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Short Communication

On the role of solvent and quencher in the type II photoelimination reactions from pentan-2-one and other ketones

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Quantum yields for the formation of acetone and removal of ketone are reported for pentanone in several solvents. Added cyclohexene quenches the reaction but the yields differ from those obtained with piperylene. It is suggested that the quencher not only affects the triplet state but has a "solvent effect" on the singlet reactions and that this can lead to difficulty in interpreting simple quenching results.

The low quantum yields and different behaviour in benzene are attributed to the reversible formation of an adduct.

Similar results are reported for 4-methylpentan-2-one and quantum yields have been measured for several other ketones.

Introduction

In the extensive studies[1–3] of type II elimination reactions in ketones, measurements of triplet yields have relied upon the quenching of the reaction by added dienes and olefins[4–8]. In a previous paper[9] we suggested that, with benzene as a solvent, the addition of cyclohexene did not cause simple quenching of the reaction; although the type II yield was diminished, the rate of consumption of the ketone increased with concentration of the olefin. We made use of this effect to measure the apparent proportion of radiationless decay in the compound.

The present paper reports attempts to extend the method to other solvents, particularly cyclohexane. There is a marked difference between the photochemical behaviour in benzene and that in cyclohexane, which indicates the incorrectness of our original interpretation. Comparison of the quenching results with those from piperylene, penta-1,3-diene, indicates the dual role of an added olefin as both solvent and quencher. It is clear that results obtained from measurements of simple quenching can only give, at best, a rough indication of the proportions of reaction which are singlet and triplet.

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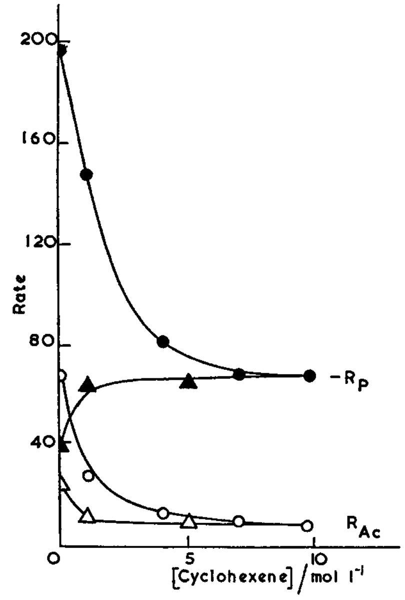
Experimental

The experiments were performed with our semi-micro method[10], in which a small sample of solution is photolyzed in a water-jacketed quartz cell stirred with a stream of nitrogen. In each run, between 5 and 10 aliquots were taken, to ensure a good estimate of the rate; they were analyzed by vapour phase chromatography. The light source was an Osram HBO 500 W high pressure mercury arc fitted with filters of potassium chromate solution (0.2 g/l, 1 cm) and Chance OX7 glass (2 mm), to pass the 313 nm line.

The quantum yields were measured with respect to a potassium ferrioxalate actinometer[11]. Pentan-2-one and octan-2-one were purified by distillation; cyclohexene was washed with $FeSO_4$ to remove peroxides, distilled and kept under N_2.

Results

Figure 1 shows the results for the decomposition of pentanone in cyclohexane and benzene. The rates are shown as a function of added cyclohexene concentration, the last point being that for pure cyclohexene. The effect in benzene



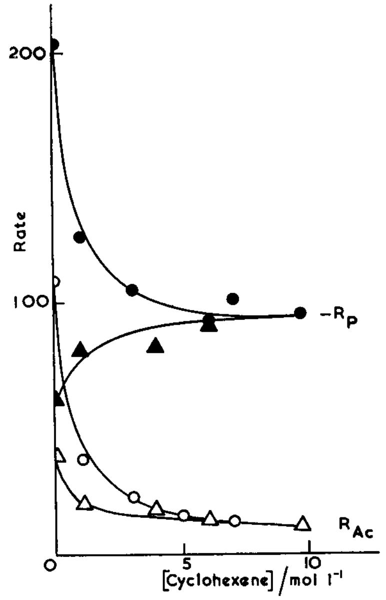


Fig. 1. Photolysis of pentan-2-one; variation of rates of formation of acetone, R_{Ac}, and consumption of ketone, R_{-p}, for solutions (0.1 mol/l) in benzene (△, ▲) and cyclohexane (○, ●), with added cyclohexene.

Fig. 2. Photolysis of 4-methyl pentan-2-one; variation of rates of formation of acetone, R_{Ac}, and consumption of ketone, R_{-p}, for solutions (0.1 mol/l) in benzene (△, ▲) and cyclohexane (○, ●), with added cyclohexene.

is as reported previously[9]; although the rate of acetone formation is diminished there is an increase in the rate of consumption of pentanone. The results in cyclohexane are in marked contrast; the rate of consumption in cyclohexane is greater and it too is diminished by cyclohexene.

Similar effects are observed with 4-methylpentan-2-one, the results for which are shown in Fig. 2.

Table 1 gives the measured quantum yields for the formation of acetone from pentanone, Φ_{Ac}, and for the removal of the ketone, Φ_{-p}. The results of several other workers are also given. Those of Yang and Feit[5] were taken from Wagner and Hammond[4], corrected for a remeasured quantum yield. There is a discrepancy between the results of Barltrop and Coyle[7], for benzene and t-butanol, and ours. As Fig. 1 shows, our results for benzene and cyclohexane are consistent with each other; if we took their value for benzene the value for cyclohexane would be well above unity; as is indicated below the difference in behaviour between benzene and the aliphatic hydrocarbons is similar to that found for benzophenone. These factors lead us to prefer our values.

Figure 3 shows the effect on the quantum yield of diluting pure pentan-2-one with cyclohexane, a comparatively "inert" solvent.

Table 2 gives the values of the quantum yield of acetone formation for several pure ketones.

TABLE 1

QUANTUM YIELDS FOR THE FORMATION OF ACETONE, Φ_{Ac}, AND REMOVAL OF KETONE, Φ_{Ac-p}, IN THE PHOTOLYSIS OF PENTAN-2-ONE IN VARIOUS SOLVENTS AND QUENCHERS

Solvent (concentration, mol/l)	Φ_{-p}	Φ_{Ac}	Φ_{Ac}/Φ_{-p}	Reference
None		0.25		*
iso-octane (0.1)		0.226		*
cyclohexane (0.1)	0.297	0.104	0.35	*
hexane (0.2)	0.44	0.30	0.68	4
hexane (0.2)†	0.27	0.18	0.67	5
n-butanol (0.1)	—	0.155	—	*
t-butanol (0.1)	—	0.29	—	*
t-butanol (0.15–5)	0.85	—	—	7
benzene (0.1)	0.049	0.03	0.6	*
benzene (0.15–5)	0.43	—	—	7
cyclohexene (0.1)	0.10	0.013	0.13	*
piperylene (0.1)**	0.05	—	—	7
piperylene (0.2)	0.05	0.04	0.8	4
piperylene (0.2)†	0.032	0.02	0.6	5

* This work.

† Values corrected by Yang and Feit[5] from those of ref. 4.

** Piperylene was 5*M* solution in t-butanol.

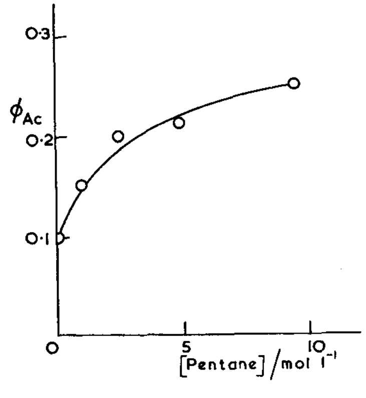


Fig. 3. Photolysis of pentan-2-one; variation of Φ_{Ac} for solutions of ketone in cyclohexane.

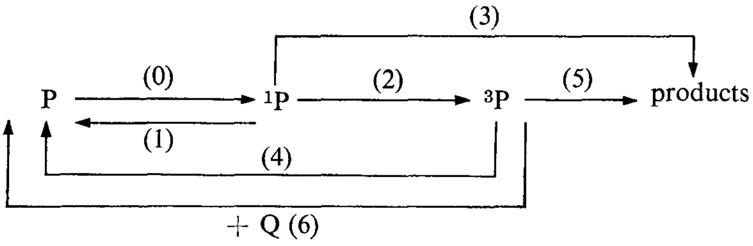
TABLE 2

VALUES FOR THE QUANTUM YIELD OF FORMATION OF ACETONE FROM VARIOUS KETONES

	Φ
Pentan-2-one	0.25
Hexan-2-one	0.08
4-Methylpentan-2-one	0.24
Heptan-2-one	0.16
Octan-2-one	0.19

Discussion

The results in Fig. 1 for the solvent cyclohexane show that cyclohexene quenches the reaction. A simple mechanism for the photolysis is:



where P, ^{1}P and ^{3}P represent the ground, excited singlet and triplet states of pentanone and Q represents the quencher molecule. Reactions (3) and (5) may be divided into type I, type II and photocyclization reactions:

$$^1\mathrm{P} \text{ or } ^3\mathrm{P} \rightarrow \mathrm{CH_3CO + C_3H_7} \qquad (7)$$

$$\rightarrow \mathrm{C_2H_4 + CH_3C(OH)CH_2} \qquad (8)$$

$$\rightarrow \mathrm{\overline{CH_2CH_2CH_2CH_2C}HOH} \qquad (9)$$

Both cyclohexene and piperylene[4,5] can apparently act as triplet quenchers, providing a parallel path (6) to reaction (4) and eliminating reaction (5) at high concentrations. They are, however, of different efficiency. Wagner and Hammond[4] found that $k_6/(k_4 + k_5)$ for piperylene was ~ 40 l/mol. If the points in Fig. 1 are linearized by plotting $(R - R(\infty))^{-1}$ *versus* [cyclohexene] where $R(\infty)$ is the rate in the pure quencher, the value of $k_6/(k_4 + k_5)$ is found to be ~ 10 l/mol from both the R(acetone) and R(−ketone) curves. A similar difference was found by Dougherty[5] in comparing the efficiencies of dichloroethylene and piperylene as quenchers for octanone. The mechanism suggests that the limiting singlet yields at high quencher concentration should be the same and, as Table 1 shows, this is not so. Neither the quantum yields nor the ratio of type II to total reaction $(\Phi_{\mathrm{Ac}}/\Phi_{-p})$ agree, and it is necessary to invoke additional effects to account for the behaviour.

A striking point about the quantum yields is the variation, from solvent to solvent of Φ_{-p} and $(\Phi_{\mathrm{Ac}}/\Phi_{-p})$. Barltrop and Coyle[7] correlated the variation with solvent polarity but this could not account for differences between aliphatic hydrocarbons. Figure 3 also shows the effect of an "inert" solvent when used to dilute pentanone. The quantum yield is reduced.

The effect of solvents on the spectra of compounds is well known and implies an intimate association of the solvent with the molecule. It is not unreasonable then that the solvent should also affect the intersystem crossing and radiationless decay rates as well as the division into different reaction channels. At high quencher concentrations the quencher will behave not only as a quencher but also as a solvent, and so the observed yields at high quencher concentration are characteristic of the molecule dissolved in the quencher, and not necessarily indicative of the yields for the molecule in the original solvent. Since it has also been shown by Wettack *et al.*[8] that piperylene can act as a quencher for the singlet state, it seems that triplet yields and so on which are determined by quenching methods in solution can only give, at best, a rough value for the proportions when quenching does not occur.

From Fig. 1 and Table 1 it is evident that benzene is a special case and is a quencher rather than a solvent in this reaction. The quantum yields are low and the yield increases as cyclohexene is added. In view of the results with cyclohexane as a solvent, our previous suggestion[9] that the triplet ketone reacts with cyclohexene, as happens with acetone[12], cannot be correct. The quantum yield for the photoreduction of benzophenone is also considerably reduced in benzene solution[13] and it has been suggested[14–16] that the triplet molecule forms an adduct with the solvent which can decompose into the original molecules. Thus a path, parallel to reaction (4), is provided which nearly quenches the almost wholly triplet reaction. If a similar reaction occurs here, the yield in benzene should indicate the extent of the singlet state reaction, but Fig. 1 shows that this cannot be simply correlated with the results in cyclohexane since again, we suggest, there is the problem of change of singlet reaction with change of solvent.

In this discussion the effect of cyclohexene on the yields has been interpreted as if it acts as a simple quencher, despite the probable unfavourable discrepancy between the triplet energies of the ketone and olefin. It may be that it quenches the reaction by intermediate compound formation, as suggested for benzene, above, but a reaction rather than a transfer would not alter the conclusions drawn on the determination of triplet yields.

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