event. For overall hydrogen abstraction from amines, the electron transfer is generally more facile than in the most favorable cases of hydrogen abstraction from alkyl groups because, at one and the same time, the $n_N\pi^*_{CO}$ and $D'_{\sigma\pi}$ states are lower than the corresponding $\pi_{CO}\pi^*_{CC}$ and $Z'_{\sigma\pi}{}^*$ states.

Support for the qualitative correctness of the basic correlation diagrams given in Figures 5 and 6 is available from qualitative calculated potential energy curves.[2a-c, 5b] For example, ab initio calculations[5b] of hydrogen abstraction from methane by formaldehyde and of the α cleavage of acetone agree completely with the qualitative diagrams presented in this paper.

Conclusion

The four experimentally significant n-initiated photochemical reactions of ketones in their various manifestations can be analyzed in a unified manner with natural correlation diagrams which can be divided in two groups. There are those which involve the formation of a new σ bond on the ketonic framework: hydrogen abstraction from alkyl groups or amines and olefin addition. In such a case, the electronically allowed valence states are the $n_O\pi^*_{CO}$ states. If no low-lying charge-transfer states exist, the reaction involves direct formation of a diradical state throughout a single PEC with a potential barrier. If there is low-lying charge-transfer state, the reaction may be a two-step process, which involves in a first step the formation of an ion-pair intermediate. It should be noted that the experimentally observed ion-pair intermediate could correspond to two situations. First, it may correspond to the potential well encountered on the PEC starting from the $n_O\pi^*_{CO}$ states in Figures 5 and 9, as already mentioned. Second it may correspond to the initial charge-transfer states ($n_N\pi^*_{CO}$, $\pi_{CC}\pi^*_{CO}$) which would have been populated by decay from the potential well corresponding to the first hypothesis. In this last hypothesis, the ion-pair intermediate has a long lifetime for the same reasons it cannot be directly populated. Thus, the subsequent hydrogen transfer or olefin addition would occur throughout a single surface linking the charge-transfer state to the ground state of the radical intermediate. Finally, there are the reactions which involve rupture of a σ bond that is α to the ketonic framework. In such a case, the electronically allowed reaction proceeds from the triplet $\pi_{CO}\pi^*_{CO}$, but reaction initiated from the $n_O\pi^*_{CO}$ states must be considered as possible pathways involving intersystem crossing or internal conversion. No charge-transfer state is possible and consequently cannot modify the general diagram in this case.

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Collision-Induced Dissociation Mass Spectrometry: Target Gas Effects upon Scattering and Charge Exchange

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Abstract: Collision-induced dissociation of polyatomic ions was studied with respect to the effects of ion and target mass and target ionization potential. Ionized argon, methane, and benzaldehyde were the projectiles, and a total of 24 target gases was examined. The relative importance of ion removal by scattering out of the collection angle of the detector, as opposed to removal by neutralization, was determined. Depending upon the target chosen, up to 40% of the initial ion beam could be neutralized and detected as unscattered fast neutrals. The cross section for neutralization showed an excellent inverse linear correlation to the ionization energy of the target. The loss of ion beam by scattering showed an approximate correlation with the mass of the target. The optimum conditions for collision-induced dissociation and charge exchange were investigated. Helium was found to be more effective than N_2 as a target for the dissociations of $CH_4{}^{+\cdot}$, $CH_5{}^+$, and $C_6H_5CHO^{+\cdot}$. In particular cases, up to 8% of the initial ion current could be collected as fragment ions.

Introduction

The effect of the target gas in high energy (keV) ion/molecule reactions of positive ions is studied as it pertains to the efficiency of collision-induced dissociation. This study is prompted by the growing use of collision-induced dissociation: in particular, its role in ion structural studies[1-13] and in the technique of mixture analysis known as MIKES (mass-analyzed ion kinetic energy spectrometry) or ms/ms (mass spectrometry/mass spectrometry).[14-16] The high-energy collision phenomena encountered here are also of interest for a number of other reasons. First, electron transfer leads to fast mass-selected molecular beams which are of use in pumped lasers and in fusion devices,[17] second, electronic

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excitation forms the basis for a translational energy spectroscopy which is analogous to optical excitation spectroscopy but free of the optical selection rules,[18] and third, a quantum mechanical description of the collision event in terms of a transient (order of 10^{-14} s) molecule consisting of both collision partners has been developed.[19] This subject also impinges upon interstellar chemistry.

The major ion/molecule reactions that occur in the kiloelectronvolt range for a positive ion (m_1^+) are listed in eq 1–4.

$$m_1^+ + N \rightarrow m_1^{+*} + N \rightarrow m_2^+ + m_3 + N \quad (1)$$

$$m_1^+ + N \rightarrow m_1^{2+} + N + e^- \quad (2)$$

$$m_1^+ + N \rightarrow m_1 + N^+ \quad (3)$$

$$m_1^+ + N \rightarrow m_1^+ \text{ (scattered)} + N \quad (4)$$

Equation 1 depicts the collisional excitation of an ion followed by the dissociation of the excited species. This reaction has been referred to as collisional activation (CA) and collision-induced dissociation (CID). The term collision-induced dissociation will be used here exclusively to describe the complete reaction in eq 1 with collisional activation being reserved to describe the first step. Preliminary work on determining the effect of the target gas on the excitation processes in eq 1 is presented elsewhere[20] with decreased energy deposition being observed with increased target mass in the laboratory frame of reference. The work reported here concentrates on the effects of target gas on charge exchange and scattering and does not usually extend to the examination of branching ratios for individual dissociation channels or to differential cross sections with respect to angle.

Charge stripping (eq 2) has a relatively small cross section in the energy range of interest, but its products have distinctive energy-to-charge ratios and some work has been done in using this reaction for ion structural characterization.[21] Charge exchange (eq 3) has been studied extensively at both low (eV range) and higher energy (keV range) for atomic, diatomic, and polyatomic species.[22] Considerable attention has gone to the use of this reaction for preparing ions with known internal energies.[23] Here we are concerned with target effects on the cross section for charge exchange of monoatomic and polyatomic systems at high kinetic energies, and the consequences this has for the efficiency of the CID process. Equation 4 refers to a process in which an ion is scattered beyond the acceptance angle of the instrument. The fast scattered product (m_1^+) is shown unchanged, but the electrical charge and the structural integrity of the scattered species are not determined in these experiments.

Kim and McLafferty[24] in a study on collision-induced dissociation observed that the efficiency of the process was related to the ionization potential (IP) of the target gas. For the reaction $CH_4^{+\cdot} \rightarrow C^{+\cdot}$, the abundance of the product ion was directly correlated with the IP of the target, and it was suggested that this might be due to changes in enthalpy for charge exchange associated with variation in the ionization potential of the target. The higher the IP, the less energetically feasible charge exchange, and hence the more favored the competitive process of dissociation. It was also suggested that differences in scattering cross sections were relatively unimportant since Ar and D_2 showed the same efficiency for CID. In earlier work Melton[25] showed that neutralization is an important ion removal process, and it is also known that different targets can selectively remove particular ions from an ion beam undergoing collision.[26]

The present study employed both a conventional geometry double-focusing mass spectrometer (Hitachi RMH-2)[27] and a reversed geometry mass-analyzed ion kinetic energy (MIKE) spectrometer.[28] The RMH-2 was modified to allow ion deflection and detection of high energy neutral particles generated in the ion/target collision. In spite of a variety of experimental options available, it was not possible to study simultaneously all the variables of interest. Consequently two types of experiments were performed separately, those in which mass analysis of the ion was done and dissociation channels followed as a function of pressure and those in which the relative amounts of neutralization and scattering were determined.

Experimental Section

Measurements were made on the Hitachi RMH-2 and on the MIKE spectrometer by using ion translational energies of 7.5 and 7.0 keV and instrumental conditions detailed elsewhere.[27,28] When the RMH-2 was used without mass analysis, product ions and neutrals were detected at an intermediate electron multiplier. For this detector, the total acceptance angle in both the plane of analysis (*xy*) and the orthogonal (*xz*) plane is 0.66°. Collision-induced dissociation products were recorded at the final detector after the ions had traversed the magnetic sector. This detector has a total acceptance angle of 0.05 and 0.26° in the *xy* and *xz* planes, respectively. The corresponding MIKES total acceptance angles are 0.05 and 0.37°, respectively. The collision cells used have nominal lengths of 25 and 22 mm for the RMH-2 and the MIKES, respectively.

Target pressures were measured in both instruments with an MKS Baratron capacitance manometer. For each target gas studied, two independent determinations of ion and neutral current were made and they typically agreed to better than 0.5%. Reproducibility checks were also made after a delay of several days, and agreement was better than 1%.

Collision gases that were obtained in liquid form were subjected to several freeze–pump–thaw cycles to remove trapped gases. The remaining gases were commercially supplied and used without further purification. For measurement of fast neutral products, ions were electrostatically removed from the beam. This was accomplished by applying potentials to two parallel stainless-steel plates located between the collision chamber and the detector in the second field free region of the RMH-2. Ion current was attenuated below the detection limit of the β multiplier by applying a potential of 700 V. The β multiplier was a 16-stage R474 Hamamatsu electron multiplier and the post magnet detector was a Galileo spiraltron, Model 4830. When the RMH-2 mass spectrometer was used to determine relative amounts of both scattering and neutralization of a precursor ion, mass analysis was not possible. Therefore, all ions formed and extracted from the EI source contributed to the experimental results. This complication and its consequences are discussed in later sections.

Three systems were studied for determining the relative effects of the target gas on scattering and charge exchange. Methane was chosen to parallel the work of Kim and McLafferty.[24] The normal 70-eV EI mass spectrum of CH_4 taken on the RMH-2 shows approximately equal intensities of $CH_4^{+\cdot}$ and CH_3^+, with these two ions accounting for more than 90% of the total ion current. The MIKES, in the chemical ionization mode, was used to generate and mass select CH_5^+ for comparison with the other methane ions. Argon was studied so as to follow the effects of removing the dissociation channel. This latter system was studied in less detail than that of methane because our primary interest lies in the CID process. Benzaldehyde was chosen as a typical organic molecule; its EI mass spectrum shows 106^+, 105^+, 77^+, and 51^+ as major ions.

Results and Discussion

This section is divided into four parts. The first contains data on scattering without mass analysis of either reactant or product ion. The corresponding results for neutralization are given in the

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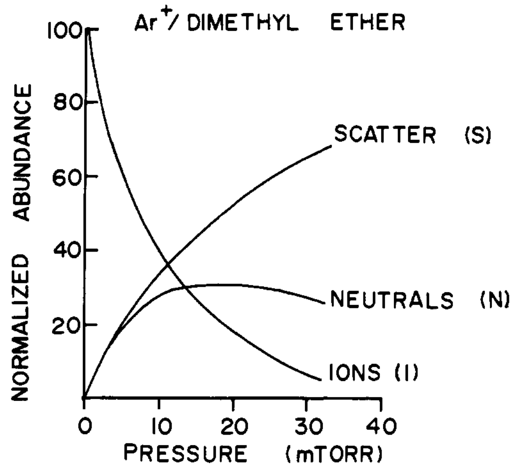

Figure 1. Reaction products for kilovolt energy argon ions colliding with dimethyl ether target gas as a function of pressure. Intensity is normalized at each target pressure.

Table I. Some Approximate Cross Sections[a]

projectile/target	σ_S	σ_N	σ_{CID}
$Ar^{+}\cdot/N_2$	2.3×10^{-16}	3.0×10^{-16}	
$Ar^{+}\cdot/He$	9.2×10^{-17}	8.8×10^{-19}	
ionized CH_4/N_2	2.3×10^{-16}	6.3×10^{-17}	5.1×10^{-17}
ionized CH_4/He	9.0×10^{-17}	1.7×10^{-17}	3.1×10^{-17}
ionized benzaldehyde/N_2	3.8×10^{-16}	1.0×10^{-16}	
ionized benzaldehyde/He	1.5×10^{-16}	6.3×10^{-17}	

[a] All values are in units of cm^2 and are calculated from data taken at a target pressure of 15 mtorr. The experiment was not designed to provide absolute cross sections and these values must be regarded as order of magnitude quantities.

second. Scattering, as discussed here, refers to the deflection of the precursor ion beam out of the collection angle of the detector. Information concerning the structural integrity, internal energy, and charge of the scattered species was not available from these experiments. The relative amount of scattering is determined by measuring the decrease in the total current at the β (intermediate) detector as a function of target pressure. As shown in the second section, a fraction of this total current is due to fast neutrals. In all of the experiments reported here, the assumption is made that the multiplier response is the same for ions and neutrals.[29] In the third and fourth sections the competition between scattering and charge exchange (neutralization) is followed for ions generated from methane and benzaldehyde. Some experiments described in these sections employed mass analysis so that particular collision-induced dissociations could also be followed, but this precluded simultaneous determination of the fate of the ions which undergo charge exchange. Most results, both with and without product mass analysis, refer to the RMH-2 mass spectrometer, but the CH_5^+ data were taken by using the reversed sector MIKES instrument.

(1) Scattering. The results for a typical collision experiment are shown in Figure 1 where $Ar^{+}\cdot$ is the projectile and dimethyl ether is the target. Shown in the figure are the normalized magnitudes of product ion current (*I*), neutral current (*N*), and the amount of total current lost to scattering (*S*). Most of the discussion in this paper will be based upon the quantities represented as *S*, *N*, and *I*. Values of cross sections are not the form in which the data of this paper are considered. They are readily derived and some representative data are provided in Table I. This gives cross sections for collision-induced dissociation (σ_{CID}) and for scatter (σ_S) and neutralization (σ_N) by helium and nitrogen.

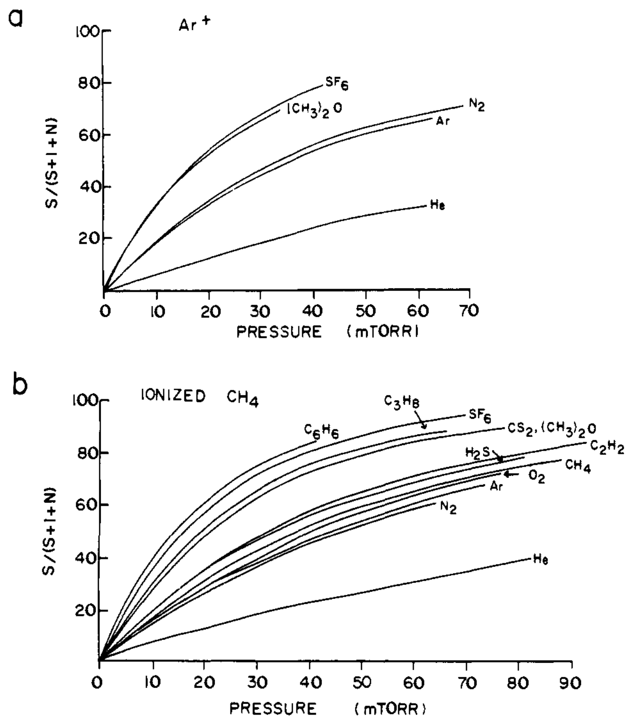

Figure 2. Scattering of (a) argon ions and (b) ionized methane and neutrals out of acceptance cone (see text) for various targets.

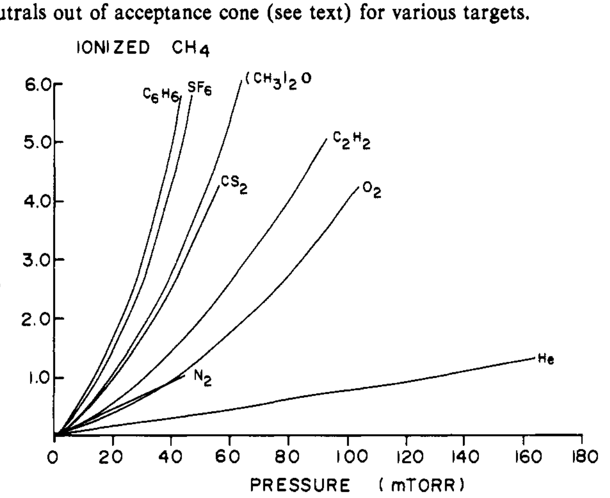

Figure 3. Ratio of species scattered out of acceptance cone to those scattered as ions (*I*) and neutrals (*N*) into the cone vs. target pressure. Projectiles are ionized methane.

The effect on the relative amount of scattering, caused by varying the collision gas, is seen in Figure 2 for the Ar and for the CH_4 systems. As expected, the amount of scattering increases with collision gas pressure. Another general trend is observed in this figure: the relative amount of scattering increases with an increase in target mass and/or size. A strict mass dependence is not observed. For example, for ionized methane, H_2S (34 amu) at 20 mtorr causes ~9% more scattering than N_2 (28 amu) while benzene, C_6H_6 (78 amu), at the same pressure causes 3% more scattering than SF_6 (146 amu).

The ionized methane data can be represented somewhat differently in order to focus on target effects on scattering. The ratio $S/(N + I)$ represents products scattered out of the collection cone vs. those scattered as both neutrals and ions within this cone. Figure 3 shows this ratio; larger and/or more massive targets favor those collisions which scatter the fast products beyond the 0.66° detector acceptance angle. It is noteworthy that benzene and dimethyl ether are more effective scatterers than their heavier but smaller counterparts, SF_6 and CS_2, respectively. Whatever

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(29) This has been shown to be valid for simple species striking the first dynode with the same kinetic energy.[30] In our experiments the ions receive additional kinetic energies of 1.5 keV over the neutrals due to the multiplier bias voltage. An exact correction for this kinetic energy effect cannot be made, but available data[31] on secondary ion emission suggests that it increases the measured ion signal by approximately 10%.

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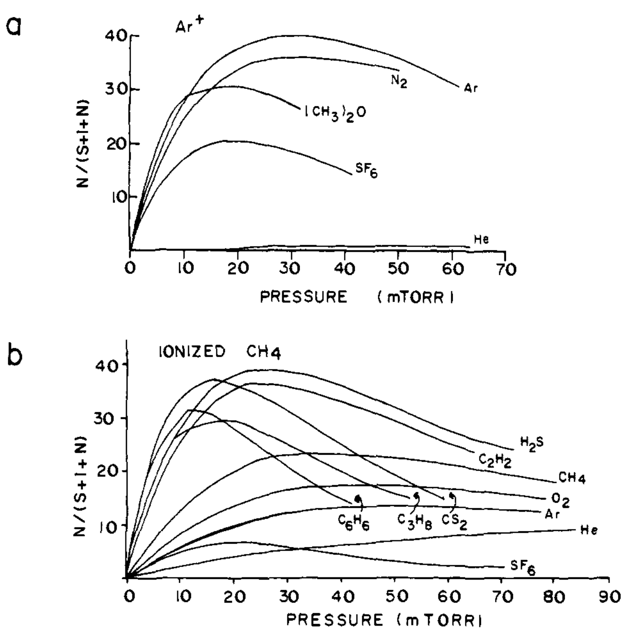

Figure 4. Ion current lost to neutralization (N) relative to all processes ($S + I + N$) for (a) Ar^+ and (b) ionized methane for various targets as a function of pressure.

the precise combination of properties that controls scattering, a qualitative decision can be made regarding which target gas to use in collisional activation. In terms of reducing the loss of ion current by scattering, it is best to use a target of low mass and small size such as helium.

(2) Charge Exchange. Electron transfer from a neutral target to a high-energy ion has been extensively studied for atomic and diatomic systems,[32,33,34] and it has been reported for some polyatomic systems that the cross section for charge exchange is larger than that for collision-induced dissociations.[13,35] (Compare σ_N and σ_{CID} in Table I.) This section deals with the effect of target gas on the propensity for charge exchange relative to other processes.

High-energy neutrals formed by charge exchange were separated from ions by applying a potential to the deflector plates, which effectively removed any contribution from an ion current to the measured signal. It is possible to produce currents due to neutrals which are up to 40% of the initial ion current. Moreover, the neutral current reported here is that due to unscattered neutral species and represents a lower limit for neutralization because the charge on the scattered particles is unknown. An example of the relative amounts of neutral current, ion current, and loss of current due to scattering is shown in Figure 1.

The relative abundances of the neutrals detected as a function of collision gas pressure are represented as $N/(S + I + N)$ in Figure 4 for the Ar and CH_4 systems. This representation of the neutralization data is analogous to the use of $S/(S + I + N)$ in Figure 2 to represent the scattering data. If the normalization excludes the scattered products, similar trends are observed (Figure 5 vs. Figure 4), but the features are more pronounced. Thus, Figure 5 shows neutralization as a fraction of the total signal detected at the β multiplier. The degree of neutralization is strongly dependent upon the nature of the target gas, with the ionization potential of the target apparently exerting the dominant influence. This is shown most dramatically by the data for helium in these plots (Figures 4 and 5).

When the ratio of neutrals to neutrals plus unscattered ions is plotted in Figure 5, the effects of scattering out of the detector cone are removed. In addition, the ratio is approximately independent of contributions from collision-induced dissociation because product ions are generated in approximately equal numbers of precursor ions (although their angular distribution may not

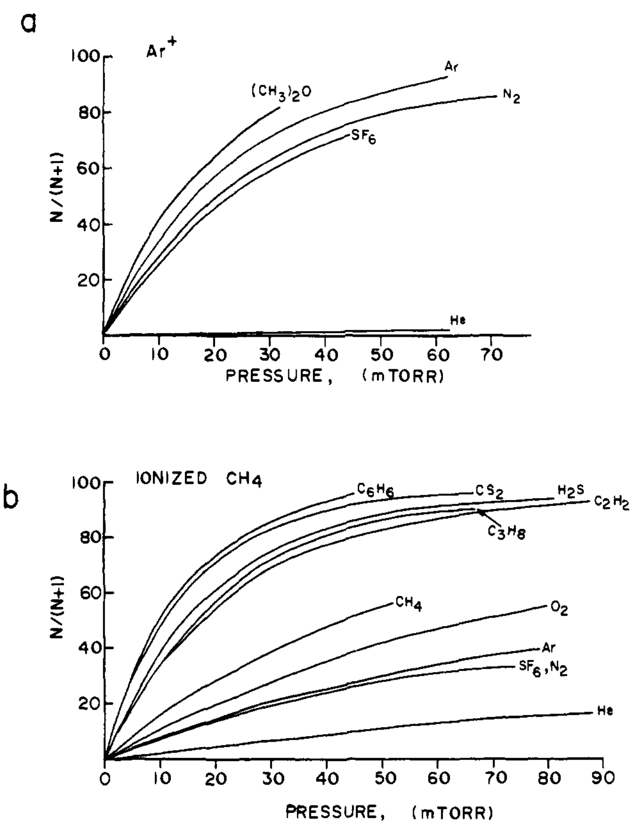

Figure 5. Neutralization (N) as a fraction of products collectable as ions (I) and neutrals (N). Data are for various target gases and pressures and for (a) Ar^+ and (b) ionized methane.

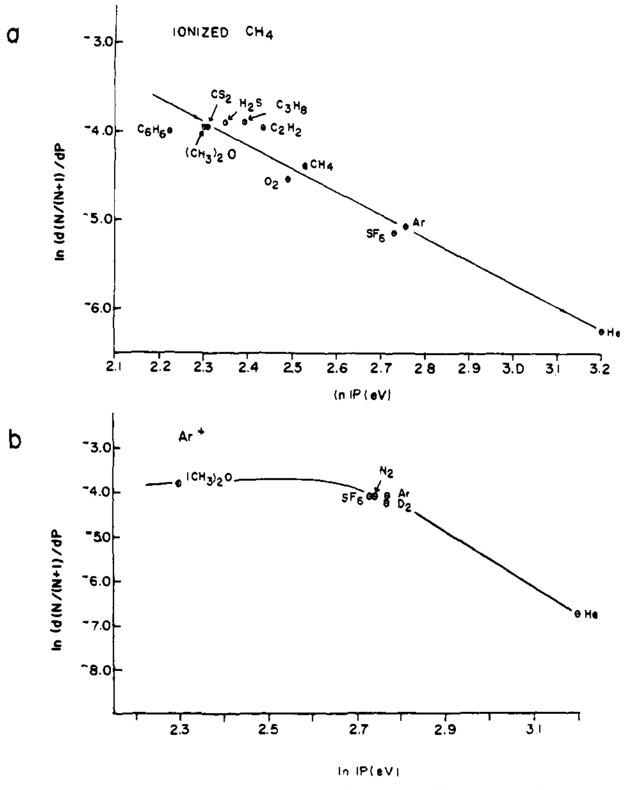

Figure 6. Logarithm of the slope, $d[N/(N + I)]/dP$, from Figure 5 vs. logarithm of target IP for (a) ionized methane and (b) Ar^+. The solid line in (a) is from a linear regression analysis which gave a correlation coefficient of -0.97.

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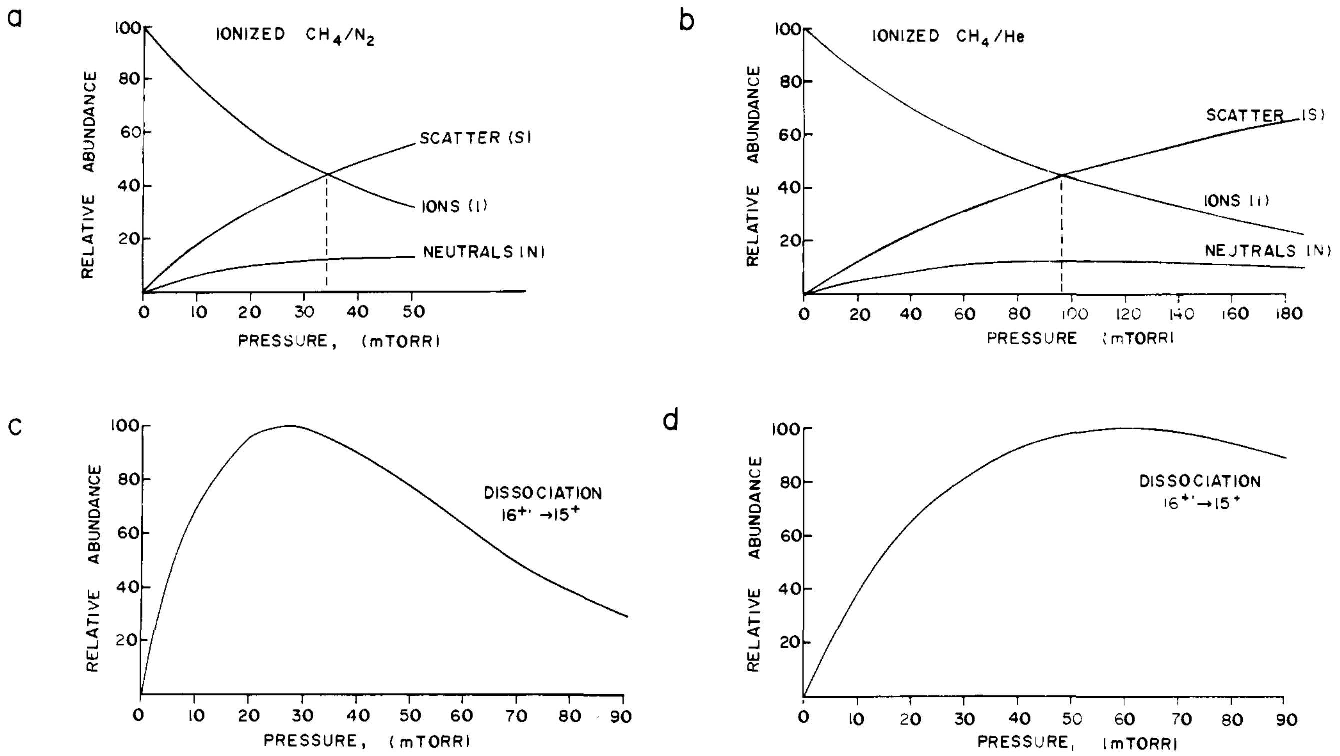

Figure 7. Reaction products for ionized methane onto (a) nitrogen target and (b) helium target vs. target gas pressure (normalized at each pressure) and relative abundance of hydrogen atom loss from $CH_4^{+}\cdot$ as a function of (c) nitrogen and (d) helium target gas pressure, normalized to maximum absolute signal.

match that of the products of charge exchange). The rate of change of the quantity $N/(N + I)$ with pressure is therefore a measure of the cross section for neutralization.[36] The linearity of the data in Figure 5 is good only up to about 40 mtorr for most gases; therefore, the slopes of these lines were determined for pressures lower than 40 mtorr. A graph of the logarithm of the slopes (cross sections) from Figure 5 vs. the logarithm of the ionization potentials of the target gases is given in Figure 6.

Work on atomic and diatomic systems[32,33,34] has shown that the cross section for neutralization is dependent in part on the energy defect for the transition, that is on the absolute value of the difference in ionization potentials (IP) for the projectile and the target. This factor may be responsible for the low cross section for He charge exchange with argon (Figure 6), but dimethyl ether is equally far removed from argon in IP and it shows a high cross section for charge exchange. The large numbers of excited states of polyatomic species allow a quasi-resonant collision and therefore account for the high cross section.[22,34]

The ionized methane results show a neutralization cross section which is approximately linearly related to target ionization potential. This may be a consequence of the presence of both $CH_4^{+}\cdot$ and CH_3^+ ions in the beam which makes a detailed interpretation impossible, but the results still allow an assessment of which target gas to use for doing collision-induced dissociation experiments. From Figure 5, it is obvious that to minimize the loss of ion current due to charge exchange, it is necessary to choose a target gas with a large ionization potential. Therefore, of the gases studied, helium provides the least amount of neutralization. This is fortunate because, as seen in the previous section, helium also produced the least amount of scattering for the target gases studied.

(3) Scattering vs. Charge Exchange in Methane. This section compares the relative amounts of scattering and charge exchange, and the effect these two processes have on the overall efficiency of collision-induced dissociation. Figure 7, parts a and b, shows the relative contributions of scattering and charge exchange to the removal of usable ion current in the CH_4 system with N_2 and He as the target gases. The target pressure at which the particular collision-induced dissociation, $CH_4^{+}\cdot \rightarrow CH_3^+ + H\cdot$, is maximized is approximately 30 mtorr for nitrogen and about twice as high for helium (Figure 7c,d). However, in both cases the losses to neutralization are similar (ca. 10%), the higher IP of helium being offset by the higher pressure. In addition, losses to scattering are also similar (30–40%), the lower mass of helium being offset by the higher pressure required to maximize collision-induced dissociation. These results do not provide any information on the extent to which the ion current (I in Figure 7) contains fragments due to collision-induced dissociation. As shown later, helium is more efficient than N_2 in producing these fragments.

Causing less scattering and less neutralization than other target gases studied, helium would be expected to be the most efficient collision gas at a given pressure for causing collision-induced dissociation. In spite of a slightly smaller cross section for CID (Table I) this was observed to be the case. This was also the case in an alternative experiment in which mass-analyzed CH_5^+ ions were dissociated by using target gases with different ionization potentials. For a specific reaction, loss of H_2, the fragment ion abundance was monitored as a function of target gas and target gas pressure on the MIKE spectrometer. The results agreed with those reported previously,[12,25,35] in that there was an increase in the abundance of fragment ions with an increase in the IP of the target gas. This correlation was observed whether the observations were made at a constant collision gas pressure or, as done by McLafferty, at pressures giving a constant reduction in the precursor ion abundance.[24] Figure 8 shows for a number of target gases the relative abundance of CH_3^+ from CH_5^+ at a constant collision gas pressure of 0.2 mtorr expressed relative to the metastable ion contribution. The relative efficiencies vary slightly, depending on whether they are plotted at constant pressure or constant reduction in precursor abundance. Other reactions, i.e., loss of H, H_3, H_4, and H_5 to give $CH_4^{+}\cdot$, $CH_2^{+}\cdot$, CH^+, and $C^{+}\cdot$, respectively, give analogous results.

From the observations on scattering and neutralization, it was also expected that higher gas pressures could be used with helium as the target gas and that this would lead to more fragmentation. This was observed in the target gas studies on both the MIKES and the RMH-2. The CID efficiency, that is the amount of main beam ion converted into fragment ions, measured on the RMH-2

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[36] Strictly the slope of $N/(N + I + S)$ with pressure; these quantities can be shown to be equivalent at low pressures where S is negligible.

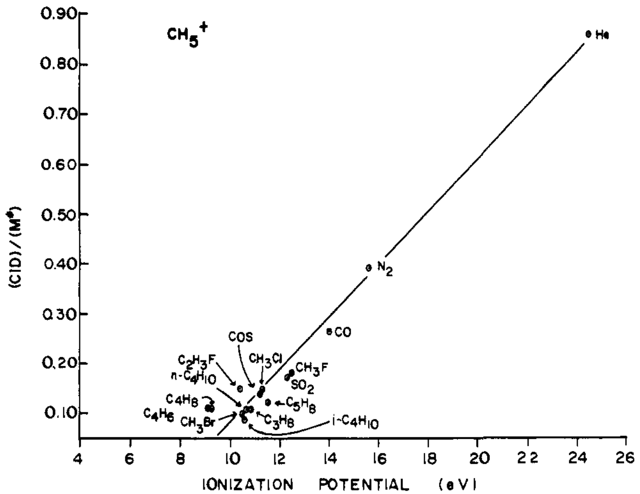

Figure 8. H_2 loss from $CH_5^{+}\cdot$; ratio of CH_3^+ produced by collision with target relative to CH_3^+ produced by unimolecular dissociation plotted against target gas IP.

for $CH_4^{+}\cdot$ was 8%.[37] This number was derived from the peak areas of the fragment ions at the optimum target pressure of nitrogen, ca. 22 mtorr. (Helium was slightly more efficient at its optimum pressure of 42 mtorr.) It is known that comparing peak heights rather than peak areas gives a lower limit to the true CID efficiency and this accounts for the fact that the number in terms of heights is 0.7% (5% given in ref 38, Figure 6, using a molecular beam target).

(4) Scattering vs. Charge Exchange in Benzaldehyde. In these experiments benzaldehyde was investigated as a typical polyatomic organic molecule. The effect of scattering and neutralization on three major collision-induced dissociations was studied. Two commonly used target gases, He and N_2, were compared.

The results (Figure 9) are very similar to those obtained for dissociation of ionized methane by the same targets. The optimum pressure for dissociation, using nitrogen, is approximately 12 mtorr. At this pressure 34% of the current is lost to scattering and 8% to neutralization. At the same pressure, the corresponding losses for helium target are only 13% and 6%, but this does not correspond to the optimum CID pressure for He. At this optimum (21 mtorr) the scatter and neutralization losses are similar to those for nitrogen. The greater efficiency of He in collision-induced dissociation at its optimum pressure must therefore be found in the fact that a larger fraction of the ion current (I) consists of fragment ions.

Conclusions

Collision-induced dissociation (CID) has been used extensively in mass spectrometry for structural determinations. The early work on this technique dealt with the fundamentals of the excitation mechanism, while later reports have been concerned mostly with applications of the method. Reported here are the results of a study on the effect of the target gas as it pertains to the efficiency of the kilovolt energy CID process. In particular, the relative amounts of scattering and charge exchange have been determined for a variety of target gases.

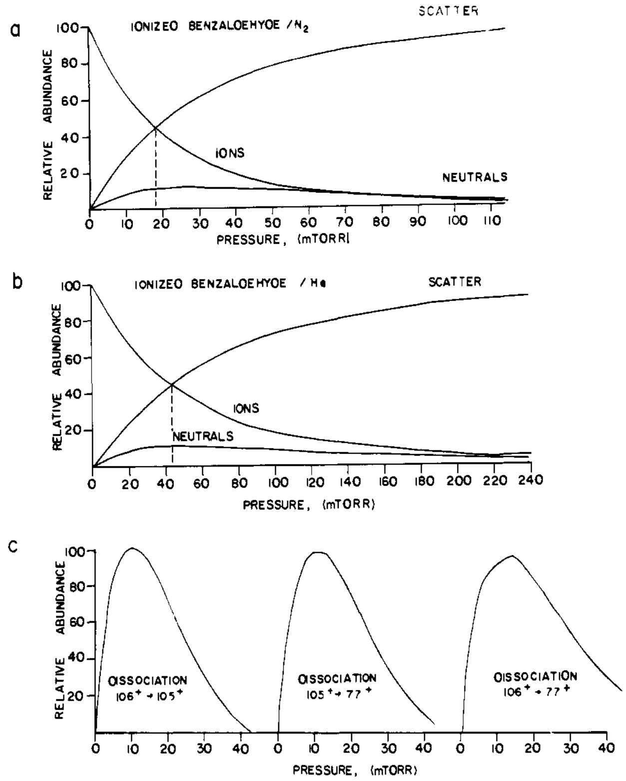

Figure 9. Reaction products for ionized benzaldehyde onto (a) nitrogen target and (b) helium target; target gas pressure and relative abundance of major CID processes as a function of nitrogen target gas pressure (c).

The CID process for high-energy collisions is relatively inefficient, often producing only a few percent of total fragment ion abundance relative to loss of precursor ion abundance. The results given here indicate that the reasons for this inefficiency are the large abundance of scattering and charge exchange relative to dissociation. The degree of scattering of the ion beam shows an approximate correlation with the mass of the target. No information has been obtained concerning the nature (charge or structural integrity) of the scattered species. Charge exchange (neutralization) shows an inverse correlation with the ionization potential of the target. These two factors result in helium being the most efficient of the target gases studied. This is true both for $CH_4^{+}\cdot$ and for the more typical organic ions derived from benzaldehyde.

These results support the work of Kim and McLafferty[24] in demonstrating that of the gases studied, helium is the most efficient target for collision-induced dissociation. This work has shown that this greater efficiency arises because both scattering and charge exchange are attenuated. It is noteworthy that helium also has a high efficiency for excitation in the course of scattering a projectile ion through a given *laboratory* angle.[39] Thus the relative efficiency of this target in CID is apparently due to a combination of a high intrinsic efficiency for energy deposition as well as its inefficiency in neutralization and scattering.

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[37] These data for efficiency can also be obtained by comparing the cross section for CID (σ_{CID}) with the sum of the neutralization, scatter, and CID cross sections ($\sigma_S + \sigma_N + \sigma_{CID}$) given in Table I.

[38] F. W. McLafferty, P. Todd, D. McGilvery, and M. Baldwin, *J. Am. Chem. Soc.*, **102**, 3360 (1980).

[39] P. H. Hemberger, J. A. Laramée, A. R. Hubik, and R. G. Cooks, submitted for publication.