Kinetics of Dissociation of the Phenylacetyl Radical in a 1:1 Acetonitrile–Water Mixture Studied by Laser Flash Photolysis of Dibenzyl Ketone

Ahmed Maouf, Helge Lemmetyinen and Jouko Koskikallio*

Laboratory of Physical Chemistry, University of Helsinki, Meritullinkatu 1 C, SF-00170 Helsinki, Finland

Mayouf, A., Lemmetyinen, H. and Koskikallio, J., 1990. Kinetics of Dissociation of the Phenylacetyl Radical in a 1:1 Acetonitrile–Water Mixture Studied by Laser Flash Photolysis of Dibenzyl Ketone. – Acta Chem. Scand. 44: 336–338.
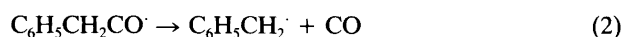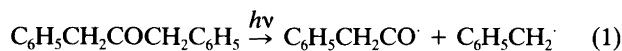
The first-order decomposition of the phenylacetyl radical to the benzyl radical and carbon monoxide was studied by laser flash photolysis of dibenzyl ketone in a 50 % acetonitrile–50 % water (v/v) mixture at temperatures from 298 to 373 K. Rate constants were calculated from the values of absorbance of the benzyl radical at 315 nm.

$$\log(k_2/\text{s}^{-1}) = 11.1 \pm 0.4 - \frac{(24.4 \pm 2.0)\ \text{kJ mol}^{-1}}{2.303\ R\ T}$$

The rate constant of the second-order combination reaction of benzyl radicals to dibenzyl was calculated in the same solvent mixture. The following equation was fitted to the rate constants:

$$\log(k_3/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = 11.3 \pm 0.2 - \frac{(6.7 \pm 1.0)\ \text{kJ mol}^{-1}}{2.303\ R\ T}$$
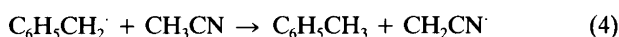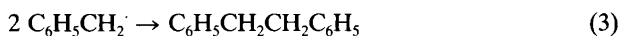
Phenylacetyl radicals are formed with high efficiency by a fast photodissociation of 1,3-diphenyl-2-propanone (DBK) from its triplet state.[1] The quantum yield of triplet DBK is approximately unity[1] and the quantum yield of fluorescence is low, 0.04 and 0.01 in hexane and acetone, respectively.[1] The lifetime of the singlet state of DBK prepared by n–π absorption is 3.6 ns, and the lifetime of triplet DBK is about 0.1 ns.[1,2] Laser flash photolysis of dibenzyl ketone with 308 nm light produces large amounts of phenylacetyl radicals in a few nanoseconds. Phenylacetyl radicals dissociate forming benzyl radicals and carbon monoxide, as in reaction (2).

$$C_6H_5CH_2COCH_2C_6H_5 \xrightarrow{h\nu} C_6H_5CH_2CO^{\cdot} + C_6H_5CH_2^{\cdot} \quad (1)$$

$$C_6H_5CH_2CO^{\cdot} \rightarrow C_6H_5CH_2^{\cdot} + CO \quad (2)$$

Lunazzi et al.[3] obtained the rate constant of reaction (2) ($k_2 = 5.2 \times 10^6\ \text{s}^{-1}$ in methanol and $k_2 = 9.1 \times 10^6\ \text{s}^{-1}$ in isooctane at 25 °C) by measuring the absorbance of the benzyl radical at 317 nm. By the same method Turro et al.[4] obtained $k_2 = 5 \times 10^6\ \text{s}^{-1}$.

The final products of the photolysis of DBK in cyclohexane were analysed by Huggenberger and Fischer.[5] The main product (98 ± 1.5 %) is 1,2-diphenylethane (diben-

zyl), formed by reaction (3), and small amounts of toluene (0.3 %) are formed by reaction (4).

$$2\ C_6H_5CH_2^{\cdot} \rightarrow C_6H_5CH_2CH_2C_6H_5 \quad (3)$$

$$C_6H_5CH_2^{\cdot} + CH_3CN \rightarrow C_6H_5CH_3 + CH_2CN^{\cdot} \quad (4)$$

Small amounts of phenylacetic acid were obtained[5] and were assumed to be formed from phenylketene. The rate of reaction (3) is close to the diffusion-controlled rate.[6]

The present work is our first investigation into the kinetics of reactions of phenylacetyl and benzyl radicals in polar solvents.

Experimental

Materials. 1,3-Diphenyl-2-propanone (DBK) (Fluka AG 98 %) was recrystallized from a methanol–petroleum ether mixture several times and found to be pure by gas-chromatography analysis. Methanol (Rathburn HPLC grade), acetonitrile (Rathburn HPLC grade) and petroleum ether (Rathburn HPLC grade) were used as received.

Methods. The flash-photolysis experiments were carried out with an excimer laser (ELIM 72, Special Design Bureau of the Estonian Academy of Science) emitting at 308 nm focused on the sample. The laser pulse width was about 10 ns, and the maximum energy was about 50 mJ/pulse.

---

* To whom correspondence should be addressed.

The laser energy was attenuated 10–100 % by grey filters when the effect of the light intensity on the reaction was being studied. Transient absorptions were monitored with a 100 W pulsed xenon lamp: the intensity of the xenon lamp pulse was constant for about 100 μs at the maximum value to within 2 %. The excitation and monitoring pulses were at right angles. The wavelength of the monitoring beam was selected with a monochromator (MDR 23). The beam was focused on the sample in a spot of about 5 mm², coinciding with the region excited by the laser. Behind the sample the monitoring beam was focused on the entrance slit of the second monochromator (MDR 23).

The signal was detected by a photomultiplier (FEU-106) which was connected to the differential amplifier (Tektronix 7 A 7) of a 500 MHz transient digitizer (Tektronix 7912 AD). In cases of low signal intensities, averages of several measurements were used. The instrumental noise due to the variation in monitoring light intensity and transient digitizer was subtracted from the measured decay curves. The influence of fluorescence on transient absorption was diminished in a similar way. In recording transient absorption spectra, decay curves were measured automatically at each chosen wavelength, stored, and presented as a function of the wavelength. The data were stored in a computer (Olivetti 24 M) for further calculations. A least-squares fitting procedure was used to calculate the rate parameters from the experimental decay curves.

The intensities of exciting radiation in stationary quantum yield experiments were measured with a potassium ferrioxalate actinometer. As a light source a 100 W high-pressure Hg lamp was used (313 nm) in combination with an MDR-2 monochromator. The yields of the photolysis products were determined by gas chromatography.

Results and discussion

A transient absorption was obtained at 315 nm in 1:1 (v/v) acetonitrile–water mixture and was ascribed to the benzyl radical. A similar narrow band of about 5 nm half-width
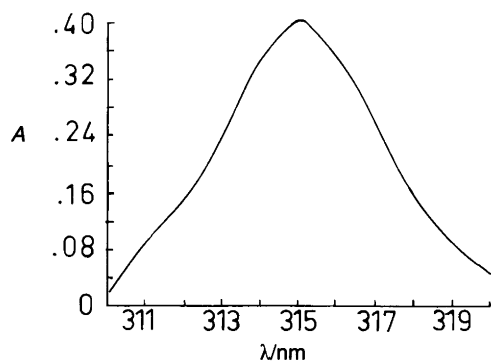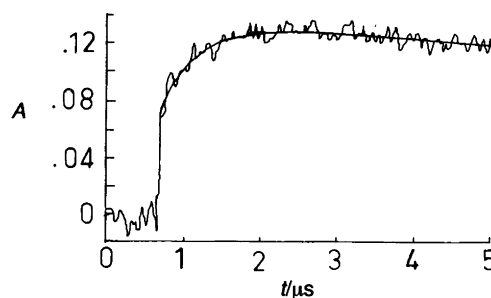

Fig. 2. Time-resolved experimental and calculated absorbance of benzyl radical in a 1:1 (v:v) acetonitrile–water mixture at 25 °C.

ascribed to the benzyl radical has been observed at 316 and 318 nm in cyclohexane,[5,7] at 317 nm in iso-octane,[3,4] at 317.5 nm in glycerol,[8] at 314 nm in methanol[6] and at 314, 315, 317, 317.5 and 318 nm in water[6,9,10–12] (Fig. 1). Owing to the fast photodissociation of triplet DBK, the benzyl radical transient was observed only immediately after a laser pulse, and the rate of formation could not be measured.

The fast increase of the transient signal was followed by a slower increase attributable to the dissociation reaction of phenylacetyl radical [reaction (2)], Fig. 2. A first-order rate equation shown by eqn. (5) was fitted to the measaured absorbance data using a computer program.

$$\ln (A_\infty - A_t) = k_2 t + \text{constant} \tag{5}$$

Constant values of the rate constant k_2 were obtained by varying the initial concentration of DBK from 3.23×10^{-2} to 18.6×10^{-2} mol dm⁻³, and the laser pulse intensity was varied from full intensity to 0.11 times the full intensity. Eqn. (6) was fitted to the values of rate constants obtained at different temperatures from 298 to 348 K.

$$\log (k_2/\text{s}^{-1}) = 11.1 \pm 0.4 - \frac{(24.4 \pm 2) \text{ kJ mol}^{-1}}{2.303\ R\ T} \tag{6}$$

The rate constant at 25 °C, $k_2 = (6.8 \pm 0.6) \times 10^6$ s⁻¹, and the values of the Arrhenius parameters are similar to the values obtained earlier by Lunazzi et al.[3] ($A = 12.0 \pm 0.3$ and $E = 28.9 \pm 1.6$ kJ mol⁻¹) and Turro et al.[4] ($A = 11.2 \pm 0.4$ and $E = 25.5 \pm 2.4$ kJ mol⁻¹).

Fig. 1. Absorbance of benzyl radical in a 1:1 (v:v) acetronitrile–water mixture 2 μs after laser flash photolysis of 0.0020 mol dm⁻³ DBK at 25 °C.

Table 1. Rate constants of reaction (3) in 1:1 (v/v) acetonitrile–water. $k_3 = \varepsilon / k_{exp}/2$, with $\varepsilon = 9000$ dm³ mol⁻¹ cm⁻¹ and $l = 2$ cm.

$T/°C$	$10^5 k_{exp}/\text{cm s}^{-1}$	$10^9 k_3/\text{mol dm}^{-3} \text{ s}^{-1}$
5	5.1±0.4	4.6±0.4
23	6.1±0.3	5.5±0.3
45	7.3±0.6	6.6±0.6

Table 2. Rate constants of reaction (3), the combination reaction of benzyl radicals, in solvents of different viscosities.[16]

Solvent	$T/^{\circ}C$	$10^2\eta/g\ cm^{-1}\ s^{-1}$	$\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$	$10^9 k_3/dm^3\ mol^{-1}\ s^{-1}$	Ref.
MeOH	25	0.542	1500	0.68	6
C_6H_6	25	0.596		4.1	15
ACN–H_2O	25	0.74	9000	5.4	This work
H_2O	25	0.890	5500	1.55	11
C_6H_{12}	25	0.90	8800	1.8	5

The R–CO bond of the phenylacetyl radical is weak, and the estimated[13] R–CO bond-breaking enthalpy is only $\Delta H = -(6 \pm 2)$ kJ mol^{-1}. The rate of R–CO bond dissociation of carbonyl radicals is sensitive to the substituent R. For example, the rate constants of R–CO dissociation reactions of C_6H_5CO and $C_6H_5C(CH_3)CO$ differ by a factor of about 10^{15}. There is an approximately linear correlation between the enthalpy and the activation energy of the R–CO bond-dissociation reaction,[13] and the value of the slope is 1.20 ± 0.10.

The relatively slow decay of the benzyl radical absorption is ascribed to the combination reaction (3) of benzyl radicals to dibenzyl. Eqn. (7) was fitted to the absorbance data obtained at about 200 ns, when the dissociation reaction (2) of phenylacetyl radical was approximately completed.

$$k_{exp} = \frac{2\,k_3}{\varepsilon\,l} = \frac{1}{t}\left(\frac{1}{A} - \frac{1}{A_0}\right) \tag{7}$$

We used the values $\varepsilon = 9000$ dm^3 mol^{-1} cm^{-1} and $l = 2$ cm in calculating the rate constant $k_3 = \varepsilon\,l\,k_{exp}/2$ (Table 1). Values of ε have been measured earlier by Huggenberger and Fischer[5] ($\varepsilon = 8800$ dm^3 mol^{-1} cm^{-1} in cyclohexane) by McAskill and Sangster[7] ($\varepsilon = 9000$ dm^3 mol^{-1} cm^{-1} in cyclohexane) and by Mittal and Hayon[8] ($\varepsilon = 9000$ dm^3 mol^{-1} cm^{-1} in water). Constant values of the rate constant k_3 were obtained when the initial concentration of DBK and the laser light intensity were varied as in the measurement of the rate constant k_2 (Table 1).

Eqn. (8) was fitted to the values of rate constants k_3 measured at different temperatures from 298 to 373 K.

$$\log(k_3/dm^3\,mol^{-1}\,s^{-1}) = (11.3 \pm 0.2) - \frac{(6.7 \pm 1.0)\ kJ\ mol^{-1}}{2.303\,R\,T} \tag{8}$$

Huggenberger and Fischer[5] found that benzyl radicals form addition products at positions 2 and 4 of the benzyl radical and rearrange to form stable dibenzyl. The rate constant of the benzyl radical combination reaction is close to the diffusion-controlled limit. The rate constant depends on the viscosity of the solvent[14] (Table 2).

The quantum yield of the main product, dibenzyl, was measured in a 1:1 (v/v) acetonitrile–water mixture at 25 °C

using a 313 nm light source. Since only minor amounts of other products are formed by photolysis of DBK, the quantum yield of 0.57 ± 0.05 can be regarded as the quantum yield of the photodissociation of DBK. Meiggs and Grossweiner[6] obtained values 0.70 and 0.71 for the quantum yield of dibenzyl when then they photolysed DBK in benzene and acetonitrile at 30 °C with 295 nm light.

Because the quantum yield[2] of the intersystem crossing from singlet to triplet and the quantum yield of triplet formation are both approximately equal to 1, the quantum yield of photodissociation of the triplet DBK must likewise be about 0.57 ± 0.05. The rate constant of triplet DBK dissociation can be calculated using the approximate value obtained for the lifetime of the triplet[1,2] $k_1 = \varphi/\tau = 0.57/0.1\times10^{-9}$ s $= 5.7\times10^9$ s^{-1}.

References

1. Robbins, W. K. and Eastman, R. H. J. Am. Chem. Soc. 92 (1970) 6076 and 6077.
2. Engel, P. S. J. J. Am. Chem. Soc. 92 (1970) 6075.
3. Lunazzi, L., Ingold, K. U. and Scaiano, J. C. J. Phys. Chem. 87 (1983) 529.
4. Turro, N. J., Gould, I. R. and Baretz, B. H. J. Phys. Chem. 87 (1983) 531.
5. Huggenberger, C. and Fischer, H. Helv. Chim. Acta 64 (1981) 338.
6. Meiggs, T. O., Grossweiner, L. I. and Miller, S. I. J. Am. Chem. Soc. 94 (1972) 7981 and 7986.
7. McAskill, N. A. and Sangster, D. F. Aust. J. Chem. 30 (1977) 2107.
8. Mittal, J. D. and Hayon, E. Nature Phys. Sci. 240 (1972) 20.
9. McCarthy, R. L. and MacLachlan, A. Trans. Faraday Soc. 56 (1960) 1178.
10. Hagemann, R. J. and Schwarz, H. A. J. Phys. Chem. 71 (1967) 2694.
11. Christensen, H. C., Sehested, K. and Hart, E. J. J. Phys. Chem. 77 (1973) 983.
12. Lilie, J. and Koskikallio, J. Acta Chem. Scand., Ser. A 38 (1984) 41.
13. Vollenwieder, I.-K. and Paul, K. Int. J. Chem. Kinet. 18 (1986) 781.
14. Lehni, M., Schuh, H. and Fischer, H. Int. J. Chem. Kinet. 11 (1979) 705.
15. Burkhart, R. D. J. Am. Chem. Soc. 90 (1968) 273.
16. Janz, I. I. and Tomkins, R. P. T. Nonaqueous Electrolytes Handbook, Vol. I, Academic Press, New York 1972.