rotation about phenyl–methoxy C–O bonds were found[27] for **9a** and **9c** than for the corresponding cyclopropyl substituted ions **9b** and **9d**, and these results were interpreted in terms of greater charge delocalization for cyclopropyl than for phenyl. However, steric repulsion between ortho hydrogens of the two phenyl groups of **9a** and **9c** should prevent these ions from becoming planar, and steric inhibition of resonance could then result in lower charge delocalization for phenyl than for cyclopropyl in these systems. Similarly, Volz and co-workers[28] have concluded from a ^{19}F NMR study of the chemical shifts in ions **10a–c** that electron release is greater for the cyclopropyl group than for phenyl. Again, this result may be a consequence of a nonplanar conformation for ion **10b**. Olah and co-workers[29] have noted that the phenyl group is generally more susceptible to steric effects than is cyclopropyl.

Conclusion

The rotational barriers determined for compounds **1**, **2**,[4] and **3**[5] by dynamic NMR spectroscopy indicate that conjugation increases in the order cyclopropyl ~ vinyl < phenyl, at least with COF at π acceptor. The opposite order may apply with BF_2 as π acceptor (compounds **4**,[11b] **5**,[22] and **6**[23]), or the apparent change may be due to inaccuracy in one or more of the barriers for these compounds. For simple cyclopropyl- or phenyl-substituted carbenium ions, conjugation with the phenyl group appears to be more important than for cyclopropyl, although steric inhibition of resonance may cause a reversal of this order.

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Radiative Lifetime of Vibrationally Excited Iodo- and Bromobenzene Ions by Two-Laser Photodissociation Spectroscopy

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Contribution from the Case Western Reserve University, Cleveland, Ohio 44106.
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Abstract: The photodissociation of iodobenzene and bromobenzene ions trapped in an ICR mass spectrometer has been enhanced by prior irradiation with a low-power infrared laser. It is concluded that the thermal or near-thermal halobenzene ions absorb 10.23-μm infrared radiation to produce vibrationally excited ions that undergo a faster visible photodissociation process than the unexcited ions. Radiative relaxation lifetimes of the excited iodo- and bromobenzene ions are defined with reference to a simple two-state relaxation kinetics model and are determined to be 500 and 200 ms, respectively. The physical significance of these values is discussed to allow comparison with other experimental results.

A new approach to exploring detailed photoprocesses and energy-transfer processes in individual molecules has been opened by the discovery of multiphoton dissociation in trapped gas-phase ions.[1] Both visible-wavelength[2,3] and infrared[4] processes can be investigated, and the conditions may be varied from collision free to collision quenched: The unique aspect of these experiments is the ability to observe events occurring on a very long time scale, ranging up to several seconds.

A recent report[5] by our laboratory of experiments combining infrared and visible irradiation of ions offers possibilities for a more detailed understanding of multiphoton photochemical kinetics. We described an effect by which infrared radiation dramatically increases the visible photodissociation of iodobenzene ions. Since then bromobenzene has been found to show similar behavior. This enhancement of photodissociation was interesting in that the infrared laser was unable to cause any dissociation on its own. It became apparent that this increased dissociation was the result of the iodobenzene ions absorbing infrared photons, with a resulting effect on the visible photon dissociation process. As the visible dissociation to yield phenyl cation plus halogen atom proceeds by a two-photon sequential process, there are several possible mechanisms for participation of IR photons in the photodissociation kinetics. These first experiments involved simultaneous irradiation by both visible and IR lasers. We report here the discovery that the visible and infrared excitation processes need not be simultaneous and discuss the new insight that these sequential-excitation results add to the understanding of ion multiphoton chemistry. Of particular interest is the question of whether a molecule needs to have sufficient internal energy to put it in the "quasi-continuum", so as to absorb IR radiation efficiently, or whether near-ground-state ions can be IR excited. The experiments used gated lasers that allowed separation of the visible and infrared irradiation period. The results clearly showed that the IR laser is optically exciting near-ground-state ions which then undergo a faster visible dissociation process; the ability to separate the IR and visible laser pulses provided information about the lifetimes of these vibrationally excited iodo- and bromobenzene ions.

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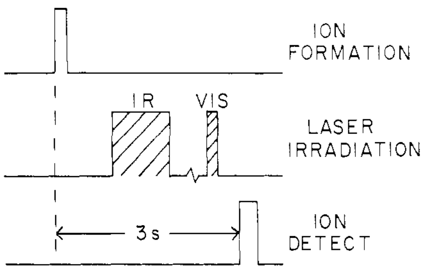

Figure 1. Illustration of experimental sequence involving separation of visible and infrared irradiation pulses to determine excited-state lifetimes.

Experimental Procedure

The production, trapping, and detection of ions in an ion cyclotron resonance (ICR) spectrometer have been described in several publications,[6-8] as have the details of ICR photodissociation techniques using both visible and infrared laser irradiation. In these experiments the trapped ions are irradiated by both an infrared (IR) laser and a visible laser, each of which is shuttered to control the irradiation times. The experimental sequence is illustrated in Figure 1.

An initial pulse of electrons produces ions that are then trapped by electric and magnetic fields for a period of 3 s. During this trapping period the ions are irradiated by a CO_2 CW IR laser and by a 100–150-ms visible laser pulse, the two laser pulses being timed so that they may overlap or be separated by a dark period of up to 1 s. At the end of the trapping period the ions are detected and the ICR is quenched of ions to begin another cycle.

The instrumentation consisted of a Varian ICR-9 spectrometer modified to operate in a pulsed mode using the trapped-ion cell configuration. The 1-s IR irradiation pulse was provided by a homebuilt CO_2 CW laser. [Decreasing the IR pulse width had no effect on the observed enhancement until the pulse width dropped below 250 ms ($C_6H_5I^+$) or 500 ms ($C_6H_5Br^+$). Apparently under these conditions the up-pumping by the IR laser is counterbalanced by relaxation processes so that steady state is established within these times.] The IR wavelength utilized in all the experiments was 10.23 μ with a power of ~12 W/cm^2 in the cell. For iodobenzene an ion-laser-pumped dye laser operating at 595 nm provided a 150-ms pulse. Bromobenzene used a 100-ms pulse at 515 nm from an argon ion laser. Accounting for beam diameters and transmission losses, the light intensities at the cell are estimated at 450 mW/cm^2 for iodobenzene and 400 mW/cm^2 for bromobenzene. The pulsing of the lasers was achieved by mechanical shutters controlled by TTL timing circuitry. The IR beam was considered to be broad enough, but the visible laser beam was spread to ~2 cm to ensure good overlap with the trapped ions. A NaCl salt window was utilized to allow the ions to be irradiated by both visible and IR laser beams. Iodobenzene and bromobenzene samples were obtained commercially and used without further purification. The ionizing electron beam energy was 2 to 5 eV above the respective ionization potential. Pressures were determined by use of a calibrated ion pump.

Results and Discussion

Kinetic Analysis of Data. Initial experiments used immediately adjacent visible and IR irradiation pulses allowing no overlap. When the order of the pulses was changed, it was found that the IR laser affected the dissociation only if it preceded the visible pulse and had no significant effect if the IR irradiation occurred after the visible pulse. This result was considered as eliminating the possibility that ions excited in some suitable way by visible irradiation are then carried over the dissociation threshold by IR pumping, and as establishing that the ions as prepared by the initial ionization process absorb IR radiation sufficiently fast to bring about the IR enhancement effect. In fact, the extent of IR enhancement for the IR pulse immediately preceding the visible pulse was not drastically less than that observed with concurrent IR visible irradiation,[5] so that this effect clearly does not depend in an essential way on the simultaneous presence of IR and visible light. It is of real concern whether the observed photochemistry involves ions that retain significant internal excitation from the ionization process. As one test, this experiment was repeated with the introduction of a 1-s cooling period between the end of the electron beam pulse and the beginning of the IR pulse. As is clear from the results described below and from previous experience with quenching of internally excited iodobenzene[9] and bromobenzene ions,[3,10] the combination of IR-radiative cooling and collisional quenching with parent neutral at these pressure gives a large internal energy decrease in 1 s. This cooling period gave no observable change in photochemical behavior.

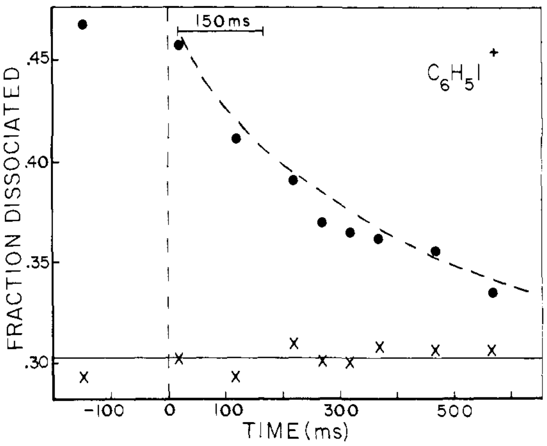

Figure 2. Plot of two-laser dissociation (●) vs. the dark period from the end of the IR irradiation to the beginning of the visible pulse for iodobenzene. The × values are visible dissociations without IR irradiation. The dashed line is a best fit to eq 2 based on an average × value (horizontal line). The value at negative time represents complete visible and IR pulse overlap.

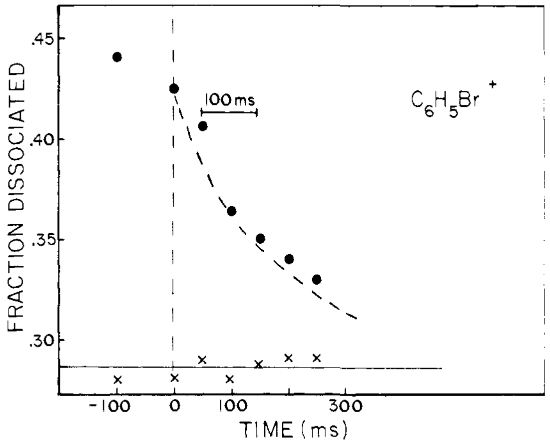

Figure 3. Plot of two-laser dissociation (●) vs. the time between the end of the IR irradiation and the beginning of the visible pulse for bromobenzene. The × values are visible dissociations without IR irradiation. The dashed line is a best fit to eq 2 based on an average × value (horizontal line). The value at negative time represents complete visible and IR pulse overlap.

The next set of experiments involved progressive separation of the IR and visible pulses. It was found that the further the pulses were separated the less effect the IR irradiation had on the dissociation: Typical results of iodobenzene and bromobenzene are shown in Figures 2 and 3, respectively. These two figures compare the fractional dissociation caused by a visible pulse only and by a visible pulse with an IR pulse preceding it by a delay time t. It is seen that the maximum effect of the IR laser is for complete pulse overlap with a monotonic decrease as the pulses are separated. After a separation of 1 s for iodobenzene and 0.5 s for bromobenzene, the level of dissociation is the same as that with visible-laser-only dissociation (within experimental errror of ~2%).

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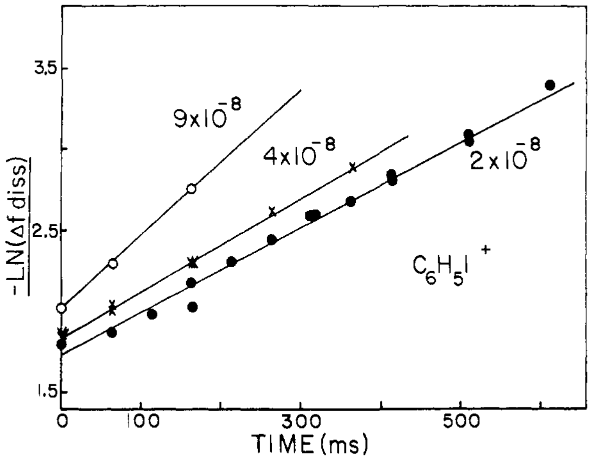

Figure 4. Plot of the logarithm of the additional fractional dissociation caused by the IR irradiation vs. the pulse separation time for iodobenzene at three different pressures (in torr).

The simplest interpretation of this persistent IR laser effect is that the IR irradiation builds up a population of vibrationally excited ions that can undergo a faster visible dissociation process. The kinetic analysis of this picture is as follows:

At the end of the IR irradiation the ion population is made up partly of excited ions (B), with the remainder being in the ground state (A). The relaxation of excited ions to the ground state is expressed by a relaxation rate k_r. For a fixed visible pulse width and intensity, one is able to dissociate specific fractions of the A and B ions, these dissociated fractions being denoted by f_{dA} and f_{dB}, respectively. As a first approximation, assume that the visible pulse is sufficiently short that ion relaxation during the pulse is negligible and that the actual finite duration of the visible is equivalent to a Δ function pulse occurring at the midpoint (in time) of the actual visible pulse. The no-light ion loss in 3 s for both iodobenzene and bromobenzene ions was observed to be small, and nonphotodissociative ion loss processes will be neglected entirely. With these highly simplified assumptions, the kinetics are governed by eq 1, where t is the time between the end of the IR

$$f_d(t) = f_{dA}f_A(t) + f_{dB}f_B(t) \qquad (1)$$

pulse and the midpoint of the visible pulse, $f_d(t)$ is the overall fraction of ions photodissociated, and $f_A(t)$ and $f_B(t)$ are respectively the fractions of ground-state and excited ions at the pulse separation time t. If one assumes simple-exponential relaxation of excited (B) ions, this yields

$$f_d(t) = [f_{dA}] + [(f_B(t = 0))(f_{dB} - f_{dA})]e^{-k_r t} \qquad (2)$$

The first term in brackets is the $t = \infty$ limit in which there are no excited ions; this limit applies to the case of a visible pulse with no previous IR irradiation. The second term in brackets is the additional dissociation caused by the IR irradiation when the two pulses overlap ($t = 0$ limit). This expression corresponds to behavior seen in Figures 2 and 3. Rearranging and taking the logarithm of both sides of eq 2 yield the convenient form:

$$\ln (\Delta f_d(t)) = -k_r t + \ln (\Delta f_d(t = 0)) \qquad (3)$$

where $\Delta f_d(t)$ is the additional fractional dissociation caused by the IR pulse ($\Delta f_d(t) = f_d(t) - f_d(\infty)$). A plot of the logarithm of $\Delta f_d(t)$ vs. the separation time t should thus be linear, with the value of k_r equal to the slope. The use of eq 3, taking t to correspond to the midpoint of the visible pulse as described above, gives good fits to both iodobenzene and bromobenzene ion data. However, it is not difficult to obtain solutions of the kinetics in a better approximation in which the finite width of the visible pulse is correctly included. This is described in the Appendix; it is found that the corrections implied by this more accurate solution can be accurately introduced into eq 3 by the simple artifice of adjusting the pulse separation parameter t. For the bromobenzene analysis via eq 3, t is best taken as the time from the end of the IR pulse to a point 40 ms from the start of the 100-ms visible pulse, while for iodobenzene, t is best taken corresponding to the point 45 ms from the beginning of the 150-ms visible pulse.

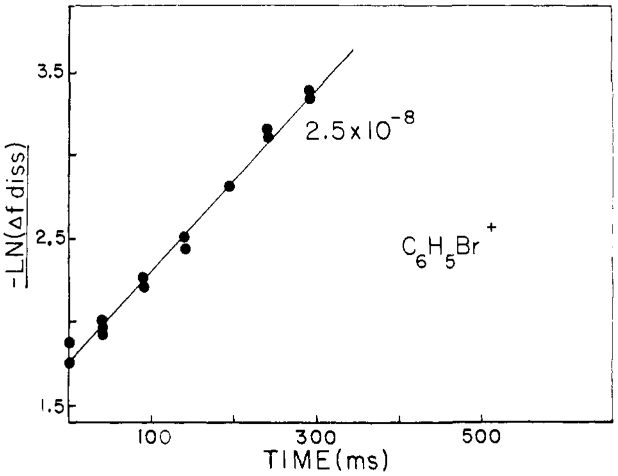

Figure 5. Plot of the logarithm of the additional fractional dissociation caused by the IR irradiation vs. the pulse separation time for bromobenzene at 2.5 × 10^{-8} torr pressure.

Table I

	pressure, ×10^{-8} torr	k_r, s^{-1}
$C_6H_5I^+$	2	2.6 ± 0.1
	4	2.95 ± 0.05
	9	4.5 ± 0.2
$C_6H_5Br^+$	2.5	5.45 ± 0.15

The results of this analysis are shown in Figures 4 and 5 for iodobenzene and bromobenzene, respectively, with the solid lines indicating a least-squares fit to the form of eq 3. A summary of Figures 4 and 5 (including iodobenzene experiments done at several pressures to determine the effect of collisions on the relaxation) is tabulated in Table I.

The pressure effect observed for iodobenzene indicates that both radiative and collisional relaxation are occurring. As the radiative and collisional rate constants add to give an overall rate k_r ($=k_{rad} + Pk_{coll}$), a weighted least-squares fit for the three iodobenzene pressures gives the following rates: for $C_6H_5I^+$, $k_{rad} = 2.0 \pm 0.1$ s^{-1} ($\tau \approx 500$ ms) and $k_{coll} = 0.25 \pm 0.03$ $s^{-1}/10^{-8}$ torr (7.5×10^{-10} cm^3/molecules s), and for $C_6H_5Br^+$, $k_{rad} = 5.0 \pm 0.2$ s^{-1} ($\tau \approx 200$ ms). Although no direct separation of radiative and collisional relaxation rates could be obtained for bromobenzene ions, past results suggest that the collisional relaxation rate for bromobenzene ion[3,10] in its parent gas is similar to that for iodobenzene[9] ion in its parent gas, and on this assumption a bromobenzene radiative rate was obtained by using the iodobenzene collisional relaxation rate.

Significance of Relaxation Rates. The physical significance of the relaxation rates obtained above for quenching of the IR enhancement effect is not entirely obvious. The analysis is based on the crude classification of ions into A and B classes, while presumably the ion population consists of a continuous spread of excitation levels. The fact that data for both iodobenzene and bromobenzene fit eq 3 quite well indicates that a simple two-level approach accounts well for the overall behavior, even though it may only be an average over a much more complicated set of kinetic equations.

The nature of the IR-pumped excited state that leads to a faster dissociation has several possibilities. Since for both iodobenzene and bromobenzene the visible photons used (2.1 and 2.4 eV, respectively) were well below the dissociation threshold (2.4 and 2.75 eV, respectively),[11,12] the visible-only dissociation must be occurring by the sequential two-photon process that has been

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[11] H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data, Suppl.*, 6, No. 1 (1977).

[12] H. M. Rosenstock and R. Stockbauer, *J. Chem. Phys.*, 73, 773 (1980).

documented for both of these ions.[3,13,14] For these ions energy from the first photon is thought to be stored as vibrational energy in a long-lived intermediate into which a second photon can be absorbed to provide the energy to dissociate the ion.

One possibility for the IR-assisted dissociation seen in these experiments is that some of the ions are absorbing at least 3–4 IR photons (10.23 μm = 0.1 eV) which would allow them to undergo a visible one-photon dissociation. The decay observed in these experiments would then reflect the relaxation from a vibrationally excited state $\geq$0.4 eV above the ground state.

Another possibility is that absorption of one or more IR photons to create a vibrationally excited ion results in an increased visible photon absorption rate with the result of speeding up the two-photon dissociation process. This question of visible photon absorption cross sections as a function of internal energy is an area of active interest. In the case of sequential two-photon visible dissociation, the second photon is envisioned as going into a highly excited ion (2–3 eV). There is some experimental evidence on the dependence of visible photon absorption cross section on the internal energy content of polyatomic ions: in the case of cyanobenzene ion,[2] two-photon kinetic analysis suggests that the second photon differs in cross section by a factor of 25 from the first photon, but this analysis does not tell which of the two photons has the larger cross section. On the other hand, similar analysis of benzene[1,15] and bromobenzene[3] ions (and recently of iodobenzene ion in our laboratory) indicates that the cross sections for the two photons do not differ by this much for these ions, probably not differing by as much as a factor of 4.

Our results would be in line with excited iodobenzene and bromobenzene ions having a faster absorption for a second visible photon that the first ($\sigma_2 > \sigma_1$). However, it would be surprising in both of these case if the small internal energy deposited by one or two IR photons could affect the visible cross section to the extent observed, and this second possibility seems less likely than the first as an interpretation of these results.

Therefore, the excited ("B") ions are required to lie above the one-photon threshold of $\sim$4000 cm^{-1} to undergo the faster one-photon dissociation. [The effective threshold, estimated as 4000 cm^{-1}, is somewhat higher than the adiabatic threshold due to an unavoidable residual kinetic shift. This question is fully explored in a forthcoming publication.] An upper limit of $\sim$20 000 cm^{-1} is set by the dissociation thresholds and the fact that no IR-only dissociation is observed. Since the IR laser undoubtedly produces a broad distribution of excited ions, it is reasonable to presume internal energies in the range of 5000–15 000 cm^{-1}. On the other hand the relaxed ("A") ions contain no more than $\sim$4000 cm^{-1} or else they would undergo the faster one-photon dissociation process. As a result, the relaxation rates measured here can be taken in broad terms to reflect the process of relaxation from an internal energy of $\sim$10 000 cm^{-1} down to $\lesssim$4000 cm^{-1}.

Within this framework it is possible to compare these results with other experiments. Radiative rates for these ions have been determined from visible two-photon dissociation experiments. Work on iodobenzene[16] suggests a radiative rate of $\sim$2 s^{-1} for the intermediate excited by visible irradiation. This agreement with the 2-s^{-1} result in these IR experiments gives some indication that both experiments are observing the same intermediate. This is in accord with the arguments made above to the effect that the IR laser pumps the ions to a high internal energy, near that supplied by the first visible photon ($\sim$16 000 cm^{-1}) in a two-photon dissociation process. For bromobenzene ion, conflicting radiation relaxation rates have been reported. van Velzen[15] and Van der Hart derive a value of 7 s^{-1} from two-photon kinetic data, while a similar but less extensive analysis in our laboratory yielded a value of 2.5 s^{-1}. An older two-photon study of Fu and Dunbar[3] did not resolve any observable radiative decay contribution to the dissociation kinetics. The uncertainties in these radiative rates make difficult any useful comparisons with the present results. The collisional relaxation rate obtained for iodobenzene is on the same order of magnitude as both the collisional quenching of the two-photon photodissociation and the orbiting collision rate. This is consistent with the charge-exchange cooling mechanism attributed to these ions when the bath gas consists of parent neutrals.[1]

It is of interest to compare our IR enhancement effects on iodobenzene and bromobenzene with the results of Wight and Beauchamp[17] on cyanobenzene. They noted no effect by the IR laser unless the visible and IR irradiation completely overlapped. They propose that after first absorbing a visible photon the photoexcited intermediate absorbs several IR photons and is promoted over the dissociation limit. Therefore, the IR absorption reflects vibrational spectroscopy of the photoexcited intermediate in their experiment while the interpretation of our experiments described above implies that our results give information about IR absorption in ions at or near their vibrational ground state.

Conclusions

In this work we have argued that the enhancement effect of IR irradiation on the visible photodissociation of iodo- and bromobenzene ions is attributable to near-ground-state ions absorbing IR photons. These vibrationally excited ions then undergo an enhanced visible photodissociation process. These experiments thus demonstrate the potentially valuable possibility of using a combination of IR and visible lasers of moderate power to obtain information concerning the vibrational spectroscopy of ions. Also obtained was information concerning the lifetime of vibrationally excited ions under collisionless conditions. The lifetimes of 500 and 200 ms determined for iodo- and bromobenzene ions, respectively, reflect the radiative lifetimes of excited states, knowledge of which is of value in understanding the photochemical behavior of gas-phase ions.

Acknowledgment. We thank Professor Paul Claspy for providing the infrared laser so essential for this work. The support of the donors of the Petroleum Research Fund, administered by the American Chemical Society, and of the National Science Foundation is gratefully acknowledged.

Appendix

Since the visible pulse was of finite duration, there occurs relaxation during the visible probe pulse. Therefore, use of the midpoint of the visible pulse to obtain the pulse separation value t for use in eq 3 may not be the best approximation. This section describes the approach used to find where in the visible pulse a Δ function approximation would be most nearly valid.

A kinetic treatment that accounts for relaxation during the visible pulse is as follows. The assumptions are that after the IR irradiation period there exists a particular fraction of excited (B) ions that begin to relax to ground-state ions (A) with a rate constant k_r. The excited ions are taken to have a larger dissociation rate constant than the ground-state species ($k_{dB} > k_{dA}$). The dissociation kinetics that account for all of these processes are given in eq A1, where t_d is the time from the end of the IR

$$f_{\text{diss}} = 1 - \left[e^{-k_{dA}T} - (f_B(t = 0))\left(\frac{k_{dB} - k_{dA}}{k_r + k_{dB} - k_{dA}}\right)(e^{k_r t_d})(e^{k_{dA}T} - e^{-k_{dB}T}) \right] \quad \text{(A1)}$$

irradiation period to the beginning of the visible pulse with pulse width T, f_B $(t = 0)$ is the fraction of excited ions at the end of the IR irradiation. A k_{dA} value can be obtained from the visible-only dissociation, and an approximate k_r can be obtained from eq 3 and use of the midpoint visible pulse approximation. This leaves two undetermined parameters, k_{dB} and $f_B(t = 0)$. It is found that the experimental results give a reasonable fit to eq A1, using a range of pairs of k_{dB} and $f_B(t = 0)$ values. (Since these pa-

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(13) R. C. Dunbar, H. H. Teng, and Emil W. Fu, *J. Am. Chem. Soc.*, **101**, 6506 (1979).

(14) N. B. Lev and R. C. Dunbar, *Chem. Phys. Lett.*, **84**, 483 (1981).

(15) P. N. T. van Velzen, Ph.D. Thesis, University of Leiden, 1980.

(16) R. C. Dunbar and J. P. Honovich, submitted for publication.

(17) C. A. Wight and J. L. Beauchamp, *Chem. Phys. Lett.*, **77**, 30 (1981).

rameters are not tightly constrained, the zero-time correction obtained below is uncertain to ~25 ms ($C_6H_5I^+$) or 10 ms ($C_6H_5Br^+$)).

Since both eq 3 and eq A1 have the same exponential behavior, the zero point of t in eq 3 may be adjusted so that eq 3 provides an equally good representation of the data. The simple description of eq 3 is properly corrected by taking the value of t to be the time from the end of the IR irradiation to a point 30 ms ($C_6H_5I^+$) or 10 ms ($C_6H_5Br^+$) before the midpoint of the visible pulse.

The treatment above is still deficient in one respect: the use of dissociation rate constants k_{dA} and k_{dB} presupposes that the A and B populations of ions photodissociate by a time-independent process, as in simple one-photon dissociation. However, the A ions (and possibly the B ions) are actually believed to dissociate by a sequential two-photon process that cannot be described exactly by a simple dissociation rate constant. A more elaborate treatment to account for this would be unwarranted on the basis of the present data, and we simply state our expectation that no major error is introduced by neglecting this effect.

Registry No. Iodobenzene radical cation, 38406-85-8; bromobenzene radical cation, 55450-33-4.

Stereodynamics of Diethylmethylamine and Triethylamine

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Abstract: Diethylmethylamine is the simplest acyclic trialkylamine that possesses the requisite symmetry that allows, in principle, the direct observation of both nitrogen inversion and isolated nitrogen–carbon bond rotation using ^1H dynamic nuclear magnetic resonance (DNMR) spectroscopy. DNMR studies of diethylmethylamine and two deuterated derivatives complemented by empirical force-field calculations reveal a comprehensive picture of the stereodynamics of this representative acyclic trialkylamine. The DNMR studies show clear evidence for pyramidal inversion at nitrogen. In addition to nitrogen inversion, the results also speak for several "families" of rotamers for diethylmethylamine that undergo very rapid, DNMR-invisible *intra*family conformational exchange via isolated $N{-}CH_2$ rotation while also undergoing higher barrier DNMR-visible *inter*family exchange also via isolated $N{-}CH_2$ rotation. The DNMR-visible $N{-}CH_2$ rotation processes involve CCH_3/N-alkyl eclipsing in the transition state while the DNMR-invisible processes involve CCH_3/lone pair eclipsing. Although the symmetry of triethylamine precludes the DNMR-observation of nitrogen inversion, ^1H DNMR evidence for restricted $N{-}CH_2$ rotation and empirical force-field calculations reveal stereodynamics for triethylamine that are highly analogous to diethylmethylamine.

There has been much previous interest in the stereodynamics of acyclic and cyclic amines. The effects of π-bonding, electronegativity, ring strain, and other structural parameters on the nitrogen inversion barrier seem to be well established.[3] However, there are *two* rate processes associated with the nitrogen atom of a trialkylamine. One of these processes is indeed pyramidal inversion, and the other is isolated rotation about the nitrogen–carbon bonds. If one is to address the inversion/rotation dichotomy incisively in such amines, information regarding inversion barriers, rotation barriers, and conformational preferences is essential. In light of the huge effort devoted to studies of nitrogen inversion,[3] there is a surprising paucity of information regarding isolated nitrogen–carbon bond rotation and rotamer preferences in simple acyclic trialkylamines.[4] Although ^1H dynamic nuclear magnetic resonance (DNMR) studies in our laboratory provided some insight into both inversion and rotation processes in a number of *tert*-butylamine and isopropylamine derivatives, such crowded molecules may not be representative of simpler acyclic trialkylamines.[5]

Diethylmethylamine is the simplest acyclic trialkylamine that possesses the requisite symmetry that allows, in principle, the direct observation of both nitrogen inversion and *isolated* nitrogen–carbon bond rotation (i.e., *no* concomitant inversion) using the ^1H DNMR method *provided* the inversion barrier is higher than the barrier for isolated rotation about the nitrogen–carbon bonds.[5] A next higher homologue, triethylamine, possesses symmetry that renders nitrogen inversion DNMR-invisible but allows, in principle, the detection of isolated nitrogen–carbon bond rotation. This paper reports the results of ^1H DNMR studies of the stereodynamics of diethylmethylamine, triethylamine, and selectively deuterated derivatives complemented by empirical force-field (EFF) calculations. For each of these two amines, the evidence suggests the existence of several "families" of rotamers that undergo very rapid,

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