Destruction of the Urea Host Lattice by the Photochemical Fragmentation of Molecular Guests

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Received May 21, 1998. Revised Manuscript Received September 2, 1998

Photochemistry in confined environments can lead to both different products and different product distributions from those observed in solution photochemistry, leaving open questions concerning the chemical involvement of the host lattice, including whether it maintains its structure. We have found that photolysis of the urea inclusion compound of 5-nonanone shows destruction of the hexagonal urea host lattice and concomitant conversion to the close-packed tetragonal urea structure. In addition, irradiation of urea-d_4/5-nonanone gives substantial deuterium incorporation, especially at the α-CH_3 of the fragmentation product, 2-hexanone. By studying both the rates of photochemical conversion of 5-nonanone and the loss of the urea host lattice in urea/5-nonanone, we deduce that the structural changes of the urea lattice are associated with fragmentation products that are too small (i.e., too volatile) to support urea inclusion compounds. Our observation of even more degradation of the urea host lattice upon photolysis of urea/2-hexanone, a reaction which leads to a greater proportion of smaller guests than for urea/5-nonanone, supports this conclusion.

Introduction

Inclusion compounds are multicomponent materials consisting of one species forming a host lattice in which the other species can reside. They can have interesting topologies, ranging from layered structures (e.g., clays and intercalates) to channels (nonintersecting channels as in the case of urea inclusion compounds or intersecting channels as in zeolites) to isolated cavities (these are clathrates, e.g., gas hydrates). The confined environments of guest species in inclusion compounds have demonstrated utility in investigations of structure−property relations,[1] and modification of the guests' physical and chemical properties,[2] including photochemical behavior.[3] In general, the host lattice is considered to be inert.

We report photochemical investigations of urea inclusion compounds, including the following findings: (1) evidence for the photochemically induced breakdown of the hexagonal urea host lattice upon irradiation of urea/5-nonanone, (2) indications of the active chemical participation of urea, and (3) signs that the structural changes of the urea lattice are associated with products that are too small (i.e., too volatile) to support urea inclusion compounds.

The industrial world production of urea is ca. 10^8 tons/year, mostly the tetragonal form of urea for use in fertilizers.[4] Urea inclusion compounds are used in the petroleum refining industry to separate hydrocarbons by extractive crystallization for production of aviation fuels and in dewaxing lubricant oils by selective inclusion of guest species.[4] In its inclusion compounds, urea forms hydrogen-bonded helices (hexagonal crystalline host lattice) in which linear hydrocarbons and many of their derivatives can be accommodated in channels of ca. 5 Å diameter, usually with no stoichiometric relationship between urea and the guest.[5] X-ray diffraction shows that urea/5-nonanone is incommensurate (i.e., the urea *c*-axis repeat distance, or a small multiple thereof, is not an integer multiple of the guest repeat distance), although the guest molecules exhibit aspects of three-dimensional ordering.[6] Pure urea forms a different structure from urea inclusion compounds: it is a hydrogen-bonded tetragonal structure in which there are no voids sufficient to accommodate guests.[7] A previous investigation of the photochemistry of 5-nonanone in its urea inclusion compound showed the predominance of Norrish Type II[8] products.[9] Although concern for the integrity of the host lattice due to the cyclic six-center transition state required for this reac-

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(2) For a review, see *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögle, F., Eds.; Pergamon: Oxford, 1996.

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(8) For a review, see: Wagner, P. J. In *CRC Handbook of Photochemistry and Photobiology*; Horspool, W. M., Song, P.-S., Eds.; CRC Press: Boca Raton, 1995; pp 449−470, and references therein.

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10.1021/cm9803713 CCC: $15.00

tion was noted, similar stereospecificity in both the primary and the secondary photochemical products suggested that the urea lattice remained intact. The main purpose of the present work was to investigate the stability of the urea host lattice after photochemical reaction of its guest species. The results of this study have implications concerning the use of urea inclusion compounds under conditions where the guest species can undergo photochemical reactions.

Experimental Methods

All samples of urea/5-nonanone for photochemical studies were thin films, prepared in situ in 1.7 mm diameter Kimax-51 capillary tubes by pumping of the solvent from an unsaturated solution [an aliquot of a solution of ≈2.6 g of urea (Fischer, 99%) dissolved in 100 mL of methanol (Aldrich, 98%), to which 12 mL of 5-nonanone (Aldrich, 98%) had been added]. After solvent removal, the capillary tubes were sealed with a flame. This procedure produced films thin enough for relatively homogeneous photolysis (as judged by photolysis of samples that were not rotated during irradiation), but thick enough to give a useful Raman signal. The tubes were sealed in order to minimize the loss of volatile products over the course of photolysis. The mole ratio of urea to 5-nonanone, determined from melting behavior by heating at 10 K/min in a Perkin-Elmer Pyris-1 differential scanning calorimeter, was 7.6 ± 0.6. [Urea/5-nonanone melts incongruently with an onset temperature of 375.9 ± 0.5 K to produce liquid 5-nonanone and solid (tetragonal) urea; further heating results in onset of melting of urea at $T = 406.3 \pm 0.5$ K; the enthalpy change associated with melting of urea is proportional to the amount of urea in the sample.] From quantitative ^{1}H NMR, the host:guest ratio was determined to be 8.0 ± 0.3.

Urea-d_4/5-nonanone was prepared in the same way as urea/5-nonanone except that urea-d_4 (Aldrich, >98% D) and methanol-*O-d* were used. Quantitative ^{1}H NMR in DMSO-d_6 (MSD Isotopes, 99.9% D) showed that the resulting samples contained urea with 94.5 ± 1% D before irradiation. Differential scanning calorimetry (urea-d_4 melts incongruently with onset temperatures of 371 ± 1 K and 404.4 ± 0.7 K) indicated a urea-d_4:5-nonanone mole ratio of 6.9 ± 0.7.

Urea/2-hexanone was prepared using the same method as urea/5-nonanone; 2-hexanone (Aldrich) was research grade (>99%).

Raman spectroscopy was used to check for transformation of the hexagonal urea inclusion compound to tetragonal urea. Raman spectra were recorded with a resolution of 4 cm^{-1} on a Bruker RFS 100 Fourier transform spectrometer; the probed area of each sample was ≈1 mm^2 with scattered light collected at 180° using a Ge diode detector. Incident light was the 1064.5 nm line of a Nd:YAG laser with a power of ≈225 mW. Raman spectra were collected for each sample tube before and after photolysis.

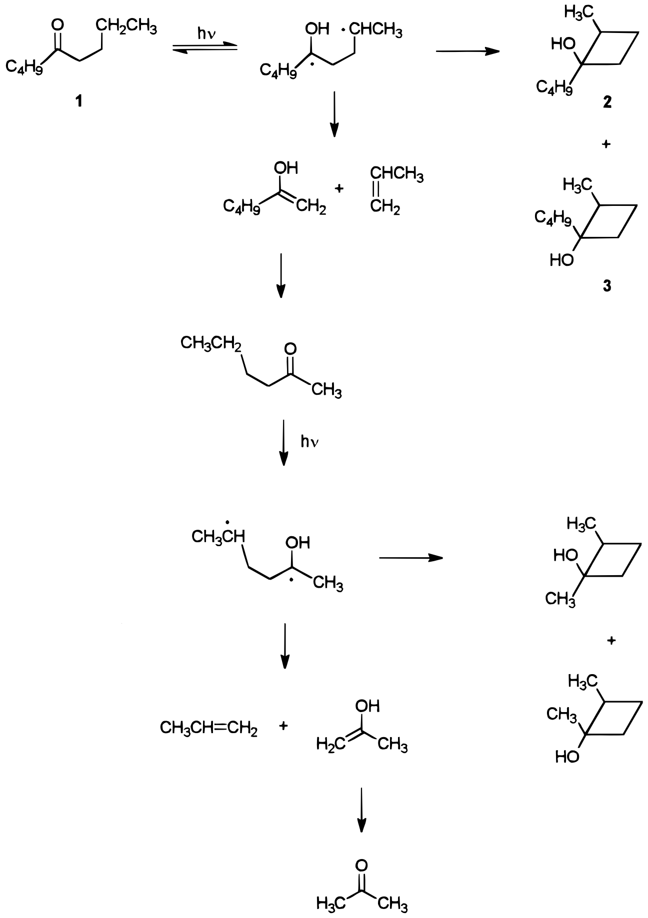
Irradiations were carried out using a 450 W medium-pressure Hg lamp encased in a Vycor filter with a surrounding water jacket. Five capillary tubes, rotated continuously during irradiation, were used for product analysis for each irradiation period. Sample heating during irradiation was negligible.

Products were analyzed by GC [Perkin-Elmer Auto-System with 15 m DB-5 (5% phenyl) methylpolysiloxane capillary column; flame ionization detection; calibrated] and GC/MS (HP 5890A GC with HP 5970 mass selective detector) analysis; all five tubes were crushed and the products were extracted. GC/MS analyses were carried out in triplicate.

Results and Discussion

Guest Photochemistry. Irradiation of urea/5-nonanone, **1**, confirmed[9] Norrish Type II photochemistry,[8] including the stereospecificity and the dominance of fragmentation over cyclization. The isomer with the methyl group cis to the hydroxyl group, **2**, is produced in about 30-fold excess over the trans isomer, **3**, consistent with the finding that boatlike transition states are more prevalent than chairlike transition states in solids.[10] (See Scheme 1 for details.)

Scheme 1



Breakdown of the Urea Lattice. We have used Raman spectroscopy to monitor the integrity of the hexagonal urea inclusion compound structure as a function of irradiation, assuming that urea is in either the hexagonal or the tetragonal form. The vibration used to monitor hexagonal/tetragonal urea was the C−N symmetric stretch, at 1022 cm^{-1} (hexagonal) and 1010 cm^{-1} (tetragonal)[11] chosen for its strong intensity, measurable shift with structural change, and lack of interference from other lines. To quantify breakdown of the hexagonal lattice, relative Raman intensities of the C−N stretch in both forms of urea were required, and these were determined by at least three measurements of each of eight ground, powdered samples prepared from measured proportions of hexagonal and tetragonal urea, in which the ratio of the absolute intensities of the hexagonal-to-tetragonal lines for this mode was found to be 8 ± 4. Raman intensities for virgin and irradiated samples in the region of the C−N symmetric stretch were fit to two Gaussian functions (one centered at 1022 cm^{-1}, the other at 1010 cm^{-1}),

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[10] Ariel, S.; Ramamurthy, V.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1983**, *105*, 6959−6960.

[11] Yamaguchi, A.; Miyazawa, T.; Shimanouchi, T.; Mizushima, S. *Spectrochim. Acta* **1957**, *10*, 170−178. Casal, H. *App. Spec.* **1984**, *38*, 306−309.

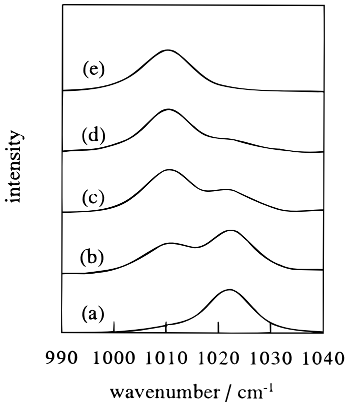

Figure 1. Raman spectra of urea/5-nonanone as a function of irradiation time: (a) before irradiation, (b) after 40 min of irradiation, (c) after 80 min of irradiation, (d) after 120 min of irradiation, and (e) pure urea.

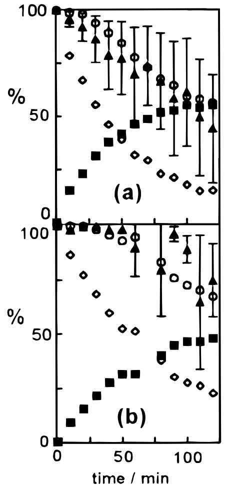

Figure 2. Urea lattice and guests as a function of irradiation time (a) for urea/5-nonanone and (b) for urea-d_4/5-nonanone: ▲, % hexagonal lattice with error bars; ◇, mole % 5-nonanone guest; ■, mole % 2-hexanone and its products; ○, mole % {5-nonanone + *cis-* and *trans*-1-butyl-2-methylcyclobutanol + 2-hexanone}.

and mole ratios were taken from peak areas relative to the calibration.

Raman analysis of irradiated urea/5-nonanone samples showed *conversion of the hexagonal urea lattice to the tetragonal form during irradiation*. Figure 1 shows the evolution of the Raman spectrum of urea/5-nonanone as a function of irradiation time, and Figure 2a quantifies the degradation of the hexagonal urea structure. We ruled out the photochemistry of urea itself by irradiation of urea/hexadecane; analysis showed no breakdown of the hexagonal urea lattice under the same irradiation conditions.

For urea-d_4/5-nonanone, the N−D$_2$ rock was the most sensitive mode to quantify breakdown of the hexagonal lattice; this vibration occurs at 983 cm^{-1} (hexagonal) and 1002 cm^{-1} (tetragonal). Calibration was carried out by at least three determinations of intensities of the 983 and 1002 cm^{-1} lines in each of four known mixtures, which showed that the tetragonal/hexagonal absolute intensity ratio for this mode was 6.3 ± 0.3; the calibration value was more certain than for unlabeled urea because crushed hexagonal and tetragonal deuterated samples mixed better, presumably because urea-d_4/5-nonanone has less propensity to form needles. Raman spectra of urea-d_4/5-nonanone are shown as a function of irradiation time in Figure 3. Loss of the hexagonal urea structure on irradiation of urea-d_4/5-nonanone (Figure 2b) was similar to that for unlabeled urea (Figure 2a).

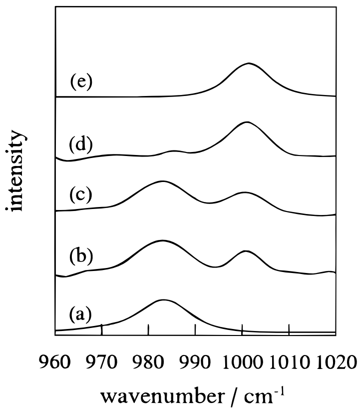

Figure 3. Raman spectra of urea-d_4/5-nonanone as a function of irradiation time: (a) before irradiation, (b) after 40 min of irradiation, (c) after 80 min of irradiation, (d) after 120 min of irradiation, and (e) pure urea-d_4.

Reaction of Urea with the Guests. Irradiation of urea-d_4/5-nonanone showed extensive, almost exclusive, deuterium incorporation at the α-methyl group in 2-hexanone. Deuterium incorporation was determined by GC/MS of products in comparison with GC retention times and MS fragmentation patterns of authentic samples including 2-hexanone-1,1,1,3,3-d_5 (prepared by repetitive reflux of 2-hexanone with D$_2$O and a trace of NaOH); 3 ± 1% deuterium incorporation was found in 5-nonanone, 5 ± 2% in *trans*-1,2-dimethylcyclobutanol, and 42 ± 4% in the α-CH$_3$ group of 2-hexanone, independent of the irradiation time. Acetone produced from secondary photochemical fragmentation was too volatile to be detected.

The very small amount of deuterium incorporation in 5-nonanone, **1**, demonstrated that urea is not very reactive with the biradical produced by ketone irradiation (Scheme 1).

Incorporation of deuterium in 2-hexanone showed a substantial isotope effect, defined as (percent ^{1}H in 2-hexanone/percent ^{1}H in urea)/(percent ^{2}H in 2-hexanone/percent ^{2}H in urea) $= [(58 \pm 4)/(5.5 \pm 1.0)]/[(42 \pm 2)/(94.5 \pm 1.0)] = 24 \pm 4$, where it has been assumed that deuterium incorporation takes place by the guest reacting with a random H/D distribution in the urea host lattice. (Isotopic compositions were determined by ^{1}H NMR in DMSO-d_6 in comparison with standard solutions, and uncertainty represents propagation of one standard deviation.) This isotope effect is consistent with participation of urea (urea-d_4 was the only source of deuterium; workup was carried out in CH$_3$OH), most likely in the ketonization step following fragmentation (Scheme 1). Ketonization likely takes place in the solid state, not in workup, because the overwhelming presence of exchangeable protons from the CH$_3$OH solvent would likely result in little incorporation of deuterium.

While “inner-molecular” reactions[12] of guest species with their host lattice are known,[13] this appears to be

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[12] Cram, D. J. 213th ACS Meeting, San Francisco, April 1997, Abstract 389.

the first report for urea inclusion compounds. Nevertheless, reaction of the urea with the guest species does not appear to be responsible for the destruction of the hexagonal urea host lattice structure, as production of 2-hexanone does not occur at the same rate as loss of hexagonal urea (vide infra).

Mechanism of Destruction of Hexagonal Urea. Two possible mechanisms for the destruction of the hexagonal urea lattice—(1) "pressure" of the biradical intermediate and (2) urea hydrogen atom abstraction in ketonization—are ruled out by the present findings (Figure 2): (1) biradical pressure would lead to similar rates of loss of the original guest and hexagonal urea (in fact, 5-nonanone disappears *faster*); (2) urea hydrogen atom abstraction would result in comparable rates of the loss of hexagonal urea and the production of ketone (we observe that 2-hexanone is produced *faster*).

To be stable, urea inclusion compounds require guests of a minimum chain length (e.g. six carbons for *n*-alkanes),[5] and some of the photochemical products made here would be too small (i.e., too volatile) to support the inclusion compound structure. Possible guests that could support the hexagonal structure in the present circumstances are 5-nonanone, 2-hexanone, and *cis*- and *trans*-1-butyl-2-methylcyclobutanol. [Although these cyclobutanols do not form urea inclusion compounds (J. C. Scaiano, personal communication, 1997), because they are formed photochemically within the urea lattice, it appears that they would support the inclusion compound structure. Both *cis*- and *trans*-1,2-dimethylcyclobutanol might also support the inclusion compound but they are minor products.] The total of these guests almost exactly tracks the proportion of hexagonal urea lattice (Figure 2), indicating that the most likely cause of hexagonal lattice disruption is the production of guests (i.e., propene and acetone) that are too small (i.e., too volatile) to support the structure of the inclusion compound.

The molecular mechanism of urea lattice disruption could be related to chemical pressure,[14] where the driving forces are closer packing of tetragonal urea and loss of volatile photochemically produced guests.

Our results are consistent with the finding that the photochemistry of urea/8-pentadecanone does not substantially disrupt the host lattice.[15] In contrast with 5-nonanone (Scheme 1), two fragmentation reactions are required for 8-pentadecanone to produce a volatile guest, and since apparently cyclization products do not interfere with the host lattice, only a small proportion of the host lattice of urea/8-pentadecanone would be expected to be disrupted, even at very long irradiation times. Furthermore, we find that irradiation of urea/2-hexanone leads to substantially enhanced destruction of the hexagonal urea host lattice: concurrent irradiation of both compounds for the same time led to loss of 19 ± 6% of the hexagonal lattice for urea/2-hexanone and less than 2% loss for urea/5-nonanone.

Concluding Remarks

The detailed mechanism of the photochemistry of ketonic urea inclusion compounds, including stereochemistry, can possibly be elucidated with other ketones where more is known about the guest−host structures.[5] Single crystal studies, using, for example, a Raman microprobe might be particularly useful.

Photochemical degradation of polymers is one of the relatively few applications of Norrish type II reactions.[16] A possible application of the chemistry described herein is photochemically induced degradation of urea inclusion compounds (with an appropriate proportion of ketonic guests), allowing timed release of (nonphotoreactive) guest species.

Acknowledgment. We are grateful to J. S. Grossert, M. Chan, H. J. P. de Lijser, and the Atlantic Region Magnetic Resonance Centre for experimental assistance and to J. C. Scaiano, L. Johnston, and J. Lusztyk for useful discussions. This work was supported by Natural Sciences and Engineering Council of Canada (M.A.W. and J.A.P.) and the Killam Trusts (M.A.W.).

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(13) For example, guests have been found to react with deoxycholic acid (Lahav, M.; Leiserowitz, L.; Popovitz-Biro, R.; Tang, C.-H. *J. Am. Chem. Soc.* **1978**, *100*, 2542−2544.) and cyclodextrin (Ablet, C. J.; Pleier, J. M. *J. Org. Chem.* **1988**, *53*, 2159−2162.).

(14) Luty, T.; Eckhardt, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 2441−2452.

(15) Casal, H. L. *Appl. Spectr.* **1984**, *38*, 306−309.

(16) Weiss, R. G. In *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song, P.-S., Eds.; CRC Press: Boca Raton, 1995; pp 471−483.