cyclohexanone–2-propanol–benzene mixtures. The rate constant for the reduction of the triplet by phenol was then determined within the scope of model (3):

(16)
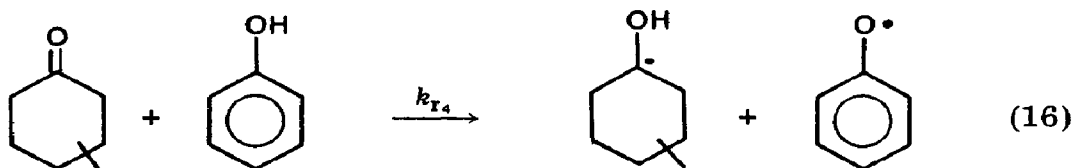
The expression for the quantum yield then becomes

$$\Phi = \frac{1}{2} \frac{k_{r_3}[\text{CPX}] + k_{r_1}[\text{RH}_2] + k_{r_4}[\text{phenol}]}{k_d[\text{C}_6\text{H}_6] + k_{d_1} + k_{r_3}[\text{CPX}] + k_{r_4}[\text{phenol}] + k_{r_1}[\text{RH}_2]} \Phi_{\text{ST}}$$

A linear dependence on the phenol concentration appears when this expression is modified as follows:

$$\frac{2\Phi}{\Phi_{\text{ST}} - \Phi} = \frac{k_{r_4}}{k_d[\text{C}_6\text{H}_6] + k_{d_1}} [\text{phenol}] + \frac{k_{r_3}[\text{CPX}] + k_{r_1}[\text{RH}_2]}{k_d[\text{C}_6\text{H}_6] + k_{d_1}}$$

The data from two series of experiments (Table 3) were used to calculate the rate constant for the triplet photoreduction by phenol ($k_{r_4} = (3.7 \pm 0.7) \times 10^7$ s^{-1} M^{-1}). As this value lies between the values of the rate constants for the photoreduction by 2-propanol ($k_{r_1} = 0.7 \times 10^6$ s^{-1} M^{-1}) and by the solvated enol ($k_{r_3} = 1.4 \times 10^9$ s^{-1} M^{-1}) it can be concluded that the hydrogen atoms of the phenolic type are more reactive than those of 2-propanol. This result is to be compared with the fluorescence and phosphorescence quenching constants of biacetyl by phenol [15] : $k_q = 3.4 \times$

TABLE 3

Effect of phenol addition on the photoreduction of 3,3,5-trimethylcyclohexanone in 2-propanol

Medium[a]	[Phenol] (M)	Φ	$\dfrac{2\Phi}{\Phi_{ST} - 2\Phi}$
A	0	0.040	0.10
	2×10^{-3}	0.049	0.12
	10^{-2}	0.049	0.12
	2×10^{-2}	0.057	0.15
	4×10^{-2}	0.063	0.16
B	0	0.23	1.07
	2×10^{-2}	0.23	1.07
	5×10^{-2}	0.25	1.31
	0.12	0.27	1.53
	0.24	0.27	1.53

[a]Medium A: ketone(6×10^{-2} M)–2-propanol(2.56 M)–benzene(8.9 M).
Medium B: ketone(13×10^{-2} M)–2-propanol(11.9 M); no benzene.

10^8 s^{-1} M^{-1}. Proton abstraction from OH bonds has been discussed theoretically by Formosinho [16] who has considered a charge transfer mechanism for phenol.

3.2. Solvent effects

The photoreducing power of the enol seems to be related to its degree of solvation, i.e. to the occurrence of the CPX complex. Experiments were carried out in three kinds of solvating photoreducing agents: amines, alcohols and ethers. Two series of samples were irradiated under the same conditions: the concentration of the photoreducing agent was about 3 M and benzene was used as a cosolvent. For each photoreduction the quantum yields for the formation of the cyclohexanols were measured for 3,3,5-trimethylcyclohexanone concentrations of 1.0 M (Φ_1) and 0.2 M ($\Phi_{0.2}$). The values of the ratio $\Phi_1/\Phi_{0.2}$ are listed in Table 4.

TABLE 4

Photoreduction quantum yields of 3,3,5-trimethylcyclohexanone in various photoreducing solvents

Photoreducing agent	$\Phi_1/\Phi_{0.2}$
NEt$_3$	1.5
(iPr)$_2$NH	1.6
EtOH	2.9
iPrOH	3
(iPr)$_2$O	2

In all the solvents possessing a heteroatom which can be bonded to the enol hydroxyl group through hydrogen bonding, the quantum yield increases with increasing ketone concentration. However, in the solvents which cannot give rise to such an association, the quantum yield does not depend on the initial cyclohexanone concentration (Table 5). In Table 5 the quantum yields are expressed with respect to that of a 0.12 M solution of 3,3,5-trimethylcyclohexanone in cyclohexane.
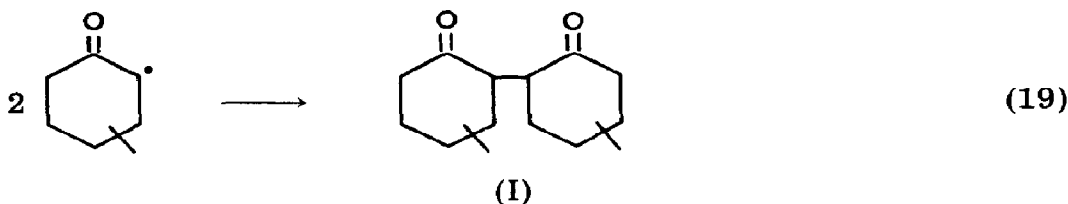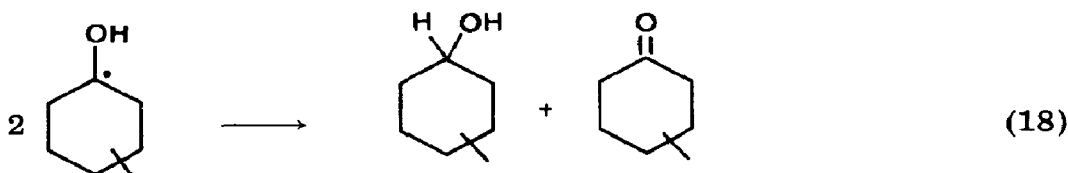
TABLE 5

Photoreduction quantum yields of 3,3,5-trimethylcyclohexanone in cyclohexane

[Cyclohexanone] (M)	$\Phi/\Phi_{0.12}$
0.25	1.1
0.60	0.95
0.94	1

3.3. Relationship between cyclohexanol and diketone (I) formation

As mentioned earlier, the reduction by the enol leads to the formation of the α-cyclohexanonyl radical:

(17)

(18)

(I)

(19)

Under these conditions there should be a relationship between the formation of cyclohexanol and that of the diketone (I). From the kinetic equations this relationship can be written as

$$\frac{[\text{diketone (I)}]}{[\text{cyclohexanol}]} = \gamma \frac{k_{r_3}[\text{CPX}]}{k_{r_3}[\text{CPX}] + k_{r_1}[\text{RH}_2]}$$

Table 6 gives the values of the proportionality factor γ which were calculated from the experimental determinations of the ratio [diketone (I)]/[cyclohexanol]. Within the limits of experimental error the proportionality factor γ remains constant. The formation of the diketone (I) is therefore due to the second process of the photoreduction, *i.e.* to the interaction between the cyclohexanone in the triplet state and its enol species.

TABLE 6

Relationship between cyclohexanol and diketone (I) formation: calculation of the proportionality factor γ

[Cyclohexanone] (M)	[RH$_2$] (M)	$\frac{[Diketone(I)]}{[Cyclohexanol]}$	$\frac{k_{r_3}[CPX]}{k_{r_3}[CPX] + k_{r_1}[RH_2]}$	γ
0.03	13.05	0.04 ± 0.02	0.08 ± 0.01	0.5 ± 0.3
0.15	12.89	0.13 ± 0.03	0.31 ± 0.04	0.4 ± 0.2
1.5	11.06	0.21 ± 0.03	0.82 ± 0.03	0.3 ± 0.2
4.5	6.99	0.28 ± 0.04	0.94 ± 0.02	0.3 ± 0.1

These data (photoreduction by phenol, solvent effects, formation of the diketone (I)) corroborate the occurrence of a photoreduction process involving an interaction between the cyclohexanone in the triplet state and its enol species which is stabilized by 2-propanol.

4. Origin of the enol

The enol species occurring in the reaction medium can be generated by several reactions: keto–enol tautomerism, photoenolization and disproportionation of the hydroxyl radicals. The rate of enol formation resulting from the direct enolization of cyclohexanone has been measured under various conditions by different authors. Some values reported in the literature are given in Table 7. Although these data are not very consistent, it appears that these enolization constants have very low values; in particular they are lower than the calculated value ($K_3 = 1.5 \times 10^{-3}$). Moreover, it should be noted that the most recent data [21, 22], which can be considered to be the most accurate [21], also lead to the lowest values.

Therefore, the enol formed through keto–enol tautomerism does not occur in sufficiently large amounts to be able to act as a photoreducing agent. However, the enol formation rate, in media such as those under investigation, can increase markedly during the irradiation by way of direct photoenolization. Direct photoenolization is a widespread phenomenon when the enol formed can be stabilized through conjugation (aromatic

TABLE 7

Values of the enol formation rate reported in the literature

$K_{\text{lit}} = [Enol]/[Ketone]$	Experimental conditions	Reference
2×10^{-4}	Water	17
1.2×10^{-2}	25% solution in methanol (extrapolated to pure cyclohexanone)	18
$(6.5 \pm 1.4) \times 10^{-5}$	—	19
4.1×10^{-6}	Water, 25 °C	20
2×10^{-6}	Water, 25 °C	21

ketones [1] or α-diketones [23]). However, as far as we know direct photo-enolization has never been reported for monocarbonylated aliphatic ketones. Moreover the dismutation reaction of the hydroxylated radicals can also give rise to the formation of enol:

(20)
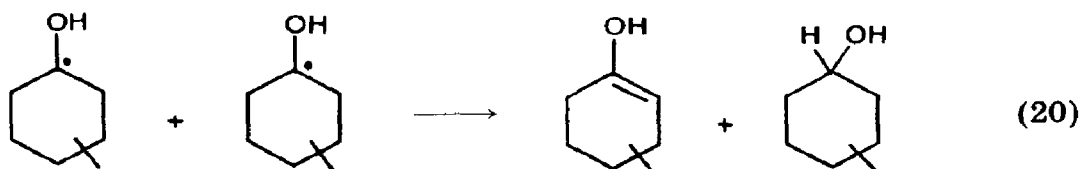
This has been shown by Laroff and Fischer as well as by Seifert [24] in the chemically induced dynamic nuclear polarization investigation of the photolysis of acetone in 2-propanol:

(21)

Anpo and Kubokawa [5] have shown that in methanol the UV irradiation leads to a much larger decrease in the intensity of the (n, π^*) band of acetone than that expected from the extent of its photolysis. This observation has been interpreted in terms of a photochemical enolization of acetone, and has been corroborated by the investigation of the reverse reaction (acetone formation). It was therefore interesting to assess whether some enol is actually formed during the irradiation of 3,3,5-trimethylcyclohexanone in 2-propanol.

4.1. Direct observation of the enol of 3,3,5-trimethylcyclohexanone by UV spectroscopy

After the irradiation of a solution of 3,3,5-trimethylcyclohexanone in 2-propanol the formation of a transient compound was observed; its spectrum is shown in Fig. 2. This unstable photoproduct has a spontaneous
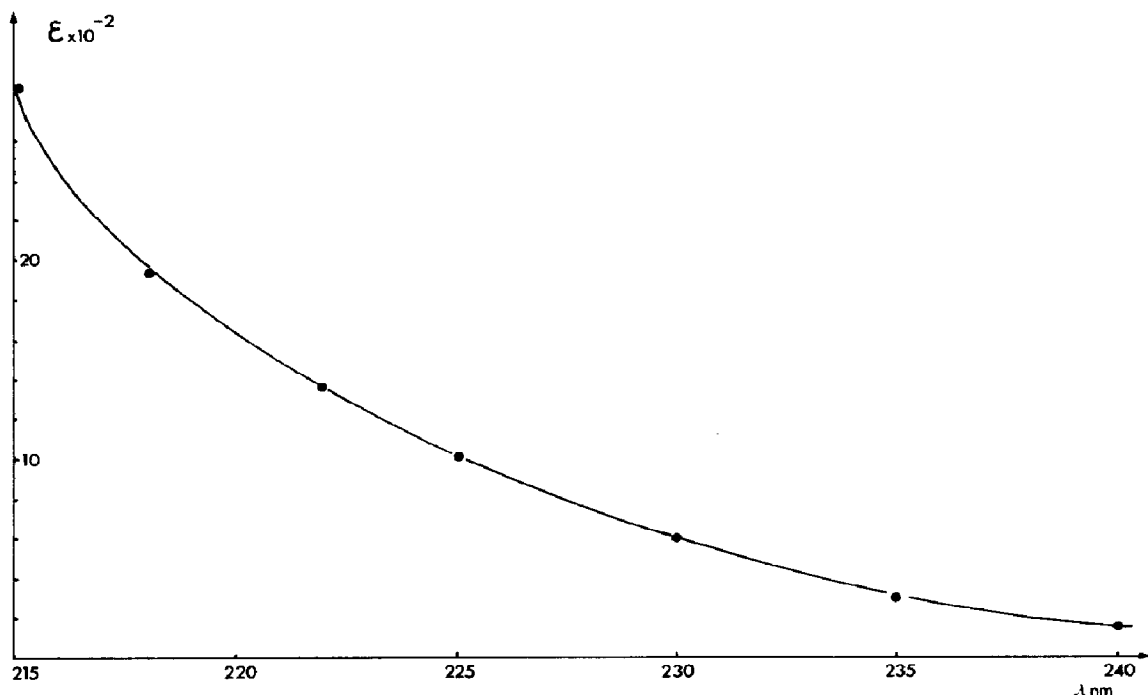
Fig. 2. A spectrum of the transient photoproduct appearing after the UV irradiation of 3,3,5-trimethylcyclohexanone (0.016 M) in 2-propanol.

deactivation rate of $(5 \pm 2) \times 10^{-4}$ s^{-1}. Corresponding to the disappearance of this absorbance as a function of time, the reappearance of the (n, π^*) band of 3,3,5-trimethylcyclohexanone could be observed at 287 nm with a rate of $(6 \pm 2) \times 10^{-4}$ s^{-1}. Both phenomena are markedly enhanced by the addition of traces of acids. They could not be observed when a non-enolizable ketone (such as fenchone) was irradiated. The transient absorbing photoproduct is therefore likely to be the enol of 3,3,5-trimethylcyclo-hexanone. Its lifetime at room temperature is about 2000 s, a value which is markedly higher than that (14 s) determined by Blank *et al.* [4] for 1-propene-2-ol in 2-propanol.

Using a value of 20.9 for the molecular extinction coefficient of 3,3,5-trimethylcyclohexanone at 287 nm, the molecular extinction coefficient of the enol at 222 nm could be calculated, *i.e.* ϵ = 1400. Under irradiation the enol reaches a steady state (Fig. 3) corresponding to 4% in extent of reaction.

The amount of photochemical enol formed depends on the initial ketone concentration; it increases as the initial ketone concentration increases (Table 8). This correlation is consistent with the involvement of the photochemical enol in the photoreduction reaction since the photoreduction quantum yields are the highest in the solutions having the highest ketone concentrations.
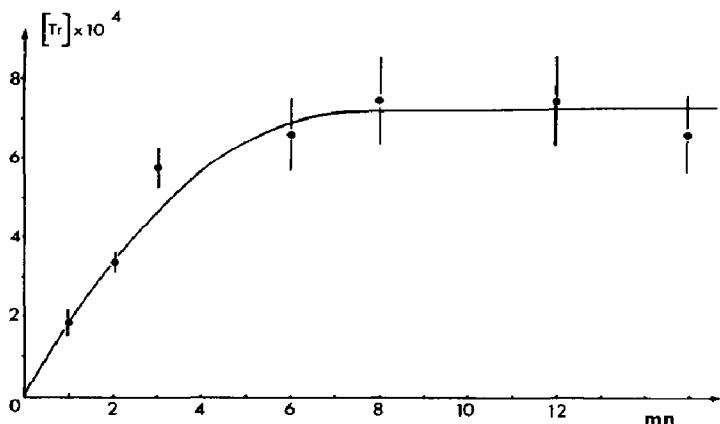
Fig. 3. The amount of enol formed as a function of the duration of the irradiation of 3,3,5-trimethylcyclohexanone in 2-propanol.

TABLE 8

Dependence of the amount of photochemical enol formed on the initial ketone concentration

$[Ketone]$[a] (M)	$[2\text{-}Propanol]$ (M)	Optical density at 222 nm	$[Enol]$ (M)	$\dfrac{[Enol]}{[Ketone][2\text{-}Propanol]}$
3.2×10^{-3}	13.20	0.09	6.4×10^{-5}	1.5×10^{-3}
16×10^{-3}	13.18	1.09	7.8×10^{-4}	3.5×10^{-3}
80×10^{-3}	13.00	2.44	1.7×10^{-3}	1.6×10^{-3}

[a] 3,3,5-Trimethylcyclohexanone in 2-propanol; 5% in extent of reaction.

TABLE 9

Calculation of the steady state concentration of CPX for various initial ketone concentrations

$[Ketone]$ (M)	$[2\text{-}Propanol]$ (M)	$[CPX](calc)$ (M)	$[CPX](exp)$ (M)
3.2×10^{-3}	13.20	2×10^{-5}	6.4×10^{-5}
1.6×10^{-3}	13.18	1×10^{-4}	7.8×10^{-4}
80×10^{-3}	13.00	3×10^{-4}	17×10^{-4}

If the enol is now assumed to be the photoreducing complex CPX, reaction (20) has to be introduced in model (3) to take into account the fact that the reactive enol is both tautomeric and photochemical. The theoretical value of the steady state concentration of CPX can then be calculated (see Section 6) and compared with the experimental value obtained by means of UV spectrophotometry. The calculated value, however, is only approximate because of the assumptions used. In that respect, the enolization constant K_{lit} has been measured by Bell and Smith [20] for cyclohexanone in water

and not for 3,3,5-trimethylcyclohexanone in 2-propanol. The amounts of CPX thus calculated for three ketone concentrations are given in Table 9. The relatively satisfactory agreement between the experimental ([CPX](exp)) values corroborates the photoreducing role of the enolic complex CPX which originates mainly from the dismutation of the hydroxycyclohexyl radicals.

5. Conclusions

The investigation of the photoreduction of cyclohexanones in 2-propanol led to a discussion of three independent kinetic models. The occurrence of cyclohexanone oxidation products (either the α-cyclohexanonyl radical or 2-(2-cyclohexanonyl)-cyclohexanone), in addition to the photoreduction cyclohexanols, is qualitatively accounted for by these reaction models. However, all the experimental data, particularly the dependence of the photoreduction quantum yields on the initial cyclohexanone concentration, can only be interpreted in terms of the reaction model involving a double photoreduction process. This model, in addition to the classical photoreduction by 2-propanol, calls upon an additional step, i.e. the interaction between the excited cyclohexanone and its enol species which is stabilized by 2-propanol ($k_{r_3} = (1.3 \pm 0.3) \times 10^9$ s^{-1} M^{-1}). The enol, with an average lifetime in the photoreducing medium of about 2000 s, originates mainly from the dismutation reactions of the hydroxycyclohexyl radicals which are generated in the course of the photoreduction reaction.

6. Experimental

6.1. Synthesis and characterization

6.1.1. Synthesis of 2-(2-cyclohexanonyl)-cyclohexanone (I)

A mixture (1:1 by weight) of cyclohexanone and tert-butyl peroxide was placed in a Pyrex tube and was degassed by bubbling N$_2$ through. After 100 h of irradiation at a wavelength of 3000 Å in a Rayonet model RPR 100 photochemical reactor, the product was purified by preparative vapour phase chromatography (VPC) (Carlo Erba; column, 10% Ucon Polar and 10% KOH on Chromosorb W 30/60; 6 m long; T = 180 °C; flow, 75 ml min^{-1}; retention time, 3.5 h). The product was characterized as follows: mass spectrometry (Riber QSM), m/e values of 194 (M), 176, 148, 137, 109, 99 and 98; ^{13}C nuclear magnetic resonance (Bruker WP 60; CHCl$_3$; internal reference, tetramethylsilane), δ (ppm) values of 25.20, 25.58 - 26.72, 28.04 - 29.19, 30.13 - 41.69, 42.25 - 50.29, 49.03 - 208.50 and 209.60 (each of the nuclear magnetic resonance signals was split indicating the occurrence of two diastereoisomers in non-equivalent amounts; the first figure corresponds to the more abundant isomer); proton magnetic resonance (Varian T 60; C$_6$D$_6$; internal reference, tetramethylsilane, δ (ppm) values of 0.8 - 2.40 (broad multiplet, 16H) and 2.8 (broad multiplet, 2H).

6.1.2. Characterization and determination of the diketone (I) in the photoreduction solutions

For this purpose, VPC (column, SE.30; $T = 120$ °C; carrier gas, helium) was coupled with mass spectrometry (Girdel–Riber; m/e values of 194 (M), 176, 148, 137, 109, 99 and 98). This identification was further corroborated by coinjection with a proper sample on two different columns A and B. (Column A; 3% Ucon Polar and 6% KOH on Chromosorb W 60/80; 4.5 m long; $T = 150$ °C; flow, 25 ml min^{-1}. Column B; 20% DEGS on Chromosorb P 60/80; 2 m long; $T = 150$ °C; flow, 20 ml min^{-1}.)

6.2. Photoreductions

6.2.1. Photoreduction in the presence of phenol

Incremental amounts of sublimated phenol were added to a solution of 3,3,5-trimethylcyclohexanone in 2-propanol. After degassing at 10^{-6} Torr by the freeze–thaw method, the samples (3.5 ml) were vacuum sealed in Pyrex tubes and were irradiated at 3000 Å in a Rayonet photochemical reactor up to 10% in extent of reaction. The 3,3,5-trimethylcyclohexanols formed were determined by VPC (column A), naphthalene being used as an internal standard. The corresponding phenol-free solutions were used as blanks for light intensity monitoring.

6.2.2. Photoreduction of 3,3,5-trimethylcyclohexanone in various solvents

The solvents used were either freshly distilled on a Büchi spinning band column (triethylamine, diisopropylamine, diisopropylether) or of spectroscopic grade (2-propanol, ethanol); in the latter case, they were used without further purification. The degassing, irradiation and analyses were carried out under the same conditions as those just described.

6.3. Spectroscopy

6.3.1. EPR spectroscopy

The EPR spectra were recorded using a Varian E spectrometer equipped with a variable temperature device. The samples were placed in quartz tubes 4 mm in external diameter and were degassed at 10^{-6} Torr by the classical method. The tubes were then sealed under vacuum and the irradiations were carried out in the EPR cavity using a Philips SP 500 lamp, a quartz lens being used for focusing. The spectra reached their maximum intensity after irradiating for a few tens of seconds at a suitably chosen temperature. Two representative solutions of a concentrated (A) or a dilute (B) medium were irradiated. (Solution A, cyclohexanone–cyclohexanol (1:2), without co-solvent (room temperature), irradiation *in situ*; spectrum, doublet of triplet 1:1:2:2:1:1; $a_1 = 17.6$ G, $a_2 = 33.5$ G; α-cyclohexanonyl radical. Solution B, 3,3,5-trimethylcyclohexanone–3,3,5-trimethylcyclohexanol–isooctane (1:5:25) ($T = -40$ °C), irradiation *in situ*; spectrum, triplet of triplet 1:2:1:2:4:2:1:2:1; $a_1 = 9.6$ G, $a_2 = 35$ G; hydroxycyclohexyl radical.)

6.3.2. Characterization of the enol by UV spectroscopy

A 4 ml quartz cell was equipped with a Pyrex side degassing bulb (10 ml). To avoid any marked variation in temperature at the level of the cell, the solution of 3,3,5-trimethylcyclohexanone in 2-propanol was transferred to the side bulb at the time of degassing. The cell–bulb set was then sealed under vacuum. During the irradiation with a wavelength of 3000 Å the solution was standing in the Pyrex bulb. Immediately after the irradiation the solution was transferred to the cell and UV spectra were recorded using a Beckman Acta M IV spectrophotometer. The standard solvent was submitted to identical conditions.

6.4. Calculations

6.4.1. Quantum yields

6.4.1.1. Model (1): ketone–radical interaction. The steady state equation for the triplet is

$$\Phi_{ST} I_a - k_{d_1}[T] - k_d[T][C_6H_6] - k_{r_1}[T][2\text{-propanol}] = 0$$

The steady state equation for the hydroxycyclohexyl radical is

$$k_{r_1}[T][2\text{-propanol}] - k_p[X][\text{ketone}] - 2k_m[X]^2 = 0$$

The equation for cyclohexanol formation is

$$k_p[X][\text{ketone}] + k_m[X]^2 = \frac{d[\text{cyclohexanol}]}{dt}$$

and the quantum yield is given by

$$\Phi = \frac{d[\text{cyclohexanol}]}{dt} I_a^{-1}$$

6.4.1.2. Model (2): ground state ketone–excited state ketone interaction. The steady state equation for the triplet is

$$\Phi_{ST} I_a - k_{d_1}[T] - k_d[T][C_6H_6] - k_{r_1}[T][2\text{-propanol}] - $$
$$- k_{r_2}[T][\text{ketone}] = 0$$

The steady state equation for the hydroxycyclohexyl radical is

$$k_{r_1}[T][2\text{-propanol}] + k_{r_2}[T][\text{ketone}] - 2k_m[X]^2 = 0$$

6.4.1.3. Model (3): ketone–CPX interaction. The steady state equation for the triplet is

$$\Phi_{ST} I_a - k_{d_1}[T] - k_d[T][C_6H_6] - k_{r_1}[T][2\text{-propanol}] - $$
$$- k_{r_2}[T][CPX] = 0$$

The steady state equation for the hydroxycyclohexyl radical is

$$k_{r_1}[T] [\text{2-propanol}] + k_{r_3}[T][CPX] - 2k_m[X]^2 = 0$$

with

$$[CPX] = \frac{K_3[\text{ketone}][\text{2-propanol}]}{1 + K_3[\text{2-propanol}]}$$

6.4.2. Computing techniques

The iterative method used is that due to Powell [25]: "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 be minimized was the mean quadratic error on Φ:

$$F = \sum_{i=1}^{N=56} \left(\frac{\Phi_i - \Phi(\text{exp})}{\Phi_i} \right)^2$$

where N is the number of experimental points, $\Phi(\text{exp})$ is the experimental value of Φ and Φ_i is the calculated value of Φ at point i in the model considered; Φ_i depends on various parameters which are said to be optimized when F is minimum. The parameters which are to be optimized are given an estimated value which has to be as close as possible to the optimal value. This estimation is based on various experimental or literature data. It could be shown that the optimal values of the parameters as well as the minimized value of F do not depend significantly on the initial values of the parameters which are to be optimized. The values found for the experimental quantum yields under various conditions are listed in Table 10.

6.4.3. Calculation of the steady state concentration of the enolic complex under irradiation

6.4.3.1. Steady state equation for the enolic complex CPX. The enolic complex CPX can result either from tautomerization or from the dismutation of the hydroxycyclohexyl radicals (reaction (20)). The complex disappears either by interacting with the cyclohexanone triplet (reaction (17)) or by giving back the initial ketone (keto–enol tautomerism):

$$\frac{d[CPX]}{dt} = k'_1[\text{ketone}][\text{2-propanol}] + \varphi k_m[X]^2 + k_{r_2}[T][CPX] = 0$$

where φ is a stoichiometric factor related to the reactivity of the hydrogen atoms α to the radical centre and $K_{lit} = k'_1/k'_{-1}$. Assuming [26] that the reactivities of the five hydrogen atoms ($2CH_2 + 1OH$) are equivalent, the value of φ is then $\frac{4}{5}$. The enol is also assumed to be solvated as fast as it is formed in the reaction medium. k'_{-1} can be calculated from the measurement of the lifetime of CPX: $k'_{-1} = 5.2 \times 10^{-4} \text{ s}^{-1}$. The value of k'_1 was derived from the data of Bell and Smith [20] who have determined the keto–enol equilibrium constant of cyclohexanone in water. The values of the

TABLE 10

Quantum yields of photoreduction *vs.* reactant concentrations

$1/\Phi(exp)$	$1/[Ketone]$	$1/[RH_2]$	$1/\Phi(exp)$	$1/[Ketone]$	$1/[RH_2]$
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

other constants are those which were determined previously when referring to reaction model (3).

6.4.3.2. Steady state equation for the triplet T. The amount of triplet formed is proportional to $I_a \Phi_{ST}$. The triplet disappears either by returning to the ground state (spontaneously or through interactions with benzene) or by interacting with 2-propanol or CPX:

$$\frac{d[T]}{dt} = I_a \Phi_{ST} - k_{r_1}[T]\,[\text{2-propanol}] - k_{r_3}[T]\,[CPX] - k_{d_1}[T] -$$

$$- k_d[T]\,[C_6H_6] = 0$$

6.4.3.3. Steady state equation for the hydroxycyclohexyl radical. The hydroxycyclohexyl radical results from photoreducing interactions at the level of the triplet and disappears through dismutation:

$$\frac{d[X]}{dt} = k_{r_1}[T] \, [2\text{-propanol}] - k_{r_3}[T] \, [CPX] - k_m[X]^2 = 0$$

From these three steady state equations, a quadratic expression for [CPX] can be derived which leads to the value of the steady state concentration of the enolic complex CPX. In these calculations the acetone enol was not taken into account as its lifetime is very short. The mixed dismutation reactions (hydroxycyclohexyl radical + hydroxyisopropyl radical) were also disregarded.

From the three steady state equations mentioned in the text, *i.e.* from

$$\frac{d[T]}{dt} = 0 \qquad \frac{d[CPX]}{dt} = 0 \qquad \frac{d[X]}{dt} = 0$$

the following expression can be written:

$$A[CPX]^2 + B[CPX] + C = 0$$

with

$$A = k'_{-1}k_{r_3}$$

$$B = k_{r_3}k'_1 [\text{ketone}] \, [2\text{-propanol}] + \frac{\varphi\Phi}{2} I_a k_{r_3} - k_{r_3}\Phi_{ST}I_a -$$

$$- k'_{-1}k_{r_1} [2\text{-propanol}] - k'_{-1}k_d[C_6H_6] - k_{d_1}k'_{-1}$$

$$C = k'_1 k_{r_1} [\text{ketone}][2\text{-propanol}]^2 + k_d k'_1 [C_6H_6] \, [\text{ketone}] \, [2\text{-propanol}] +$$

$$+ k_{d_1}k'_1 [\text{ketone}] \, [2\text{-propanol}] + \frac{\varphi}{2} I_a k_{r_1} [2\text{-propanol}] +$$

$$+ \frac{\varphi}{2} \Phi I_a k_d[C_6H_6] + \frac{\varphi}{2} k_{d_1}\Phi I_a$$

and $k'_{-1} = 5.2 \times 10^{-4}$ s^{-1}, $k'_1 = 2.1 \times 10^9$ s^{-1} M^{-1}, $k_{r_1} = 0.7 \times 10^6$ s^{-1} M^{-1}, $k_{r_3} = 1.35 \times 10^9$ s^{-1} M^{-1}, $\varphi = 0.8$, $I_a = 2.85 \times 10^{-6}$ $(1 - 10^{-7.5[\text{ketone}]})$ einstein l^{-1} s^{-1}, $k_d = 1.25 \times 10^6$ s^{-1} and $k_{d_1} = 1.15 \times 10^7$ s^{-1}. Φ is the quantum yield of photoreduction and $\Phi_{ST} = 0.89$. This equation was solved using a Hewlett–Packard HP.97 desk calculator.

6.5. Determination of the lifetime and concentration of the photochemical enol

The transient lifetime and the amplitude of the signal of the photochemical enol of 3,3,5-trimethylcyclohexanone in 2-propanol were determined at 222 nm. This wavelength was chosen so as to obtain a balance between two contradictory criteria: a sufficiently high value of the molecular extinction coefficient and a good linearity in the response of the

UV spectrophotometer. The UV spectra (215 - 300 nm) were recorded as a function of time using a Beckman Acta M IV spectrophotometer equipped for kinetic measurements. The kinetic calculations were performed on a Tektronix 4051 minicomputer using a least-squares Guggenheim program [27].

References

1 J. Chilton, L. Giering and C. Steel, *J. Am. Chem. Soc.*, *98* (1976) 1865.
2 G. D. Abbott and D. Phillips, *Mol. Photochem.*, *8* (4 - 5) (1977) 289.
   P. Colman, A. Dunne and M. F. Quinn, *J. Chem. Soc., Faraday Trans. I*, *72* (11) (1976) 2605.
   J. A. den Hollander, A. J. Hartel and P. H. Shippers, *Tetrahedron*, *33* (1977) 211.
3 D. I. Schuster, G. C. Barile and K. Liu, *J. Am. Chem. Soc.*, *97* (1975) 4441.
4 B. Blank, A. Henne, G. P. Laroff and H. Fischer, *Pure Appl. Chem.*, *41* (1975) 475.
5 M. Anpo and Y. Kubokawa, *Bull. Chem. Soc. Jpn.*, *50* (8) (1977) 1913.
6 B. Despax, J. C. Micheau, N. Paillous and A. Lattes, *J. Photochem.*, *7* (1977) 365.
7 J. C. Micheau, N. Paillous and A. Lattes, *Tetrahedron*, *31* (1975) 441.
   B. Despax, E. Alipour, N. Paillous, J. C. Micheau and A. Lattes, *Tetrahedron*, *34* (1978) 3579.
8 R. Simonaitis, G. W. Cowell and J. N. Pitts, Jr., *Tetrahedron Lett.*, *38* (1967) 3751.
9 D. I. Schuster, T. M. Weil and M. R. Topp, *Chem. Commun.*, (1971) 1212.
10 C. Corvaja, G. Giacometti and G. Sartori, *J. Chem. Soc., Faraday Trans. II*, *70* (1974) 709.
11 B. C. Gilbert, R. O. C. Norman and R. C. Sealy, *J. Chem. Soc., Perkin Trans. II*, (1973) 2174.
   J. C. Chang and T. F. Thomas, *J. Photochem.*, *9* (1978) 312.
12 G. Porter, S. K. Dogra, R. O. Loufty, S. E. Sugamori and R. W. Yip, *J. Chem. Soc., Faraday Trans. I*, *69* (8) (1973) 1462.
13 M. L. Josien and P. Pineau, *C.R. Acad. Sci.*, *250* (1960) 2559.
14 D. M. Camaioni, H. F. Walter, J. E. Fordan and D. W. Pratt, *J. Am. Chem. Soc.*, *95* (1973) 7978.
15 H. D. Becker, *J. Org. Chem.*, *32* (1967) 2140.
   A. J. Elliot and J. K. S. Wan, *J. Phys. Chem.*, *82* (1978) 444.
   N. J. Turro and R. Engel, *J. Am. Chem. Soc.*, *91* (1969) 7113.
16 S. J. Formosinho, *J. Chem. Soc., Faraday Trans. II*, *72* (1976) 1313.
17 G. Swartzenbach and C. Wittwer, *Helv. Chim. Acta*, *30* (1947) 656.
18 A. Gero, *J. Org. Chem.*, *26* (1961) 3156.
19 J. E. Dubois and G. Barbier, *Bull. Soc. Chim. Fr.*, (1965) 682.
20 R. P. Bell and P. W. Smith, *J. Chem. Soc. B*, (1966) 241.
21 J. P. Guthrie and P. A. Cullimore, *Can. J. Chem.*, *57* (1979) 240.
22 G. E. Lienhard and T. C. Wang, *J. Am. Chem. Soc.*, *91* (1969) 1146.
23 J. Lemaire, *J. Phys. Chem.*, *71* (1967) 2653.

24 G. P. Laroff and H. Fisher, *Helv. Chim. Acta, 56* (1973) 2011.
    K. G. Seifert, *Chem. Ber., 107* (1974) 3749.
25 M. J. D. Powell, *Comput. J., 7* (1964) 155.
26 R. Haag, J. Wirz and P. J. Wagner, *Helv. Chim. Acta, 60* (1977) 2595.
27 D. F. Detar, *Computer Programs for Chemistry*, Vol. 1, Benjamin, New York, 1968, p. 117.