PHOTOCHEMISTRY OF PHENYL ALKYL KETONES ADSORBED ON ZEOLITE MOLECULAR SIEVES.

OBSERVATION OF PRONOUNCED EFFECTS ON TYPE I/TYPE II PHOTOCHEMISTRY.

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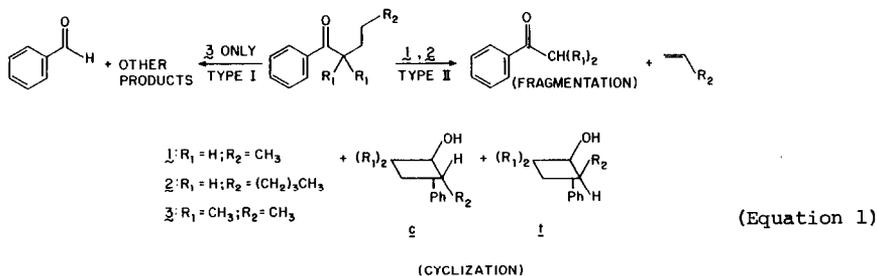New York, NY 10027, USA

Summary: The photolysis of phenyl alkyl ketones adsorbed on a number of commonly avail-
able zeolites(molecular sieves) can result in dramatic changes in Type I/Type II
photochemistry.

The photochemistry of ketones in ordered environments is a topic of current interest[2-4].
Environmental effects can have important influence on the conformational flexibility of
organic molecules, which in turn can affect the outcome of photochemical reactions[5]. Two
recent reports[2,3] on the Norrish Type II reaction in ordered media prompts us to report our
initial studies of the photochemistry of a number of phenyl alkyl ketones adsorbed in
zeolites.

Zeolites are crystalline aluminosilicates of usually well-defined structure[6]. Within
the zeolite framework are a system of channels and cavities of varying dimensions (2 - 13Å)[6],
some of which are capable of adsorption of large organic molecules(e.g.,substituted benzenes).
Thus the possibility that the internal spaces (or void volumes) of zeolites can exert
topological control on organic photochemical reactions warrants investigation, since it is
well-known that zeolites display shape-selective catalytic and adsorptive properties in
important industrial chemical processes[10]. However, only a handful of reports of photochem-
ical reactions on zeolites are known[4,7-9]; the majority of these concern the catalytic
splitting of water[9]. In this study, several commonly available zeolites were studied, and
the results are compared to those obtained in homogeneous solution.

Phenyl alkyl ketones $\underline{1}$ - $\underline{3}$ were employed in this study. The photochemistry of
valerophenone ($\underline{1}$), octanophenone ($\underline{2}$),and α,α-dimethylvalerophenone ($\underline{3}$) is relatively well-
understood in solution[11-13]. For $\underline{1}$ and $\underline{2}$, the photobehaviour is characterized by Type II
reaction, to give a triplet 1,4-biradical, which can either fragment, to give acetophenone,
or cyclize, to give cis and trans cyclobutanols(eqn. 1). Type I reaction is not observed.
In solution, the ratio of fragmentation to cyclization (F/C) products is ∿ 4 for $\underline{1}$ and $\underline{2}$.
In general, the trans isomer dominates, with t/c = 3 - 5 in benzene, and decreasing to a
limit of 1 in more polar solvents (MeOH or micelles)[11-13]. For $\underline{3}$, Type I reaction is obser-
ved in addition to Type II. The ratio of Type I/Type II products has been reported to be 0.3
in benzene without added thiol, and 0.6 with added thiol[11].

Ketones $\underline{1}$ and $\underline{3}$ were deposited on Zeolites Na^+-A, Na^+-X, Na^+-Y, Na^+-Mordenite and

$\underline{1}: R_1 = H; R_2 = CH_3$

$\underline{2}: R_1 = H; R_2 = (CH_2)_3 CH_3$

$\underline{3}: R_1 = CH_3; R_2 = CH_3$

(Equation 1)

(CYCLIZATION)

Silicalite[14] by adding a known amount of ketone (dissolved in CH_2Cl_2) to a pre-weighed quantity of adsorbant. After removal of the solvent by vacuum pumping, the samples were photolyzed with a Hanovia 450 W lamp(Pyrex filter) for 15 min - 1 h, depending on the zeolite. After photolysis, the zeolite samples were extracted with CH_2Cl_2 for 3 - 5 h on a Soxhlet apparatus. The product ratios as determined by GLC are summarized in Table 1.

The results presented demonstrate that dramatic effects in Type I/Type II photoreaction can be effected by adsorption in zeolites. The effects observed in this study are more dramatic than those reported by de Mayo, et al.[2], and Scheffer, et al[3], which were studies of the Type II photoreaction of 5-nonanone in urea inclusion complex and α-cyclohexylaceto-phenone in the solid state, respectively.

Although additonal studies are warranted before the details of the effect of zeolite adsorption on Type II photochemistry can be fully delineated, the results of this work can most simply be interpreted in terms of the degree of molecular flexibility (or mobility) of the ketone allowed by adsorption into these materials. It is well-known that conformat-ional effects are critical to the outcome of Type II reaction[5]. Previous studies[5,11,12] have shown that fragmentation of the 1,4-biradical requires a conformation in which both singly occupied p-orbitals can overlap significantly with the central σ-bond being broken. If this conformation cannot be achieved, the cyclization pathway may be favoured. However, cycli-zation requires extensive molecular motion in that the pedant aryl, hydroxyl and alkyl groups of the 1,4-biradical must sweep a relatively large volume of space before bond formation can occur; fragmentation, on the other hand, requires much less motion(Figure 1).

Silicalite is a relatively new zeolite[15] that is organophilic and hydrophobic and is capable of adsorbing benzene[15] (main channel dimensions 5.2 X 5.8 Å). Because the kinetic diameter of the pore (∿ 6Å) is just sufficient for the benzene ring, once $\underline{1} - \underline{3}$ are adsorb-ed into this zeolite, one would expect these molecules to undergo very little motion. For $\underline{1}$ and $\underline{2}$, in which Type I reaction is not competitive, those molecules adsorbed that have the correct conformation for hydrogen abstraction via a 6-membered transition state, will react to give a 1,4-biradical that is highly constrained from undergoing closure to form cyclobutanol. A slight twisting of one bond, however, will result in a conformation that resembles B (Figure 1), which can fragment without much additional motion. Cyclization from a conformation resembling B still requires motion of the p-orbitals inward, and it would appear even this motion is restricted on Silicalite. Fragmentation from a conformation

resembling $\underline{C}$ is also possible, from which cyclization is prohibited. For $\underline{3}$, Type I reaction is known to compete with the Type II process[11]. Adsorption of this ketone on Silicalite results in reaction via the least-motion pathway, namely Type I reaction, to give benzaldehyde as the aromatic product. Thus the behaviour of this ketone on Silicalite is quite consistent with the explanation offered for $\underline{1}$ and $\underline{2}$.

Na$^+$-Y is a large pore zeolite, with a pore diameter of $\sim$8 Å and an internal cavity (supercage) of $\sim$13 Å[6]. Additionally, we have found from related studies[16] that of the zeolites capable of adsorbing benzene-type molecules studied in this work, Na$^+$-Y allows the greatest degree of molecular mobility for photogenerated benzyl radicals. Thus the observed F/C ratios of less than unity for this zeolite probably reflects the increased mobility of the photogenerated 1,4-biradical, allowing it to undergo ring closure readily. Interestingly, this zeolite also gave an inverse t/c ratio for cyclobutanols of $\underline{2}$.

The results for the other zeolites are not readily distinguishable from those observed in solution, although two of these (Na$^+$-X and Na$^+$-Mordenite) are capable of adsorbing $\underline{1}$ - $\underline{3}$[6]. In any event, these two zeolites offer a medium for Type I/Type II reaction which essentially duplicate the behaviour in solution without the presence of solvent. Additional studies are in progress to further study the use of zeolites as a medium for photochemical reactions.

References and Notes

1. Present address: Department of Chemistry, University of Victoria, Victoria, Canada V8W 2Y2.
2. H.L. Casal, P. de Mayo, J.F. Miranda and J.C. Scaiano, J.Am.Chem.Soc.,1983,105,5155.
3. S. Ariel, V. Ramamurthy, J.R. Scheffer and J. Trotter, J. Am.Chem.Soc.,1983, 105,6959.
4. H.L. Casal and J.C. Scaiano, Can.J.Chem.,1984,62,628.
5. P.J. Wagner, Acc.Chem.Res.,1983,16,461.
6. D.W. Breck,"Zeolite Molecular Sieves",Wiley, New York,1974.
7. S.L. Suib, A. Kostapapas and D. Psaras, J.Am.Chem.Soc.,1984,106,1614, and references therein.
8. B.H. Baretz and N.J. Turro, J.Photochem., 1984,24,201.
9. (a) P.A. Jacobs, J.B. Uytterhoeven and H.K. Beyer, J.Chem.Soc.,Chem.Commun.,1977,28;
   (b) K. Chandrasekaran, T.K. Foreman and D.G. Whitten, Nouv.J.Chem.,1981,5,275, and references therein.
10. V.J. Smith,in "Zeolite Chemistry and Catalysis", J.A. Rabo(Ed.),American Chemical Society, Washington,D.C.,1983; Monograph Ser. No. 171.
11. F.D. Lewis and T.A. Hilliard, J.Am.Chem.Soc.,1972,94,3852.
12. P.J. Wagner, Acc.Chem.Res.,1971,4,168.
13. N.J. Turro, K.-C. Liu and M.F.Chow, Photochem.Photobiol.,1977,26,413.
14. Zeolites were Linde molecular sieves obtained from Union Carbide and were activated by heating to 200°C for 10 h.
15. E.M. Flanigen, J.M. Bennett, R.W. Grose, J.P. Patton, R.M. Kirchner and V.J. Smith, Nature, 1978, 271,512.
16. N.J. Turro and P. Wan, to be published.

Table 1. Product Ratios for Phenyl Alkyl Ketones 1 - 3 Adsorbed on Zeolites[a].

Zeolite	1 F/C[c]	---- 2 ---- F/C[c]	t/c[d]	------------ 3 ------------ Type I/Type II[e]	F/C[f]	pore size[g]
Na⁺-A (4A)	2.7	2.3	2.2	0.30	0.50	4 Å
Na⁺-Y (LZ-Y52)	0.82	0.83	0.72	0.38	0.47	8 Å
Na⁺-X (13X)	3.2	3.8	--[h]	--	--	8 Å
Na⁺-Mordenite(LZ-M5) (large-port)	2.5	2.2	2.3	--	--	7 Å
Silicalite (S-115)	>50[i]	>50[i]	N.A.	>50[j]	N.A.	6 Å

(a) Ratios were determined via GLC on a Varian Aerograph model 3700 gas chromatograph after Soxhlet extraction of the photolyzed zeolite sample. Ratios are uncorrected for detector response. Zeolite loading was 2% wt/wt. Estimated error ± 10% of quoted value.
(b) Designation in brackets are Union Carbide product codes.
(c) Ratio of acetophenone to cyclobutanols. For 1 , trans and cis cyclobutanols could not be separated clearly for calculation of t/c ratios.
(d) Ratio of trans to cis cyclobutanols.
(e) Ratio of benzaldehyde to total Type II photoproducts(without added thiol).
(f) Ratio of α,α-dimethylvalerophenone(fragmentation product) to cyclobutanols. Ratio of t/c cyclobutanols not determined.
(g) Approximate kinetic diameter of zeolite(from refs. 6 and 15).
(h) Thermal isomerization between trans and cis cyclobutanols occurs on this zeolite.
(i) No detectable cyclobutanol. Control experiments indicate that cyclobutanols, if formed on this zeolite, can be extracted.
(j) Benzaldehyde is the only observed product. Control experiments indicate that both fragmentation and cyclization products can be extracted out of this zeolite, if formed in the photoreaction.
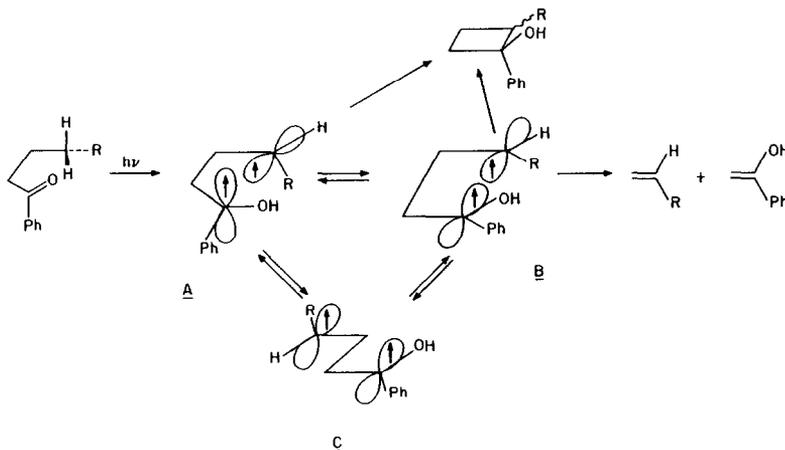

Figure 1. Reaction of the photogenerated 1,4-biradical. A = initially formed conformation in which the half-filled p-orbitals are nearly perpendicular to each other; B = a conformation in which the two p-orbitals are lined up with the central σ-bond; C = an alternative conformation from which fragmentation can occur.