

ON THE ROLE OF THE SOLVENT IN TYPE II PHOTOREACTIONS FROM ALIPHATIC KETONES

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Summary

The photochemistry of 4-methylpentan-2-one, heptan-2-one, 5-methylheptan-3-one and 5-methylhexan-2-one has been investigated in several solvents. A treatment of the data is given that allows a differentiation of the solvent effect from the quenching by the solvent. Cyclohexane, cyclohexene and benzene, when employed as solvents, quench excited triplet states with pseudo first-order constants of 4×10^6 , 2×10^8 and 7×10^7 s^{-1} respectively. On the other hand, cyclohexene is the only solvent investigated that is able to partly quench the excited singlet state. By considering the effect of the different solvents upon the photochemistry of ketones having widely different mean lives, it is concluded that the change in behaviour with solvent is due almost entirely to quenching of the excited states and not to a "solvent effect".

The behaviour of both singlet and triplet biradicals is similar in n-hexane, cyclohexane, cyclohexene and benzene.

Introduction

The effect of the solvent upon the photochemistry of aliphatic ketones which decompose predominantly by a Norrish type II mechanism is complex. The available experimental data are frequently contradictory [1], and it is not enough to provide a clear picture of the relationship between photochemical behaviour and solvent properties. Most of the difficulties found in analyzing the experimental data can be related to two factors: (i) the number of species which can interact with the solvent, and (ii) the number of ways in which the solvent can interact with a given species.

Regarding the first point, the solvent can interact with the excited singlet, the excited triplet, the singlet biradical and the triplet biradical. Each one of these interactions can modify the rate constants involved

(a "solvent effect"), introduce new photochemical processes (*i.e.* photoreduction) or provide new channels for the non-radiative processes (*i.e.* through the formation of an exciplex). In the last two cases, the solvent is behaving as "quencher". There are several systems where all the effect of the solvent has been related to a single interaction [2], but in most cases the solvent interacts with more than one species providing more than one reaction path for each species [1, 3]. Lately, the work of Borrell and Holmes has emphasized this multiple effect [1], casting doubts on the validity of several experimental methods generally employed to analyze the photochemical behaviour of ketones (*i.e.* the *cis* to *trans* isomerization of 1,3-diolefins). These authors have investigated the behaviour of two closely related ketones (pentan-2-one and 4-methylpentan-2-one) in several solvents. In the present work we extend the study to ketones of widely different mean life and introduce a simple method for deciding whether the solvent influences the photochemistry as a "solvent" or as a "quencher". This method is based on the assumption that a "solvent effect" would modify the photochemical behaviour almost regardless of the lifetime of the excited state, while a "quencher" would have an effect that must be directly related to the lifetime of the excited state.

Experimental

Most of the experimental details have been reported elsewhere [4]. Triplet quantum yields were obtained by the *cis* to *trans* isomerization of 1,3-pentadiene. The diolefin concentration was always less than 1 *M*. Acetone was employed as standard and it was assumed that its triplet quantum yield in *n*-hexane and benzene was one [5, 7]. The decay ratio of the excited diolefin was found to be the same in benzene and *n*-hexane solution. The triplet quantum yields in cyclohexene were obtained assuming a similar value for the decay ratio of the excited diolefin.

Cyclohexene was washed with FeSO_4 and distilled under nitrogen. Chloroform (Uvasol) was washed, dried and distilled to eliminate the alcohol.

Quantum yields of the photoproducts were obtained relative to heptan-2-one. For this ketone 0.2 was taken as the propylene quantum yield in *n*-hexane solution [6].

$\Phi_{\text{II}}^{\text{S}}$ (type II fragmentation from the singlet state) was measured in the presence of enough 1,3-pentadiene to quench all triplet reactions. The quantum yields of the photoproducts were measured at several 1,3-pentadiene concentrations. All the ketones showed a range of 1,3-pentadiene concentrations where the Φ_{II} was independent of 1,3-pentadiene concentration. The value of $\Phi_{\text{II}}^{\text{S}}$ was taken as the Φ_{II} value obtained under these conditions.

TABLE 1
Experimental results

Ketone	Solvent	Φ_{II}	Φ_{II}^S	Φ_{II}^T	Φ_T	$k_Q \tau_T^a$
pentan-2-one	n-hexane ^b	0.23	0.023	0.21	0.84	2500
	benzene	0.054	0.019	0.035	0.81 ^h	80
4-methylpentan-2-one	n-hexane ^c	0.22	0.031	0.19	0.78	1260
	benzene	0.061	0.028	0.033	0.83	100
	cyclohexane	0.18	0.030	0.15	—	610
	cyclohexene	0.038	0.024	0.014	0.65	38 ^d
	chloroform	0.16	0.030	0.13		
heptan-2-one	n-hexane	0.20	0.082	0.12	0.31	50
	benzene	0.18	0.081	0.095	0.31	30
	cyclohexane	0.19	0.081	0.11	0.31 ^e	38
	cyclohexene	0.14	0.080	0.060	0.30	28
	chloroform	0.11				
octan-2-one	n-hexane	0.20	0.070	0.13		
	benzene	0.18	0.075	0.10		40(30 ^f)
	cyclohexane	0.19	0.076	0.11		
5-methylheptan-3-one	n-hexane	0.11	0.057	0.053	0.26	42
	benzene	0.10	0.054	0.042	0.28	33
	cyclohexene	0.09	0.055	0.038	0.29	28
	chloroform	0.07				
5-methylhexan-2-one	n-hexane	0.16	0.11	0.05	0.14	10(4.0 ^g)
	benzene	0.16	0.11	0.05	0.14	8.5(13 ^h , 5 ^f)
	cyclohexene	0.14	0.10	0.04	0.14	7.7
	cyclohexane	0.16	0.11	0.05	0.14 ^e	8
	chloroform	0.08				

^a Measured from the change in Φ_{II} with added 1,3-pentadiene.

^b Ref. [4].

^c Ref. [12].

^d From the quantum yield of *cis* to *trans* isomerization as a function of *cis*-1,3-pentadiene concentration.

^e Assumed.

^f Ref. [2].

^g Ref. [8]; n-heptane solution.

^h Ref. [7].

Results

Table 1 gives the experimental data obtained. For the sake of consistency, all the discussion will be carried out employing data obtained in this laboratory. Some of the data previously reported have been included in Table 1 in order to estimate the reliability of our results.

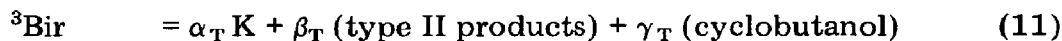
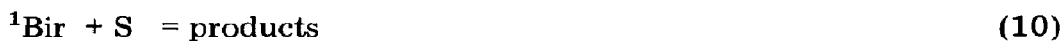
Discussion

From the data shown in Table 1 it can be concluded that the results obtained in n-hexane, cyclohexane, cyclohexene and benzene conform to a simple pattern. The results obtained in these solvents approach similar values when the reactivity of the excited states increases (*i.e.* when a tertiary γ hydrogen is present). These results suggest that the solvent is behaving as a quencher of the excited states. The results obtained in chloroform are included as an example of a solvent showing a completely different behaviour. For this solvent there is no relationship between the decrease in Φ_{II} and the reactivity of the excited state. These results will be discussed elsewhere.

The results obtained can be interpreted quantitatively by the following treatment. The reaction scheme for the photolysis of a ketone (K) in a solvent (S) must consider the following reactions:



and the secondary reactions of the biradicals (Bir) produced:



In this scheme, all the rate constants and the α , β , and γ values could depend upon the solvent S.

Dependence of ${}^1\text{Biradical}$ behaviour upon the solvent

If we assume that owing to the relatively short lifetime of the singlet biradical, this species is not trapped by the solvent (*i.e.* $\nu_{10} \ll \nu_9$), the proposed reaction scheme leads to:

$$\beta_S = (1/\epsilon)\Phi_{II}^S/(1 - \Phi_T) \quad (13)$$

where ϵ is defined by:

$$\epsilon = \Phi_{1\text{Bir}}/(1 - \Phi_T) = k_2/(k_2 + k_3 S + k_4 S) \quad (14)$$

TABLE 2

Dependence of the biradical behaviour on the solvent

Ketone	Solvent	β_S	β_T
heptan-2-one	n-hexane		0.39
	cyclohexane		0.35
	cyclohexene		0.35
	benzene		0.39
5-methylhexan-2-one	n-hexane	0.12	0.37
	cyclohexane	0.12	0.37
	cyclohexene	0.12	0.34
	benzene	0.12	0.37

The factor ϵ would tend to one when k_2 increases. If we assume that for 5-methylhexan-2-one, owing to the high value of k_2 , $\epsilon = 1$, we obtain the values of β_S given in Table 2. We can conclude then that the behaviour of the singlet biradical is independent of the solvent. This result is in agreement with the low sensitivity of ratios of rate constants for free radical reactions to the solvent employed [9]. Furthermore, it must be pointed out that if the internal conversion from the excited singlet is important [10], our results imply that its contribution must be independent of the solvent.

Interaction of the excited singlet with the solvent

Borrell and Holmes suggested that, when employing cyclohexane and benzene as solvent, the reactions of the excited singlet could be solvent dependent [1]. Since we can assume that $\epsilon = 1$ in n-hexane, eqn. (13) allows the estimation of β_S for any ketone in this solvent. Furthermore, since we have shown that β_S does not change with the solvent, the value of ϵ in a given solvent S can be obtained employing eqn. (15):

$$\epsilon_S = (\Phi_{II}^S)_S / [(1 - \Phi_T)_S \times (\beta_S)_{\text{hex.}}] \quad (15)$$

The values of ϵ_S thus obtained are given in Table 3. The data given in this Table show that benzene and cyclohexane can be considered as inert solvents towards the excited singlet. On the other hand, cyclohexene is able to partly quench long lived excited singlets.

The value of (k_2/k_5) can be obtained employing eqn. (16):

$$(k_2/k_5) = \epsilon(1 - \Phi_T)/\Phi_T \quad (16)$$

If we assume that $\epsilon = 1$, and that β_S is independent of the solvent, values of (k_2/k_5) can also be obtained employing eqn. (17):

$$(k_2/k_5)_S = (\Phi_{II}^S)_S / [(\beta_S)_{\text{hex.}} - (\Phi_{II}^S)_S] \quad (17)$$

Data obtained employing these equations are shown in Table 4. We can conclude from this Table that, for the four solvents considered, (k_2/k_5)

TABLE 3
Values of ϵ_S

Solvent	4-methylpentan-2-one	heptan-2-one	5-methylheptan-3-one
cyclohexane ^a	1.07	1.0	1.0
cyclohexene	0.5	0.95	1.0
benzene	1.1	0.98	0.95

^a Obtained assuming that $(\Phi_T)_{\text{cyclohexane}} = (\Phi_T)_{\text{hexane}}$.

TABLE 4
Values of (k_2/k_5)

Solvent	MP	2-H	M-H	M-Hex
n-hexane	0.28	2.2	2.8	6.0
cyclohexene	0.27	2.2	2.4	6.0
benzene	0.23	2.3	2.4	6.0
cyclohexane ^a	0.27	2.0		6.0

^a Values in cyclohexane obtained employing eqn. (17). MP = 4-methylpentan-2-one; 2-H = heptan-2-one; M-H = 5-methylheptan-3-one; M-Hex = 5-methylhexan-2-one.

can be considered as solvent independent. Since all the data available suggest that the intersystem crossing rate is largely solvent independent [11], this result indicates that k_2 can also be considered as nearly solvent independent.

For 4-methylpentan-2-one in cyclohexene we have obtained (see Table 3) that:

$$k_2 \approx (k_3 + k_4)S$$

By introducing in this relationship the value of k_2 determined in n-hexane solution [12], we obtain that:

$$(k_3 S + k_4 S)_{\text{cyclohexene}} \approx 1.1 \times 10^8 \text{ s}^{-1}$$

For the other solvents employed, we can conclude that the pseudo first-order interaction of the solvent with the excited singlet (measured by $(k_3 S + k_4 S)$) must be less than $0.2 \times 10^8 \text{ s}^{-1}$.

Triplet reactions

Since we have measured the $(k_Q \tau_T)$ values we can employ a different approach to determine the influence of the solvent. The lifetime of a given triplet in a given solvent S will be given by:

$$\tau_T = 1/(k_S + k_6) \quad (18)$$

where k_S , defined by:

$$k_S = k_7 S + k_8 S \quad (19)$$

is the pseudo unimolecular quenching of the triplet. If it is assumed that activated complex theory can be applied to reaction (6) [12, 13], the value of k_6 will be given by:

$$(k_6)_S = (k_6)_{\text{gas}} (\gamma_{3K})_S / (\gamma_{\ddagger})_S \quad (20)$$

where $(k_6)_{\text{gas}}$ is the gas phase rate constant; and $(\gamma_{3K})_S$ and $(\gamma_{\ddagger})_S$ are the activity coefficients of the triplet and activated complex in the solvent considered.

If we compare the values of k_6 in two solvents S_1 and S_2 , we obtain:

$$(k_6)_{S_1} = (k_6)_{S_2} \times [(\gamma_{\ddagger})_{S_1} / (\gamma_{\ddagger})_{S_2}] \times [(\gamma_{3K})_{S_2} / (\gamma_{3K})_{S_1}] \quad (21)$$

which, if S_2 is taken as a reference solvent, can be rewritten:

$$(k_6)_S = k_6 (\gamma_{3K}) / \gamma_{\ddagger} = f \times k_6 \quad (22)$$

where k_6 is the specific rate constant in the reference solvent, and (γ_{3K}) and γ_{\ddagger} are the activity coefficients of 3K and the activated complex in a scale which employs the infinitely diluted solution in the reference solvent as reference state.

The value of f measures the change in free energy of activation with the solvent and, in a first approximation, can be considered as being determined by the type of reaction involved and independent of the ketone employed.

For the ketones employed in the present work, we have that in n-hexane solution:

$$k_6 \gg k_S$$

In this solvent we can consider then that:

$$1/(\tau_T)_{\text{hex}} = (k_6)_{\text{hex}} \quad (23)$$

Furthermore, since the energy of the excited triplet is rather insensitive to β or γ substitution, the value of k_6 will be determined almost exclusively by the solvent and can be considered independent of the ketone. We then have that, for a given ketone in a given solvent:

$$1/(\tau_T)_S = (f/(\tau_T)_{\text{hex}}) + k_S \quad (24)$$

where f is measured relative to the n-hexane solution. In this equation, f and k_S are considered to be determined exclusively by the solvent. Measurement of $(\tau_T)_S$ and $(\tau_T)_{\text{hex}}$ for two ketones will then allow the evaluation of f and k_S for a given solvent.

Since we have only measured $(k_Q \tau_T)$ values, the k_Q values have to be assumed to be capable of evaluating f and k_S from eqn. (24). A steady state treatment of the quenching reaction leads to:

$$(1/k_Q) = (1/k_{\text{diff}}) + \delta \quad (25)$$

where k_{diff} is the rate constant for the diffusion process, and δ is related to the rate of quenching between molecules that are nearest neighbours and to the equilibrium concentration of excited molecule quencher pairs.

As a first approximation we can consider that δ is independent of the solvent. With this assumption and taking:

$$(k_Q)_{\text{hexane}} = 10^{10} M^{-1} s^{-1}$$

and the k_{diff} values given by eqn. (26) [14]:

$$k_{diff} = 8RT/2000 \quad (26)$$

we can obtain a set of k_Q values for the solvents employed. With these values and the data reported in Table 1 for 4-methylpentan-2-one and 5-methylhexan-2-one, the solution of eqn. (24) gives the values of f and k_S shown in Table 5.

The values of f are close to one, showing that the intramolecular hydrogen abstraction is not significantly affected by the solvent. We can conclude then that the reactivity of both singlet and triplet excited states is the same in all the solvents considered in the present work.

The values obtained for k_S can provide values of the bimolecular quenching rate constant since:

$$k_{bim} = k_S/S \quad (27)$$

where S is the solvent concentration. The values so obtained have been included in Table 5. For benzene and cyclohexene these values are higher than those reported for the same quenchers in diluted solution (see Table 5). This difference can explain the upward curvature of the Volmer plot reported for the quenching of pentan-2-one triplets at high benzene concentration [4].

Dependence of ³Biradical reaction upon the solvent

The proposed reaction scheme leads to:

$$(\beta_T)_S = (\Phi_{II}^T)_S [1 + k_S(\tau_T)_{\text{hex}}/f]/(\Phi_T)_S \quad (28)$$

if reaction (12) is disregarded. The data obtained for 5-methylhexan-2-one and heptan-2-one are particularly suited to estimate the influence of the solvent upon β_T owing to the small contribution of the quenching by the solvent. The values of β_T obtained are shown in Table 2. We can conclude from these data that the β_T values can also be considered independent of the solvent. Furthermore, the constancy of the β_T values obtained applying eqn. (28) supports the assumption that reaction (12) can be disregarded.

The change of (Φ_{II}^T) with the solvent shown in Table 1 must then be related to the importance of reactions (7) and (8). This is supported by the data obtained which show that: (i) for a given ketone, Φ_{II}^T follows the order: n-hexane > cyclohexane > benzene > cyclohexene, as expected from the relative values of k_S in these solvents; (ii) for a given solvent, the

TABLE 5

Experimental values of f and k_S

Solvent	f	k_S/s^{-1}	$k_{\text{bim}}^a/M^{-1} s^{-1}$	$k_{\text{bim}}^b/M^{-1} s^{-1}$
cyclohexane	0.86	4×10^6	4.4×10^5	3.4×10^{5c}
cyclohexene	0.8	2×10^8	2×10^7	0.9×10^{7c} 0.8×10^{7d}
benzene	0.85	7×10^7	6.3×10^6	1.7×10^{6c} 2.0×10^{6e}

^a $k_{\text{bim}} = k_S/S$.^b $k_{\text{bim}} = (k_7 + k_8)$ in diluted solution.^c Ref. [15] quenching of acetone triplets in acetonitrile solution.^d Ref. [16] quenching of 4-methylpentan-2-one triplets in n-hexane solution.^e Ref. [4] pentan-2-one triplets in n-hexane solution.

value of $(\Phi_{\text{II}}^T)_S / (\Phi_{\text{II}}^T)_{\text{hex}}$ increases when the reactivity of the hydrogen increases. We can see that when the γ hydrogen is tertiary, the only solvent that diminishes (Φ_{II}^T) appreciably is cyclohexene (the one having the higher k_S value).

Change in ketone consumption with solvent

Most of Borrell and Holmes interpretation of the experimental data relies on the change in quantum yield of ketone consumption (Φ_{-K}) with solvent. Even with the simplified mechanism proposed in the present work the expression for the parent ketone consumption is complex and will be given by:

$$\Phi_{-K} = [k_4 + k_2(1 - \alpha_S)]\tau_S + [k_8 + k_6(1 - \alpha_T)]\Phi_T\tau_T \quad (29)$$

The following qualitative considerations can be derived from this equation:

- (1) benzene, although quenching 3K , decreases Φ_{-K} owing to the fact that $k_7 \gg k_8$ for this solvent [17];
- (2) cyclohexene is an efficient quencher (k_S is high) but, since it is a mixed quencher ($k_7 \approx k_8$ [15]), Φ_{-K} remains relatively low;
- (3) cyclohexane is a rather poor quencher but, since $k_7 \ll k_8$ [15], Φ_{-K} increases when cyclohexane is added [1].

In conclusion we consider that: (i) the behaviour of the singlet and triplet biradicals is not appreciably modified by the solvents considered in the present work; (ii) it is possible to differentiate the effect of the solvent from its behaviour as a quencher by considering two ketones of widely different mean life; (iii) cyclohexane and benzene do not react with the excited singlet. Cyclohexene is able to partly quench long-lived singlets (*i.e.* that of 4-methylpentan-2-one) with a pseudo first-order rate constant of approximately $1.1 \times 10^8 s^{-1}$; (iv) cyclohexane, cyclohexene and benzene quench excited triplets with pseudo first-order rate constants of 7×10^6 , 1.6×10^8 , and $4.6 \times 10^7 s^{-1}$ respectively; and (v) for the hydrocarbon solvents employed, the "solvent effect" is negligible either for the singlet or triplet state.

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