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LOW-ENERGY COLLISIONAL ACTIVATION OF POLYATOMIC IONS WITH DIFFERENT TARGET GASES *

KEVIN L. SCHEY, HILKKA I. KENTTÄMAA **, VICKI H. WYSOCKI ***
and R. GRAHAM COOKS **

Department of Chemistry, Purdue University, West Lafayette, IN 47907 (U.S.A.)

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ABSTRACT

The dependence of collision-activated dissociation spectra on the nature of the target gas was examined by activating the molecular ions of tetraethylsilane, tungsten hexacarbonyl, furan, and 2,2′-bithiophene, as well as the chromium pentacarbonyl radical cation, by 5–30 eV collisions with various mono- and polyatomic target gases. Average internal energies were estimated for the activated ions from the collisional activation spectra by utilizing a knowledge of the sequence and energetics of dissociation. For all of the ions studied, the data indicate that the amount of internal energy deposited increases as a function of the kinetic energy of the molecular ion. For some of these systems, the internal energy of the parent ions can also be increased by using a heavier target. However, for ionized furan, ionized tetraethylsilane, and the chromium pentacarbonyl radical cation, smaller internal energy deposition is observed at a given center-of-mass energy (E_{cm}) when heavier targets are used. This unexpected result appears to be due to significant ion loss caused by scattering of the fragments beyond the acceptance cone of the instrument when the mass of the target (M_t) is large compared to that of the parent ion (M_p). Another result is that the use of polyatomic targets leads to less extensive fragmentation of $[(C_2H_5)_4Si]^{+\cdot}$ and ionized furan than does the use of monatomic targets of similar mass. The relatively large number of internal degrees of freedom in the polyatomic targets appears to favor distribution of a significant amount of the excitation energy into the internal modes of the target. Conversion of translational energy to vibrational energy is observed to be constant (15 ± 5%) over the center-of-mass kinetic energy range 4–16 eV for nearly all targets. Practical consequences of these target effects are discussed.

INTRODUCTION

Collision-activated dissociation (CAD) of gas-phase ions is controlled by several experimental parameters, such as the collision energy and the nature

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* Dedicated to Professor Harry J. Svec.

** Authors to whom correspondence should be addressed.

*** Present address: Naval Research Laboratory, Code 6112/Chemistry Division, Washington, DC 20375-5000, U.S.A.

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and pressure of the target gas. These effects have been the subject of numerous studies [1–19]. It is generally accepted that helium is the target of choice for high energy (keV) collisions because its use minimizes the major processes competing with collision-activated dissociation of the projectile ion, i.e., neutralization and scattering beyond the acceptance angle of the mass spectrometer [1–3]. Nonetheless, the low efficiency of internal energy deposition in the small angle collisions with helium makes other targets such as nitrogen of comparable value in keV energy experiments [3]. In the low energy (eV) regime, the nature of the target can be expected to play a different role from that found for high-energy collisions since (i) a different excitation mechanism (vibrational excitation) is in operation, and (ii) a much larger fraction of the maximum available energy, or center-of-mass kinetic energy, is converted to internal energy of the projectile ion ($E_{cm} = E_{lab}M_t/(M_t + M_p)$) [20]. In low-energy collisional activation, large scattering angles are common and scattering losses are often minimized through the use of a focussing collision chamber, particularly an r.f.-only quadrupole [19].

Some recent results obtained for low-energy collisional activation of polyatomic ions by using He, H_2, N_2, Ar, and Kr as the collision targets provide support for the simple expectation that heavier targets are preferred over light targets because they provide a larger E_{cm} [12–14]. For example, collisions with He were found to deposit only very small amounts of energy [12–14] in comparision with collisions with N_2, Ar, or Kr. Furthermore, there is a limited amount of data which suggests that collisions with polyatomic targets result in a smaller energy deposition than is obtained for monoatomic targets of the same mass [7,8].

In most of the studies published to date, target effects were examined by assuming a correlation between the relative abundances of two fragment ions and the average internal energy of the activated parent ion. This approach is based on several assumptions, principally that the relative abundances of the fragment ions vary monotonically with internal energy as depicted in the breakdown curves obtained by independent methods. For example, the abundance ratio of the fragment ions of masses 29 and 31 has been used to follow the internal energy of activated methanol molecular ions as a function of collision energy and/or scattering angle [2]. Because of the shortcomings of this method, two more refined approaches are presented here for studies of target effects in collision-activated dissociation. The first, an extension of the simple method described above, is to determine the center-of-mass energies at which two fragment ions are equal in abundance (a "cross-point" in the energy-resolved tandem mass spectrometry (MS/MS) spectra obtained by varying the kinetic energy of the parent ion prior to collision). This method allows one to set the experimental conditions so as to reproducibly access a particular but unknown, internal energy which is defined by the unit ion abundance ratio. Limitations are imposed on this approach by the fact that for widely different internal energy distributions, the dependence of the relative abundances of the fragment ions on the average internal energy is not easy to predict. However, since the same fragmenting ion is being studied in all cases under generally similar conditions, it is unreasonable to expect grossly different shapes in the $P(E)$ distributions [21].

A more refined method of estimating the average energy deposited by different targets was also employed. In these experiments the internal energy distribution present in activated parent ions after collisions with different targets was estimated. This was done by using carefully selected model ions which fragment by a series of similar reactions (e.g., reaction 1). The fragment ion abundances obtained for an activated parent ion allow calculation of approximate internal energy distributions and average internal energies for those parent ions which produce observable fragments [21].

$$[\mathrm{Cr(CO)_5}]^{+\cdot} \rightarrow [\mathrm{Cr(CO)_4}]^{+\cdot} \rightarrow [\mathrm{Cr(CO)_3}]^{+\cdot} \rightarrow [\mathrm{Cr(CO)_2}]^{+\cdot} \rightarrow [\mathrm{Cr(CO)}]^{+\cdot} \rightarrow [\mathrm{Cr}]^{+\cdot} \qquad (1)$$

EXPERIMENTAL

The experiments were carried out with a Finnigan triple quadrupole mass spectrometer [22]. The instrument was set to perform daughter scans, i.e., the first mass analyzer was set at the mass value of the parent ion of interest, and the second mass analyzer was scanned to record the fragments. Ionization was effected by 70-eV electron impact. Special attention was paid to the adjustment of the pressure of the collision target to make sure that single-collision conditions predominated in the r.f.-only collision quadrupole. A linear increase in fragment ion abundances with pressure (but no changes in relative fragment ion abundances) after metastable contributions were subtracted was taken as the criterion for single-collision conditions [12–14]. A series of experiments was carried out by using ionized tetraethylsilane colliding with two target gases (Ar and Xe) at different pressures to verify that the target effects observed were not dependent on the exact pressure chosen. Collision-activated dissociation spectra were recorded for the molecular ions of tetraethylsilane, tungsten hexacarbonyl, furan, and 2,2′-bithiophene, as well as the chromium pentacarbonyl radical cation (generated by electron ionization from chromium hexacarbonyl). Helium, neon, argon, krypton, xenon, furan, benzene, and thiophene were used as targets in collisional activation of the furan molecular ion. Tetraethylsilane was activated by collisions with neon, argon, xenon, methane, propane, isobutane, n-heptane, sulfur hexafluoride, and carbon tetrachloride. All other ions were activated by collisions with argon and xenon targets. The compounds were obtained commercially and used without purification.

The potential difference between the ion source and the collision quadrupole determines the axial kinetic energy of the parent ion, which to a good approximation is equal to the laboratory collision energy. In the energy-resolved experiments, successive daughter spectra were recorded as the collision energy was increased in ca. 5-eV intervals from about 5 eV up to 30 eV (laboratory frame). Approximate breakdown graphs were constructed based on peak intensities normalized to total fragment ion abundance at each collision energy, unless otherwise specified.

RESULTS

Energy-resolved MS/MS daughter spectra of ionized furan, activated by collisions with four different targets, are presented in Figure 1. The activation energies for formation of the major fragment ions of *m/z* 40, *m/z* 39, and *m/z* 29 are 2.7 eV, 3.2 eV and 4.3 eV, respectively [23]. The relative ion

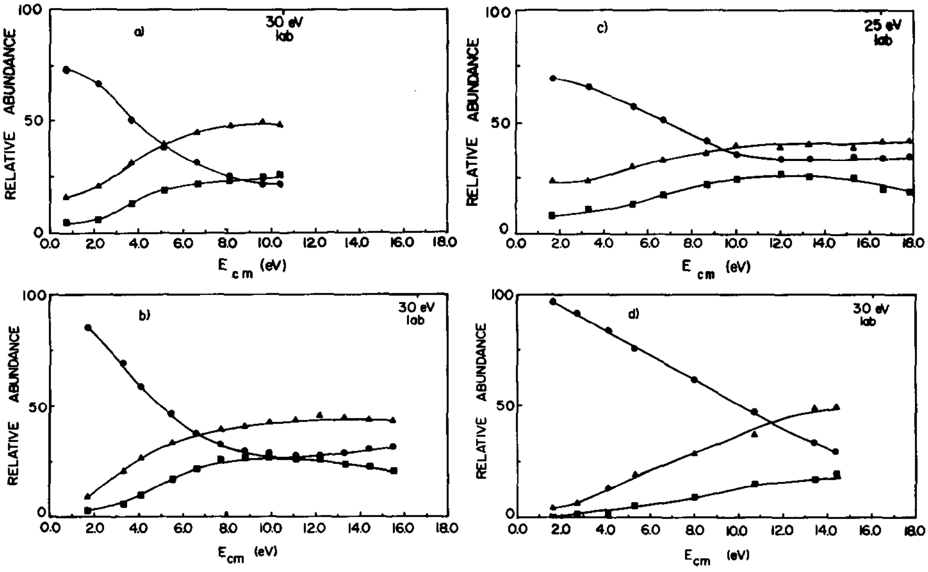


Fig. 1. Energy-resolved MS/MS data (a single collision, 2–30 eV lab energy) obtained for ionized furan by collisional activation with (a) argon, (b) krypton, (c) xenon, and (d) benzene target gas in the triple quadrupole instrument. Relative abundances are normalized to the sum of the abundances of the three fragment ions shown. Data obtained in a single experiment are presented: (●), *m/z* 40; (▲), *m/z* 39; (■), *m/z* 29.

TABLE 1

The cross-points (average of several experiments) obtained for fragments of ionized furan colliding with different target gases (ion kinetic energies were varied between 5 and 30 eV, lab)

Target	Cross-point E_{cm} (eV)		Maximum E_{cm} available (eV)
	$40^+/39^+$	$40^+/29^+$	
He	–	–	0.9
Ne	5.7	–	6.8
Ar	5.1	8.1	11.1
Kr	6.6	10.5	16.6
Xe	9.5	–	19.8
Furan	10.0	–	15.0
Benzene	11.5	–	16.0
Thiophene	12.2	–	16.6

kinetic energies (E_{cm}) where the abundances of two fragment ions are equal, i.e., the cross-points in the energy-resolved data, as well as data for other gases, are presented in Table 1. While the data obtained for He, Ne and Ar targets follow trends expected from a consideration of the center-of-mass energy, collisions with Ar cause more extensive fragmentation at a given E_{cm} than do collisions with the remaining atomic and polyatomic targets which are all heavier than argon. Indeed, the spectrum obtained for ionized furan at $E_{cm} = 6$ eV by using an Ar target is similar to that obtained at $E_{cm} = 18$ eV with Xe [Ar: *m/z* 29(50%), *m/z* 39(100%), *m/z* 40(84%), *m/z* 42(6%); Xe: *m/z* 29(56%), *m/z* 39(100%), *m/z* 40(83%), *m/z* 42(13%)]. It is noteworthy that charge exchange reactions were observed in collisions of ionized furan with polyatomic targets though the products formed were of relatively low abundance (< 5% of the total ion current) at ion kinetic energies greater than 10 eV (lab). The largest amount of charge exchange was observed for the thiophene target which upon < 2 eV (lab) collisions with ionized furan gave 25% of ionized thiophene as estimated from the ion current due to fragment ions.

Energy-resolved MS/MS daughter spectra of ionized 2,2′-bithiophene activated by collisions with Ar and Xe are presented in Figure 2. The E_{cm} value for the cross-point of the major products, *m/z* 134 and *m/z* 121, is the same (within experimental error) for Ar ($E_{cm} = 3.3.$ eV) and Xe ($E_{cm} = 3.1$ eV). This is in striking contrast with the behavior of the furan molecular ion which showed a significant difference between center-of-mass energies of the cross-points obtained for these two targets.

The average internal energies deposited in $[(C_2H_5)_4Si]^{+\cdot}$, $[W(CO)_6]^{+\cdot}$, and $[Cr(CO)_5]^{+\cdot}$ upon low-energy collisions with the aforementioned targets were

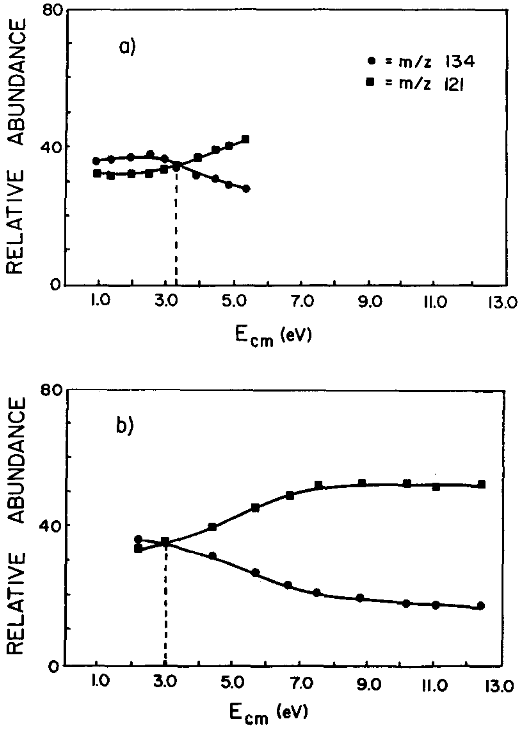


Fig. 2. Energy-resolved MS/MS data obtained for ionized 2,2′-bithiophene by collisional activation with (a) argon and (b) xenon target gas in the triple quadrupole instrument. Only the two most abundant ions are shown. Normalization includes all fragment ions over 1% relative abundance.

calculated according to a method published previously [21] and described briefly here. The major fragmentation pathway of each of the selected molecular ions consists of several consecutive dissociations with known activation energies and similar entropy requirements. It was assumed that all except the most obvious kinetic effects are negligible, viz., all the parent ions which have enough internal energy to dissociate do so, and undergo the most endothermic reaction available to them. To estimate the average internal energy, the distribution of internal energies was estimated and a weighted average calculated. Under single-collision conditions, as used here, the percentage of the parent ions which undergo a collision but do not acquire enough energy to fragment is unknown. Therefore, that part of the energy distribution in the range below the lowest activation energy for fragmentation was not considered. The average internal energies were corrected (i) for metastable ion contributions, and (ii) for the estimated maximum internal energy present in the parent ion prior to collision by subtracting the activation energy for the lowest-energy fragmentation which for $[W(CO)_6]^{+\cdot}$

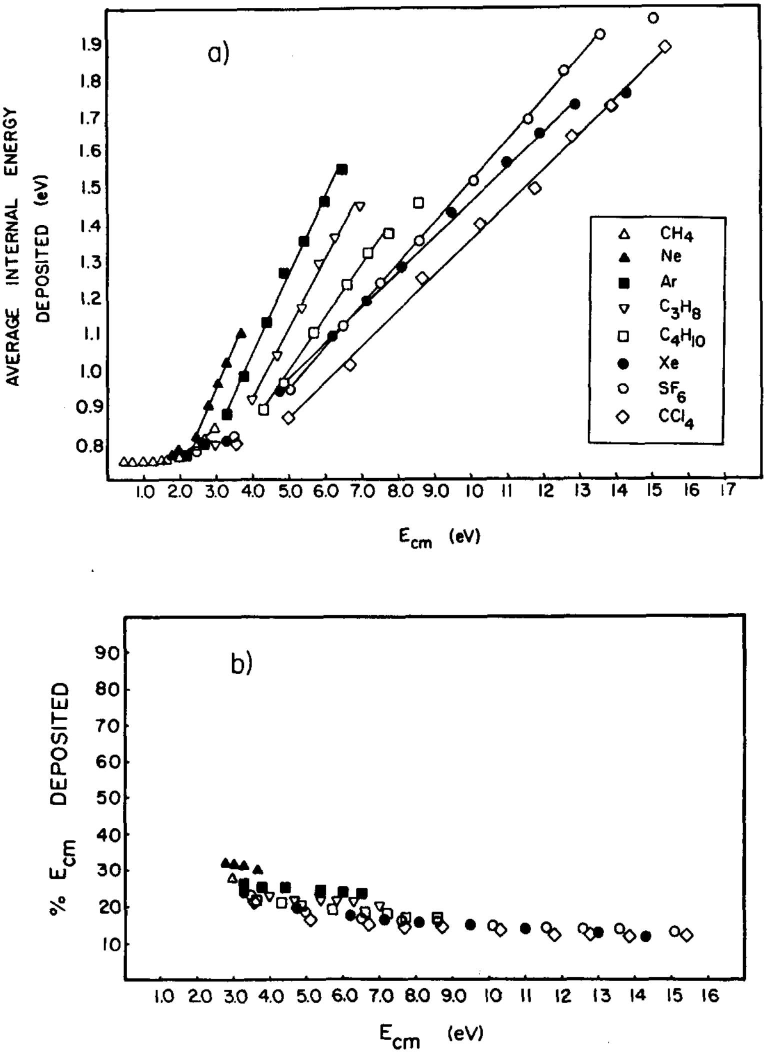


Fig. 3. (a) Average internal energy of collisionally activated $[(C_2H_5)_4Si]^{+\cdot}$ as a function of the relative kinetic energy of the collision $[E_{cm} = E_{lab}\ M_t/(M_t + M_p)]$ for a variety of targets. (b) Efficiency of internal energy deposition into $[(C_2H_5)_4Si]^{+\cdot}$ ions is presented as a function of the relative kinetic energy (E_{cm}) for a variety of targets.

is 1.2 eV [23], for $[(C_2H_5)_4Si]^{+\cdot}$ 0.5 eV [24], and for $[Cr(CO)_5]^{+\cdot}$ 0.2 eV [25].

For all targets studied, the internal energy of fragmenting $[(C_2H_5)_4Si]^{+\cdot}$ ions increases linearly as a function of the ion kinetic energy (Fig. 3a). Preliminary data from another laboratory indicate that this linear increase occurs over the large laboratory energy range of 0–200 eV [26]. Quite unexpectedly, collisions with light atomic targets are seen to result in a larger average energy deposition than collisions with heavier atomic targets, at a given E_{cm}. This is reminiscent of the furan results already discussed. Analogous findings were obtained for $[Cr(CO)_5]^{+\cdot}$. In contrast to $[(C_2H_5)_4Si]^{+\cdot}$, $[Cr(CO)_5]^{+\cdot}$, and ionized furan, collisions of the larger $[W(CO)_6]^{+\cdot}$ ion with Xe were found to result in more internal energy in the parent ion than collisions with Ar at each E_{cm} examined (data not shown). For example, at $E_{cm} = 2.5$ eV, the average energy deposited in collisions with Ar is 1.2 eV, and with Xe 1.3 eV. Another noteworthy result is that the use of polyatomic targets (with the exception of SF_6) in collisional activation of $[(C_2H_5)_4Si]^{+\cdot}$ (Fig. 3a) results in less internal energy at a given E_{cm} than the use of a monatomic target of similar mass (e.g., Ne vs. CH_4, Ar vs. C_3H_8, and Xe vs. CCl_4). This confirms the more tentative observation reported earlier [7,8].

Differing slopes of the linear portions of the internal energy vs. center-of-mass collision energy curves (Fig. 3a) indicate that the sensitivity of the observed fragmentation of $[(C_2H_5)_4Si]^{+\cdot}$ to variation of E_{cm} depends on the target used. For example, a small change in E_{cm} for a Ne target results in a larger change in internal energy deposition than would an equivalent E_{cm} change for the Xe target. The curvature at small E_{cm} values in the data obtained for $[(C_2H_5)_4Si]^{+\cdot}$ (Fig. 3a) is an artifact of the method used to calculate the internal energy deposited. At very low E_{cm} values, only one fragment ion appears in the daughter spectra, and the method fails to give an accurate average energy [21]. Note that the lack of knowledge of the internal energy distributions for energies below the lowest activation energy for fragmentation also causes an error in the absolute values, but not in the

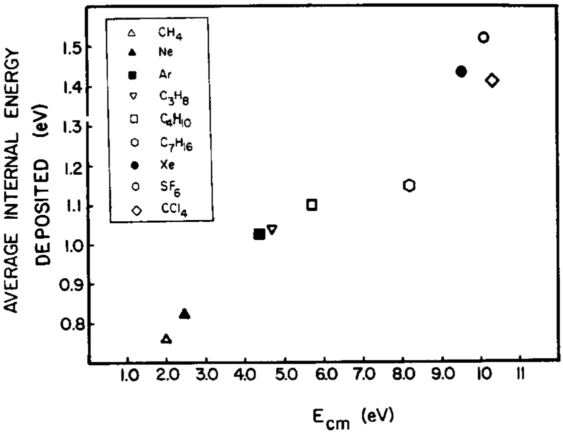


Fig. 4. Average internal energy of $[(C_2H_5)_4Si]^{+\cdot}$ activated by a 20-eV collision with different target gases is presented as a function of E_{cm}.

relative values, of internal energy. This results in non-zero intercepts of the linear parts of the curves in Fig. 3a (the largest deviation from zero is 0.4 eV).

Figure 3b shows the percentage of the maximum available internal energy (E_{cm}) which is deposited into $[(C_2H_5)_4Si]^{+\cdot}$ upon collisions with different targets. The results indicate that the efficiency of kinetic-to-internal energy conversion is nearly independent of the target, for this system. Note also that a decreasing fraction of the maximum available energy is deposited in the ion as the center-of-mass energy increases, although a nearly constant value of $15 \pm 5\%$ occurs over a wide range of E_{cm} values (4–16 eV).

Figure 4 shows the average energy of fragmenting $[(C_2H_5)_4Si]^{+\cdot}$ after collisions with various targets at a fixed laboratory kinetic energy (20 eV). The internal energy deposited increases when E_{cm} is increased by using targets of greater mass. Thus, the amount of energy deposited in $[(C_2H_5)_4Si]^{+\cdot}$ can be increased (i) by using a heavier target at a given laboratory (as opposed to E_{cm}) energy (Fig. 4), or (ii) by increasing the laboratory kinetic energy while using the same target (Fig. 3a).

DISCUSSION

The results presented here indicate that the use of a heavier target in low-energy collisional activation of polyatomic ions may result in less extensive observable fragmentation at a fixed center-of-mass energy. Furthermore, collisions with polyatomic targets seem to deposit a smaller amount of internal energy in the parent ion than collisions with mono- or diatomic targets of approximately the same mass, as evidenced for both ionized furan and $[(C_2H_5)_4Si]^{+\cdot}$. While the results suggest that the use of Ar as a target is preferable to the use of Xe in that the former results in greater internal energies in fragmenting parent ions at a fixed E_{cm}, the same is not true for a fixed laboratory ion kinetic energy (see Fig. 4). Many instruments are limited to a relatively narrow laboratory kinetic energy range, as is the case for the triple quadrupole instrument used in the present study (up to 30 eV). At the maximum laboratory ion kinetic energy, the use of Xe or SF_6 as the collision target provides a larger E_{cm}. This was found to result in a somewhat larger energy deposition in ionized tetraethylsilane, ionized tungsten hexacarbonyl, and chromium pentacarbonyl cation, but not in ionized furan.

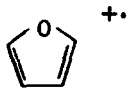
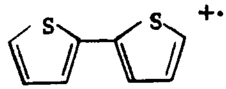
Several factors may contribute to the behavior described above by affecting the observed product distributions of collision-activated dissociation using different targets. (i) The intrinsic efficiency of conversion of translational energy to internal energy may be different for different targets, even when the center-of-mass energy, E_{cm}, is the same. The efficiency may depend on the size of the target, the polarizability of the target, and the nature of the collision complex. (ii) The target atom or molecule may itself become activated during collision. Heavy mono- and polyatomic targets typically have lower ionization energies than do lighter targets, and may become internally excited or ionized. Polyatomic targets may also become vibrationally excited upon collision with a projectile ion. The results for ionized furan provide evidence for ionization of the polyatomic target molecules. Unfortunately, the cross-sections for the charge exchange reactions between the parent ions and the targets studied are not known. Moreover, the observed energy deposition, the relative abundances of the ionized target (results obtained for furan), and the difference between the recombination energy of the parent ion and the ionization potential of the target, did not reveal any trends bearing upon target ionization. (iii) Heavier targets may cause a significant amount of scattering of ions beyond the acceptance angle of the instrument. Note also that kinetic energy released in dissociation may cause scattering of the fragment ions, but this is not expected to be target dependent. The extent to which each of these factors (i–iii) affects the product distributions is difficult to predict and the intrinsic efficiency of kinetic-to-internal energy conversion for each target, perhaps the most interesting parameter, cannot be measured by methods now in hand.

While unequivocal correlation of the amount of energy deposited in a projectile ion and the scattering angle associated with production of a fragment is difficult, the unexpected target effects observed in this study are consistent with scattering of a significant amount of the activated parent ions and their dissociation products out of the acceptance cone of the third quadrupole. It is well-established that low-energy collisions may result in very large scattering angles [7,10]. Crossed-beam studies have demonstrated that scattering efficiencies increase for different targets as follows: Ar < Kr < Xe [1,17]. Moreover, greater energy transfers are known to correlate with larger scattering angles [8,10,20,27,28]. The difference has been found to be more pronounced for Kr target than for Ar, and even more so for polyatomic targets, such as propane [7]. Thus, scattering of product ions is affected by both the relative masses of the collision partners and the endothermicity of the reaction.

The relative masses of the collision partners studied here are presented in Table 2 as the ratio of the mass of the target (M_t) to the mass of the parent ion (M_p). Anomalous target effects were found for those collision partners with a relatively large mass ratio ($M_t/M_p > 1.0$), as for example furan ion colliding with Kr or Xe. The furan ion also has relatively high activation energies for fragmentation. Therefore, the fragmenting ions have necessarily obtained a large amount of internal energy upon collision, and are more

TABLE 2

Mass ratios (M_t/M_p) for collisions of the model ions with different target gases

Ion	M_p	Target	M_t	(M_t/M_p)
$[(C_2H_5)_4Si]^{+\cdot}$	144	CH_4	16	0.11
		Ne	20	0.14
		Ar	40	0.28
		C_3H_8	44	0.31
		C_4H_{10}	58	0.40
		Xe	131	0.91
		SF_6	146	1.01
		CCl_4	154	1.07
$[Cr(CO)_5]^{+\cdot}$	192	Ar	40	0.21
		Xe	131	0.68
$[W(CO)_6]^{+\cdot}$	352	Ar	40	0.11
		Xe	131	0.37
	68	He	4	0.06
		Ne	20	0.29
		Ar	40	0.59
		Furan	68	1.00
		Benzene	68	1.15
		Thiophene	84	1.24
		Kr	84	1.24
		Xe	131	1.93
	166	Ar	40	0.24
		Xe	131	0.79

likely to be scattered through larger angles than the non-fragmenting parent ions which only received small amounts of internal energy. Smaller scattering effects are expected, and were found, for collisions of the relatively massive tungsten hexacarbonyl molecular ion which has small mass ratios, and for ionized tetraethylsilane which has low activation energies for fragmentation.

CONCLUSIONS

The use of heavy mono- or polyatomic targets in low-energy collision-activated dissociation of polyatomic ions may not always be advantageous. For some of the systems studied, the amount of energy present in those collisionally activated parent ions which produce observable fragment ions can be increased by replacing the commonly used Ar target with a heavier target. However, the amount of extra average internal energy gained in this way was found to be small at best (about 0.2 eV for ionized tetraethylsilane at 30 eV, the highest laboratory ion kinetic energy available). Moreover, the use of a target heavier than Ar results in a smaller energy deposition in some ions. This phenomenon was observed for relatively light parent ions colliding with heavier targets, and is probably due to scattering of fragment ions beyond the acceptance angle of the mass spectrometer. However, the use of heavy collision targets may become important when attempting to fragment very large ions which are less likely to scatter. Most of the polyatomic targets studied appear to be less favorable for efficient energy deposition than monoatomic targets of similar mass, probably because of a degrees-of-freedom effect favoring distribution of the excitation energy into the internal modes of the target. However, contributions from charge exchange reactions cannot be excluded.

A further conclusion of this study is that the methods used here for estimating internal energies are likely to have value quite apart from the study of target effects. The simple expediency of setting fragment ion abundance ratios to a fixed value (unity) to define an ion internal energy was evaluated by comparison with a method which utilizes ion abundances and known energetics of fragmentation to estimate the internal energy distributions. The latter method is not applicable to all systems, but it gives more reliable results. Moreover, the ratio method was found to be very sensitive to small differences in ion internal energy. Therefore it provides a useful tool for studies of collision-activated dissociation of polyatomic ions, particularly when inquiring into fundamental aspects of the phenomenon.

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