ORGANIC CHEMISTRY AT HIGH PRESSURE : CAN UNSATURATED BONDS SURVIVE 10 GPa ?

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Résumé - Quand le naphthalène en solution dans des mélanges d'alcanes ou d'alcools est irradié à des longueurs d'onde ≤ 315 nm, il est détruit par une série de réactions qui sont fortement accélérées à haute pression. Les analyses GC-MS des photoproduits recouverts après montée à très haute pression (>5 GPa) montrent que plusieurs réactions sont impliquées : 1) la photolyse sensibilisée des molécules de solvant en radicaux alkyles et alkoxyes ; 2) la réduction du naphthalène en tétrahydronaphthalène et radicaux hydronaphtyles ; 3) la polymérisation des radicaux hydronaphtyles et alkyles en dimères, trimères et polymères ; 4) la photoaddition des radicaux du solvant sur le naphthalène ; et 5) l'échange H-D entre le naphthalène et les molécules de solvant. La variation de l'intensité d'excitation en fonction de la vitesse de disparition du naphthalène montre que l'étape photochimique primaire est la formation biphotonique des intermédiaires triplets du naphthalène sensibilisant la production des radicaux libres qui, à haute pression, sont des consommateurs efficaces de liaisons insaturées. Les conséquences de ces phénomènes (ainsi que d'autres décrits dans la littérature) sur la stabilité des composés organiques insaturés, à haute pression, sont discutées.

Abstract - When solutions of naphthalene in mixed alkanes or alcohols are irradiated at 315 nm or shorter wavelengths, naphthalene is destroyed by a series of reactions whose rates are greatly accelerated at high pressures. Analyses of the photoproducts recovered from diamond-anvil high pressure cells by gas chromatography-mass spectrometry demonstrate that several reactions are involved: 1) sensitized photolysis of solvent molecules to alkyl and alkoxy radicals; 2) reduction of naphthalene to tetrahydronaphthalene and hydronaphtyl radicals; 3) polymerization of the hydronaphtyl and alkyl radicals to dimers, trimers and higher polymers; 4) photoaddition of solvent radicals to naphthalene; and 5) H-D exchange between naphthalene and the solvents. The dependence of rate of disappearance of naphthalene on the excitation intensity shows that the primary photochemical step involves two-photons and triplet naphthalene intermediates that sensitize production of the free radicals which, at high pressures, are efficient consumers of unsaturated bonds. Implications of these and other phenomena described in the high pressure literature for the stabilities of unsaturated organic compounds at high pressures are discussed.

The chemistry of organic materials at high pressures is of interest for producing diamonds, high-strength plastics, and other hard materials; selectively accelerating chemical syntheses; understanding explosives; and making new metals and superconductors. Unusual transformations have been reported for specific systems, including: cooking proteins [1]; polymerizing CO [2], CS₂ [3], and benzene [4]; synthesizing tetrathiofulvane directly from CS₂ and C₂H₂ [5]; and converting polyacetylenes from semiconductors to insulators [D. Schiferl and K. Syassen, personal communications]. Except for reaction kinetics at relatively low pressures, these phenomena have not been correlated in a systematic way. Indeed, sub-microgram samples are so difficult to analyze that organic and photochemistry are essentially unexplored at pressures above 3 GPa.

Recently, we [6,7] observed that naphthalene became unusually photoreactive at pressures of the order of 5 GPa. This was unexpected since, with few exceptions, aromatic hydrocarbons are generally stable to ultraviolet (uv) radiation [8-22]. The few photoadditions and photoreductions of aromatic hydrocarbons in "inert" solvents that have been reported [23-26] occur with low yields and at low temperatures.

In order to characterize the high pressure reaction, we developed the techniques to recover the photoproducts for mass spectroscopic analysis that are briefly reviewed here. These analyses showed that major products were derivatives of tetralin (1,2,3,4-tetrahydronaphthalene) [7]; that is, most of the products result from a four-electron reduction. Consideration of the probable mechanisms of these reactions led us to examine more generally the chemistry of the unsaturated carbon-carbon bond at high pressures and to formulate the thesis of this paper, that unsaturated C-C bonds become thermodynamically and kinetically unstable with respect to saturated products at pressures of the order of 10 GPa.

I - EXPERIMENTAL

The photochemistry was excited with either a synchronously-pumped, cavity-dumped dye laser excitation source at 270 or 290 nm or the uv output of 100-W short arc mercury lamp, isolated by a Corning 7-54 filter. Progress of the reaction was monitored by measuring the fluorescence spectra or lifetimes of the solution.

A diamond-anvil high pressure cell was modified for these experiments by attaching with epoxy two stainless steel ring (3.0-mm diameter and 0.6-mm high) around the diamonds to form microcontainers with volumes of about 5 μ l (Figure 1) for recovering reaction products. Naphthalene (Fisher N128 or Aldrich naphthalene-dg) solutions (in absolute ethanol, Publicker Industries, Inc.; methanol, Mallinckrodt AR; pentane, Mallinckrodt spectAR; isopentane, Aldrich spectrophotometric grade), that had been deaerated, were loaded into the cell by placing the cell inside a small stainless steel box, flooding the lower part of the cell including the lower diamond and gasket with the solution, and sealing the sample with the upper diamond. These operations were performed inside of a nitrogen-filled glove box to minimize the exposure of the solution to oxygen. The resulting sample contains only a very small amount of naphthalene, about 80 nanograms or 4×10^{14} molecules.

Figure 1. Cross-section of diamond anvil cell that shows the locations location of the microcontainers (cross-hatched) used to confine the liquid solvent that entraps the sample when the cell is opened.

The small samples and high volatility of naphthalene and the solvents at room temperature forced us to develop special procedures for collecting the products. These procedures were performed in a cold room (at -15° C) where the cell, solvent, and tools had been stored for at least two hours. The collection procedure began by rinsing the area surrounding the diamond anvils with 5- μ l aliquots of solvent, either uv-grade hexane (Burdick & Jackson Lab., Inc.) or methanol. These solvents were injected with a syringe into the microcontainers, sucked back by the same syringe, and transferred to a 5-mm diameter Pyrex tube. This operation was repeated until about 0.1 ml was collected. The rinsings were combined and analyzed by GC-MS in order to detect impurities and residual naphthalene surrounding the diamonds.

Next, in an almost continuous series of operations, 5- μ l of fresh solvent was

injected into microcontainers in order to surround the diamonds with solvent (Figure 1); the pressure was slowly released; the upper piston was lifted, removed and turned over; and a few more microliters of the solvent were quickly delivered to each microcontainer to cover the tips of the diamonds. The gasket was then rinsed with about 10 μ l of solvent by squeeze-suck cycles of a pipet, and each diamond and its microcontainer were rinsed with the same pipet. The rinse solutions were transferred to a second Pyrex tube.

The solutions in the Pyrex tubes then were reduced in volume to about 2 μ l by flowing a gentle stream of helium from a pipet over the solution. These concentrated solutions were immediately drawn into a 10- μ l syringe and injected into a KRATOS MS-25 gas chromatograph-mass spectrometer (GC-MS) with a 0.256 mm x 30 m DB5 fused silica capillary column (J & W Scientific, Inc.). The oven temperature program for the GC column usually was: initial temperature, 32° C for 10 min; ramp rate, 16° C/min; final temperature, 280° C for 10 min. A Data General Nova computer system was interfaced with the GC-MS for data analysis. The detection limit of the KRATOS MS-25 GC-MS, about 2 ng, is adequate for the photoproduct analyses. Gas chromatographs were obtained with a Hewlett-Packard 5710A gas chromatograph (GC) with a hydrogen flame ionization detector and a 0.256 mm x 30 m SE-52 fused silica capillary column (J & W Scientific, Inc.). Mass spectra (MS) were recorded on an AEI MS902 mass spectrometer.

II - RESULTS

Calibration and Background Studies. GC-MS elution patterns of a sample of the hexane solvent used to rinse the diamond cell and a naphthalene sample recovered from the diamond cell without exposure to uv radiation are shown in Figure 2. The heavier components in the uv-grade hexane are retained preferentially when the solution is concentrated. Thus, the C_n impurity peaks are more intense in the concentrate than in the original hexane. Quantitative studies without uv exposure showed that between 26 and 33 ng out of 80 ± 10 ng of naphthalene loaded into the diamond cell could be recovered.

High Pressure Photochemistry. When 5×10^{-2} M naphthalene in 1:1 pentane:isopentane was compressed to 4.7 GPa and irradiated for 30 minutes at 310 nm with a mercury arc, two new photoproduct bands appeared in the emission spectra [6]. The broad (300-to-550 nm) band has a 5 nsec lifetime, while the structured band at shorter wavelengths (280-310 nm) has a lifetime of 12-to-15 nsec. After short exposures, the growth of the intensity of the broad band (relative to the naphthalene emission) could be partially reversed by heating the sample to 180 °C for one hour. However, after irradiation for two hours, the naphthalene emission could not be restored by heating. This behavior suggests that some weakly-bound naphthalene dimers form during the early stages of the photochemistry. At the same time, naphthalene reacts with solvent molecules to form reduction and addition products. However, with prolonged irradiation, all of the naphthalene, even the weakly-bound dimers, reacts irreversibly to form at least two different types of products. These products were identified by MS and GC-MS methods.

The lighter products were determined by GC-MS analysis of the type illustrated in Figure 3-5. These data were collected from a 5×10^{-2} M solution of naphthalene in 1:1 pentane:isopentane that had been irradiated with a mercury arc for 3 hours and collected with methanol. Naphthalene is clearly absent. The mass spectra for three photoproducts, GC peaks #487, 528 and 532, have the same abundance maxima (at m/z 129 and 130), the mono- and di-hydronaphthyl ions. The higher mass fragments in the spectra show that naphthalene reduction occurs by addition of solvent molecules. Each naphthalene molecule incorporated in these addition products retains only one aromatic ring; thus, the emission band at 280-to-310 nm can be attributed to them. Although it was difficult to determine the total amount of products recovered by this procedure, experience with recovering samples that had not reacted suggested that these "light" products represented about 25% of the initial naphthalene.

Figure 2. GC-MS elution patterns of (a) concentrated hexane used to rinse the surroundings of the diamonds and (b) naphthalene recovered in hexane from diamond cell without photochemistry.

Another type of product was found by carefully examining the diamond tip and gasket after the lighter molecules had been collected. These surfaces were thinly coated with a white precipitate that was insoluble in either hexane or methanol. Because epoxy was used to form the microcontainers, stronger solvents could not be used to rinse them. By mass spectral analysis of similar deposits obtained from atmospheric pressure experiments, these products were identified as high molecular weight compounds in which several solvent and aromatic moieties are linked. The permanent, broad (300-to-550 nm) emission spectra are attributed to this material.

Photochemistry at Atmospheric Pressure and Room Temperature. When a broad, bright white emission was observed during an unintentionally prolonged 315-nm irradiation of a solution of naphthalene in methanol contained in a Pyrex tube, experiments were conducted with naphthalene or naphthalene-d₈ in 4:1 methanol:ethanol or 1:1 pentane:isopentane [7]. For all combinations of naphthalene and solvent (naphthalene or naphthalene-d₈, alcohols or alkanes, deaerated or aerated), a precipitate with a the same bright fluorescence formed, and most of it deposited on the tube wall. (Similar deposits did not form in quartz tubes which suggests that an early step in the formation of the deposit can be reversed by short wavelength uv.)

Figure 3. GC-MS elution pattern of a 5×10^{-2} M solution of naphthalene in 1:1 pentane:isopentane collected by methanol from the diamond cell after a 3-hour irradiation with an Hg arc.

Figure 4. Mass spectrum for GC peak #487 of Figure 3, trihydronaphthalene.

Figure 5. Mass spectrum for GC peak #528 of Figure 3, pentyl-bi-dihydronaphthalene.

The chemistry of these deposits was studied by irradiating samples with a new, tightly-focussed mercury arc for one or more days, diluting the resulting solution fivefold with additional solvent, and injecting 500-nl aliquots of the diluted solutions into the GC-MS system. These analyses, which are described in detail in References 9 and 29, showed that, in 4:1 methanol:ethanol, almost all of the naphthalene photoreacted within 24 hours, whereas, in 1:1 pentane:isopentane, only small portion of naphthalene reacted during 30-to-60 hours. (For comparison, reaction at high pressures were complete within a couple of hours and were more rapid in the alkane solvents.)

The product analyses clearly demonstrated that the chemistry begins when naphthalene is photoreduced to a hydronaphthyl or alkyl-naphthyl radical. These radicals then combine with each other to produce dimers or react further with other naphthalene or solvent molecules to form adducts. All of the naphthalene photoproducts found in the solution is estimated to contain less than half of the original naphthalene. More than half of the naphthalene ends up in the precipitate.

Similar photoproducts were obtained with naphthalene-d₈ in perprotonated pentanes; however, all of the GC-MS fragmentation patterns were broadened. These patterns indicated that, during the photoreaction, one to three deuteriums exchange with hydrogens from the solvents. Other fragmentation patterns suggested that deuterated pentane radicals, which came from the H-D exchange reaction, reacted with protonated pentane to form deuterated C₁₀.

The precipitates would not elute at the highest temperature of the GC column and could not be analyzed by GC-MS. They were characterized by direct mass spectra, nmr, and luminescence spectroscopy. Direct mass spectra were measured as these solids slowly evaporated while they were heated from 200 to 400° C. Figure 6 shows a mass spectrum of the precipitates from a 36-hour irradiation of naphthalene in 4:1 methanol:ethanol. The fragmentation pattern clearly shows monomers (m/z 129), dimers (m/z 258), trimers (m/z 387) and tetramers (m/z 516) of hydronaphthalenes with extensive ion series of -(CH₂)- or -(CH₂)OH. The dominant ions, from m/z 128 through 132, imply multiple reductions. Multiple peaking throughout the spectra implies that the precipitate is a mixture of polymerized hydronaphthalenes and solvent molecules. Precipitates from alkane solutions had similar spectra.

Figure 6. Mass spectra of the precipitates obtained from a 5×10^{-2} M solution of naphthalene in 4:1 methanol:ethanol after a 36-hour irradiation with an Hg arc under oxygen-free conditions.

This interpretation was confirmed by the nmr spectra and fluorescence spectra of the precipitates. The broad fluorescence spectra were similar to those of aromatic polymers (see, for example, the spectrum of polystyrene in ethyl acetate [28] or poly-2-vinylnaphthalene at 10^{-3} M in 2-vinylnaphthalene [29]). These broad emission bands result from intra-chain overlapping and coiling of the aromatic rings that enhance interactions among the pi orbitals.

III - PHOTOCHEMICAL MECHANISM

That the initial steps of the photoprocess forms solvent radicals by energy transfer from a triplet state of naphthalene excited by sequential absorption of two photons has been suggested by several studies [25, 30-34] and by the measured 2.0 ± 0.3 -power dependence of the rate of reaction on the intensity of excitation. [7] However, direct ionization of the excited triplet aromatic or the direct H abstraction by the excited triplet aromatic from the solvents cannot be excluded. Whether the efficiency of the two-photon pumping process increases or decreases with pressure depends critically upon pressure dependences of the rates of intersystem crossing from the singlet state excited by the first photon and of non-radiative decay of the intermediate triplet. Offen's studies of rigid solutions [35] imply that the pumping efficiency increases slightly with increasing pressures. However, those results may not be transferable to fluids where the reduction in diffusional quenching of the intermediate triplet with increasing solvent viscosity may increase the pumping rate.

The subsequent processes have not been carefully considered in earlier studies, but a likely reaction scheme is illustrated in Figure 7. After a solvent molecule dissociates to a hydrogen atom and solvent radical, at least one of these radicals adds to naphthalene molecule(AH) to form a hydronaphthyl radical, $\cdot\text{AH}_2$, or alkyl naphthyl radical, $\cdot\text{AHR}$. The volume of activation and overall volume change for the dissociation step should be positive, and the rate and yield of this step would be expected to decrease with increasing pressures. This adverse effect might be compensated by close coupling of the dissociation to the addition step with its negative volume of activation and overall volume change.

The reversible dimerization of naphthalene also may be important early in the photochemistry. Bonds between the molecules of the dimer destabilize the pi-bonds of each naphthalene moiety. Thus, dimers should photoreact more readily with radicals than monomers. Furthermore, dimer production would be enhanced at high pressure. In such a circumstance, the hydronaphthyl naphthalene radical ($\cdot\text{AH}_2\text{-AH}$) would be the key intermediate. After photoreduction or photoaddition, the dimer might dissociate; or the relation might persist to the final product.

Figure 7. Proposed scheme of the two-photon induced radical reactions.

Formation of reduced naphthyl radicals open up several radical chain propagating and terminating reactions that consume naphthalene. For instance, $\cdot\text{AH}_2$ may react with an H atom or $\cdot\text{R}$ to form adducts, AH_3 or AH_2R . These adducts can react further with H atoms or solvent radicals to form tetrahydronaphthalene (AH_5), trihydronaphthyl adducts (AH_4R), or multiadducts ($\text{AH}_2\text{RR}'$). Two $\cdot\text{AH}_2$ radicals may combine to give hydronaphthyl dimers ($\text{AH}_2\text{-AH}_2$). Hydronaphthyl radicals also may attack naphthalene to form dimer radicals of reduced naphthalenes that may attack other naphthalenes to form trimer radicals and eventually polymers, and the reductive photoadducts may represent side reactions to the main polymer chain. H atoms from the dissociation of protonated solvents can attack naphthalene-d₈ and replace D atoms to form naphthalene-d_i ($i < 8$), and the D atoms can react with the solvent molecules. Two solvent radicals also can combine to yield longer molecules which may explain the large amounts of C₁₀ alkanes found in some pentane runs.

With the glaring exception of derivatives of dihydronaphthalene, most of the products that can be derived from the scheme in Figure 7 were detected by GC-MS analyses. This suggests that dihydronaphthalene derivatives that formed were efficiently converted to tetrahydronaphthalene derivatives. This can be readily understood in terms of the enthalpies and volumes of activation and reaction for the relevant steps:

If both HR and HR' add to the same ring of the original naphthalene, the standard

enthalpies of reactions for these steps at atmospheric pressure should be about +100 and -130 kJ/mol, respectively, since the difference between the resonance energies of naphthalene and benzene must be supplied in reaction (1). At low pressures, both steps have positive enthalpies of activation; but, again in this respect, step (1) should be more endoergic than step (2). Thus, since the photoexcitation supplies radicals of sufficient energy for the more endoergic step (1), the similar but less endoergic step (2) should proceed facily under the same conditions to convert dihydroderivatives to tetrahydroderivatives. Further conversion from tetrato hexahydroderivatives involves an even more endothermic step in which the resonance energy of benzene must be supplied. This may not be possible for the excitation conditions of these experiments.

Pressure should strongly affect the kinetics of these addition-propagation steps of the mechanism. Each intermolecular addition decreases the molar volume of the system by between -10 and -20 cm³ because short intermolecular bonds replace long intermolecular bonds. The volumes of activation should have similar signs and magnitudes. Thus, for each step, the enthalpies of activation and reaction decrease by between -10 and -20 kJ/GPa; and the rate of each step increases by about a factor of e^4 per gigapascal. Thus, by pressures of the order of 10 GPa, step (1) should be exothermic. At somewhat higher pressures, conversion of the tetrahydroderivatives to non-aromatic species cannot be neglected.

These observations also can explain high pressure phenomena as diverse as the shock-induced polymerizations of benzene and naphthalene reported by Dremm [35] or the loss of metal-like reflectivity of the polyacetylenes, for examples. During shock compression, pressure lowers the activation barriers and local heating by the high stress gradients activates molecules over this lower barrier to produce radicals that consume unsaturated bonds until the sample is quenched. The mobile charges of the polyacetylenes also are radicals that want to cross-link neighboring chains. Pressure increases the concentration of these reagents by decreasing the bandgap and also facilitates the interchain reactivity by bringing adjacent chains closer. If the intrachain mobility of the radicals increases with pressure, the reactivity also will be enhanced since, within any time interval, the reactive radicals will sample a larger number of potential reaction sites.

Thus, the implications of this work are general. Just as graphite is thermodynamically unstable with respect to diamond at pressures of the order of 5 GPa, aromatic C-C bonds become thermodynamically unstable with respect to production of large saturated molecules at pressures of the order of 5 to 10 GPa. (Of course, the isolated, unsaturated double and triple C-C bonds of the ethylenes and acetylenes are unstable even at atmospheric pressure.) Furthermore, there is no qualitative difference whether the an unsaturated bond is saturated by addition of an unsaturated or a saturated species. Until somewhat higher pressures, unsaturated bonds may remain kinetically stable. Nevertheless, unsaturated C-C bonds will not survive pressures much higher than 10 GPa.

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