

A COMPARISON BETWEEN GAS AND LIQUID PHASE PHOTOCHEMISTRY OF 2-PENTANONE

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Summary

The triplet lifetime of 2-pentanone has been measured in the gas phase and in n-hexane solution at very low conversion. The values obtained, 6×10^{-7} s and 2.5×10^{-7} s respectively, are much longer than the presently accepted values. From the triplet quantum yields and an analysis of the photo-products arising from the singlet and triplet state it is concluded that the triplet 1,4-biradical behaves similarly in both phases. On the other hand, the singlet photoreactions are significantly different.

The effect of total pressure in the photodecomposition quantum yield has been measured. It is concluded that all the "hot" photodecomposition arises from the singlet state.

Introduction

There exist conflicting data for the lifetime of the triplet of 2-pentanone in solution [1]. Most of the reported differences can be attributed to different experimental conditions (*i. e.* solvent, conversion, 2-pentanone concentration) although the influence of these factors has not been completely elucidated [2]. The only data reported for the lifetime of the triplet state in the gas phase were obtained without keeping the total pressure constant [2, 3], and they are based on an assumed unity efficiency for the triplet quenching reaction. Since this is an unlikely assumption [4, 5], we have redetermined the triplet lifetime.

The reported triplet quantum yields are completely different for the two phases. Reported values are 0.25 (benzene solution [6]), 0.63 (n-hexane [7]), 0.81 (benzene [8]) and 0.16 (48 °C, gas phase [9]). Similar discrepancies are found regarding the fraction of type II reaction arising from the singlet state [1, 6, 9]. We have re-investigated the gas phase photolysis in order to determine if the low triplet yield and increased singlet photodecomposition found in the gas phase are a consequence of incomplete deactivation of the vibrationally hot molecules.

Experimental

The experimental conditions employed in the gas phase studies have been reported elsewhere [10].

Runs in the liquid phase were carried out in a "merry-go-round" with absorbed light in the 3130 Å region.

2-Pentanone (Chem. Service or B. D. H.) was employed after distillation. No impurities could be detected by gas-liquid chromatography.

Several benzene samples were employed: Hopkin and Williams (pure), Merck (for molecular weight determinations), Merck (spectroscopic), Merck (spectroscopic, photobrominated and distilled) and B. D. H. (Analar). No differences could be detected among them.

Results and Discussion

The photolysis of 2-pentanone in the presence of a triplet quencher, Q, can be interpreted in terms of the following mechanism [10]:



where for simplicity "concerted" reactions are not included. They are considered as arising from the biradical prior to its geometrical equilibrium. This assumption is indistinguishable from a true concerted reaction. The type I reactions have also been neglected [3, 7, 11]. Neither assumption would modify significantly the following discussion.

Decomposition from ${}^1A^$*

The question of the competitiveness between fluorescence and type II photodecomposition has not been totally solved [12]. In Fig. 1 we show

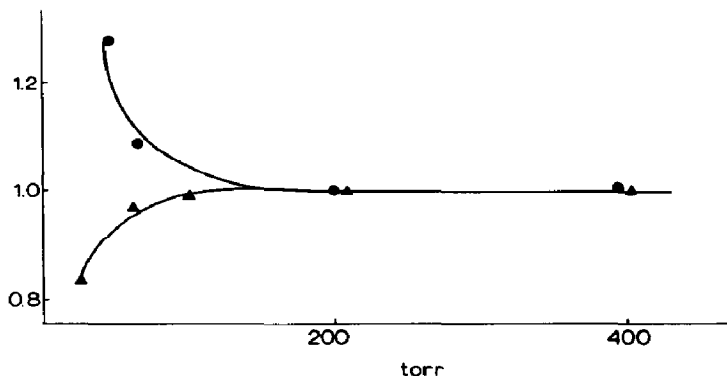
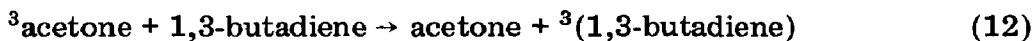


Fig. 1. Effect of total pressure upon the ethylene quantum yield at total thermal triplet quenching. ●, $\Phi_{C_2H_4}/(\Phi_{C_2H_4})_{P_\infty}$: 2-pentanone pressure, 20 Torr; 1,3-butadiene pressure, 38 Torr; butane added, room temperature, 3130 Å. ▲, $I_F/(I_F)_\infty$ (from ref. 12): 2-pentanone pressure, 25 Torr; butane added, 25 °C, 3130 Å.

values of $\Phi_{C_2H_4}/(\Phi_{C_2H_4})_\infty$ obtained for total triplet quenching and at different total pressures. The similarity between these data and those reported previously for the change in fluorescence quantum yield with total pressure [12] (also shown in Fig. 1), strongly suggest that even at 3130 Å there is decomposition from high vibronic levels of the singlet manifold and that, at the pressures studied, there is no evidence of "hot" triplet decomposition [13 - 15]. It has to be stated that the effect shown in Fig. 1 cannot be related to a change in the singlet biradical behaviour with total pressure since it has been shown that Φ_{II} does not depend upon total pressure [16].

Gas phase triplet lifetime

The data shown in Fig. 1 indicate that at the pressures used by Wettack and Noyes [3], there is a change in Φ_T (the triplet quantum yield) with pressure due to the thermalization of the hot singlet. The data given in Fig. 3 of their work show then the effect of 1,3-butadiene on both $^1A^*$ and 3A . In order to obtain meaningful values of $k_{11}\tau_T$, all the data have to be obtained at constant total pressure. Results obtained under these conditions are shown in our Fig. 2. If we assume that k_{11} is similar to the rate constant for reaction (12) [4],



we obtain $\tau_T = 6 \times 10^{-7}$ s.

This lifetime is an order of magnitude longer than those reported in solution [1], but is similar to that suggested by the data of Fig. 1 and Table 1 of Michael and Noyes [17]. Furthermore, the value obtained implies that the triplet lifetime of 2-pentanone lies between those of 3-pentanone and methyl butanone [14]. This is in agreement with qualitative data reported by Ausloos and Rebbert [18].

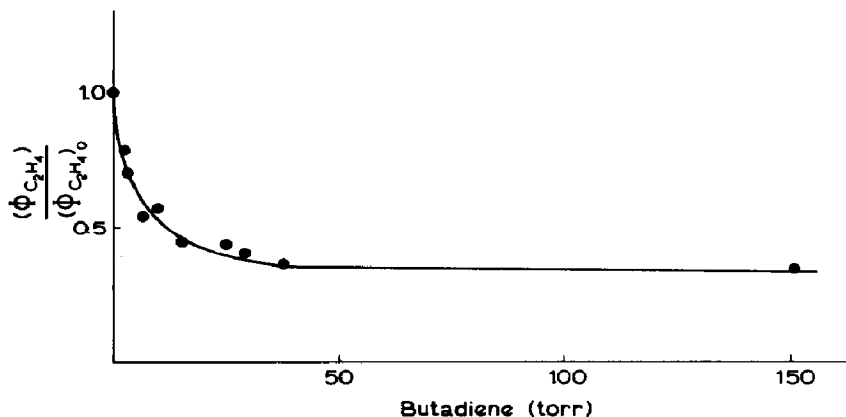


Fig. 2. Effect of 1,3-butadiene upon the ethylene quantum yield. 2-pentanone pressure, 20 Torr; temperature, 26 °C; total pressure, 200 Torr; 3130 Å.

The difference between the triplet lifetimes reported in solution and in the gas can be due to a pressure dependence of reaction (10) [13, 14], experimental errors, or to a real phase dependence. We have carried out some measurements which show that the triplet lifetime is not pressure dependent under the conditions employed. The proposed mechanism indicates that, at pressures higher than 100 Torr and at constant 1,3-butadiene pressure:

$$\Phi_{C_2H_4} = a + b/\tau_T \quad (13)$$

where the parameters a and b are independent of total pressure. Results obtained with 6.5 Torr of 1,3-butadiene and total pressures ranging from 100 to 500 Torr show that $\Phi_{C_2H_4}$, and hence τ_T , is not pressure dependent.

Triplet lifetime in *n*-hexane solution

It has been shown that the value of τ_T obtained in solution is sensitive to the extent of conversion [2]. The source of this dependence, as well as the conditions which have to be employed to obtain meaningful results, have not been fully determined. We found that "extent of conversion" is not the main parameter to be considered and that the results seem to be dependent mainly on the reaction time and absorbed light intensity. Typical results obtained are shown in Fig. 3. They show that there are probably two sources of error which tend to give low values of $\Phi_{Acetone}^0 / \Phi_{Acetone}$ at high conversion: product accumulation (downward curvature in the photolysis of 2-pentanone alone) and quencher consumption (upward curvature in the photolysis of 2-pentanone/1,3-pentadiene mixtures). The first effect has been previously reported by Ausloos and Rebert [16]. The consumption of 1,3-pentadiene was confirmed by measuring its concentration after the photolysis. The value of $k_Q \tau_T$ obtained from data extrapolated to zero conversion is shown in Table 1 together with the most reliable data previously reported. The value of τ_T obtained is nearly an order of magnitude longer than that reported by Wettack [2], showing the great importance of working at extremely low conversion.

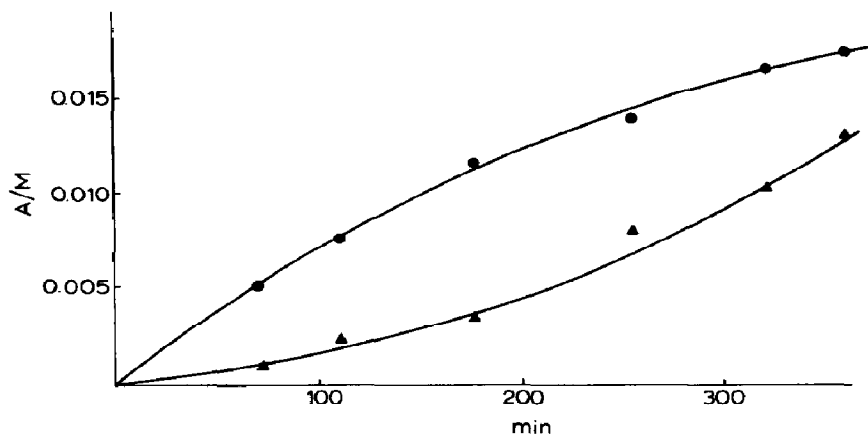


Fig. 3. Acetone production in the photolysis of 2-pentanone. Solvent, n-hexane; temperature, 20 °C. 2-Pentanone concentration, 0.115 M; ●, 2-pentanone alone; ▲, 2-pentanone and 0.00345 M 1,3-pentadiene.

TABLE 1

Experimental data for 2-pentanone

Solvent	$k_Q\tau_T^a$	$(\Phi_{II})_{\text{singlet}}/\Phi_{II}$	Φ_T	τ_T	Ref.
n-hexane	-	0.09	0.63		7
n-hexane	2500	0.1	-	2.5×10^{-7}	this work
n-heptane	380	0.2	-	4×10^{-8}	2
benzene	390	-	0.81	8×10^{-8}	8
benzene	44	0.14	-	0.9×10^{-8}	20
benzene		0.35	-		this work
gas phase	5000	0.37	0.55	6×10^{-7}	this work

^a1,3-Diolefins as quencher.

Triplet lifetime in benzene solution

The results reported previously in benzene solution show significant differences (see Table 1). In this case, besides the factors discussed in the previous section, solvent impurities can be an extra source of error. The most reliable result is probably that reported by Wagner [8] since it gives the longer lifetime and although the experimental conditions have not been reported, the method employed implies very low conversions.

If we compare the behaviour of 2-pentanone in n-hexane and in benzene solution, we can see from Table 1 that: (a) $(\tau_T)_{\text{benzene}} < (\tau_T)_{\text{n-hexane}}$; and (b) $(\Phi_{II})_S/\Phi_{II}$ is higher in benzene than in n-hexane.

Furthermore, we find that the higher value of $(\Phi_{II})_S/\Phi_{II}$ obtained in benzene is due almost exclusively to a reduction in $(\Phi_{II})_T$. All these results are compatible with some triplet quenching by the benzene. (The fact that we could not detect any differences between different benzenes, even after photobromination, would argue against the presence of reactive impurities.)

The rate of benzene quenching of 2-pentanone triplets was evaluated by measuring the effect of added benzene upon Φ_{II} in n-hexane. At benzene concentrations lower than 1 M a normal Volmer's plot was obtained with $k_Q \tau_T = 0.55$. This value gives, for reaction (14) in n-hexane solution, $k_{14} = 2.2 \times 10^6 M^{-1} s^{-1}$.



For acetone, and by a completely different method, it has been reported [19 b] that $k_Q = 1.7 \times 10^6 M^{-1} s^{-1}$. The similarity between these two values lends support to the occurrence of reaction (14). We can conclude then that the photochemical behaviour of 2-pentanone in benzene solution is influenced by a reaction between the triplet and the solvent and that the results obtained under these conditions cannot be employed directly to obtain information on the rate of internal abstraction. This effect will be less important with ketones of shorter triplet lifetimes and could explain the small difference obtained by Barltrop and Coyle for the triplet lifetimes of 2-pentanone and 2-octanone in benzene solution [20].

Comparison between gas phase and solution photochemistry

The triplet lifetime obtained in n-hexane solution is nearly three times shorter than the gas phase value. This difference can not be completely due to photoreaction with the solvent [7], since the results of Wagner and Hammond indicate that 2-pentanone consumption is similar to the amount of acetone and cyclobutanol produced [21]. Furthermore, for acetone in n-hexane solution the triplet lifetime is nearly 10^{-6} s [19b, 22].

The ethylene quantum yield in the gas phase is nearly 0.3 and almost independent of total pressure [2, 4], wavelength and temperature [3, 11, 16]. This value is similar to that obtained in inert solvents [1], showing that Φ_{II} is not very sensitive to the experimental conditions. Nevertheless, there are striking differences between the proportion of type II reaction arising from the singlet state in both phases. At 3130 Å in the gas phase it has been reported that 0.4 of the type II reaction arises from the singlet state [3]. Our data shown in Fig. 2 indicate that this value depends upon the total pressure and that, at high pressures, it reaches a value of 0.37. The data reported in solution are more conflicting. Reported values range from 0.09 [7], to 0.24 [6]. Furthermore, a re-interpretation of previous data favours a value as high as 0.3 [23]. Our data, obtained at very low conversion and under conditions where singlet quenching can be completely disregarded, show conclusively that, at least in n-hexane, the low value is correct and that the differences are outside the experimental error. The reduced value of $(\Phi_{II})_S / \Phi_{II}$ obtained in solution can be due to a higher value of Φ_T , to a different biradical behaviour in both phases or to a different degree of "concerted" reaction. The most reliable data for the triplet quantum yield in solution are given in Table 1. The value of $\Phi_T = 0.25$ reported in benzene solution [6] can be an underestimate since it is based on the assumption that only chem-

TABLE 2

Biradical behaviour

	Triplet biradical			Singlet biradical		
	Solution		Gas	Solution		Gas
	a	b		a	b	
α	0.37	0.51	0.48	0.91	0.81	0.70
β	0.44	0.34	0.34	0.06	0.13	0.26
γ	0.19	0.15	0.18	0.02	0.04	0.04 ^c

^a Assuming $\Phi_T = 0.63$.

^b Assuming $\Phi_T = 0.81$.

^c From data of ref. 16.

ical quenching takes place between 2-pentanone triplets and cyclohexene [19b]. Furthermore, the value of 0.16 reported for the gas phase triplet quantum yield is based on the opposite assumption (that only electronic energy transfer takes place between 2-pentanone triplets and *cis*-2-butene) and can also be an underestimate [9]. We have measured Φ_T from the sensitized biacetyl emission at pressures between 4 and 5 Torr and total pressure higher than 100 Torr. We obtain $\Phi_T = 0.55$. Under these conditions, the 2-pentanone triplets can be considered as completely quenched [17], without significant singlet quenching [18]. The value obtained is not too far from that reported in n-hexane and shows that the increase in $(\Phi_{II})_S$ obtained in the gas phase cannot be explained only in terms of a reduced triplet yield.

The biradicals must disappear by one of the following reactions:



If we define

$$\alpha = k_{15}/(k_{15} + k_{16} + k_{17})$$

$$\beta = k_{16}/(k_{15} + k_{16} + k_{17})$$

$$\gamma = k_{17}/(k_{15} + k_{16} + k_{17})$$

we obtain the values shown in Table 2. It can be seen that for the triplet biradical, where a "concerted" reaction can be disregarded [1, 24], and the radical lifetime is long enough to assure statistical geometrical configuration, the reactivity pattern is strongly similar in both phases. This is in agreement with the small sensitivity of related unimolecular free radical reactions to phase changes. On the other hand, noticeable differences exist between the behaviour of singlet and triplet biradicals and that of the singlet biradical in both phase. We have to conclude that: (a) the "concerted" reaction favours

the internal conversion and it is more important in solution than in the gas phase, or (b) from the singlet state some fraction of the biradical goes back to 2-pentanone before internal rotations separate the hydroxylic hydrogen from the carbon carrying the unpaired electron. This fraction is higher in solution than in the gas phase.

The second alternative is particularly interesting since the solvent could increase the time that both reaction centers remain close enough to make the back hydrogen abstraction possible.

Our main conclusions can be summarized as follows.

(1). In benzene, the triplet lifetime is reduced by solvent quenching.

(2). In the gas phase, the triplet lifetime is of the same order of magnitude as that obtained in inert solvents (*i. e.* n-hexane). The value obtained is nearly 2.5 times longer but not too much significance must be attached to this number in view of the uncertainties of the method employed (based on "assumed" rates of 2-pentanone triplets by diolefins). Both values (gas phase and n-hexane solution) are considerably longer than those presently accepted.

(3). The triplet quantum yield and the behaviour of the triplet biradical are similar in the gas phase and in n-hexane solution.

(4). The products arising from the excited singlet are different in the gas phase and n-hexane solution, the most noticeable difference being an increase of the type II reaction in the gas phase.

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