contribution from such a process.[28]

It has been shown[23] in one previous case (nitrostyrene on platinum catalyzing dibromostilbene reduction) that an increase in i_{CAT} occurs as Γ increases, but that this limits at $\Gamma \approx 4$ nmol cm^{-2}. The surprising aspect of the present case is that the "limit" where inhibition takes over occurs at such small Γ values. These values correspond to about one close-packed monolayer of monomer. Various explanations for this result can be imagined and some of these will be tested in further studies.

In all the above experiments the first CV sweep was initiated only after the electrode El had been immersed in the buffered NADH solution for several minutes. An intriguing aspect of the kinetics was revealed by an experiment in which the first sweep was initiated as soon as the electrode was immersed. Instead of observing the usual gradual decrease of i_p with successive sweeps, an increase was seen. Thus, background subtracted i_p^a for El in the presence of 1 mM NADH ($\nu = 0.2$ V s^{-1}, pH 4.1) was initially 5.8 μA, then 6.6 μA on sweep five and 7.2 μA on sweep ten, and steady state was 7.4 μA. A time-dependent phenomenon of this kind was not observed for El in the absence of NADH. Therefore, we tentatively explain the observation by an initially slow access of NADH to catalyst sites. With time, access to these quinone sites improves and the current increases. We have observed a number of such unexpected time- and/or potential-dependent phenomena with adsorbed polymers and the three-dimensionality of the polymer layers seems responsible.

The success of the NADH catalysis and the unexpected Γ dependence of i_{CAT} make this and related systems of interest for further study. Reports on this work will be forthcoming.

Experimental Section

Cyclic voltammetry was performed by using a PAR Model 173 potentiostat in conjunction with a PAR 175 universal programmer. Voltammograms were recorded on a Varian F-80A x–y recorder. The current integral was measured by the "copy, cut and weigh" method after background subtraction.

NADH was used as received from Sigma Chemical. A fresh solution was prepared for each run and voltammograms were recorded within minutes after the NADH was added. The vitreous carbon was Lorraine V25, 3.0-nm diameter disks sealed into glass. Britton–Robinson buffer solutions were used for pH 2–10. At pH 0.7, 0.2 N H_2SO_4 was used.

The carbon electrodes were cleaned by abrasion with silicon carbide paper (3M brand NH43 600), wiping with a Kimwipe, abrasion with a 0.3-μ alumina on paper disk (ESCIL Type A3), rinsing with water and acetone and air drying, and rinsing with pyridine and air drying. Background CV curves were run, typically from −0.5 to +0.6 V for ten cycles. The electrode was then recleaned by using alumina, water, acetone, air, pyridine, and air and used to record NADH curves or dip coated with polymer. The dip time was generally 2 min in a 0.02% solution (w/v) of **1** in pyridine.

Polymer 1. Dopamine hydrobromide (1.87 g, 8×10^{-3} mol) was dissolved in 2 mL of hot DMF. An equivalent amount of triethylamine was added and the triethylammonium bromide which formed was filtered after addition of 20 mL of acetone. The acetone was evaporated under vacuum and 20 mL of DMF was added. This solution was dried by using alumina, the alumina was filtered off, and the filtrate was added to 209 mg off methacryloyl chloride (Polysciences). After refluxing for 24 h, water was added and a precipitate collected. After careful washing with water 160 mg of beige powder remained. The elemental analysis suggested 41% loading, i.e., $x = 0.41$, $y = 0.59$ in **1**, and no chlorine remained in the material. Anal. Calcd: C, 61.4; H, 6.88; N, 4.0. Found: C, 61.52; H, 6.51; N, 4.04.. This material is insoluble in acetone and was slightly soluble in pyridine, and shows the expected infrared bands (KBr disk or Nujol mull) from hydroxyl, carboxylic acid, and amide functionalities. In the carbonyl region were bands at 1715 (rel intensity 53), 1660 (65), and 1520 cm^{-1} (49).

The ultraviolet spectrum of the polymer in 40% ethanol/60% water was determined at several pH values. The solution was buffered with 0.1 M Britton–Robinson buffer. In acidic solution the polymer absorbed with $\lambda_{\max}$ 281 nm. Assuming that the loading was 41%, log ϵ per hydroquinone unit was 3.54. The monomer dopamine had $\lambda_{\max}$ 280 nm (log ϵ 3.45). In basic solution, e.g., pH 10.7, the polymer had $\lambda_{\max}$ 287 nm (log ϵ 3.68 per hydroquinone unit). Dopamine at pH 10 had $\lambda_{\max}$ 287 nm (log ϵ 3.67). The pK_a for loss of the first hydroquinone proton from polymer sites was computed from these UV spectra to be 8.90. The dopamine pK_a was 8.1.

Acknowledgments. This work was supported by the NSF and the CNRS. Travel funds for C.D. were supplied by a NATO fellowship.

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Absorption Spectra and Photochemical Rearrangement of Cycloheptatriene Cation to Toluene Cation in Solid Argon

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Abstract: The toluene and cycloheptatriene cations have been produced and trapped in solid argon by matrix photoionization techniques. Toluene experiments gave a photosensitive 430-nm absorption and weak 480-nm band, the cycloheptatriene studies yielded a broad 480-nm absorption and a weak 430-nm band; these matrix bands are slightly red shifted from the photodissociation spectra (PDS) peaks for the corresponding parent cations. Visible photolysis in cycloheptatriene experiments decreased the 480-nm band and increased the 430-nm absorption, indicating that cycloheptatriene cation can be photochemically rearranged to toluene cation. The toluene cation absorption bandwidth is more than an order of magnitude less in solid argon than in ICR experiments; this may be due to quenching excess vibrational energy in the ground-state ion by the matrix and/or a reduction in the rate of internal conversion from the excited-state ion in the matrix owing to rapid relaxation to lower vibrational levels of the excited state where the density of states for vibronic coupling is less. The reduced photolysis rate of toluene cation in the matrix is consistent with the latter point and an efficient removal of vibrational energy from the vibrationally excited ground-state ion resulting from internal conversion.

Introduction

The toluene radical cation and its dissociation products are among the most widely studied ions in mass and photodissociation spectroscopies. The observation of extensive hydrogen scrambling in mass spectra of isotopically labeled toluenes has prompted investigation of the possible isomerization of $C_7H_8^+$ cations produced from toluene and other C_7H_8 compounds. Mass-spectroscopic studies with labeled precursors have been explained by isomerization of the parent cations to a common intermediate for toluene, cycloheptatriene, and norbornadiene.[1-7] Ion cyclotron

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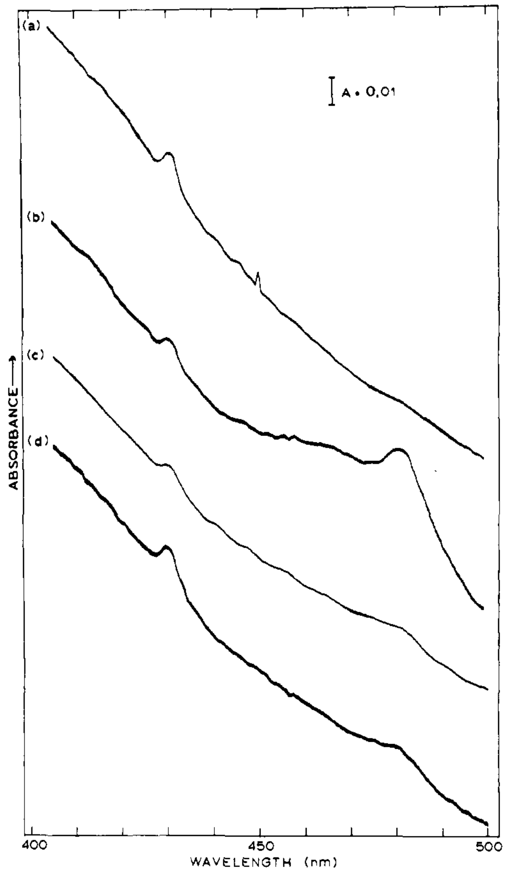

Figure 1. Absorption spectra from 400 to 500 nm following matrix photoionization and further dilution of argon/reagent = 100/1 samples from 3-mm diameter orifice discharge tube during condensation at 22 ± 2 K. Spectra recorded on 0.1 absorbance range of Cary 17: (a) toluene, (b) cycloheptatriene, (c) norbornadiene, and (d) *n*-butylbenzene.

resonance (ICR) studies of toluene cation have produced a strong photodissociation spectrum beginning near 538 nm with a peak at 417 nm and have demonstrated that hydrogen randomization before dissociation is almost complete even with energies near the threshold.[8-12] However, an ICR study employing chemical reactions of isomeric $C_7H_8^+$ cations showed that nondissociating cations from toluene and cycloheptatriene do not interconvert on a time scale of milliseconds,[13] and another ICR investigation revealed different photodissociation spectra (PDS) for these isomeric cations.[14]

Since excess internal energy appears to be the essential prerequisite for interconversion of isomeric $C_7H_8^+$ parent cations, which are thought to be in equilibrium at relatively low internal energies,[10,15,16] the low-temperature matrix isolation technique was employed to trap these cations in their different isomeric structural forms without excess internal energies for observation of their characteristic absorption spectra. Matrix photoionization methods have been used to produce and trap a number of cations, allowing observation of infrared and optical absorption spectra and photochemical behavior, including parent ions like CF_3Cl^+ and CCl_4^+, which readily photodissociate.[17-19] Analogous experiments with C_7H_8 precursors are described in the following report.

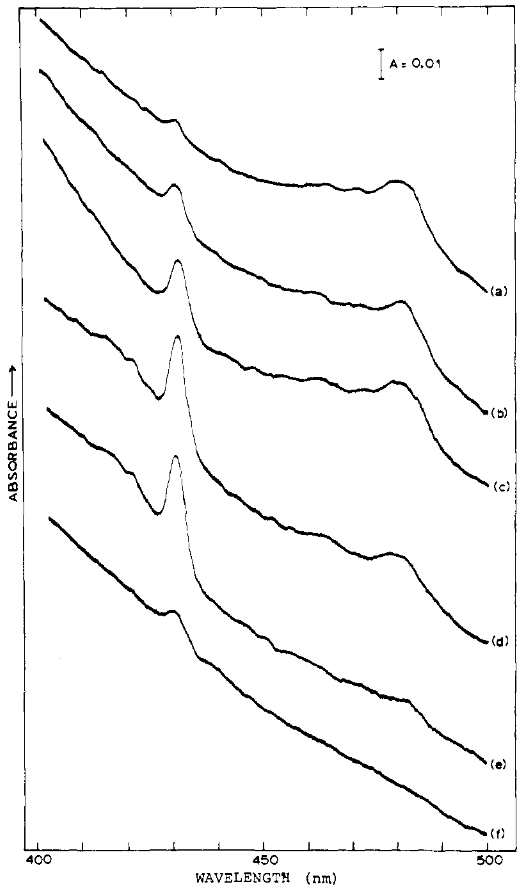

Figure 2. Absorption spectra of cycloheptatriene sample subjected to matrix photoionization, trace (a). Scan (b) recorded after photolysis with 590-nm cutoff filtered high-pressure mercury arc light. Trace (c) recorded after photolysis with 520-nm cutoff filter. Spectra (d), (e), and (f) recorded after 470-, 420-, and 290-nm photolyses, respectively, for identical 15-min periods.

Experimental Section

The cryogenic apparatus and matrix photoionization experiments have been described in previous reports.[20,21] Reagent-grade chemicals were vacuum distilled from glass beads, and argon/reagent = 100/1 samples were prepared. These samples were deposited on a 22 ± 2 K sapphire substrate at 1 mmol/h for 4–7 h with concurrent vacuum ultraviolet irradiation from a similar amount of argon, flowed through a 3-mm orifice quartz tube and excited by a microwave discharge. Thus, the argon/reagent ratio in the matrix was ≈200/1. Spectra were recorded on a Cary 17 spectrophotometer from 280 to 800 nm and regions of special interest were recorded on the 0.1 absorbance range. The light from a high-pressure mercury arc (1000 W, Illumination Industries, Inc., BH-6-1) was reflected from an ultraviolet mirror (Special Optics, reflects 90% between 220 and 1000 nm with decreasing reflection in the near infrared), through colored glass filters, and onto the matrix sample, and additional absorption spectra were recorded.

Results

The spectrum from a toluene experiment employing sample deposition and irradiation for 7 h is illustrated in Figure 1a. Of

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Table I. Visible Absorption Band Intensities (Absorbance Units) for Cycloheptatriene Codeposited at 22 K for 4 h with Argon Resonance Photoionization and Following Filtered Mercury Arc Photolysis for 15-min Periods

absorption	480 nm	430 nm	416 nm
init deposit	0.025	0.005	0.000
590[a]	0.022	0.010	0.000
520	0.020	0.021	0.004
470	0.012	0.040	0.010
420	0.005	0.038	0.010
290	0.000	0.007	0.000
220	0.000	0.000	0.000

[a] Short-wavelength cutoff glass filters used in photolysis.

particular interest are the broad 430-nm band (*A* = absorbance units = 0.010) and the broad, weak 480-nm band (*A* = 0.001). The sharp, weak 449.6-nm band and a strong, sharp 310.5-nm absorption are due to benzyl radical, and a 317-nm band (not shown) has been attributed to C_7H_9 radical.[22] Mercury arc photolysis with 420-nm cutoff light for 30 min decreased the 430-nm band (to *A* = 0.004) and destroyed the 480-nm band without producing any absorption between 400 and 420 nm, and full arc photolysis (220–1000 nm) destroyed the 430–nm band. A similar krypton matrix experiment was performed with toluene, using krypton resonance photolysis and a 30 ± 2 K substrate to minimize light scattering by the sample. After 2 h of sample deposition, new benzyl radical bands were observed at 313.0 and 451.0 nm and C_7H_9 radical was observed at 320 nm, and a weak new broad absorption was detected at 435 nm (*A* = 0.002) above the scattering background.

Two identical cycloheptatriene studies were performed by using 4 h of simultaneous sample deposition and argon discharge irradiation. The spectrum from the first one of these experiments is shown in Figure 2a. A new product absorption was observed at 480 nm (*A* = 0.030) trailing to the blue; the weak 430-nm (*A* = 0.006) band was again observed along with broad, very weak absorption from 410 to 420 nm. Upon photolysis with 520- and 470-nm cutoff mercury arc radiation, the 480-nm band *decreased* and the 430-nm absorption *increased*; 420-nm photolysis halved the 480-nm band and slightly decreased the 430-nm absorption; 290-nm irradiation destroyed the former and almost destroyed the latter. This experiment was repeated to more thoroughly explore this interesting photochemistry. Absorption spectra from the second experiment are shown in Figure 2, and the band absorbance units are listed in Table I; observations from the two experiments were almost identical. Photolysis with 590-nm cutoff light for 15 min reduced the 480-nm band by 10% and doubled the 430-nm band, as can be seen from comparison of traces (a) and (b) in Figure 2; this trend continued with 520- and 470-nm photolysis, shown in scans (c) and (d), which also produced a broad 410–422-nm band peaking at 416 nm. At maximum intensity (*A* = 0.040), the band peaked at 430.5 nm and had a 428–432-nm (~220 cm^{-1}) full width at half-maximum and a threshold at 436 ± 2 nm (22 940 ± 100 cm^{-1}). As in the previous experiment, 420-nm radiation decreased the 430-nm absorption, trace (e). The visible photolysis sequence produced new bands at 301 (*A* = 0.035), 310.5 (*A* = 0.002), and 315 nm (*A* = 0.045). Irradiation at 290 nm almost destroyed the 430-nm band, trace (f); the 310- and 315-nm bands were destroyed and the 301-nm absorption increased. A final full-arc irradiation for 15 min destroyed all absorptions except the 301-nm band, which was substantially decreased. A krypton matrix experiment was also done with cycloheptatriene. New broad, weak bands were observed at 483 and 435 nm (*A* = 0.002) with the sharp benzyl radical band at 451.0 nm (*A* = 0.004). Photolysis with 470-nm cutoff light destroyed the 483-nm band without affecting the weak 435-nm absorption.

Two additional cycloheptatriene experiments were performed by using an 8-mm i.d. orifice discharge tube photoionization source for 3 h and the product bands were more intense. The absorption maximum centered at 479 nm (*A* = 0.066) was flanked by broad structure at 461 (*A* = 0.036) and 444 nm on the higher energy and 498, 519, and 542 nm on the lower energy side. This series of broad bands spaced 810 ± 20 cm^{-1} forms a smooth Franck–Condon profile. The 430- (*A* = 0.024) and 415-nm (*A* = 0.006) bands were also observed. In one experiment initial 650-nm cutoff photolysis with a new, stronger mercury arc lamp reduced the 479-nm band by one third; in the other, photolysis with 750-nm cutoff radiation reduced the 479-nm band by 10%. As in the previous experiments with cycloheptatriene, 470-nm photolysis substantially reduced the 479-nm band system; however, growth in the 430-nm band was limited to 20% in these later photolysis studies.

Norbornadiene (bicyclo[2.2.1]hepta-2,5-diene) was studied and the spectrum after matrix photoionization is illustrated in Figure 1c. Weak, broad bands were observed at 430 and 480 nm (*A* = 0.005). Photolysis with 590-nm radiation produced a weak, broad 416-nm band (*A* = 0.002), increased the 430-nm absorption, and decreased the 480-nm absorption. The photolysis sequence described above had the same effect in this experiment except that the ultraviolet bands were not produced; a final 290-nm irradiation destroyed all product absorptions.

An experiment was performed with *n*-butylbenzene to see if the McLafferty rearrangement product ion,[23] resulting from the loss of propylene, could be detected by an absorption distinctly different from those observed in toluene and cycloheptatriene experiments, as has been found in a recent ICR study.[24] The absorption spectrum, shown in Figure 1d, contains product bands at 430 (*A* = 0.012) and 480 nm (*A* = 0.006); in addition ultraviolet bands were observed at 310.4 (*A* = 0.036) and 316 nm (*A* = 0.024). Photolysis of this sample with the glass-filtered 750–2750-nm light from a 500-W tungsten lamp for 45 min had no effect on the spectrum. Photolysis with 450-nm cutoff light from a high-pressure arc for 15 min reduced the 480-nm band slightly (to *A* = 0.005), increased the 430-nm absorption (to *A* = 0.014), and produced a broad, weak band centered at 416 nm (*A* = 0.005), similar to that shown in Figure 2d. No detectable absorption was observed in the 500-nm region.

Discussion

The matrix photoionization products will be identified and compared to gas-phase observations, and their photochemistry will be considered with regard to possible structural rearrangement processes.

Identification. The 430-nm argon matrix absorption is assigned to the toluene cation (hereafter called T^+) produced by photoionization of toluene molecules (IP = 8.9 eV)[25] with argon resonance radiation (11.6–11.8 eV) and trapped in the condensing argon matrix, as described previously for other parent ions.[17–19,21] This observation of toluene cation is supported by several considerations: (a) the argon matrix absorption energy is in very good agreement with the 3.0-eV energy difference between the onset of ionization and the second band in the photoelectron spectrum;[25] (b) the 430-nm band is in excellent agreement with the PDS band peak at 417 nm for toluene cation;[9] (c) the 430-nm band is photosensitive to 420-nm radiation, as required by the PDS results. The observation of the same 430-nm absorption from three isomeric C_7H_8 precursors provides further evidence for this solid-phase identification of the toluene cation. The marked photochemical growth of the 430-nm absorption (Figure 2) at the expense of the 480-nm absorption in cycloheptatriene experiments, the latter of which can reasonably be assigned to the isomeric cycloheptatriene cation (hereafter called C^+), confirms assignment of the 430-nm argon matrix absorption to the toluene cation.

The 480-nm argon matrix absorption is in excellent agreement with the 470-nm peak in the cycloheptatriene PDS band in ICR studies.[14] These absorptions are in agreement with the energy

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difference between the first and third photoelectron bands for cycloheptatriene.[26] Accordingly, the 480-nm argon matrix absorption is assigned to C$^+$. The 810 ± 20 cm^{-1} progression observed in the stronger C$^+$ spectrum is probably due to the symmetric ring stretching mode, which has been observed near 980 cm^{-1} for benzene cation in the photoelectron spectrum of benzene and at 908 cm^{-1} in the Raman spectrum of cycloheptatriene.[27]

The photodissociation spectrum of norbornadiene did not give a definite band peak; the photodissociation rate increased slightly from blue to red in the visible region.[14] The matrix absorption spectrum of norbornadiene photoionization products revealed only weak bands for the isomeric T$^+$ and C$^+$ cations in the 300–1000-nm region.

Matrix photoionization and photolysis of *n*-butylbenzene produced the 430-nm T$^+$ band in slightly greater yield than the toluene experiments; the 480-nm C$^+$ band was also observed. No absorptions were produced which could be attributed to the *n*-butylbenzene cation,[9] presumably owing to competitive photodissociation processes and rearrangement after photoionization. In the ultraviolet region, the strongest band of benzyl radical was observed at 310.4 nm.[20] The 316-nm product feature cannot be identified with certainty, although it is likely due to a cyclohexadienyl type of radical,[28] found at 310 nm in similar benzene matrix studies,[29] and 317 nm in toluene experiments.[22] No evidence was found for the McLafferty rearrangement product[23] methylenecyclohexadiene cation, which gave a distinctly different PDS than the toluene and cycloheptatriene cations,[24] both of which were observed in the matrix spectrum. It is suggested that the McLafferty rearrangement process takes place upon matrix photoionization of *n*-butylbenzene, but that the methylenecyclohexadiene cation formed is photochemically converted mostly to T$^+$ with a smaller amount of C$^+$, as revealed by the absorption spectrum. However, the mercury arc photochemistry which converts C$^+$ into a T$^+$ also produces a new 416-nm absorption, which could be due to the methylenecyclohexadiene cation as will be discussed below.

Photochemistry. The toluene cation photodissociation spectrum peaks at 417 nm in the gas phase;[9] hydrogen-atom elimination gives $C_7H_7^+$ ions with the benzyl and tropylium structures depending upon photon energy.[10] Photolysis of the 430-nm argon matrix T$^+$ band with 420-nm cutoff light is in agreement with the gas-phase PDS, although the product daughter cation spectrum was not observed. Benzyl cation is reported to absorb at 363 nm in solution[30] or at 290 nm in PDS studies[31] and should have been observed if produced (assuming that the absorption cross section is comparable to T$^+$); however, the more likely product tropylium cation absorbs very strongly at 217 and strongly at 273 nm in concentrated H_2SO_4,[31,32] and these product absorptions would be obscured by the very intense toluene precursor bands.

Photolysis behavior in the cycloheptatriene experiments was carefully studied. As is illustrated in Figure 2, 590-nm cutoff radiation, just to the long-wavelength side of the C$^+$ absorption, caused a photochemical rearrangement to T$^+$. This rearrangement was more pronounced with 520-nm light and most effective with 470-nm radiation which includes the absorption maximum. This photolysis behavior shows that T$^+$ can be produced from C$^+$, which strongly supports their identifications. The photochemical rearrangement of C$^+$ to T$^+$ is clearly competitive with photodissociation of C$^+$ in the matrix. In addition to the T$^+$ band, a broad 410–422-nm absorption with a maximum at 416 nm was observed. The methylenecyclohexadiene cation PDS peaks at 410 nm in the gas phase,[24] which is just below the 417-nm peak for T$^+$ in the gas phase.[9] We tentatively assign the 416-nm argon matrix band to methylenecyclohexadiene cation. This different $C_7H_8^+$ isomer is produced in matrix experiments by photochemical rearrangement of the C$^+$ ion. Continued photolysis of cycloheptatriene samples with 420-nm cutoff radiation substantially diminished C$^+$, began to decrease T$^+$, as expected, and produced new ultraviolet bands at 301, 310, and 315 nm, which were decreased by short-wavelength photolysis. The absorbers responsible for these relatively sharp ultraviolet bands are uncertain; hydrogen addition radicals C_7H_9, like cyclohexadienyl,[27] and hydrogen elimination cycloheptatrienyl radical C_7H_7 are possibilities. The weaker 310-nm band is, however, due to benzyl radical.

The norbornadiene and *n*-butylbenzene experiments provided no new photochemical information. Weak T$^+$ and C$^+$ absorptions were observed and their photochemistry, including production of the weak 416-nm absorption, was similar to that of the cycloheptatriene studies described above.

Gas-Phase Comparisons. It is interesting to compare the gas-phase photodissociation spectra and the matrix absorption spectra for T$^+$ and C$^+$. Our most intense T$^+$ band ($A = 0.04$) in Figure 2d peaks at 430.5 nm (23 289 cm^{-1}) and exhibits a full width at half-maximum of 220 cm^{-1} and a threshold of 22 940 ± 100 cm^{-1}; this is in contrast to the gaseous T$^+$ peak at 417 nm (23 981 cm^{-1}) with a 3000-cm^{-1} full width at half-maximum and threshold at 18 590 ± 70 cm^{-1}. For the C$^+$ species, the matrix band peaks at 480 nm (20 833 cm^{-1}), with a 700-cm^{-1} half-width, and the gaseous ion PDS peaks at 470 nm (21 277 cm^{-1}), with a half-width of approximately 2800 cm^{-1}. The argon matrix peaks for C$^+$ and T$^+$ are red shifted 444 and 692 cm^{-1}, respectively, from the gaseous maxima, both slightly more than the 234-cm^{-1} matrix shift for the sharp origin of the strong $C_6F_6^+$ transition.[34]

The markedly decreased bandwidth in solid argon is of interest, particularly for the extensively studied T$^+$ ion. The major difference between the gaseous and matrix-isolated T$^+$ ions is effective quenching of vibrational energy by the matrix, and this will affect the ground-state ion and the dissociation dynamics. Even though the dye-laser PDS study in the threshold region used 10-eV electron-impact ionization and retained the ions for 150 ms to undergo approximately 30 collisions with neutrals,[12] it is still conceivable that a "few tenths" of an electronvolt of vibrational energy, particularly in totally symmetric modes, might be retained by T$^+$ in an ICR cell; the T$^+$ ions in solid argon at 22 K are surely vibrationally quenched. This may account, in part, for the bandwidth and the 4300 cm^{-1} between the lower energy gaseous and higher energy matrix thresholds for T$^+$ absorption and dissociation. Since the dissociation of T$^+$ involves photoexcitation to a bound excited state, followed by rapid internal conversion to the vibrationally hot ground electronic state, which then eliminates a hydrogen atom, the gaseous PDS may, in fact, be lifetime broadened.[35] A very important effect of the solid argon lattice interacting with the guest T$^+$ ion is to quench vibrational excitation in the excited electronic state to lower vibrational levels where the density of states for vibronic coupling is less; this may reduce the internal conversion rate, which would tend to sharpen the absorption spectrum and retard the photodissociation process. The matrix T$^+$ absorption bandwidth is more than an order of magnitude less than the gaseous PDS bandwidth, consistent with this hypothesis.

Although quantitative comparison of the photolysis rates for T$^+$ in the gas and matrix phases is difficult, an approximate comparison can be made. Irradiation at 420 nm through a 10-mm band-pass interference filter, using a 2500-W Hanovia xenon arc, destroyed virtually all T$^+$ in 0.5 min,[10] whereas 420-1000-nm photolysis of the matrix sample through a Corning 3389 filter (transmits 40% at 430 nm) and the argon matrix (background

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transmits 40% at 420 nm), using a 1000-W high-pressure mercury arc, destroyed only 60% of the T$^+$ in 30 min. Even if the matrix photolysis procedure is only 5% as effective as that used in the gas-phase experiments, photolysis of T$^+$ in the matrix is substantially less efficient than in the gas phase. The observed photochemical rearrangement of C$^+$ to T$^+$ also suggests a reduced rate of photodissociation for C$^+$ in the matrix. Since hydrogen atoms can diffuse freely through solid argon at 22 K without being retained by the matrix cage,[36] recombination of photolysis products in the matrix cage is an unlikely explanation for reduced photodissociation in the solid argon matrix. More likely, vibrational predissociation is rendered less effective in the matrix, owing to faster vibrational relaxation in the ground electronic state reached by internal conversion.

The matrix host provides an efficient sink for internal energy which is necessary to stabilize the T$^+$ and C$^+$ parent cations. Argon resonance radiation (11.6–11.8 eV) exceeds the threshold for production of $C_7H_7^+$ daughter ion from toluene (11.6 eV) and cycloheptatriene (10.1 eV);[37] however, the matrix quenches internal energy at a rate competitive with unimolecular decomposition and enables the parent cation to be stabilized. While internal energy is being quenched from the original parent cation formed, rearrangements of both T$^+$ and C$^+$ have been observed as C$^+$ was found in toluene studies (Figure 1a) and T$^+$ in cycloheptatriene experiments (Figure 1b).

The rearrangement of C$^+$ to T$^+$ on visible photolysis demonstrates that the balance between internal energy from visible light absorption by the ions and internal energy quenched by the matrix provides sufficient internal energy for rearrangement of the ions without dominant unimolecular decomposition. MINDO/3 calculations of the overall activation energy for C$^+$ → T$^+$ rearrangement gave 39.8 and 39.2 kcal/mol (718 and 729 nm) for two different processes.[38] This is slightly lower than the first absorption detected at 542 nm, although the electronic band could tail additional vibrational quanta to the red. The matrix photolysis of C$^+$ with 750-nm radiation (38 kcal/mol) is in excellent agreement with the calculated activation energy for the C$^+$ → T$^+$ isomerization. The observation of C$^+$ rearrangement with 750-nm photolysis at a finite rate in solid argon suggests that the activation energy for this rearrangement may in fact be somewhat lower. An extensive progression in the C$^+$ absorption, probably involving the symmetric carbon–carbon ring breathing mode, indicates a geometry change on excitation; this structural change may aid the rearrangement process. Finally, the C$^+$ $\rightleftarrows$ T$^+$ isomerization documented here by optical spectroscopy provides support for the conclusion from gas-phase experiments[10,15,16] that C$^+$ and T$^+$ are in equilibrium at relatively low internal energies.

Conclusions

The toluene and cycloheptatriene cations have been produced by argon resonance photoionization and trapped upon condensation at 22 K with excess argon. A 430-nm absorption in toluene experiments photolyzed with 420-nm cutoff light and is slightly red shifted from the 417-nm peak of the toluene ion PDS in the gas phase. Cycloheptatriene experiments produced a broad 480-nm absorption, near the 470-nm PDS peak for cycloheptatriene cation, and a small yield of the 430-nm absorption, which were clearly resolved. Visible photolysis *decreased* the 480-nm band and *increased* the 430-nm absorption, indicating that photochemical rearrangement of cycloheptatriene cation to toluene cation is competitive with photodissociation in these experiments.

The absorption spectroscopic observation of C$^+$ in toluene experiments and T$^+$ in cycloheptatriene studies supports the previously proposed equilibrium between C$^+$ and T$^+$ at relatively low internal energies. The toluene cation absorption bandwidth is more than an order of magnitude less in solid argon than in the gas phase. The sharper matrix band may be due to the absence of excess vibrational energy and/or a reduction in the rate of internal conversion from the excited state owing to efficient vibrational relaxation by the matrix. The slower photolysis rate for toluene cation in the matrix is consistent with the latter point and an efficient removal of vibrational excitation from the vibrationally hot ground state produced by internal conversion. The solid argon matrix is a useful medium for trapping large molecular ions for spectroscopic and photochemical studies under conditions where vibrational relaxation is a fast process. These matrix studies suggest that internal energy makes an important contribution to the bandwidth and photodissociation rate in ICR experiments.

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Reactions of Fluorine with Methane upon Photolysis and Diffusion in Solid Argon. Infrared Spectra of HF Hydrogen-Bonded Complexes

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Abstract: Argon/methane and argon/fluorine samples were codeposited at 15 K. Mercury arc photolysis produced new absorptions assigned to the $CH_3F\cdots HF$ hydrogen-bonded complex characterized by an H–F stretching mode at 3774 cm^{-1}, significantly below the 3962-cm^{-1} isolated HF value, and a C–F stretching mode at 1003 cm^{-1}, also below the 1040-cm^{-1} CH_3F value. Sample warming to 25 K to allow diffusion and reaction of fluorine atoms produced additional new absorptions assigned to $H_3C\cdots HF$ characterized by an H–F stretching mode at 3764 cm^{-1}. The reaction of F atoms with CH_4 without radiation in solid argon at 25 K shows that this reaction requires practically zero activation energy.

Introduction

Fluorine reacts explosively with methane at room temperature; in fact, the low-pressure reaction of F_2 with $^{13}CH_4$ diluted in argon has been used to synthesize $^{13}CF_4$.[1] If, however, these reagents are condensed in solid argon, the reaction requires photochemical initiation, and the products of one fluorine molecule and one

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