and no energy gap should be present. Experimentally, no energy gap is found. The E_{00} band of the emission spectrum is at about 13 850 cm^{-1}; the absorption spectrum has its initial intensity at about 14 000 cm^{-1}.[4,5,19]

It has been shown that the energy gap and the vibronic spacing in the electronic spectra of the $[PtCl_4]^{2-}$ ion are explained by an excited-state distortion in a non-totally symmetric mode. The 315-cm^{-1} MIME frequency results from the distortion in the 329-cm^{-1} A_{1g} mode and the 304-cm^{-1} B_{1g} mode. The low intensity in the energy gap is a result of slow wavepacket spreading along the B_{1g} coordinate.

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Registry No. $K_2[PtCl_4]$, 10025-99-7.

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[19] Kroenig, R. F.; Rush, R. M.; Martin, D. S.; Clardy, J. C. *Inorg. Chem.* **1974**, *13*, 1366.

Gas-Phase Heats of Formation of $C_7H_7^+$ Isomers: *m*-Tolyl, *p*-Tolyl, and Benzyl Ions

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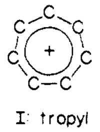
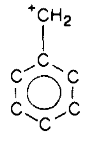
Abstract: The dissociation onsets of $C_7H_7^+$ formation from the ionic precursors of benzyl bromide and *m*- and *p*-nitrotoluene have been investigated by photoelectron photoion coincidence in order to determine accurate heats of formation of the resulting $C_7H_7^+$ ion structures. These parent ions are known to produce 100% benzyl and tolyl ions, respectively. Because the benzyl bromide ion dissociation was found to be rapid, the dissociation onset was determined from the crossover energy in the breakdown diagram and appropriately corrected for the precursor thermal energy. The nitrobenzene ions dissociate slowly near the dissociation onset, so that the thermochemical onset was found by extrapolating the measured decay rates with the RRKM/QET statistical theory. The rate data indicate that *p*- and *m*-nitrotoluene ions do not isomerize to a common structure prior to dissociation. This suggests that the *p*- and *m*-tolyl ions also exist as unique structures. However, no information about the *o*-tolyl ion was obtained. The derived ionic heats of formation were $\Delta H_f{}^\circ{}_{298}$(*m*-tolyl) = 1054 ± 10 kJ/mol, $\Delta H_f{}^\circ{}_{298}$(*p*-tolyl) = 1074 ± 10 kJ/mol, and $\Delta H_f{}^\circ{}_{298}$(benzyl) = 897 ± 5 kJ/mol. An upper limit for the heat of formation of $C_6H_4CH_3O^+$, the NO loss product from the *p*-nitrotoluene ion, was determined to be 890 kJ/mol. These heats of formation allow the methyl and ring C–H bond energies in the toluene ion to be calculated. They are 2.18 and 3.9 eV, respectively.

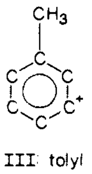
I. Introduction

The structures and energies of the $C_7H_7^+$ ions have fascinated chemists ever since the discovery by Doering and Knox[1] that the seven-membered cyclic structure known as the tropylium ion is stable in solution and that cycloheptatrienyl bromide appears to be ionized in the solid form.[2] The origin of this stability has been attributed to aromaticity, in which cyclic compounds with $4n + 2$ ($n = 1-3$, etc.) electrons are particularly stable. The tropylium ion has six π electrons, similar to the benzene molecule. In addition to the tropylium ion, there are many other possible structures of $C_7H_7^+$. Among the most stable are the benzyl and tolyl ions.

Investigations of gas-phase $C_7H_7^+$ ions have been carried out for a number of years by a variety of techniques including mass spectrometry,[3-7] collisional activation (CA),[8-13] ion cyclotron resonance (ICR),[14-17] photoionization (PI),[18-22] and photoelectron photoion coincidence (PEPICO),[23] as well as by molecular orbital calculations.[24,25] These studies show that there are three primary $C_7H_7^+$ structures that are produced in the dissociative ionization of various precursor molecules. These are, in order of increasing energy, the tropylium (I), the benzyl (II), and the tolyl (III) ions.


I: tropyl


II: benzyl


III: tolyl

Ion III has three different isomers, which differ in the position of the charge site on the ring relative to the methyl group. There

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(1) Doering, W. v. E.; Knox, L. H. *J. Am. Chem. Soc.* **1954**, *76*, 3203.
(2) Hine, J. *Physical Organic Chemistry*; McGraw-Hill: New York, 1962; p 27.
(3) Brown, P. *J. Am. Chem. Soc.* **1968**, *90*, 4461.
(4) Yeo, A. N. H.; Williams, D. H. *J. Chem. Soc., Chem. Commun.* **1970**, 886.
(5) Stapleton, B. J.; Bowen, R. D.; Williams, D. H. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1219.
(6) Tajima, S.; Tsuchiya, T. *Org. Mass Spectrom.* **1974**, *9*, 265.
(7) Leung, H. W.; Ichikawa, H.; Li, Y. H.; Harrison, A. G. *J. Am. Chem. Soc.* **1978**, *100*, 2479.
(8) McLafferty, F. W.; Winkler, J. *J. Am. Chem. Soc.* **1974**, *96*, 5182.
(9) McLafferty, F. W.; Bockhoff, F. M. *Org. Mass Spectrom.* **1979**, *14*, 181.
(10) Dymerski, P. P.; McLafferty, F. W. *J. Am. Chem. Soc.* **1976**, *98*, 6070.
(11) McLafferty, F. W.; Proctor, C. J. *Org. Mass Spectrom.* **1983**, *18*, 193.
(12) Buschek, J. M.; Ridal, J. J.; Holmes, J. L. *Org. Mass Spectrom.*, in press.
(13) Olesik, S.; Baer, T.; Ridal, J. J.; Buschek, J. M.; Holmes, J. L.; Morrow, J. C., to be submitted for publication in *Org. Mass Spectrom.*
(14) Jackson, J. A. A.; Lias, S. G.; Ausloos, P. *J. Am. Chem. Soc.* **1977**, *99*, 7515.
(15) Dunbar, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 1382.
(16) Honovich, J. P.; Dunbar, R. C. *Int. J. Mass Spectrom. Ion Processes* **1982**, *42*, 33.
(17) Fu, E. W.; Dymerski, P. P.; Dunbar, R. C. *J. Am. Chem. Soc.* **1976**, *98*, 337.
(18) Akopyan, M. E.; Vilesov, F. K. *Russ. J. Phys. Chem.* **1966**, *40*, 63.
(19) McLoughlin, R. G.; Morrison, J. D.; Traeger, J. C. *Org. Mass Spectrom.* **1979**, *14*; 104.
(20) McLoughlin, R. G.; Morrison, J. D.; Traeger, J. C. *Org. Mass Spectrom.* **1978**, *13*, 483.
(21) Traeger, J. C.; McLoughlin, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 7351.
(22) Lifshitz, C.; Goldenberg, M.; Malinovich, Y.; Peres, M. *Org. Mass Spectrom.* **1982**, *17*, 453.

0002-7863/88/1510-5633$01.50/0

appears to be little agreement concerning the energetics of the $C_7H_7^+$ ions beyond the order of the ion energies. Apart from the benzyl ion, the values for the heats of formation of the $C_7H_7^+$ isomers are not well established, and the isomerization barriers among the three structures are not known.

The tolyl ion is the least well-known of the three isomers. No experimental heat of formation for the tolyl ion has been reported. The only calculations are of the MINDO type, which indicate that the heats of formation of the ortho, meta, and para isomers are 970, 987, and 992 kJ/mol, respectively.[24] However, it is not clear whether the three tolyl isomers are stable or freely interconvert.

The benzyl ion heat of formation is far better established. A reliable value comes from the combination of the $\Delta H_f°_{298}(C_6H_5CH_2^•)$ = 200 ± 6 kJ/mol[26] with the radical ionization energy of 7.2[27] or 7.27[28] eV. Using the newer IE value of 7.20 eV leads to a $\Delta H_f°_{298}(C_6H_5CH_2^+)$ = 895 ± 8 kJ/mol. Other values reported are considerably less certain because they result from the dissociative ionization onsets obtained from substituted benzenes. In these cases, the product ion was probably not 100% benzyl. Thus, the H loss from toluene, studied by PEPICO, led to a heat of formation of 913 kJ/mol.[23] Simple photoionization onsets from ethylbenzene and benzylchloride led to the higher values of 929 and 974 kJ/mol, respectively.[18] However, the ethylbenzene result is probably too high because of a kinetic shift. Finally, two calculations also appear to give high values. A MINDO approach predicted 922 kJ/mol,[24] while an ab initio calculation gave 908 kJ/mol.[25]

The many reported values for the tropylium ion heat of formation range from 820 to 985 kJ/mol.[5,14,18-25] The difficulty in establishing this value is a result of the fact that most ions investigated do not produce solely the tropylium ion. Furthermore, tropylium ion production generally proceeds with the release of kinetic energy, which indicates that its production is accompanied by a reverse activation barrier.[12,13] The only precursors that are known to give pure tropylium ion with no reverse activation energy are salts such as tropylium tetrafluoroborate.[12] However, the study of such compounds by photoionization has not been attempted, in part because they do not have a significant vapor pressure. Thus, the tropylium ion heat of formation remains largely unknown.

A considerable body of collisional activation (CA) data exists[8-13] on the $C_7H_7^+$ ion structures. These studies have shown that benzyl bromide ions dissociate near threshold exclusively to the benzyl ion structure and that *m*- and *p*-nitrotoluene ions dissociate exclusively to the tolyl ion structure.[9,12,13] In this investigation we use these dissociation reactions to confirm the previously reported benzyl ion heat of formation and to establish for the first time the heats of formation of the *m*- and *p*-tolyl $C_7H_7^+$ ion energies. The PEPICO technique is used to measure the dissociation rate of *m*- and *p*-nitrotoluene ions from which an onset energy, corrected for the kinetic shift, can be determined. The benzyl bromide ion dissociation is fast so that no rate data were collected. Its energetics could be obtained directly from the dissociation onset in the breakdown diagram.

Unfortunately, the *o*-nitrotoluene ion loses OH at its dissociation threshold, and no NO_2 loss signal is evident at energies corresponding to the slow reaction. Thus, we are unable to report any results on the *o*-tolyl isomer.

II. PEPICO Experiments: Breakdown Diagrams and Dissociation Rates

The photoelectron photoion coincidence (PEPICO) experiment has been described previously.[29-32] Briefly, ions were produced by light from a hydrogen-discharge lamp dispersed by a 1-m monochromator with slits set at 200 μm, which yield a resolution of about 17 meV at 1200 Å. When a sample is ionized with photons of energy $h\nu$, the resulting ions have a distribution of internal energies ranging from the ionization potential (IP) to $h\nu$ - IP. However, by conservation of energy and momentum, the ion internal energy, E_{ion}, is associated with an ejected electron of a particular kinetic energy (E_{el}). E_{ion} is given by $h\nu$ - IP - E_{el} + E_{th}, where E_{th} is the ion internal energy due to the thermal internal energy of the precursor molecule at a temperature T. Thus, by measuring ions in coincidence with electrons of initially zero energies, we collect only ions that contain the energy $h\nu$ - IP + E_{th}.

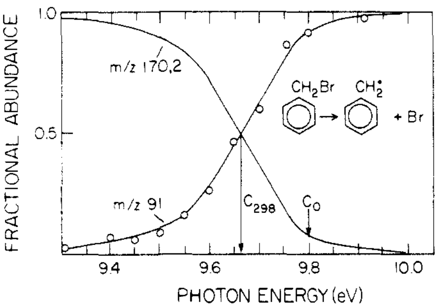

Figure 1. Breakdown diagram of benzyl bromide. The two isotopes, *m/z* 170 and 172, were not resolved. These data were collected in two PEPICO laboratories: one at the University of North Carolina and the other at the University of Paris, Orsay (LURE).

Zero-energy electrons are detected by passing them through a set of collimated holes with a length to diameter ratio of 40. Ions are accelerated in the opposite direction by the applied field of 12 V/cm in the 4-cm-long acceleration region. After traversing an 8-cm-long drift region, they are detected by a spiraltron electron multiplier. The electron and ion signals provide, respectively, the start and stop inputs to a time to pulse-height converter. This output signal then goes to a multichannel pulse-height analyzer. The resulting spectrum is a time of flight (TOF) distribution for all ions formed from the parent ion at a selected internal energy.

The breakdown diagram displays the fractional abundance of the ions produced as a function of the ion internal energy. It is obtained by collecting PEPICO mass spectra at various parent ion internal energies. Such diagrams are useful especially when the ion lifetimes are short compared to the time necessary to collect the ion, i.e. microseconds. However, the shape of the breakdown diagram is very instrument dependent when the ion dissociations are slow. Slowly dissociating ions, which fragment during the course of acceleration, result in times of flight that are in between those of the rapidly produced product ion and the parent ion. The analysis of the resulting asymmetric TOF distribution can thus be used to determine the dissociation rate.

The breakdown diagram of benzyl bromide was obtained in the Chapel Hill PEPICO apparatus as well as in the very different coincidence experiment at the synchrotron radiation facility (LURE) at the University of Paris in Orsay. The electron energy resolution and suppression of energetic electrons are superior in the latter apparatus. Nevertheless, the two sets of data were virtually indistinguishable.

III. Results

A. $C_7H_7^+$ Dissociation Onset from the Benzyl Bromide Ion. The CA results have shown that the benzyl ion is exclusively formed in the threshold dissociation of benzyl bromide ions. Thus, the benzyl ion heat of formation can be calculated from the measured appearance energy. If an ion dissociated rapidly at the dissociation onset with no, or little, release of kinetic energy, the most accurate method for determining the fragmentation onset is from the crossover energy in the breakdown diagram. This diagram in the vicinity of the dissociation limit is shown in Figure 1.

From the symmetric $C_7H_7^+$ fragment ion TOF distribution, we know that the dissociation rate of benzyl bromide is rapid. Thus, the extended energy range over which the product and parent ions

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(23) Bombach, R.; Dannacher, J.; Stadelmann, J. P. *Chem. Phys. Lett.* **1983**, *95*, 259.

(24) Cone, C.; Dewar, J. S.; Landman, D. *J. Am. Chem. Soc.* **1977**, *99*, 372.

(25) Abboud, J. L. M.; Hehre, W. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 6072.

(26) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(27) Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3290.

(28) Lossing, F. P. *Can. J. Chem.* **1971**, *49*, 357.

(29) Baer, T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 1, Chapter 5.

(30) Baer, T. *Adv. Chem. Phys.* **1986**, *64*, 111.

(31) Butler, J. J.; Baer, T. *J. Am. Chem. Soc.* **1980**, *102*, 6764.

(32) Fraser-Monteiro, M. L.; Fraser-Monteiro, L.; Butler, J. J.; Baer, T.; Hass, J. R. *J. Phys. Chem.* **1982**, *86*, 739.

(33) Green, J. H. S. *Spectrochim. Acta, Part A* **1970**, *26A*, 1913.

(34) Green, J. H. S. *Spectrochim. Acta* **1962**, *18*, 39.

Table I. Molecular Ion and Transition-State Vibrational Frequencies

$C_6H_4CH_3NO_2$[a]	2940 (7) 405 (3)	1495 (8) 265 (1)	1345 (5) 180 (1)	1040 (11) 140 (1)	820 (3)	635 (5)
$C_6H_4CH_3NO_2$ (TS)[b] (loose)	2940 (7) 320 (3)	1495 (8) 200 (1)	1345 (5) 120 (1)	1040 (10) 70 (1)	820 (3)	600 (5)
$C_6H_4CH_3NO_2$ (TS)[c] (tight)	2940 (7) 600 (3)	1495 (8) 500 (1)	1345 (5) 490 (1)	1040 (10) 400 (1)	820 (3)	700 (5)
$C_6H_5CH_2Br$[d]	2940 (7) 470 (4)	1475 (7) 250 (2)	1200 (5) 220 (1)	1040 (4) 150 (1)	940 (4)	720 (4)
$C_6H_5CH_2^+$ or $C_6H_4CH_3^+$[d]	2940 (7) 485 (4)	1480 (7) 370 (1)	1210 (5)	1045 (4)	940 (4)	730 (4)

[a] Derived from frequencies of nitrobenzene and chlorobenzene.[33] [b] Transition-state frequencies for NO_2 loss from p-$C_6H_4CH_3NO_2^+$. [c] Transition-state frequencies for NO loss from p-$C_6H_4CH_3NO_2^+$. [d] Derived from the frequencies of the halotoluenes.[33,34]

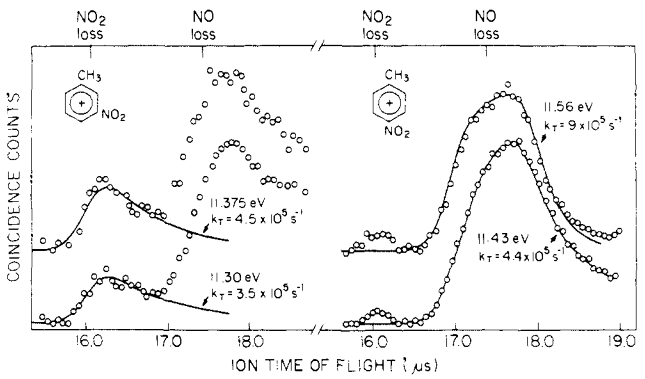


Figure 2. $C_7H_7^+$ ion coincidence TOF spectrum from the dissociation of m- and p-nitrotoluene at several ion internal energies. The points are the experimental data, while the lines are calculated TOF distributions for the indicated rates.

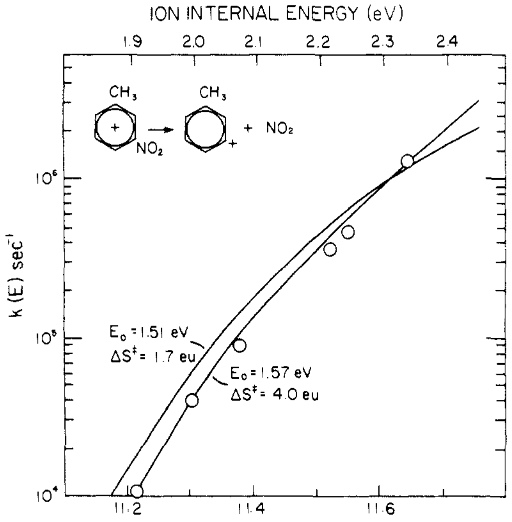
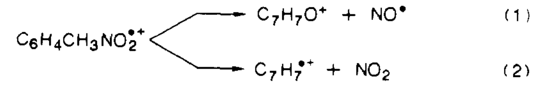


Figure 3. Experimental rates of NO_2 loss from m-nitrotoluene ions (points). The solid lines are two RRKM/QET calculations with different transition-state frequencies and assumed activation energies. The indicated $\Delta S^\ddagger$ values, evaluated at 1000 K, are a measure of the tightness of the assumed transition state.

appear is a result only of the thermal energy distribution of the parent molecule. At the crossover energy precisely half of the parent ions have sufficient energy to dissociate and half do not. This energy is the median energy in the thermal energy distribution and is close to the mean thermal energy. Thus, the crossover energy at 0 K (C_0) is obtained simply by adding the median thermal energy of 0.14 eV to the crossover energy at 298 K (C_{298}). The average thermal energy is the sum of the rotational energy ($^3/_2RT$) and the average vibrational energy in the benzyl bromide molecule at the temperature of our experiment (~300 K). The average vibrational energy was calculated from the vibrational frequencies listed in Table I. Each normal mode contributes $h\nu/[\exp(h\nu/kT) - 1]$ to the total vibrational energy. The use of the breakdown diagram is the most accurate method for obtaining dissociation onsets because it avoids the problems associated with defining an onset in a curve that rises slowly and smoothly from the background noise. The C_{298} and C_0 values for bromine loss from benzyl bromide were found to be 9.66 and 9.80 eV, respectively.

B. Dissociation Rates and RRKM/QET Calculations of Nitrotoluene Ions. The nitrotoluene ions are metastable near their dissociation thresholds. Thus, the thermochemical dissociation limit cannot be obtained by measuring the breakdown diagram. Instead, the dissociation rates at several ion internal energies were measured and then modeled with the statistical theory of unimolecular decay. The analysis of these rate measurements was hampered by the competing dissociation channels of the nitrotoluene ion, which, near the dissociation threshold, are shown in eq 1 and 2. The onset for reaction 1 is considerably lower than



$$C_6H_4CH_3NO_2^{\bullet +} \longrightarrow C_7H_7O^+ + NO^\bullet \quad (1)$$
$$C_6H_4CH_3NO_2^{\bullet +} \longrightarrow C_7H_7^{\bullet +} + NO_2 \quad (2)$$

for reaction 2 so that the NO loss channel dominates at low energies. In the case of m-nitrotoluene, it was possible to determine the rate of NO_2 loss by modeling the $C_7H_7^+$ time of flight (TOF) distribution. However, in the case of the p-nitrotoluene ion, the competition favors the NO formation to such an extent that the $C_7H_7^+$ production was too small to monitor the rate in this manner. Examples of several TOF distributions are shown in Figure 2.

In the case of dissociation reactions with several competing product channels, the total rate constant, k_T, is given by the sum of the individual rate constants, i.e., $k_T = k_1 + k_2$. The TOF profile of either the $C_7H_7O^+$ or the $C_7H_7^+$ ion should give the same result, which is the total rate constant. The individual rates can then be derived from the ratio of the $C_7H_7O^+$ and $C_7H_7^+$ signals. The total rate could be determined from each of the product TOF distributions in the case of the m-nitrotoluene ion. These rates were verified to be the same, thereby establishing the existence of a competitive reaction to the two channels. The rate for NO_2 loss was then determined from the ratio of ion intensities. These rates as a function of the ion internal energy are shown in Figure 3. The dissociation rate of the p-nitrotoluene ion could only be determined from the NO loss channel. However, this was sufficient to obtain the NO_2 loss rate from the peak ratios, which could be determined with good accuracy. These rates are shown in Figure 4.

The dissociation rates of the m- and p-nitrotoluene ions at the same absolute energy scale [$h\nu + \Delta H_f^\circ(C_6H_4CH_3NO_2)$] are not identical. This shows that these two ions do not isomerize to a common structure prior to dissociation. This is also evident from the different branching ratios for NO and NO_2 loss in Figure 3. These results strongly suggest that the product tolyl ions retain their distinct structures.

Two energy scales are shown in Figures 3 and 4, the photon energy at the bottom and the ion internal energy at the top. At a given photon energy, the ion internal energy is given by $h\nu + E_{th} - IE$, where E_{th} is the average thermal energy in the nitrotoluene molecule and IE is its ionization energy. The average thermal energy of the two nitrotoluene molecules, determined from the vibrational frequencies listed in Table I, is 0.143 eV. The same set of frequencies was used for the meta and para isomers. The

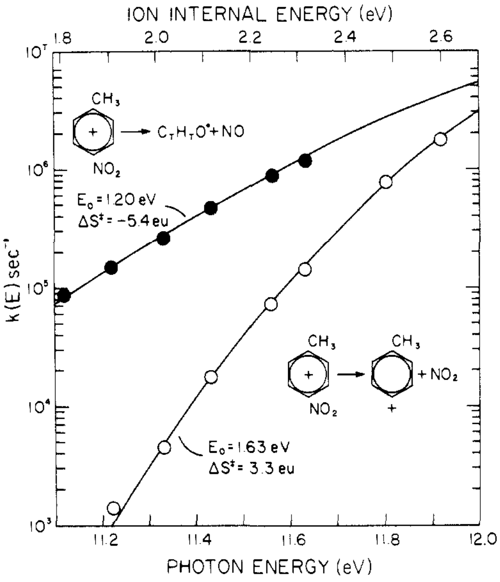


Figure 4. Experimental rates (points) and the RRKM/QET calculated rates (solid lines) for the dissociation of *p*-nitrotoluene ion to the two indicated product channels. The total rates were measured with respect to the NO loss channel and the rates to the separate channels derived from the ratio of the NO and NO_2 loss signals.

adiabatic ionization energies, as determined from the onset of the photoionization efficiency curves, were found to be 9.45 eV (meta) and 9.46 eV (para). The ion internal energy as measured from the zero-point energy of the ground-state ion is the energy used in the RRKM/QET calculations.

The dissociation rate, $k(E)$, in the statistical theory (RRKM[35] or QET[36]) is given by eq 3 in which E and E_0 are the ion internal

$$k(E) = \sigma W^{\ddagger}(E - E_0)/\rho(E) \qquad (3)$$

energy and the activation energy, respectively, $W^{\ddagger}(E - E_0)$ is the sum of internal energy states in the transition state from 0 to $E - E_0$, $\rho(E)$ is the parent ion density of states at energy E, and σ is the number of equivalent dissociation paths. The molecular parameters required for evaluation of the rates are the vibrational frequencies of the transition state and the parent ion and the activation energy, E_0. The vibrational frequencies of the ions and transition states are not known. As a result, we have derived the approximate parent ion frequencies (Table I) from the frequencies of the neutral nitrobenzene and the halotoluene molecules. The transition-state frequencies can be treated as adjustable parameters. A tight transition state, generally associated with a reaction proceeding with a reverse activation barrier, would have slightly higher frequencies than the parent ion. On the other hand a loose transition state, generally associated with a reaction for which the products resemble the reactant ion and which proceeds with no reverse activation energy, has frequencies that are slightly lower than those of the parent ion.

The character of the transition state is conveniently represented by the entropy of activation (eq 4) in which the total partition

$$\Delta S^{\ddagger} = k \ln Q^{\ddagger}/Q = k \ln (\Pi q_i^{\ddagger}/\Pi q_i) \qquad (4)$$

function, Q, is the product of the individual vibrational partition functions, $q_i = [1 - \exp(h\nu/kT)]^{-1}$. Thus, $\Delta S^{\ddagger} < 0$ for a tight transition state, while $\Delta S^{\ddagger} > 0$ for a loose transition state.

Although a total of 89 vibrational frequencies of the molecular ion and its transition state must be specified in carrying out the RRKM/QET calculations, the individual values are less important than the average values of the frequencies in the transition state and the molecular ion. Thus, there are only two independent parameters, the activation energy, E_0, and the entropy of activation, $\Delta S^{\ddagger}$. These parameters were varied until the fits shown by the lines in Figure 3 and 4 were obtained. The estimated vibrational frequencies of the transition-state ions are shown in Table I. The C–NO_2 stretching frequency of 1040 cm^{-1} was chosen as the reaction coordinate. One of these frequencies is thus missing from the transition-state frequencies.

Two RRKM/QET calculations with slightly different values for E_0 and $\Delta S^{\ddagger}$ are shown in Figure 3. These calculations indicate the sensitivity of the derived results to the assumed activation energy. On this basis, the uncertainty in the derived energy is believed to be ±0.05 eV. The $\Delta S^{\ddagger}$ for both calculations are positive, indicating that the transition state is "loose".

It is noteworthy that the dissociation onset, E_0, is 0.46 eV below the lowest energies at which the rate data could be obtained. This is a result of the well-known kinetic shift.[37] The onset for dissociation, as measured by an appearance energy, is typically associated with rates between 10^2 and 10^4 s^{-1}.[38] The precise location depends on the signal to noise limit. However, it can also be shifted by secondary processes such as collision-induced dissociation. Figure 3 shows clearly that the appearance energy for NO_2 loss would be between 1.8 and 1.9 eV, which is well above the true onset of 1.56 ± 0.05 eV.

The rates for both NO and NO_2 loss from *p*-nitrotoluene ions are shown in Figure 4. RRKM/QET calculations were performed for both reactions using the same molecular ion vibrational frequencies. However, very different transition-state frequencies were required. The "tight" transition state associated with the NO loss channel is typically of a reaction that involves a rearrangement and has a reverse activation energy. An analysis of the $C_7H_7O^+$ peak width indicated that the kinetic energy released in the dissociation is 0.9 ± 0.06 eV and that the distribution is sharply peaked around this value. The large negative $\Delta S^{\ddagger}$ of −5.4 cal/K is entirely consistent with these facts.

The NO_2 loss channel is overshadowed at low energies by the NO loss reaction but becomes dominant at high energies. This behavior is typical of direct cleavage reactions that are associated with loose transition states, and the positive $\Delta S^{\ddagger}$ of 3.3 cal/K is reasonable. It is also reassuring that both the E_0 and $\Delta S^{\ddagger}$ values for the NO_2 loss from *m*- and *p*-nitrotoluene ions are similar, as indeed they are expected to be.

IV. Derived Heats of Formation

A. Benzyl Ion. In order to determine the $C_7H_7^+$ ion heats of formation, it is necessary to know the neutral precursor thermochemistry. The gas-phase benzyl bromide $\Delta H_f°_{298}$ is well established at 63.3 kJ/mol.[39] The $\Delta H_f°_{298}$ (*p*-nitrotoluene) of 31 kJ/mol in the gas phase[39] is somewhat less well-known. Only the liquid phase of value of −31.5 kJ/mol for the *m*-nitrotoluene heat of formation is listed in Pedley et al.[39] Thus, the gas-phase value of $\Delta H_f°_{298}$ of 18 ± 2 kJ/mol shown in Table II was derived from *m*-nitrotoluene vapor pressure data.[40]

The conversion of the 298 K heats of formation to 0 K was carried out in the usual manner,[32,41,42] using the vibrational frequencies listed in Table I. The parent ion heats of formation, shown in Table II, were determined by adding the ionization energy to either the 0 or 298 K neutral heats of formation.

The 0 K crossover energy in Figure 1 can now be used in conjunction with the neutral 0 K heats of formation to determine the benzyl ion heat of formation by

$$\Delta H_f°_0(\text{benzyl}) = \text{AE}(0\text{ K}) + \Delta H_f°_0(C_6H_5CH_2Br) - \Delta H_f°_0(\text{Br}) = 919 \pm 5 \text{ kJ/mol}$$

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(35) Marcus, R. A.; Rice, O. K. *J. Phys. Colloid Chem.* **1951**, *55*, 894.

(36) Rosenstock, H. M.; Wallenstein, M. B.; Warhaftig, A. L.; Eyring, H. *Proc. Natl. Acad. Sci. U.S.A.* **1952**, *38*, 667.

(37) Chupka, W. A. *J. Chem. Phys.* **1959**, *30*, 191.

(38) Fraser-Monteiro, M. L.; Fraser-Monteiro, L. F.; deWit, J.; Baer, T. *J. Phys. Chem.* **1984**, *88*, 3622.

(39) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.

(40) *Handbook of Chemistry and Physics*, 56th ed.; Weast, R. C., Ed.; CRC: Cleveland, OH, 1975; p D-198.

(41) Rosenstock, H. M. In *Kinetics of Ion-Molecule Reactions*; Ausloos, P., Ed.; Plenum: New York, 1979.

(42) Traeger, J. C.; McLoughlin, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 3647.

(43) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data, Suppl.* **1982**, *11*, 2.

Table II. Gas-Phase Heats of Formation (kJ/mol) and Ionization Energies (eV)

	molecule			ion	
molecule/ion	$\Delta H_f{}^\circ{}_{298}$	$\Delta H_f{}^\circ{}_0{}^a$	IP[b]	$\Delta H_f{}^\circ{}_{298}{}^c$	$\Delta H_f{}^\circ{}_0$
$C_6H_5CH_2Br$	63.3 ± 2[d]	92	8.99 ± 0.015	931	959
m-$C_6H_4CH_3NO_2$	18 ± 2[e]	47.8	9.45 ± 0.1	930	959
p-$C_6H_4CH_3NO_2$	31 ± 4[d]	60.8 ± 4	9.46 ± 0.05	944	973
Br	111.88[f]	117.94[f]			
NO_2	33.18[g]	35.98[g]			
NO	90.25[g]	89.75[g]			

[a] Converted from 298 K value using the frequencies in Table I. [b] From this study. [c] Converted from 0 K ion value using the frequencies in Table III. The Rosenstock convention[41] in which the electron energy at 298 K is zero was used. To convert to JANAF convention, add 6.2 kJ/mol. [d] Pedley et al.[39] [e] Determined from the liquid-state value of −31.5 kJ/mol[39] using vapor pressure data from ref 40. [f] Wagman et al.[43] [g] Rosenstock et al.[44]

Table III. Derived $C_7H_7^+$ Heats of Formation (kJ/mol)

	this work			
$C_7H_7^+$ structure	$\Delta H_f{}^\circ{}_0$	$\Delta H_f{}^\circ{}_{298}$	$\Delta H_f{}^\circ{}_{298}$	lit. values
$C_6H_4CH_3^+$ (tolyl)			970 (ortho)	MINDO calculation[24]
meta	1074 ± 10	1054 ± 10[a]	987 (meta	MINDO calculation[24]
para	1094 ± 10	1074 ± 10[a]	992 (para)	MINDO calculation[24]
$C_6H_5CH_2^+$ (benzyl)	919 ± 5	897 ± 5[a]	895 ± 6[b]	
			913	toluene PEPICO results[23]
			922	MINDO calculation[24]
			908	ab initio calculation[25]
			929	PI onset from ethylbenzene[18]
			974	PI onset from benzyl chloride[18]

[a] Zero-energy electron convention. To convert to the JANAF convention, add 6.2 kJ/mol. [b] Determined from the IP of 7.2 eV[27] and the $\Delta H_f{}^\circ(C_6H_5CH^\bullet)$ = 200 kJ/mol.[26]

This value can be converted to 298 K by the standard procedure using the assumed vibrational frequencies of the benzyl ion.

The derived benzyl ion heat of formation compares very well with one that is obtained from the ionization energy of the benzyl radical and the radical heat of formation (see Table III). The agreement between these two very different approaches thus firmly establishes the benzyl ion heat of formation. The other published values are all somewhat uncertain because of the mixture of product ions formed in the dissociative ionization of toluene and other substituted benzenes.

B. *m*- and *p*-Tolyl Ions. The tolyl ion heats of formation can be calculated in a similar manner from the analysis of the rate data in Figures 3 and 4 by using the derived activation energies in the following relation:

$$\begin{aligned}\Delta H_f{}^\circ{}_0(\text{tolyl}) &= \Delta H_f{}^\circ{}_0(C_6H_4CH_3NO_2{}^+) + E_0 - \Delta H_f{}^\circ{}_0(NO_2)\\ &= 1074 \pm 10\ \text{kJ/mol}\ (m\text{-tolyl})\\ &= 1094 \pm 10\ \text{kJ/mol}\ (p\text{-tolyl})\end{aligned}$$

These values are then also converted to their 298 K counterparts.

The derived 0 and 298 K heats of formation are listed in Table III, where they are compared with those of other workers. The tolyl ion heats of formation we report here are the first experimental values obtained. The MINDO calculations give results that are more than 0.8 eV lower than the experimental values. However, these calculations do predict the experimentally obtained ordering of the heats of formation of the two isomers. The difference in the two experimentally found isomer energies is 20 kJ/mol, whereas the MINDO calculations predict only 5 kJ/mol. The question arises as to how significant the 20 kJ/mol energy difference is. On the one hand, the uncertainty in the total heat of formation is estimated to be ±10 kJ/mol. Yet the difference in energies of the two isomers may be given much more accurately since any systematic errors in data reduction would presumably cause similar magnitude errors in the same direction. The difference of 20 kJ/mol arises from two sources. The neutral *p*-nitrotoluene molecule is 13 kJ/mol less stable than the meta isomer. This difference remains about the same in the nitroluene ions. However, the different activation energies for NO_2 loss increase the discrepancy in the tolyl ion energetics by another 7 kJ/mol. The large difference in the heats of formation of the two tolyl ions confirms the previous conclusion that the two tolyl isomers indeed have distinct structures and energies.

It is unfortunate that the *o*-nitrotoluene ion dissociation did not produce a sufficient signal of $C_7H_7^+$ for the *o*-tolyl ion heat of formation to be compared to the others. The MINDO[24] predictions are that the heat of formation of this ion is about 20 kJ/mol below those of the other two. However, it is not known whether this ion is even stable. Rearrangement to the benzyl ion, which is 1.8 eV more stable, via a simple 1,3 H atom transfer is certainly a very probable process.

C. C–H Bond Energies in the Toluene Ion. There are two types of C–H bonds in the toluene ion: the three methyl C–H bonds and the five C–H bonds on the benzene ring. It is possible to calculate the methyl C–H bond energy in the toluene ion with the benzyl ion heat of formation. This value, along with the toluene ion 0 K heat of formation of 924 kJ/mol[23] and the H atom heat of formation of 216 kJ/mol,[44] leads to a C–H bond energy of 211 kJ/mol, or 2.18 eV. This is very small when compared to the corresponding C–H bond energy in neutral toluene of 368 kJ/mol[26] or the C–H bond energy in the benzene ion of 357 kJ/mol.[45] It is a reflection of the energy gained by the change from a tetrahedral methyl group to a planar CH_2^+ group.

The energy of the C–H bond located on the toluene ion ring can be determined in a similar manner by using the tolyl ion heat of formation. This leads to an average C–H bond energy at the meta and para positions of 376 ± 15 kJ/mol, or 3.9 eV. This energy can be compared to other benzene ring C–H bond energies, which in benzene, chlorobenzene, and bromobenzene are 357,[45] 376,[46] and 372.[46] From this agreement with other benzene ring C–H bond energies, we conclude that the structure of the tolyl ion is very similar to that of the phenyl ion. The agreement also lends further support to the derived tolyl ion heat of formation.

D. $C_6H_4CH_3O^+$ Ion. As was pointed out before, the NO loss from *p*-nitrotoluene is accompanied by the release of 0.90 ± 0.06 eV of kinetic energy, and this energy distribution is sharply peaked at this energy. A previous determination of this kinetic energy was reported by Beynon et al.,[47] on the basis of a MIKES study,

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(44) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl.* **1977**, *6*, 1.

(45) Rosenstock, H. M.; Dannacher, J.; Liebman, J. F. *Radiat. Phys. Chem.* **1982**, *40*, 7.

(46) Olesik, S.; Baer, T.; Morrow, J. C. *J. Phys. Chem.* **1986**, *90*, 3563.

who found the release energy to be 0.96 eV with a slight contribution from a low-energy release channel. It is impossible to determine the heat of formation of the $C_7H_7O^+$ ion from the derived dissociation limit because we do not know the fraction of the reverse activation energy that appears as kinetic energy of the departing fragments. However, we can determine an upper limit to the heat of formation for the resulting $C_6H_4CH_3O^+$ ion by subtracting the kinetic energy release from the NO loss dissociation limit. This yields a $\Delta H_f{}^\circ{}_0 < 910$ kJ/mol, which translates to a 298 K value of 890 kJ/mol.

It is interesting to compare this derived heat of formation with that of the similar ion, $C_6H_5O^+$, which is the product of the NO loss from the nitrobenzene ion.[48] The 298 K heat of formation of $C_6H_5O^+$ was calculated to be 874 kJ/mol from the ionization energy (8.56 eV) of the phenoxy radical[49] and its neutral radical heat of formation (46 kJ/mol).[50] We can estimate the effect of adding a methyl group to a benzene ring from the difference in the heats of formation of the benzene ion (975 kJ/mol) and the toluene ion (901 kJ/mol).[44] Thus, we estimate that the $\Delta H_f{}^\circ{}_{298}(C_6H_4CH_3O^+)$ should be about 874 - 74 = 800 kJ/mol. Thus, the upper limit of 890 kJ/mol for the heat of formation of $C_6H_4CH_3O^+$ obtained in this study is indeed an upper limit. However, the discrepancy of 90 kJ/mol suggests that the release energy represents only 50% of the total reverse activation energy.

V. Conclusions

The PEPICO experiments on the dissociative ionization of benzyl bromide ions have confirmed the previously reported heat of formation of the $C_7H_7^+$ benzyl ion on the basis of the ionization energy of the benzyl radical. The benzyl ion heat of formation at 298 K can now be considered established at 896 ± 4 kJ/mol. The PEPICO measurements of the *m*- and *p*-nitrotoluene ion dissociation rates modeled with the statistical theory (RRKM/QET) have been used to establish for the first-time experimental values for the tolyl ion heats of formation. The meta and para isomers were found to have 298 K heats of formation of 1054 and 1074 ± 10 kJ/mol, respectively. No experimental information about the stability and thermochemistry of the *o*-tolyl ion is available.

Aside from the *o*-tolyl ion, the major mystery in the $C_7H_7^+$ story yet to be solved is the heat of formation of the tropyl ion. This must await an experiment in which the dissociation limit of a precursor such as the tropylium tetrafluoroborate ion is measured. However, such a study will also require the heat of formation of the neutral salt.

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(47) Beynon, J. H.; Bertrand, M.; Cooks, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 1739.

(48) Panczel, M.; Baer, T. *Int. J. Mass Spectrom. Ion Processes* **1984**, *58*, 43.

(49) Dewar, M. J. S.; David, D. E. *J. Am. Chem. Soc.* **1980**, *102*, 7387.

(50) DeFrees, D. J.; McIver, R. T.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 3334.

Intramolecular Determinants of Conformation and Mobility within the Antibiotic Vancomycin

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Abstract: The conformations of the N-terminal region of the glycopeptide antibiotic vancomycin, and *N*-acetylvancomycin, in DMSO solution are discussed. A 180° rotation of the central amide unit of the carboxylate binding pocket is observed. It is shown that the anomalously rapid exchange of the N-terminal amide proton with the residual water within the solvent is dependent upon the basic N-terminal amine.

The structure of the clinically important glycopeptide antibiotic vancomycin (**1**) has been elucidated by a combination of methods. Following the solution of the crystal structure of the degradation product, CDP-I,[1] the proposed structure of vancomycin was revised with high-field ^{1}H NMR[2] and chemical studies.[3] The geometry of the binding of vancomycin to bacterial cell wall precursor analogues di-*N*-acetyl-L-Lys-D-Ala-D-Ala (tripeptide) and *N*-acetyl-D-Ala-D-Ala (dipeptide) has also been studied by ^{1}H NMR.[4-6] Within these structural studies, the solution conformation of the rigid C-terminal region of vancomycin has been well-defined, but little has been reported about the more flexible N-terminal region. This paper will deal with our observations concerning the conformations and motion of the N-terminal region as studied by ^{1}H NMR. For convenience, we define the binding pocket side of vancomycin as the "front" face and the nonbinding side as the "back" face. The code used to designate the protons of vancomycin is that used previously[6] and is shown in Figure 1. The constituent amino acid residues are numbered 1-7 starting from the N-terminus. The observed chemical shifts of the proton resonances are listed in Table I, and the nuclear Overhauser effects (NOEs) mentioned in the text are shown in Table II. It should

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(1) Sheldrick, G. M.; Jones, P. G.; Kennard, O.; Williams, D. H.; Smith, G. A. *Nature (London)* **1978**, *271*, 223.

(2) Williamson, M. P.; Williams, D. H. *J. Am. Chem. Soc.* **1981**, *103*, 6580.

(3) Harris, C. M.; Kopecka, H.; Harris, T. M. *J. Am. Chem. Soc.* **1983**, *105*, 6915.

(4) Williams, D. H.; Butcher, D. W. *J. Am. Chem. Soc.* **1981**, *103*, 5697.

(5) Williams, D. H.; Williamson, M. P.; Butcher, D. W.; Hammond, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 1332.

(6) Rajamoorthi, K.; Harris, C. M.; Harris, T. M.; Waltho, J. P.; Skelton, N. J.; Williams, D. H. *J. Am. Chem. Soc.* **1988**, *110*, 2946.

0002-7863/88/1510-5638$01.50/0