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An Ionic Heavy-Atom Effect in the Solid State Photochemistry of a β,γ-Unsaturated Ketone

Bozena Borecka,[†] Anna D. Gudmundsdottir,[†]
Gunnar Olovsson,[†] V. Ramamurthy,[‡] John R. Scheffer,[*,†] and
James Trotter[†]

Department of Chemistry, University of British Columbia
2036 Main Mall, Vancouver, Canada V6T 1Z1
Central Research and Development
Experimental Station, The DuPont Company
Wilmington, Delaware 19880-0328

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The heavy-atom effect has been widely used to promote triplet state photophysical and photochemical behavior in cases where singlet–triplet intersystem crossing is otherwise inefficient following direct irradiation.[1,2] In the present communication, we report an unprecedented heavy-atom effect that takes place in the *crystalline state* during the solid state photochemistry of a β,γ-unsaturated ketone. Parallel photochemical studies in the cavities of heavy alkali cation containing zeolites are also reported.

The compound chosen for study was the β,γ-unsaturated keto acid **1** (Scheme 1), which had been shown by Coffin, Cox, Carlson, and Givens to undergo a 1,3-acyl shift (1,3-AS) reaction upon direct photolysis in solution to give compound **2** and to afford the cyclopropyl ketone derivative **3** upon triplet-sensitized irradiation.[3] This latter process is an example of a very general and synthetically useful reaction of β,γ-unsaturated ketones that has come to be known as the oxadi-π-methane (ODPM) photorearrangement.[4] Motivated by a desire to study the ODPM photorearrrangement in the crystalline state in order to establish detailed structure–reactivity relationships for the process, we reasoned that alkali metal salts of keto acid **1** might react this way upon direct irradiation by virtue of the heavy-atom effect. At the outset, this seemed like an unlikely prospect, as previous solution phase studies of both the internal[5] and the external[6] heavy-atom effect in the photochemistry of β,γ-unsaturated ketones had found no evidence for enhanced ODPM behavior upon direct photolysis. Nevertheless, the Li+, Na+, K+, Rb+, and Cs+ salts of compound **1** were prepared, recrystallized, and subjected to direct photolysis, both in the crystalline state and in aqueous solution;[7] X-ray crystal structures were obtained for the K+ and Rb+ members of the series.[8]

Scheme 1

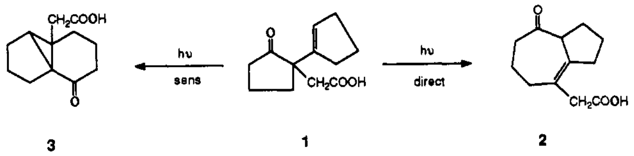

Table 1. Photolysis of Keto Acid **1** and Its Salts in Various Media[a]

entry	M+	**2**:**3** (soln)	**2**:**3** (cryst)
1	H+	85:15 (hexane)	95:5
2	H+	5:95 (acetone)	95:5
3	Li+	>99:1 (H_2O)	90:10
4	Na+	>99:1 (H_2O)	48:52
5	K+	>99:1 (H_2O)	35:65
6	Rb+	>99:1 (H_2O)	40:60
7	Cs+	>99:1 (H_2O)	60:40

[a] Irradiated through Pyrex under nitrogen with a 450-W Hanovia lamp; solution photolyses were carried out at ca. 10^{-2} M to conversions of 35–60%; crystal photolyses were conducted on powders to <12% conversion. The product ratios were determined by capillary gas chromatography following acidification and diazomethane workup to form the methyl esters of compounds **2** and **3**. The K+ and Rb+ product ratios are probably not significantly different from one another within experimental error.

Table 1 summarizes the photochemical results. As can be seen, there is indeed a significant cation effect in the crystalline state but none in aqueous solution. The lack of a heavy-cation effect in solution is not surprising, as the salts are presumably dissociated, and Chandra, Turro, Lyons, and Stone have shown that the external heavy-atom effect is operative only at short distances.[9]

In order to confirm the existence of a heavy-atom effect in the photochemistry of β,γ-unsaturated ketone **1**, we turned to studies in M+ Y zeolites, where M+ = Li+, Na+, K+, Rb+, Cs+, and Tl+. Previous studies by Ramamurthy et al. had shown that such zeolites exert strong heavy-atom effects on the *photophysical* behavior of included aromatic and olefinic compounds,[10] as well as on the bimolecular photoreactions of acenaphthylene.[11] To the best of our knowledge, however, the use of heavy-metal-containing zeolites to perturb *unimolecular* photochemical behavior is unreported. The results are summarized in Table 2. In these experiments, the methyl ester of keto acid **1** was used in order to facilitate extraction of the photoproducts from the zeolites following photolysis. Once again there is a marked heavy-atom effect, both on the photophysical properties and on the product distribution, and in this case the thallium-containing zeolite exerts the strongest influence, a result that is consistent with its remarkable ability to alter photophysical behavior.[10]

The results summarized in Table 1 are intriguing in that, contrary to expectation,[1] the **2**:**3** product ratios are not related directly to the atomic numbers of the heavy ions. One factor that undoubtedly contributes to this involves differences in the crystal and molecular structures of the salts. For example, while the K+ and Rb+ salts have nearly identical conformations in the solid state, as shown by X-ray crystallography,[8] the closest C═O···K+ distance is 2.79 Å, whereas the shortest C═O···Rb+ contact is 3.43 Å.[12] With regard to the zeolite studies, the decrease in the singlet lifetimes and fluorescence intensities and the increase in the phosphorescence intensities with increasing atomic number of the cation are consistent with a heavy-atom effect. Interestingly, however, the product ratio within Cs+ Y does not follow the expected trend. It is possible that a nonuniform distribution of guests within the zeolite may be responsible for this result. The

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[†] University of British Columbia.

[‡] DuPont Company.

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(7) The salts were characterized by IR and ^{1}H NMR spectroscopy, mass spectrometry, and elemental analysis. The cesium and rubidium salts crystallized with one molecule of water in the asymmetric unit, and the potassium salt crystallized with two.

(8) K+ salt: $P\bar{1}$; $a = 6.5913(4)$ Å, $b = 18.417(1)$ Å, $c = 6.4595(4)$ Å; $\alpha = 92.189(6)°$, $\beta = 114.349(4)°$, $\gamma = 80.358(6)°$; $Z = 2$; $R = 3.5\%$. Rb+ salt: $P2_1/a$; $a = 12.112(1)$ Å, $b = 6.6947(8)$ Å, $c = 16.570(2)$ Å; $\beta = 96.835(9)°$; $Z = 4$; $R = 2.7\%$. Full crystallographic details will be published separately.

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(12) The difference in these two contacts is much larger than the difference in the ionic radii of K+ (1.33 Å) and Rb+ (1.48 Å).

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Table 2. Photophysical Properties and Photochemical Behavior of the Methyl Ester of **1** in M^+ Y Zeolites

zeolite[a]	**2**:**3** ratio	fl:ph ratio[b]	S_1 lifetime,[c] ns
Li^+ Y	>99:1	10:1	9.2
Na^+ Y	>99:1	10:1	8.9
K^+ Y	58:42	5:1	8.2
Rb^+ Y	47:53	2:1	6.9
Cs^+ Y	82:18	2:1	5.8
Tl^+ Y	38:62	0.2:1	4.4

[a] The zeolites were prepared as described previously.[10] Zeolite inclusion was achieved by stirring 10 mg of keto ester with 300 mg of zeolite in hexane. Following 6 h of stirring, the complex was filtered and washed thoroughly with hexane. The resulting white powders were placed in Pyrex tubes, degassed at 10^{-4} mm, and sealed, and the contents were irradiated with a 450-W mercury arc lamp. The photoproducts were extracted by stirring the irradiated powders overnight in ether. Excellent mass balances indicated complete extraction of the products whose ratios were determined by capillary GC. [b] Two emissions, one with short lifetime (nanosecond range, λ_{max} = 378 nm) and the other with long lifetime (millisecond range, λ_{max} = 430 nm), were recorded at 77 K. Both emissions had the same excitation spectra at 77 K. At room temperature, the longer wavelength emission was absent. The short wavelength emission is attributed to the S_1 state and the long wavelength one to the T_1 state. The fluorescence emission intensity, measured in terms of "counts" utilizing a SPEX fluorometer, decreased with increasing atomic number of the cation, and the phosphorescence intensity increased. [c] The singlet lifetimes were measured at 77 K on an Edinburgh single photon counting spectrometer.

zeolites used were not fully exchanged,[10] and it is quite likely that the guest molecules would prefer cages containing Na^+ rather than cages containing the much larger Cs^+. Studies of the photophysical behavior of aromatic compounds in zeolites have been interpreted in exactly this way.[13] It is also possible, as Turro and Zhang have suggested for dibenzyl ketone,[14] that, in the increasingly crowded supercages of alkali ion-exchanged zeolites, one reaction pathway may be progressively favored over the other as a result of steric constraints. Arguing for the heavy-atom interpretation in the present case, however, is the fact that Tl^+, which is comparable in size to Rb^+ but has a higher atomic number, has a greater influence on the photoproduct distribution.

It is now well accepted that the 1,3-AS process in β,γ-unsaturated ketones originates not only from S_1 (n,π^*) but from T_2 (n,π^*) as well, and that the ODPM rearrangement occurs primarily from T_1 (π,π^*).[15] While internal heavy-atom-enhanced $T_1 \rightarrow S_0$ radiationless decay has been demonstrated by Givens, Chae, and Matuszewski,[5b] and external heavy-atom-induced $S_1 \rightarrow T_2$ intersystem crossing has been reported by Schuster and Calcaterra,[6] the present results provide the first experimental evidence for heavy-atom-assisted $S_1 \rightarrow T_1$ intersystem crossing in a β,γ-unsaturated ketone. Current work is devoted to demonstrating the same effect in crystalline salts formed between amine-containing β,γ-unsaturated ketones and hydrogen halides. The present studies now enable both the 1,3-AS and ODPM reactions of β,γ-unsaturated ketones to be investigated by the powerful crystal structure–reactivity correlation method,[16] and this aspect of the project will be reported in the near future.

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