J. Am. Chem. Soc. 1981, 103, 99-103

Ultraviolet Absorption Spectra and Photochemical Rearrangements of Benzyl and Tropylium Cations in Solid Argon

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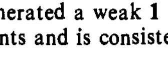
Abstract: New ultraviolet absorptions were produced at 353 and 263 nm upon cocondensation of benzyl bromide vapor with excess argon from an open-ended discharge tube on a sapphire plate at 22 K. Agreement with the pulse-radiolysis solution spectrum of benzyl cation at 363 nm and the 274-nm absorption of tropylium salts in concentrated acid identifies the argon matrix products. Photolysis in the benzyl cation (**1**) absorption band, which is below the dissociation threshold, rearranged **1** to tropylium cation (**2**), and photolysis in the **2** absorption, which is above the dissociation threshold, destroyed the **2** band and regenerated a weak **1** absorption. The photochemical interconversion of **1** and **2** supports their identification in these experiments and is consistent with **1** $\rightleftarrows$ **2** equilibrium at low internal energies in gas-phase studies.

Introduction

Many investigators have been concerned with the structures of gas-phase $C_7H_7^+$ ions produced from different aromatic compounds.[1,2] It has been shown by a number of workers that the $C_7H_7^+$ ion population contains reactive and unreactive fractions and that the two populations probably have different structures,[3-7] which have been identified as the benzyl **1** and tropylium **2** cations, respectively.[5,7]



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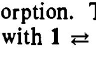

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The first spectroscopic studies of $C_7H_7^+$ ions identified **2** in concentrated H_2SO_4 by strong absorption at 274 and 217 nm.[8-10] Although several methyl-substituted derivatives of **1** have been observed in superacid solutions,[11] **1** itself is sufficiently reactive to require pulse-radiolysis and submicrosecond observation of a 363-nm absorption in dichloroethane solution.[12] Very recent gas-phase photodissociation spectroscopic studies have assigned a 310-nm band to α-methylbenzyl cation[13] and a 290-nm band has been attributed to benzyl cation.[14]

Matrix photoionization methods have been used to produce and trap unstable and reactive cations such as CCl_4^+ and $C_7H_8^+$ for spectroscopic and photochemical study.[15-17] In a recent matrix investigation of the cycloheptatriene system, both cycloheptatriene and toluene cations were observed by absorptions at 480 and 430 nm, respectively, and visible photolysis rearranged the cycloheptatriene cation to the toluene cation.[17] Here follows a matrix photoionization study of benzyl bromide which provides ultraviolet absorption spectra and information on the photochemical rearrangement between **1** and **2**.

Experimental Section

The cryogenic equipment and matrix photoionization techniques have been described in earlier papers.[18,19] Due to the low volatility of benzyl bromide (Aldrich), its equilibrium vapor (approximately 1 torr) was codeposited neat through a flow-regulating needle valve (Nupro, M series) with argon flowing through a 3-mm orifice quartz discharge tube. The argon flow rate was about 0.5 mmol/h, which gave pressures between 0.125 and 0.150 torr as measured on a thermocouple gauge 90 cm ahead of the microwave discharge; the discharge was excited by an Evenson-Broida cavity and 60–80% power with a nominal 125-W magnetron diathermy unit. Thus, benzyl bromide vapor was mixed with argon emerging from an open discharge on a 22 ± 2 K sapphire plate, and spectra were recorded from 200–800 nm on a Cary 17 spectrophotometer. 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 Corning colored glass filters, and onto the matrix sample, and additional absorption spectra were recorded.

Results

Matrix photoionization experiments with benzyl bromide and other precursors will be described.

Benzyl Bromide. One experiment was performed codepositing an argon/benzyl bromide ~100/1 sample with argon from the 3-mm discharge tube for 3 h; the spectrum revealed broad, weak bands at 495 (A = absorbance = 0.03) and 540 nm (A = 0.04) and a strong, broad asymmetric band centered at 338 nm (A = 0.35) in addition to completely absorbing precursor at 220–230 nm. Photolysis by 520-nm cutoff radiation with the sample warmed to 25 K reduced the 338-nm band (to A = 0.25), the 495-nm absorption (to A = 0.02), and the 540-nm band (to A = 0.03).

All subsequent experiments described here employed the new technique involving neat codeposition of benzyl bromide vapor through the needle valve and spray-on line with argon from the 3-mm discharge tube. In the first experiment, codeposition of equilibrium benzyl bromide vapor for 1 h with undischarged argon entering the tube at about 150-mtorr pressure produced only a precursor absorption at 220–230 nm (A = 0.15) as a shoulder on the steeply rising sample background. This procedure was con-

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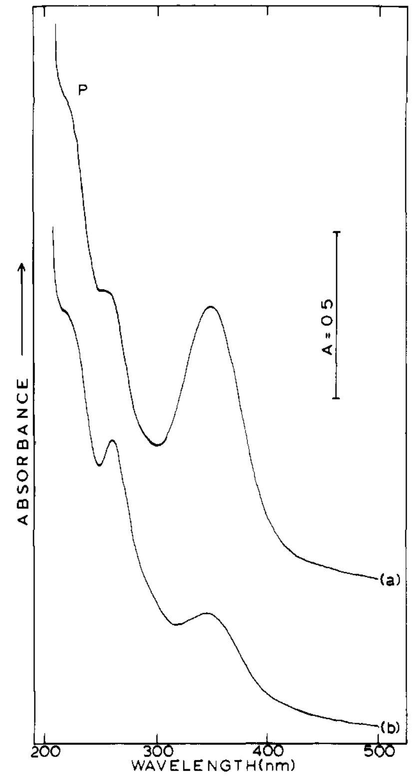

Figure 1. Ultraviolet spectra of sample prepared by 22 K codeposition of benzyl bromide vapor with argon subjected to microwave discharge: (a) after 2-h codeposition with full, rich discharge; (b) after Pyrex-filtered photolysis (290-nm cutoff) for 30 min. P denotes precursor absorption.

Table I. Product Band Intensities (Absorbance) and Photochemistry in Benzyl Bromide Experiments

P, mtorr[a]	λ, nm[b]	t, min[c]	353 nm	263 nm
125	105	60	0.30	0.05
	340–600	30	0.05	0.09
	290	30	0.02	0.12
	220	30	0.03	0.04
140	105	60	0.36	0.24
	380	10	0.10	0.33
	340–600	10	0.02	0.37
	290	10	0.00	0.35
	220	10	0.05	0.06
125	105	46	0.30	0.05
	420	15	0.22	0.08
	380	15	0.13	0.08
	340–600	15	0.05	0.08
	290	15	0.01	0.10
	220–360	15	0.04	0.00
	290	15	0.02	0.04
	220	15	0.03	0.01

[a] Argon pressure entering discharge tube. [b] Photolysis wavelength range or short-wavelength cutoff (nm) used to produce listed product band intensities. [c] Time period for given photolysis: vacuum UV during condensation, UV-Vis after condensation.

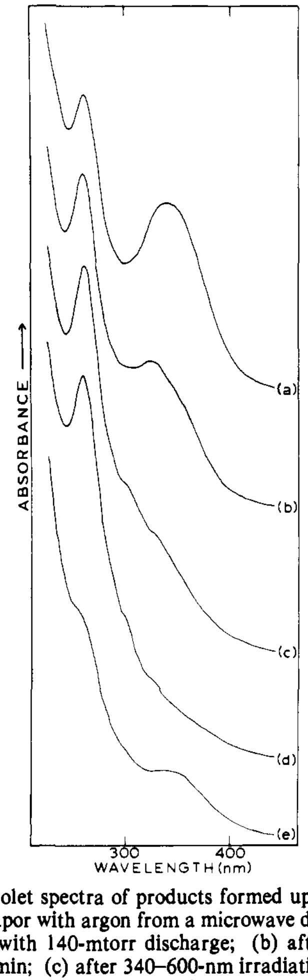

Figure 2. Ultraviolet spectra of products formed upon codeposition of benzyl bromide vapor with argon from a microwave discharge: (a) after 1-h codeposition with 140-mtorr discharge; (b) after 380-nm cuttoff photolysis for 10 min; (c) after 340–600-nm irradiation for 10 min; (d) after 290-nm photolysis for 10 min; (e) after full-arc photolysis for 10 min (lamp has no output at wavelengths shorter than 220 nm).

tinued for 1 h more with the same flow rates and the argon was energized by a microwave discharge. A strong, broad symmetrical band was observed beginning at 430 nm with a maximum and band center at 353 nm ($A = 0.60$) (fwhm = full width at half-maximum = 4300 cm^{-1}) and a minimum at 300 nm on a background with little slope (increase 0.15 absorbance from 430 to 300 nm). A weak shoulder was detected at 263 nm ($A = 0.06$) on the side of the 225 nm ($A = 0.25$) precursor absorption. The sample was photolyzed with unfiltered mercury-arc radiation and the 353-nm absorption was reduced (to $A = 0.17$) and the 263-nm absorption was destroyed. The next experiment codeposited benzyl bromide vapor neat with argon from a lean discharge for 1 h, which produced a weak 353-nm band ($A = 0.05$). This experiment was continued for 2 h more using a full, rich discharge, which produced the 353-nm band with increased intensity ($A = 0.55$) and the 263-nm band as a shoulder ($A = 0.10$) on the 225-nm precursor absorption superposed on the steeply rising ultraviolet sample background (Figure 1a). Pyrex-filtered mercury-arc photolysis (290-nm short-wavelength limit) for 30 min reduced the 363-nm band (to $A = 0.10$) and increased the 263-nm absorption (to $A = 0.20$) (Figure 1b).

Ten more similar experiments were performed with benzyl bromide to search for the optimum argon pressure flowing into the discharge to maximize the product yield and maintain ultraviolet transmission of the sample. One of these experiments employed codeposition of benzyl bromide vapor with argon entering the tube at 150 mtorr for 30 min and only the 225-nm ($A = 0.16$) precursor absorption was observed. The argon discharge was then maintained for 30 min, and the precursor absorption increased (to $A = 0.26$) and new bands again appeared centered at 353 ($A = 0.15$), 310 ($A = 0.002$), and 263 nm ($A = 0.10$, fwhm = 2900 cm^{-1}). A full-arc photolysis markedly reduced the major product absorptions, 353 (to 0.04) and 263 nm (to 0.01), but left the weak 310-nm band, due to benzyl radical,[16] unchanged.

In the final trio of benzyl bromide experiments performed on three successive days, an argon film was deposited first and precursor was introduced after starting the discharge. In an experiment using an argon inlet pressure of 125 mtorr, codeposition for 1 h produced the 353- ($A = 0.30$) and 263-nm ($A = 0.05$) product bands. Photolysis with 340–600-nm radiation for 30 min reduced the 353-nm band (to $A = 0.05$) and increased the 263-nm absorption (to $A = 0.09$); an additional 30-min irradiation with 290–1000-nm light continued this trend, 353 nm (to $A = 0.02$)

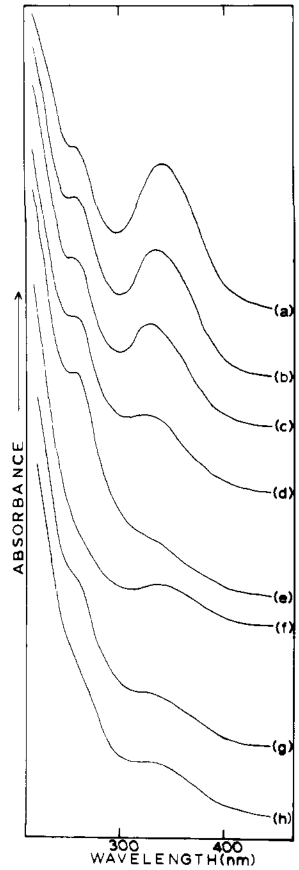

Figure 3. Ultraviolet spectra of benzyl bromide vapor codeposited with argon from an open microwave discharge and after filtered photolysis for 15-min periods: (a) after sample deposition for 46 min with 125-mtorr discharge; (b) after 420-nm photolysis; (c) after 380-nm photolysis; (d) after 340–600-nm photolysis; (e) after 290-nm photolysis; (f) after 220–360-nm photolysis; (g) after 290-nm photolysis (repeated); (h) after 220-nm photolysis (repeated).

and 263 nm (to $A = 0.12$); however, full-arc (220–1000 nm) photolysis for 30 min *reversed* this trend and increased the 353-nm band (to $A = 0.03$) and decreased the 263-nm band (to $A = 0.04$). Table I summarizes the intensity changes on photolysis.

The next experiment employed an argon inlet pressure of 140 mtorr and the spectrum after codeposition of benzyl bromide vapor with discharged argon for 1 h is illustrated in Figure 2a; the product yields were increased, 353 nm (band center, $A = 0.36$) and 263 nm ($A = 0.24$), as Table I indicates. Photolysis with 380-nm cutoff radiation for 10 min markedly reduced the 353-nm band (to $A = 0.10$) and produced a new maximum at 325 nm ($A = 0.10$) and increased the 263-nm band (to $A = 0.33$), Figure 2b. Irradiation through the 340-600-nm band-pass filter for 10 min further reduced the 353- and 325-nm bands (to $A = 0.02$), revealed a weak 300-nm absorption, and increased the 263-nm band (to $A = 0.37$), Figure 2c. Exposure of this sample to 290-nm light for 10 min destroyed the 353-nm band, leaving weak 325- and 300-nm absorptions ($A = 0.01$), and slightly reduced the 263-nm absorption (to $A = 0.35$), Figure 2d. A final full-arc photolysis for 10 min produced a new absorption centered at 353 nm ($A = 0.05$), markedly reduced the 263-nm band (to $A = 0.06$), and destroyed the 325-nm band, Figure 2e.

The last experiment in this sequence repeated the 125-mtorr inlet argon pressure, and the spectrum after 46 min of sample deposition, shown in Fugure 3a, was almost identical with the first 125-mtorr run described above and listed in Table I. An extensive sequence of filtered photolyses was performed for 15-min periods; the initial irradiation employed a 420-nm cutoff filter, which just catches the long-wavelength tail of the 353-nm absorption. The 353-nm absorption was slightly reduced with its band center shifted to 340 nm and the 263-nm band was slightly increased, as shown in Figure 3b. Photolysis with 380-nm radiation, Figure 3c, reduced the 340-nm absorption and shifted the maximum to 330 nm, leaving the 263-nm absorption unchanged. A similar photolysis with 340–600-nm light reduced the 330-nm band substantially without observable change at 263 nm; however, 290-nm irradiation almost destroyed the 330-nm absorption and increased the 263-nm band to its maximum value ($A = 0.10$), Figure 3e. The use of a $CoSO_4$–$NiSO_4$ solution filter to minimize irradiation in the long-wavelength product band (passes from 220 to 360 nm) completely destroyed the 263-nm absorption and produced a new band centered at 353 nm ($A = 0.04$), Figure 3f. An additional 290-nm photolysis halved the 353-nm band and produced a new 263-nm absorption ($A = 0.04$), Figure 3g, and a final exposure to the full arc slightly reduced the 263-nm absorption and increased the 353-nm band, Figure 3h, as observed in the earlier photolysis studies.

In one experiment, benzyl bromide vapor was codeposited with argon for 1 h and then discharged argon was deposited on top of this sample for 3 h, exposing the sample to vacuum ultraviolet argon discharge radiation. A weak new band centered at 325 nm ($A = 0.07$) was produced.

Other Precursors. Several experiments were performed with benzyl chloride codepositing the vapor with discharged argon. A weak band was observed at 469 nm and no absorption was detected at 353 nm. A series of five investigations was done with *p*-methylbenzyl bromide; these experiments produced a weak 315-nm band, and broad absorptions centered at 343 and 485 nm. Photolysis with 420-nm radiation for 30 min destroyed both broad bands without affecting the 315-nm band.

Discussion

The new absorptions will be identified and the photochemistry will be considered in light of possible rearrangement processes.

Identification. The strong 353-nm absorption in solid argon is assigned to the benzyl cation, **1**, on the basis of agreement in position and line width with the 363-nm band (fwhm = 3800 cm^{-1}) produced by pulse radiolysis of several benzyl compounds in 1,2-dichloroethane solution.[12] Typically solution spectra are red shifted from argon matrix spectra, which are in turn red shifted from gas-phase spectra. A representative example is benzyl radical, observed at 305.3 nm in the gas phase, 310.5 nm in solid argon at 22 K, and 318.2 nm in glassy matrices at 77 K.[16,20,21] Likewise, the 263-nm band produced on photolysis of the 353-nm absorption is assigned to the tropylium cation, **2**, owing to agreement with the 274-nm absorption (fwhm = 2400 cm^{-1}) of tropylium salts in concentrated acid solutions; the stronger 217-nm absorption of **2** in acid solutions is probably displaced to near 208 nm in solid argon, where it is obscured by the benzyl bromide absorption and the steeply scattering background in this region. Considering the matrix shift observations for benzyl radical, it is reasonable to expect spectra of **2** to red shift from gas to solid argon to solution phases, particularly in the latter case of a cation in an aqueous acid medium. Since the ionization energies of benzyl radical (7.2 eV)[22] and tropyl radical (6.2 eV)[23] are relatively low compared to that of argon (15.8 eV), **1** and **2** should not interact significantly with the argon matrix, and the argon matrix spectra should be representative of the gas phase. Further evidence supporting these spectroscopic observations of **1** and **2** is found in their photochemical interconversion, to be discussed in a later section.

The weak 310-nm absorption in several experiments is due to benzyl radical.[16] A similar absorption in α-bromo-*p*-xylene experiments at 315 nm is due to the *p*-methylbenzyl radical which absorbs 5 nm higher than benzyl radical in glassy solutions.[21] The photosensitive 495- and 540-nm absorptions in the prediluted benzyl bromide experiment have been assigned to the *p*-bromotoluene cation formed upon rearrangement of the benzyl bromide parent ion, which absorbs further to the red.[24] An analogous

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photosensitive absorption at 485 nm in the α-bromo-p-xylene experiments is attributed to the similar rearranged 2-bromo-p-xylene cation. The broad absorption centered at 343 nm in this experiment was destroyed upon 420-nm photolysis, and it is tentatively assigned to the p-methylbenzyl cation. It is anticipated that a p-methyl substituent will stabilize the benzyl cation ground state slightly, but not as much as two α-methyl groups; the $C_6H_5C(CH_3)_2^+$ cation has been observed at 326 nm in superacid media.[11]

Benzyl cation **1** is formed by energy from the argon discharge in these experiments, reaction 1. Argon metastable atoms produced by the discharge with 11.6–11.8-eV energies are in excess of the 9.1-eV appearance potential of $C_6H_5CH_2^+$ from benzyl bromide.[25] Either argon resonance photoionization or Penning ionization by collision with metastable argon atoms on the surface of the matrix, where the argon and benzyl bromide vapor are codeposited from separate sources, could be the mechanism for reaction 1. The electrons produced are probably captured by bromine atom products or dissociatively captured by benzyl bromide to give bromide ion, which is also trapped in the matrix sample. It is perhaps noteworthy that passing an argon–benzyl bromide mixture *through* the discharge produced no observable products.

$$C_6H_5CH_2Br + 11\ \text{eV} \rightarrow C_6H_5CH_2^+ + Br + e^- \qquad (1)$$

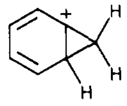
The effect of codepositing the sample vapor neat with argon from the discharge, as compared to prediluting the sample with argon, is to increase the yield of the ionic product species. In the present studies, the 350-nm product was 3–6 times stronger using neat sample vapor. In similar investigations with toluene, the 430-nm toluene cation absorption was threefold stronger with the neat technique depositing approximately equal quantities of toluene.[16] Apparently the argon used to predilute the sample partially screens reagent molecules from the ionizing radiation or ionizing collisions and, in this manner, reduces the yield of charged product species.

Increasing the argon pressure in the discharge tube increases the total flux of argon resonance radiation emerging from the tube.[19] Table I shows that the yield of **1** is relatively unaffected in the 125–140-mtorr pressure range; however, the yield of **2** is substantially enhanced at the higher pressure. A possible explanation for the increased production of **2** is increased photoisomerization of **1** to **2** by radiation from the discharge.

Photochemistry. The figures show five general photochemical observations that are of interest here: (1) the 353-nm benzyl cation band photolyzes with an appreciable rate within the absorption band beginning at 420 nm (the longest wavelength used here); (2) brief photolysis with 420- and 380-nm cutoff radiation produces a new species absorbing at 325 nm; (3) photolysis with 340–600- and 290–1000-nm light reduces the benzyl cation band symmetrically and produces the 263-nm tropylium cation absorption; (4) photolysis with 220-nm radiation destroys **2** and regenerates a small yield of **1** without any 325-nm absorption; and (5) continued ultraviolet photolysis decreases both **1** and **2** absorptions, owing to neutralization by electrons photodetached from bromide ion electron traps. These observations will be discussed in turn.

(1) The postulated equilibrium between **1** and **2** at relatively low internal energies in the gas phase[3-7] suggests a ready rearrangement of **1** upon excitation. MINDO/3 calculations predict an activation energy of 33 kcal/mol[26] and experimental energy relationships give approximately the same barrier[3] for the **1** → **2** isomerization, which is exceeded by absorption at 420 nm (68 kcal/mol). The least endothermic dissociation process, $C_7H_7^+$ to $C_5H_5^+$ and C_2H_2, however, requires 95 kcal/mol (300 nm).[3] The near-ultraviolet electronic absorption of **1** provides ample internal energy for rearrangement but insufficient energy for photodissociation.

(2) The interconversion between **1** and **2** may involve intermediate $C_7H_7^+$ isomeric species with different structures. Calculations have predicted local minima for norcaradienyl cation and 1-cycloheptatrienyl cation (**9** and **10** in ref 26) with activation energies of 18 and 23 kcal/mol for their formation;[26] these required energies are exceeded by the matrix photolysis. Furthermore, evidence has been presented for norbornadienyl cation as a stable species in the gas phase[3] and in acid solutions,[27] and photolysis of **2** in solution has produced norbornadienyl cation with a mechanism suggested to involve a bicyclo[3.2.0]heptadienyl cation intermediate.[28a] The 325-nm absorption formed on 380-nm photolysis of **1** (Figure 2b) is assigned to a $C_7H_7^+$ structure different from **1** and **2**; the weak absorption revealed at 300 nm on 340- and 290-nm photolysis (Figure 2c,d) may be due to a still different structure. Since norbornadienyl cation exhibits no absorption above the 330-nm cutoff of liquid SO_2,[27] it is unlikely that the 325-nm matrix absorption is due to norbornadienyl cation. More likely, the 325-nm argon matrix absorption may be due to norcaradienyl cation **3**, which can be readily formed upon photoexcitation of **1** in the matrix. Supporting evidence for this possible assignment is found in the 325-nm absorption of benzonium ion, $C_6H_7^+$, in acid media.[28b] This $C_7H_7^+$ structure also contributes to the spectrum in the prediluted benzyl bromide experiment.



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(3) Photolysis with 290–1000-nm radiation gives essentially complete destruction of absorption in the 300-nm region, which results in a maximum in the 263-nm absorption of **2**. The **1** → **2** rearrangement is complete insofar as the competitive photoneutralization process will allow.

(4) The full mercury arc provides photon energies up to about 125 kcal/mol, which clearly exceed the 95 kcal/mol activation energy[3] for dissociation of **2** to $C_5H_5^+$. Nevertheless, a small amount of **1** is re-formed from **2**, although dissociation clearly dominates (Figure 2d). The rearrangement process can be cycled back and forth (Figure 3 shows **1** → **2** → **1** → **2** → **1**), but both absorptions are reduced in the process, owing to the favorably competitive dissociation pathway. The role of the matrix in quenching internal energy makes it possible for some **2** → **1** rearrangement to be observed.

The photochemical isomerization of **2** → **1** in solid argon is analogous to the previous matrix observation of the photoisomerization of cycloheptatriene cation to toluene cation.[17] In the $C_7H_8^+$ studies, visible photolysis in the 480-nm cycloheptatriene cation absorption, above the dissociation threshold, produced the 430-nm toluene cation band. After absorption by cycloheptatriene cation at 480 nm, the argon matrix effectively reduced internal energy, which allowed rearrangement to toluene cation to be competitive with dissociation.

(5) The final point in these photolysis studies is that, when the 369-nm photodetachment threshold[29] of the bromide ion electron trap is exceeded, photoneutralization of all isolated cations will proceed. Experiments with CF_3^+ and Br^- have shown that this is a relatively slow process (approximately 30% reduction in 125 min);[30] hence the dominant process with the present brief 220–1000-nm photolysis studies is ion photodissociation.

Gas-Phase Comparisons. Recent photodissociation studies have been performed on gaseous $C_7H_7^+$ ions in an ICR trap produced by 17-eV electron impact of toluene or 70-eV electron impact of benzyl chloride.[14] This method of preparing $C_7H_7^+$ ions has been

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shown in previous work to give a major fraction of a "reactive form" of $C_7H_7^+$, which is believed to have the **1** structure, and a minor fraction of an "unreactive form", thought to have the **2** structure;[4–7] however, $C_7H_7^+$ ions produced in this manner are likely to contain substantial excess internal energy, and the reactive population may consist of more than one structural form. The broad PDS band peaking at 290 ± 10 nm, which arises from photodissociation of >50% of the $C_7H_7^+$ ions in the population, is not compatible with the pulse-radiolysis observation of **1** at 363 nm in solution or the present 353-nm argon matrix absorption. Furthermore, the PDS is not compatible with **2** since the gaseous spectrum of **2** is expected to the blue of the acid solution (and solid argon) observations. The ICR experiment has the advantage of precise knowledge of the ion mass and the disadvantage of possible excess internal energy, which can facilitate structural rearrangement of many ions in the population. The cryogenic matrix technique certainly quenches internal energy and the pulse-radiolysis method gives a spectrum on a 10^{-6}-s time scale, although neither can absolutely prevent the observation of benzyl cation reaction products. However, the pulse-radiolysis observation of the same 363-nm transient absorption with the different dibenzylmercury and benzyl bromide precursors in solution strongly favors identification of the 363-nm band as a common fragment and not a reaction product with the precursor. Further kinetic studies[31,32] of **1** in solution are consistent with this identification. As discussed above, the 353-nm argon matrix and 363-nm pulse-radiolysis identifications of **1** are mutually supportive. It is therefore suggested that the $C_7H_7^+$ population giving rise to the broad 350- to 260-nm PDS band is complicated by more than one structural form different from **1**.

The photoelectron spectrum of benzyl radical[22] contains no band in the region 3.5 eV above ionization which would correspond to a 353-nm absorption for the ion. This suggests that the 3.5-eV transition for **1** involves an electron promotion type of transition such as $\pi \rightarrow \pi^*$ or, less likely, that the structure of **1** is substantially different from benzyl radical.

Several exploratory experiments have been performed codepositing benzyl bromide vapor with argon from a separate source onto the sapphire window and an electrode positioned in the center of the window.[33] Applying +300 V dc to the electrode to sustain a discharge on the surface of the sample during codeposition gave no products; however, a 30-min codeposition with a Tesla coil discharge on the electrode produced a substantial 263-nm absorption ($A = 0.2$) without significant absorption in the 350-nm region. Apparently, the tropylium structure is the most stable isomer under electrical discharge conditions.

Conclusions

Codeposition of benzyl bromide vapor with argon emerging from a microwave discharge onto a sapphire plate at 22 K produced new absorptions at 263 and 353 nm. Agreement with the 274-nm absorption of tropylium salts in concentrated acid and the 363-nm absorption of benzyl cation in 1,2-dichloroethane solution identifies the argon matrix absorptions. Photolysis in the **1** absorption, which is below the dissociation threshold, isomerizes **1** to **2**, possibly involving another $C_7H_7^+$ structure absorbing at 325 nm. Further photolysis in the **2** absorption, which is above the dissociation threshold, destroys the **2** band and reproduces a small **1** absorption. The matrix quenches internal energy and makes some $\mathbf{2} \rightarrow \mathbf{1}$ rearrangement possible. The photochemical interconversion of **1** and **2** supports their identification in these experiments and is consistent with $\mathbf{1} \rightleftarrows \mathbf{2}$ equilibrium at low internal energies in gas-phase studies.

Acknowledgment is made to the National Science Foundation for support of this research under Grant CHE 79-10966.

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Intramolecular Electron Transfer and Dehalogenation of Anion Radicals. 3. Halobenzonitriles and Cyanobenzyl Halides[1–3]

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Abstract: One-electron reduction of halobenzonitriles and cyanobenzyl halides produces the anion radicals which then undergo intramolecular electron transfer leading to dehalogenation. Kinetic spectrophotometric pulse radiolysis allowed the observation of the halobenzonitrile anion radicals and the determination of their dehalogenation rates. The rates varied from 10^4 to $>10^7$ s^{-1} depending on the halogen and its position relative to the cyano group. The production of X^- was measured in steady-state radiolysis experiments, and the participation of cyanophenyl radicals as intermediates was also deduced from observation of chain reactions. The anion radicals of cyanobenzyl halides were not observed since they dehalogenate very rapidly. The cyanobenzyl radicals produced by this process were monitored spectrophotometrically. The rates of dehalogenation of the anion radicals studied here are at least 5 orders of magnitude higher than the corresponding values determined previously for analogous nitro derivatives, but the pattern of reactivities is similar in both series of radicals.

Introduction

Anion radicals of nitroaromatic compounds, containing a halogen atom at various positions on the ring or on a side chain, were found in certain cases to undergo an intramolecular electron transfer and to release halide ions.[2,3] Rates of dehalogenation in the range of $1-10^6$ s^{-1} were determined for the anion radicals of various nitrobenzyl and nitrophenacyl halides. The rates were strongly dependent on the nature of the halide and its position relative to the nitro group.[2,3] On the other hand, when the halogen was further removed from the ring or attached directly to the ring, no significant C–X bond scission was observed. These findings were explained by differences in C–X bond strength and by the charge distribution on the ring. The rate of dehalogenation should

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(1) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2149 from the Notre Dame Radiation Laboratory.
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