

Influence of the intrazeolite microenvironment on the fate of the radical pairs formed by photolysis of 3-bromo-4-chromanone

M. Consuelo Jiménez, Miguel A. Miranda *, Rosa Tormos

Departamento de Química, Instituto de Tecnología Química UPV-CSIC, Universidad Politécnica de Valencia, Camino de Vera s/n, Apartado 22012, E-46071 Valencia, Spain

Received 14 June 1994; accepted 9 August 1994

Abstract

The photochemistry of 3-bromo-4-chromanone (**1**) is significantly modified by inclusion within an NaY zeolite. Disproportionation of the α -carbonyl radical **I**, to give equimolar amounts of chromone (**2**) and 4-chromanone (**3**), occurs to a lower extent than in solution. By contrast, generation of the cation **II**, which leads to chromone (**2**) and subsequently to 2-cyclohexyl-4-chromanone (**4**), is enhanced in the heterogeneous medium.

Keywords: Intrazeolite microenvironment; Radical pairs; Photolysis; 3-Bromo-4-chromanone

1. Introduction

The internal cavities of zeolites have been used as vessels of molecular dimensions to achieve a variety of chemical transformations [1]. These microenvironments have been found to be especially suitable for controlling the photobehaviour of adsorbed organic guests due to the combined effect of several factors, such as spatial limitations, restricted diffusion and variations in the spin-orbit coupling parameter [2].

A number of well-known processes have been used as probes to explore the possibilities of zeolites as hosts for organic photoreactions. In this context, the Norrish type I photolysis of carbonyl compounds has attracted much attention as a prototype for cleavage into radical pairs and subsequent disproportionation or radical-radical recombination [3,4]. Other photochemical studies have dealt with cis-trans isomerizations [5], [2+2] dimerizations [6] and Norrish type II reactions [7].

In this work, 3-bromo-4-chromanone (**1**) [8] has been used as a molecular probe to gain further understanding of the restrictions imposed by the internal structure of zeolites on the course of photochemical reactions. In this case, the characteristic β -cleavage of α -haloketones [9–15] affords α -carbonyl/halogen radical pairs, whose

fate is significantly influenced by adsorption in the solid support.

2. Experimental details

2.1. General irradiation procedures

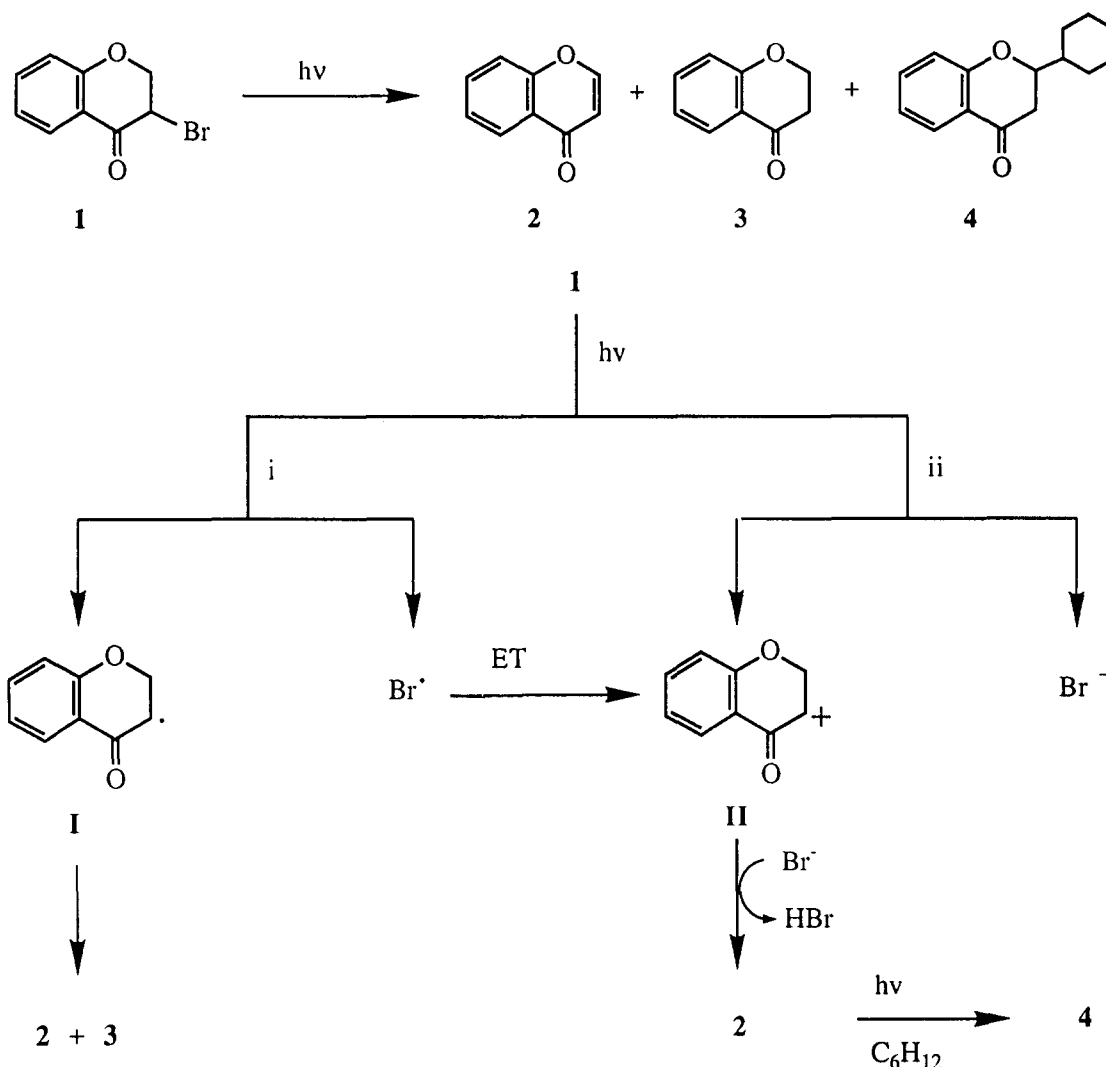
2.1.1. Homogeneous media

Solutions of 0.2 mmol of the substrate in 2 ml of methylene chloride, cyclohexane and acetonitrile were placed into Pyrex test-tubes surrounding a centrally positioned quartz cooling jacket containing a 125 W medium-pressure Hg lamp, and irradiated for 1 h. These reaction mixtures were analysed by gas chromatography-mass spectrometry (GC-MS).

2.1.2. Heterogeneous media

A solution (30 ml) of **1** (0.02 g) was poured onto NaY zeolite (0.50 g) previously activated by calcination at 773 K for 12 h. The suspension was stirred for 2 h and centrifuged. The amount of **1** included was calculated from the difference between the initial and recovered weights. Direct photolysis was carried out by resuspending compound **1** within NaY in fresh solvent (5 ml), and irradiating with Pyrex-filtered light from a 125 W medium-pressure mercury lamp for 1 h. At the end of irradiation, the solid was thoroughly extracted

* Corresponding author.



with CH_2Cl_2 and the mixture was analysed by GC–MS. Further details can be found elsewhere [16,17].

2.2. 2-Cyclohexyl-4-chromanone (4)

This compound is a viscous oil. MS (m/z , %): 230 (M^+ , 19), 147 (43), 121 (100), 120 (20), 92 (12). *Fourier transform IR (FTIR)* (ν , cm^{-1}): 2939, 2866, 1713 ($\text{C}=\text{O}$), 1610, 1467, 1320, 1230, 1116, 1031, 888, 760. Proton nuclear magnetic resonance (^1H NMR, 400 MHz) (δ , ppm): 1.10–2.00 (m, 11 H, C_6H_{11}), 2.69 (m, 2H, COCH_2), 4.21 (m, 1H, $-\text{OCH}$) 6.97–7.88 (m, 4H, ArH). Exact mass, 230.1309; calculated for $\text{C}_{15}\text{H}_{18}\text{O}_2$, 230.1306. Analysis: C 78.24, H 7.95; calculated for $\text{C}_{15}\text{H}_{18}\text{O}$: C 78.23, H 7.88. An alternative method of synthesis is given in Refs. [18,19]. A mixture of *o*-hydroxyacetophenone (1.00 g, 7.4 mmol), cyclohexane-carboxaldehyde (1.10 g, 9.0 mmol) and pyrrolidine (0.15 g, 2.0 mmol) was allowed to stand for 5 days at room temperature. The desired product was isolated by evaporation of the solvent at reduced pressure and further purification by column

chromatography on silica gel, using methylene chloride as eluent. Yield, 0.65 g (38%).

3. Results and discussion

In the first stage, the photolysis of 1 was carried out in homogeneous media, using solutions of the substrate in methylene chloride, acetonitrile and cyclohexane (Table 1, entries 1, 2 and 3). Chromone (2) was always obtained as the major product, together with minor amounts of 4-chromanone (3). In cyclohexane, the conversion was lower and the yield of 3 was higher than in the other solvents. Since the spatial arrangement of the halogen atom (axial vs. equatorial) appears to play a key role in the photochemistry of α -halocyclohexanones [12], we decided to perform a careful ^1H NMR study of substrate 1 in the corresponding deuterated solvents, in order to determine whether the two possible conformers were differentially populated. The data presented in Table 1 show that bromine was

Table 1
Photochemistry of the bromoketone **1** in solution and adsorbed on NaY zeolite

Entry	Solvent	Conversion (%)	Product distribution (%)			¹ H NMR of 1 δ (H ₃), ppm (J, Hz)
			2	3	4	
1	CH ₂ Cl ₂	99	98	2	–	4.65 (2.8, 4.4)
2	CH ₃ CN	98	97	3	–	4.75 (2.8, 5.2)
3	C ₆ H ₁₂	78	79	21	–	4.39 (2.8, 5.2)
4	NaY/C ₆ H ₁₂	59	90	5	5	

axial in all cases, as indicated by the coupling pattern (no vicinal trans-diaxial coupling constant). Nonetheless, the protons of the pyran ring (especially that bound to C-3) became significantly deshielded in more polar solvents, which can be accounted for in terms of a higher polarization of the carbon–halogen bond.

The adsorption of **1** on NaY zeolite was achieved by stirring a cyclohexane solution of the bromoketone with the activated inorganic support for 2 h. After filtering and washing, the dry solid was analysed by FTIR and diffuse reflectance UV–visible spectrophotometry. The presence of **1** was shown by the characteristic carbonyl band at 1685 cm^{−1} and an absorption spectrum comparable with that obtained in cyclohexane solution (see Fig. 1). The amount of substrate included was calculated from the difference between the initial and recovered weights.

It is known that conformational changes in cyclic α -bromoketones are associated with significant variations in the IR spectra [20]. Thus the conformers with an equatorial halogen display their carbonyl bands at higher frequencies than the corresponding axial analogues ($\Delta\nu \approx 12$ cm^{−1}). Since such variations are not observed in the case of **1** ($\nu_{C=O}$ in cyclohexane, methylene chloride or acetonitrile solution is 1690 ± 5 cm^{−1}), the axial conformation of this compound appears to be preserved in the heterogeneous medium.

The photolysis of **1**/NaY (Table 1, entry 4) was performed after resuspending the dry bromoketone-containing zeolite in cyclohexane to form a well-stirred slurry. Under these conditions, chromone (**2**) and chromanone (**3**) were also formed, together with the cyclohexane-derived product **4**.

It is known that photochemical breaking of the carbon–halogen bond leads to radical and/or ion pairs [15]. Furthermore, the primary bond cleavage can be followed by electron transfer, so that the interconversion between both types of intermediates is possible [10]. Thus compound **2** would be obtained by deprotonation of cation **II**, while **3** would be the product of hydrogen abstraction by radical **I**. Another route leading to **2** + **3** would involve disproportionation of **I**. Since much more

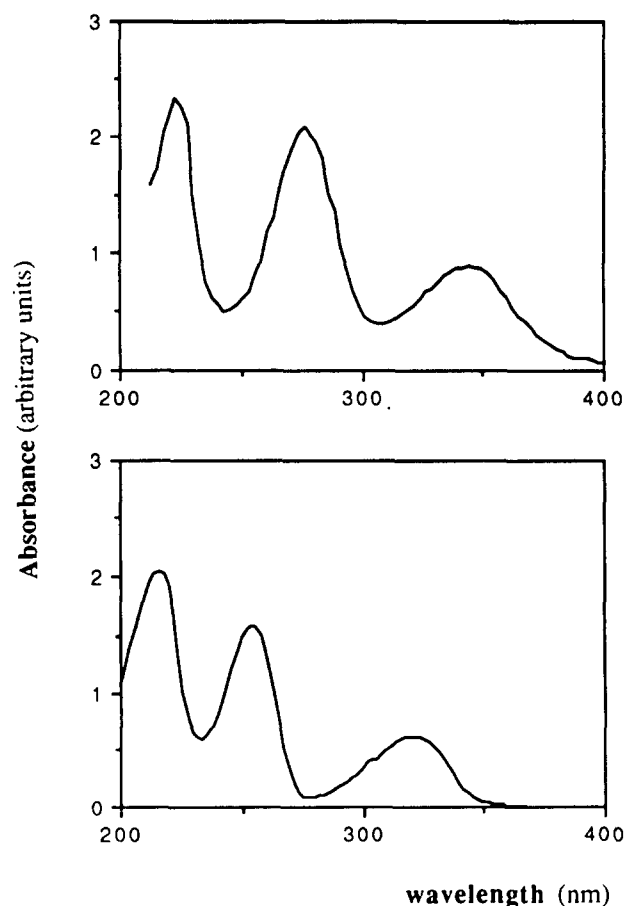


Fig. 1. (a) Diffuse reflectance UV–visible spectrum of **1**/NaY. (b) UV–visible spectrum of **1** in cyclohexane solution (approximately 10^{-4} M).

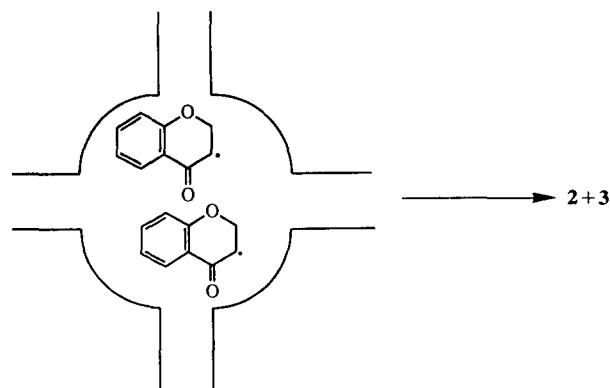


Fig. 2. Schematic representation of the disproportionation of the α -carbonyl radical **I** inside the zeolite, leading to **2** + **3**.

chromone is formed, this route should operate together with the abovementioned deprotonation of **II**.

To determine the origin of chromanone, a series of parallel experiments were carried out using deuterated solvents (CD₂Cl₂, CD₃CN and C₆D₁₂). Analysis of the photomixtures by GC–MS revealed that no deuterium atom had been incorporated into product **3**. The same was true for the irradiation of **1** on NaY zeolite, with C₆D₁₂ as solvent. These observations led to the con-

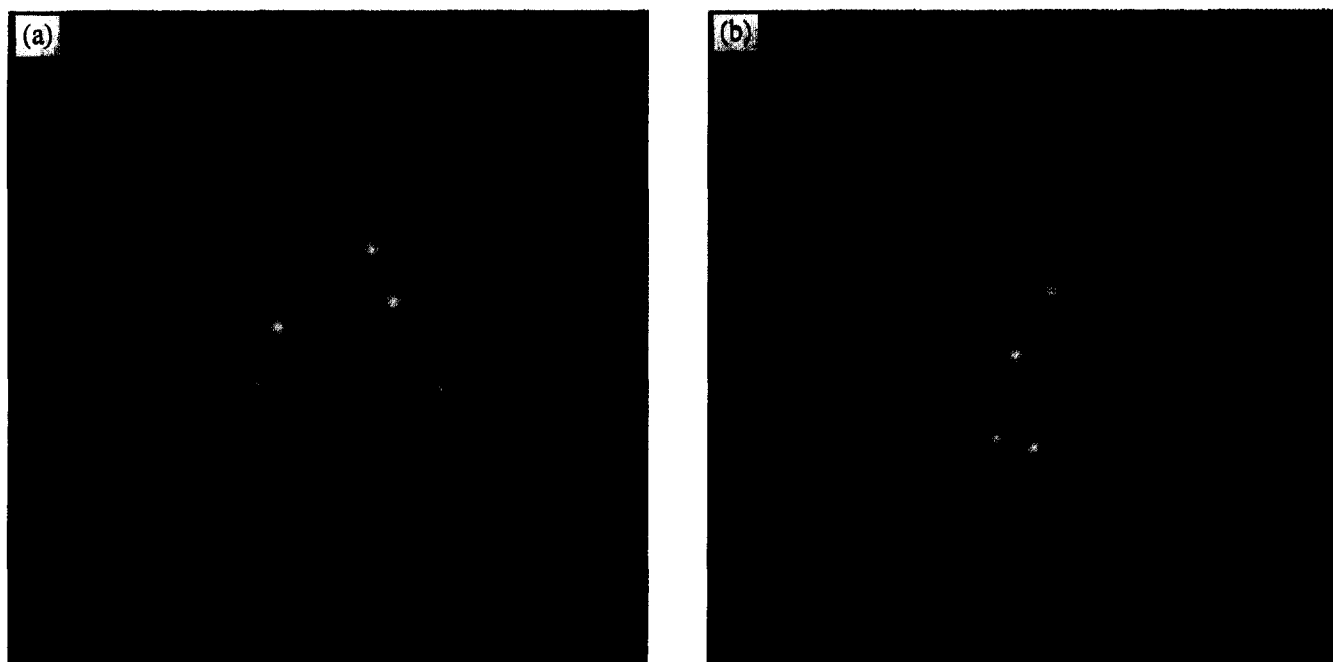


Fig. 3. Different views of two bromoketone units inside the cavity of an NaY zeolite, according to molecular modelling (Biosym Insight II package). The interactions of these molecules with the zeolite framework (and also with each other) are minimized in this arrangement.

clusion that chromanone is mainly formed through the disproportionation route. Since the mobility of radicals I inside the zeolite framework must be severely restricted [21–23], disproportionation probably requires accommodation of two bromoketone units within the same supercavity (Fig. 2). Molecular modelling using the Biosym Insight II package (Fig. 3) shows that such an arrangement is indeed possible.

A further point of interest was the formation of the cyclohexyl derivative 4. Since the abstraction of a cyclohexane hydrogen by bromine is thermodynamically unfavourable by approximately 7 kcal mol^{-1} , cyclohexyl radicals cannot be generated in this way. An alternative route to 4 might involve solvent addition to the enone moiety of 2 [24]. This was confirmed by separate irradiation of the chromone (2) in cyclohexane, which produced a detectable amount of 4.

Entries 3 and 4 (Table 1) clearly show that the contribution of the ionic pathway (ii), which gives rise to 2 (and 4), is markedly higher inside the zeolite cavity than in solution. Taking into account that the radical pathway (i) leads to equimolar amounts of 3 and 2, the relative ratios (ii)/(i) are 90/10 in heterogeneous medium vs. 58/42 in homogeneous medium. This correlates well with previous findings on the photochemistry of benzyl chloride, where the cage effect and the electrostatic fields characteristic of the zeolite microenvironment appear to enhance single electron transfer within the radical pair formed by primary homolysis of the carbon–halogen bond [16].

In summary, the above results show that the photochemistry of 3-bromo-4-chromanone (1) is significantly

altered by inclusion within an NaY zeolite. The radical pairs formed by primary carbon–halogen bond cleavage are strongly affected by adsorption in the solid support.

Acknowledgements

We wish to thank Dr. Vicente Fornés and Ms. Rosa Torrero for the FTIR spectra of 1/NaY and Mr. Vicente Martí for his assistance in molecular modelling.

References

- [1] V. Ramamurthy (ed.), *Photochemistry in Organized and Constrained Media*, Verlag Chemie, New York, 1991.
- [2] V. Ramamurthy, *Chimia*, 46 (1992) 359.
- [3] N.J. Turro, C.C. Cheng, L. Abrams and D.R. Corbin, *J. Am. Chem. Soc.*, 109 (1987) 2449.
- [4] M.A. García-Garibay, Z. Zhang and N.J. Turro, *J. Am. Chem. Soc.*, 113 (1991) 6212.
- [5] V. Ramamurthy, J.V. Caspar, D.R. Corbin, D.F. Eaton, J.S. Kaufman and C. Dybowski, *J. Photochem. Photobiol. A: Chem.*, 51 (1990) 259.
- [6] G. Lem, N.A. Kaprinidis, D.I. Schuster, N.D. Ghatlia and N.J. Turro, *J. Am. Chem. Soc.*, 115 (1993) 7009.
- [7] V. Ramamurthy, D.R. Corbin and L. Johnston, *J. Am. Chem. Soc.*, 114 (1992) 3870.
- [8] J.A. Donnelly and D.E. Maloney, *Tetrahedron*, 35 (1979) 2883.
- [9] P.C. Purohit and H.R. Sonawane, *Tetrahedron*, 37 (1981) 873.
- [10] Y. Izawa, Y. Watoh and H. Tomioka, *Chem. Lett.*, (1984) 33.
- [11] H. García, R. Martínez-Utrilla and M.A. Miranda, *Liebigs Ann. Chem.*, (1985) 589.
- [12] H. Morrison and L. Cárdenas, *J. Org. Chem.*, 52 (1987) 2590.

- [13] W.G. McGimpsey and J.C. Scaiano, *Can. J. Chem.*, **66** (1988) 1474.
- [14] M. Zupan and B. Sket, *Collect. Czech. Chem. Commun.*, **53** (1988) 1745.
- [15] N. Zupancic and B. Sket, *J. Photochem. Photobiol. A: Chem.*, **63** (1992) 303.
- [16] M. Alvaro, A. Corma, H. García, M.A. Miranda and J. Primo, *J. Chem. Soc., Chem. Commun.*, **13** (1993) 1041.
- [17] A. Corma, H. García, M.A. Miranda, J. Primo and M.J. Sabater, *J. Org. Chem.*, **58** (1993) 6892.
- [18] H.J. Kabbe and A. Widdig, *Angew. Chem. Int. Ed. Engl.*, **21** (1982) 247.
- [19] M.C. Jiménez, M.A. Miranda, J. Soto and R. Tormos, *Tetrahedron*, **50** (1994) 7635.
- [20] N.L. Allinger, J. Allinger, L.A. Freiberg, R.F. Czaja and N.A. Lebel, *J. Am. Chem. Soc.*, **82** (1960) 5876.
- [21] V. Ramamurthy, D.R. Corbin and D.F. Eaton, *J. Org. Chem.*, **55** (1990) 5269.
- [22] L.J. Johnston, J.C. Scaiano, J.L. Shi, W. Siebrand and F. Zerbetto, *J. Phys. Chem.*, **95** (1991) 10 018.
- [23] N.D. Ghatlia and N.J. Turro, *J. Photochem. Photobiol. A: Chem.*, **57** (1991) 7.
- [24] L. Fillol, M.A. Miranda, I.M. Morera and H. Sheikh, *Heterocycles*, **31** (1990) 751.