

KETONE PHOTOCHEMISTRY ON SOLID SILICA. A DIFFUSE REFLECTANCE LASER FLASH PHOTOLYSIS STUDY

Nicholas J. TURRO, Ian R. GOULD, Matthew B. ZIMMT and Chen-Chih CHENG

Chemistry Department, Columbia University, New York, NY 10027, USA

Received 15 April 1985

Using diffuse reflectance laser flash photolysis, the lifetimes of the triplet states of valerophenone and diphenylbutyrophenone adsorbed on solid silica have been determined to be 0.3 and 0.9 μs respectively. These lifetimes are at least two orders of magnitude greater than those found in homogeneous solution. Quenching of the triplet states by gas-phase oxygen and butadiene is observed.

1. Introduction

Recently the photophysics and photochemistry of several organic molecules adsorbed onto different types of solid silica surfaces have been reported [1,2]. These studies have provided information concerning the nature of the adsorbate/surface interactions [1], the effects of additives [1], and the extent to which the silica surface restricts the mobility of the transient intermediates formed in photochemical reactions [2]. Until now only emission spectroscopy or product studies have been used to characterize the influence of solid silica surfaces on photoinduced processes. We now report the direct observation of transient intermediates in the type II photoreaction of the ketones valerophenone (VAL) and diphenylbutyrophenone (DPB) on a solid silica surface using the technique of diffuse reflectance laser flash photolysis [3,4]. This technique has previously been used to observe the triplet states of naphthalene adsorbed onto an alumina surface [3], and the triplet states of various organic molecules in the microcrystalline form [4]. The results of the experiments on VAL and DPB are compared to those obtained for the relatively unreactive triplet states of acetophenone (ACP) and benzophenone (BZP). In addition we report the effect of gas phase triplet quenchers on the lifetimes of the adsorbed triplet species.

2. Experimental

Samples were prepared by adsorbing ≈ 1 mg of ketone onto 300 mg silica from pentane, followed by slow solvent removal and evacuation to 1×10^{-3} Torr. The silica used was a synthetic material which was prepared as described previously [5]. The material has a surface area of $78 \text{ m}^2 \text{ g}^{-1}$ and an average pore diameter of 255 Å as determined by BET(N_2) measurements [5]. We estimate that only $\approx 5\%$ of the surface area available to nitrogen is covered by ketone.

Steady-state photolysis was performed by irradiating the sample in a rotating evacuated quartz vessel with either a medium pressure mercury arc lamp with a 313 nm filter, or with an excimer laser at 308 nm. After photolysis the samples were extracted using methylene chloride and analysed using gas chromatography.

Transient absorption studies were performed using an apparatus which is similar to that described by Wilkinson [4] (fig. 1). A Lambda Physik excimer laser (EMG 101, 308 nm, 50 mJ, 15 ns) was used as the excitation source. The monitoring light was a 450 W xenon arc lamp with a PRA 301 power supply and a PRA 305 pulser. Monitoring light which was diffusely reflected 45° to the angle of incidence, and normal to the surface of the sample (fig. 1) was detected using an RCA 4840 photomultiplier tube. The signals were digitized using a Tektronix 7912 AD transient digitizer, and the

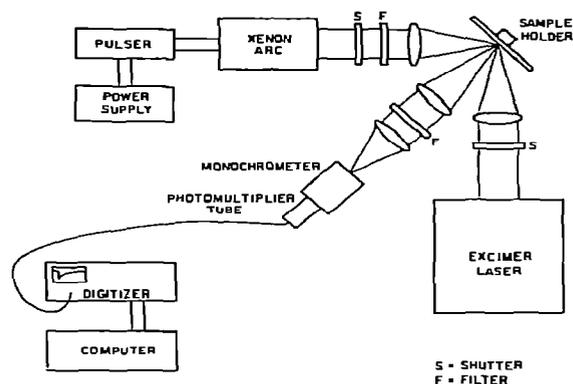


Fig. 1. Schematic diagram of apparatus used for diffuse reflectance transient absorption spectroscopy.

data analysed using a Digital PDP 11/23 computer. The samples were contained in 2 mm internal diameter suprasil cuvettes which were equipped with a side arm for vacuum degassing. The front face of the sample holder consisted of a thin brass plate with a 2 mm diameter hole so that only a small portion of the sample was irradiated at any time. The laser beam was defocused so that the sample was irradiated with a pulse of only ≈ 4 mJ. Data analysis was performed as described by Wilkinson [4].

3. Results and discussion

Laser flash photolysis of VAL or ACP on solid silica leads to very similar transient absorption spectra for each ketone, as shown in fig. 2. The time-resolved absorption at 350 nm decays with a clean first order lifetime of 310 ns to within 5% of the prepulse level for VAL. For ACP $\approx 80\%$ of the absorption at 350 nm decays by first-order kinetics with a lifetime of 1.5 μ s. Flash photolysis of DPB on the silica results initially in a similar transient absorption spectrum to those observed for VAL and ACP, which evolves with time into a spectrum with maximum adsorption at 330 nm (fig. 2). In this case $\approx 60\%$ of the absorption at 350 nm fits first-order kinetics with a lifetime of 900 ns, the remaining absorption decays with a lifetime of $>100 \mu$ s. For benzophenone (BZP) a transient absorption spectrum very similar to that reported pre-

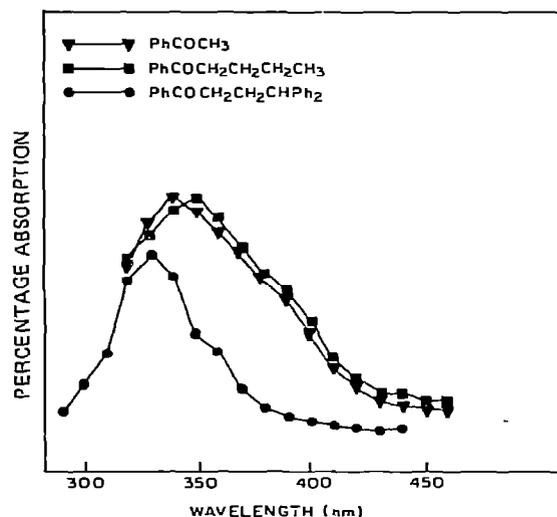


Fig. 2. Transient absorption spectra observed for pulsed laser photolysis of acetophenone, valerophenone and diphenylbutyphenone on solid silica.

viously for microcrystalline BZP, with maximum absorption at 525 nm was observed [4]. In this case $\approx 80\%$ of the decay fits first-order kinetics and a lifetime of 1.8 μ s is determined.

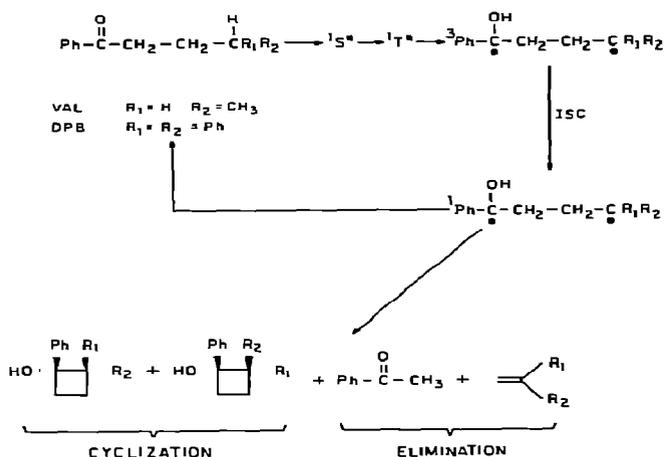
In the presence of gaseous butadiene the rate of decay of the absorptions from ACP, VAL and BZP depend linearly upon the pressure of this triplet quencher. From the slopes of plots of the decay rates versus butadiene pressure, very similar rate constants for quenching for each ketone were determined as summarized in table 1. These absorptions were also quenched by gaseous oxygen with much smaller rate constants (table 1). Beck and Thomas determined a similar rate constant for oxygen quenching of naph-

Table 1
Rate constants for quenching of ketone triplets adsorbed onto solid silica by gas phase quenchers

Ketone	k_q (Torr $^{-1}$ s $^{-1}$)	
	oxygen	butadiene
benzophenone	$(4.5 \pm 0.1) \times 10^4$	$(5.0 \pm 0.2) \times 10^7$
acetophenone	$(4.6 \pm 0.2) \times 10^4$	$(3.9 \pm 0.2) \times 10^7$
valerophenone	$(3.9 \pm 0.2) \times 10^4$	$(3.4 \pm 0.2) \times 10^7$

thalene triplet adsorbed onto an alumina surface [4]. The fast decay observed for DPB was also quenched by butadiene and oxygen, although in this case the transient decays did not fit cleanly to first-order kinetics presumably because of the overlapping absorption of the slowly decaying species. However, the pressures of butadiene or oxygen which are required to effect significant quenching of the fast decay are the same as those required for the other ketones.

The photochemistry of VAL and DPB can be described according to scheme 1. In homogeneous solu-



Scheme 1.

tion rapid intra-molecular hydrogen abstraction takes place to form a 1,4-biradical which can be detected using transient absorption spectroscopy [6]. The biradical lifetime is probably determined by the rate of intersystem crossing to the singlet biradical [6], from which the products are formed [7]. The triplet state of acetophenone in polar solvents has an absorption maximum at 340 nm [8] and thus we assign the absorptions observed on the silica for ACP to its triplet state. The observed quenching by both oxygen and butadiene effectively rules out either radicals or ionic species as the 340 nm transient. Because of the similarity between the absorption spectra and quenching behaviour observed for ACP, VAL and the fast decay of DPB, the transients for these latter two ketones are also assigned to their corresponding triplet states. These results are remarkable since the lifetimes of the triplet states of these ketones have been estimated to

be <5 ns in homogeneous solution, due to rapid intra-molecular hydrogen abstraction [6,9]. The triplets are longer lived on the silica surface presumably because the binding to the surface severely restricts the accessibility of the conformations required for intra-molecular hydrogen abstraction [10]. Presumably the DPB triplet is longer lived than the triplet of VAL because the former is strongly adsorbed to the surface at both ends of the molecule due to the two γ -phenyl groups, whereas the valerophenone has only a short alkyl chain and thus may find the correct conformation for reaction more easily [11].

The 1,4-biradicals derived from VAL and DPB have absorption maxima at 300 and 330 nm, respectively, in homogeneous solution and their lifetimes in methanol are 102 and 222 ns [6,9]. If we assume that the differences in the triplet lifetimes of ACP and VAL and DPB are due to the hydrogen abstraction process then we can estimate a quantum yields of ≈ 0.8 and ≈ 0.4 for biradical formation for VAL and DPB. However for VAL there is no evidence of transient absorptions due to the triplet biradical. We conclude that the conformational restrictions which drastically increase the lifetime of the triplet state do not operate on the biradical. This is understandable since only one conformation (chair) is appropriate for the hydrogen abstraction process [10] whereas many conformations may be permissible for intersystem crossing from the triplet to the singlet biradical, which may subsequently undergo fast reaction [12]. Thus in homogeneous solution the triplet state of VAL is shorter lived than the triplet biradical, whereas the opposite is true on the silica surface, presumably because of the conformational restrictions which are characteristic of binding to the surface. Similar conclusions concerning the effect of conformational control have been reached for the photochemistry of several organic molecules adsorbed onto zeolites [13].

Long-lived absorptions are observed for photolysis of DPB and furthermore these absorptions exhibit a maximum absorption at 330 nm, the reported maximum for the triplet biradical. However these cannot be assigned to the biradical unequivocally since the absorption spectrum tails into the visible whereas the spectrum in homogeneous solution does not [9]. No quenching by butadiene is observed, and upon the addition of oxygen the transient absorption spectrum of the slowly decaying species changes and so we can not determine

Table 2
Products observed upon photolysis of valerophenone on the solid silica surface

Medium	Light source	E/C ^{a)}	t/c ^{b)}
silica	laser (308 nm)	4.2	1.6
silica	lamp (313 nm)	4.2	1.6
benzene ^{c)}	lamp (313 nm)	4.5	4.0
t-butanol ^{c)}	lamp (313 nm)	7.3	2.0

a) The ratio of elimination to cyclization products (scheme 1).

b) The ratio of trans- to cis-cyclization products (scheme 1).

c) Ref. [14].

without doubt whether the long-lived absorptions are indeed quenched by oxygen. If the long-lived absorptions are due to a triplet biradical then this species is remarkably long lived.

Steady-state photolysis using either lamp or laser excitation, of VAL or DPB on the silica surface leads to the expected products for VAL (scheme 1) (table 2). For DPB on the silica surface only elimination products are observed, as in homogeneous solution [9]. These results confirm that the expected type II photochemistry does take place, and that the laser does not significantly influence the chemistry. The ratios of the cyclization to elimination products for VAL are similar to those found in non-polar solvents [14], however the ratio of the two cyclobutanols indicates a more polar environment [14]. Clearly the factors which influence the product distribution in homogeneous solution need not be important on the silica surface where the influence of surface binding on the accessibility of various conformers must play an important role.

The triplet energy of butadiene is 65 kcal mol⁻¹ [15] and so quenching of each of the ketones in the present study by this species will be diffusion controlled in homogeneous solution. Oxygen is known to quench many triplet states with rate constants approximately one order of magnitude less than the diffusion control rate constant [16]. For triplet states adsorbed onto the silica surface we find that *gas phase oxygen quenching is three orders of magnitude less efficient than gas phase quenching by butadiene* (table 1). This is an interesting result and could be interpreted as a reflection of the local concentration of the gaseous quencher which is seen by the adsorbed ketone triplet. The higher quenching efficiency by butadiene compared to oxygen could be due to a higher concentra-

tion of the hydrocarbon quencher, absorbed from the gas phase, at the sites of adsorption of the ketones. However Beck and Thomas have found that for excited states bound to alumina in which similar triplet quenching constants to those of the present work were found, oxygen quenched singlet excited states with rate constants of $\approx 10^7 \text{ Torr}^{-1} \text{ s}^{-1}$ [3]. Although the differences in quenching efficiency are clearly not understood, it is obvious that the processes which determine quenching efficiency in homogeneous solution and on the solid surface are not the same.

4. Conclusion

The factors which influence the mechanisms of photochemical processes of organic species adsorbed onto solid silica surfaces are different from those for processes in homogeneous solution [1,2]. In the present work these effects are observed in the efficiencies of triplet quenching by oxygen and butadiene, and in the lifetimes of reactive triplet states. In the latter case the effects of restricted conformational flexibility can account for the observed behaviour.

Acknowledgement

The authors thank the National Science Foundation, the I.B.M. Corporation, and the Air Force office of Scientific Research for their generous support of this research. MBZ thanks the NSF for a predoctoral fellowship. We would also like to thank C. Doubleday Jr. for helpful discussions, and Dr. Walter Mahler of the duPont Corporation for providing us with samples of synthetic silicas.

References

- [1] P. deMayo, Pure Appl. Chem. 54 (1982) 1623; P. deMayo, A. Nakamura, P.W.K. Tsang and S.K.J. Wong, J. Am. Chem. Soc. 104 (1982) 6824; P. deMayo, L.V. Natarajan and W.R. Ware, Chem. Phys. Letters 107 (1984) 187; R.K. Bauer, P. deMayo, L.V. Natarajan and W.R. Ware, Can. J. Chem. 62 (1984) 1279; U. Even, K. Rademann, J. Jortner, N. Manor and R. Reisfeld, Phys. Rev. Letters 52 (1984) 2164.

- [2] R.K. Bauer, R. Borenstein, P. deMayo, K.K. Okada, M. Rafalska, W.R. Ware and K C Wu, *J Am Chem. Soc.* 104 (1982) 4635;
N.J. Turro, C.-C. Cheng and W. Mahler, *J. Am. Chem. Soc.* 106 (1984) 5022
- [3] G Beck and J.K. Thomas, *Chem. Phys Letters* 94 (1983) 553
- [4] F. Wilkinson and C.J. Wilsner, *Chem. Phys. Letters* 104 (1984) 272;
R.W. Kessler, G Krablicher, S. Uhl, D. Oelkrug, W.P. Hagan, J. Hyslop and F. Wilkinson, *Opt. Acta* 30 (1983) 1099.
- [5] W. Mahler and M. Bechtold, *Nature (London)* 285 (1980) 27.
- [6] J.C Scaiano, *Accounts Chem Res* 15 (1982) 252,
R.D. Small and J C Scaiano, *J. Phys Chem.* 81 (1977) 2126.
- [7] P.J. Wagner, *Accounts Chem. Res.* 4 (1971) 168.
- [8] H. Lutz, E. Brehardt and L Lindquist, *J. Phys. Chem* 77 (1973) 1758.
- [9] R.A. Caldwell, T. Majima and C. Pac, *J. Am Chem. Soc.* 104 (1982) 629.
- [10] P.J. Wagner, *Accounts Chem. Res.* 16 (1983) 461.
- [11] A.V. Kiselev, Y. Koutetski and I. Chizhek, *Proc. Acad. Sci. USSR Phys. Chem. Sect. Engl. Transl.* 147 (1962) 769.
- [12] C. Doubleday Jr., *Chem. Phys. Letters* 77 (1981) 131;
79 (1981) 375;
C. Doubleday Jr, J.W. McIver Jr. and M Page. *J. Am. Chem. Soc.* 104 (1982) 6533.
- [13] N.J. Turro and P. Wan. *Tett. Letters* (1984) 3655;
H.L. Casal and J.C. Scaiano, *Can. J. Chem* 62 (1984) 628.
- [14] P.J. Wagner, P.A. Kelso, A.E. Kemppainen, J.M. McGrath, H.N. Schott and R.G. Zepp, *J Am. Chem. Soc.* 94 (1972) 750.
- [15] D F. Evans, *J. Chem. Soc* (1960) 1735.
- [16] O.L.J. Gajzman, F. Kaufman and G. Porter, *J. Chem Soc. Faraday II* 69 (1973) 708.