With Al$_{25}^+$ we made some rough estimates of the binding energies, and there appeared to be a qualitative correlation between the predictions of Shustorovitch's model and the measured activation barriers. With Si$_{25}^+$ any estimates of the binding energies we can make appear so unreliable that a meaningful comparison cannot be made at this time. Another factor that is certainly important in determining the size of activation barriers for dissociative chemisorption on atomic clusters is the electronic structure of the metal. Transition metal clusters with a partially filled d shell chemisorb hydrogen with no significant activation barrier.[6,37] With aluminum and silicon clusters there are substantial activation barriers. Finally, there is the role of geometric structure. Several recent papers have argued that geometric structure or shape are important factors in controlling the reactivity of atomic clusters.[38,39] Geometry and electronic structure are intimately related and their effects difficult to separate, but the role of geometry is probably considerably more subtle than the other factors we have discussed above.

As can be seen from Figure 8, although the activation barriers for chemisorption on Si$_{25}^+$ and Al$_{25}^+$ show the same qualitative trends, there are significant differences. The activation barriers for chemisorption of D$_2$ and CH$_4$ are quite similar, but those for CO and N$_2$ are significantly larger for Si$_{25}^+$ than for Al$_{25}^+$. This may indicate that Si$_{25}^+$ is considerably less effective as a π donor than Al$_{25}^+$, but the clusters are roughly equivalent as σ donors.

Summary and Conclusions

In this paper we have presented the results of a detailed study of the reactions of Si$_{25}^+$ with a range of simple molecules. Many of the reactions studied show substantial activation barriers and so they can only be studied using methods, such as the ion beam technique, where a wide range of collision energies are accessible. Activation barriers for chemisorption of D$_2$, CH$_4$, O$_2$, C$_2$H$_4$, CO, and N$_2$ on Si$_{25}^+$ were derived from the experimental data. In many cases chemical reactions, resulting in cluster fragmentation, followed chemisorption. These chemical reactions often result in fission of the cluster, similar to the dissociation processes recently observed for the bare clusters. The data for the reactions of Si$_{25}^+$ were compared with our recently published results for Al$_{25}^+$. There are obvious similarities between the reactions of Al$_{25}^+$ and Si$_{25}^+$, despite the large differences expected in the bonding of these clusters. The activation barriers show the same qualitative trends, but there are also significant differences. Al$_{25}^+$ does not undergo the fission processes observed with Si$_{25}^+$. The activation barriers for chemisorption on both Al$_{25}^+$ and Si$_{25}^+$ show a qualitative correlation with the cluster HOMO → molecule LUMO promotion energy, suggesting that charge-transfer stabilization of the transition state is an important factor in determining the size of the activation barriers for chemisorption on atomic clusters. The electronic structure of the metal cluster and the strength of the bonds being broken and formed are probably also important.

Acknowledgment. We are grateful for a number of helpful comments by the reviewers, and by M. L. Mandich.

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Isomeric Characterization of Gaseous Ions. Minimizing C$_4$H$_8^{\bullet +}$ Rearrangement by Dissociating the Corresponding Neutrals

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Abstract: With use of neutralization–reionization (NR) mass spectrometry, five gaseous C$_4$H$_8^{\bullet +}$ isomers can be structurally characterized by neutralization with sodium to produce excited C$_4$H$_8$ molecules whose dissociation products are reionized to both negative and positive ions. Such NR mass spectra are less characteristic when produced by Cs neutralization, which forms more highly excited C$_4$H$_8$, or by Hg neutralization followed by dissociation of C$_4$H$_8$ using multiple collisions; on average each collision adds $\sim$1.7 eV to the molecule, so that isomerization may occur between collisions. The Na NR spectra show that C$_4$H$_8^{\bullet +}$ ions from all butyl acetate isomers have the expected structure except that 2-C$_4$H$_8^{\bullet +}$ is formed from *n*-butyl acetate. 2-C$_4$H$_8^{\bullet +}$ and methylcyclopropane$^{\bullet +}$ appear to be the major products from methylcyclopentane$^{\bullet +}$. 1-Butanol$^{\bullet +}$ and cyclohexane$^{\bullet +}$ predominantly form cyclobutane$^{\bullet +}$, while β- and γ-valerolactone$^{\bullet +}$ give 1-C$_4$H$_8^{\bullet +}$ and methylcyclopropane$^{\bullet +}$, respectively, as major products.

Recent impressive advances in the chemistry of gaseous ions, and the applications of this chemistry to synthesis and analysis, have depended heavily on techniques for ion structural characterization.[1,2] For example, valuable new information on simple ions in plasmas has come from laser spectroscopy.[3] However, a long-term problem for the identification of isomeric cations, especially those of hydrocarbons, has been their low isomerization barriers,[4] both low in absolute terms (13–30 kcal mol^{-1} for C$_4$H$_8^{\bullet +}$ isomers, Table I) and low relative to the isomerization barriers for the corresponding neutrals (64–73 kcal mol^{-1} for C$_4$H$_8$ iso-

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Table I. Thermochemical Data of C_4H_8 and $C_4H_8^{\bullet+}$ Isomers

	1-C_4H_8	2-C_4H_8	*i*-C_4H_8	c-$C_3H_5CH_3$	c-C_4H_8
			C_4H_8		
IE(eV)[a]	9.58	9.10	9.19	9.46	10.06
$\Delta H^\circ{}_f$[b]	0	−3	−4	6[c]	6
E_a, isomeriz.[d,e]	70[c]	73[c]	73	64[c]	68
E_a, $H^\bullet$ loss[d]	83	86	86[f]	97	97
E_a, $CH_3^\bullet$ loss[d]	75	97[g]	99[h]	95	95[i]
			$C_4H_8^{\bullet+}$		
$\Delta H^\circ{}_f$[a]	221	208	208	224	239
E_a, isomeriz.[d,j]	23[k]	30[l]	30[l]	13[m]	16[m]
E_a, $H^\bullet$ loss[a,d]	37	50	55	46	25
E_a, $CH_3^\bullet$ loss[a,d]	39	82	57	44	21

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mers). To minimize isomerization and other reactions, ESR studies of $C_4H_8^{\bullet+}$ isomers were carried out in frozen matrices.[5]

$CH_3CH_2CH{=}CH_2$

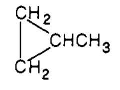
1-C_4H_8

$CH_3CH{=}CHCH_3$

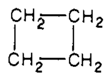
2-C_4H_8

$(CH_3)_2C{=}CH_2$

i-C_4H_8



c-$C_3H_5CH_3$



c-C_4H_8

The electron ionization (EI) mass spectra[6] of C_4H_8 isomeric molecules are closely similar, as are the collisionally activated dissociation (CAD)[7] mass spectra[8] of the $C_4H_8^{\bullet+}$ isomers (e.g., Figure 1A,B), which seriously compromises their analytical and mechanistic utility.[9] These similarities arise (Figure 2) from the near equilibration of the molecular ions to a common structure(s) before or during dissociation.[4] Isomeric differences increase for higher energy dissociations, as their looser activated complexes make them more competitive with isomerization reactions; CH_3 and C_2H_4 losses from $C_4H_8^{\bullet+}$ isomers taking place in ~10^{-11} s occur with negligible rearrangement.[10] This correspondingly high-energy (>5 eV) deposition requirement is also reflected in the poor isomeric characterization of such alkene ions by photodissociation[11] using 3–5-eV photons; laser photodissociation of

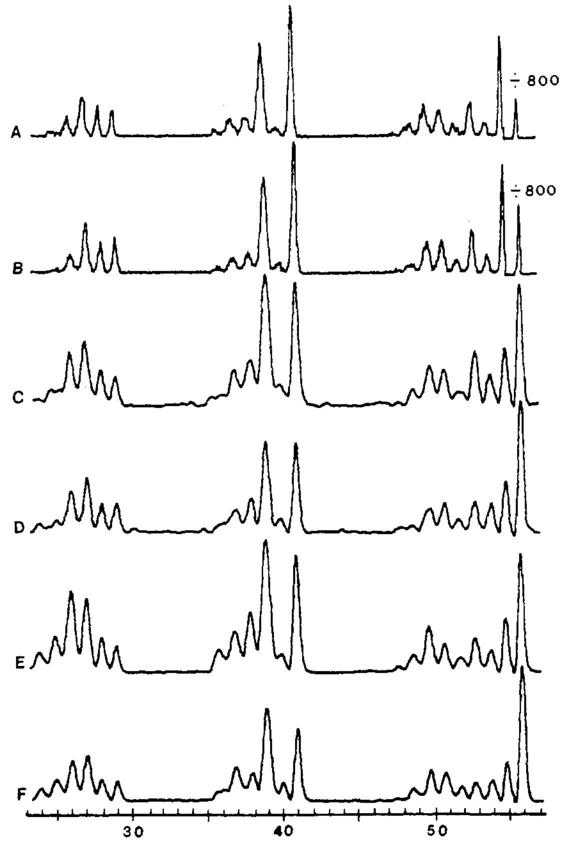


Figure 1. Comparative spectra of (A, C, E) 1-$C_4H_8^{\bullet+}$ and (B, D, F) 2-$C_4H_8^{\bullet+}$: (A, B) CAD, He (30% T); (C, D) $^+NR^+$, Hg (80% T)/NO (30% T); (E, F) $^+NCR^+$, Hg (80% T)/He (30% T)/NO (30% T). $[39^+]/I_0$ values = (A) 2.8×10^{-3}; (B) 1.7×10^{-3}; (C) 1.6×10^{-5}; (D) 3.1×10^{-5}; (E) 2.0×10^{-5}; (F) 1.6×10^{-5}.

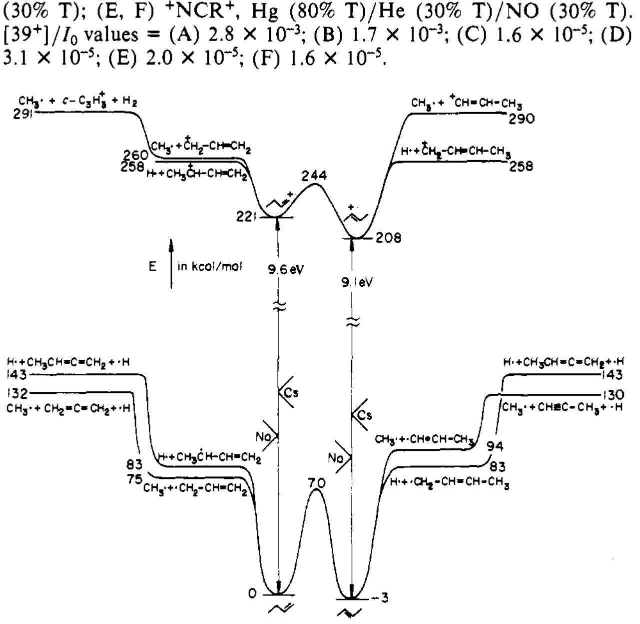


Figure 2. Potential energy surface for 1-C_4H_8, 2-C_4H_8, 1-$C_4H_8^{\bullet+}$, and 2-$C_4H_8^{\bullet+}$. Wedges indicate the differences in ionization energy values of 1- and 2-C_4H_8 and the values of Na and Cs.

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(9) For example, differentiating 1- and 2-C_4H_8 using EI spectra is possible only under carefully controlled experimental conditions, and such conditions could not be achieved for CAD differentiation of 1- and 2-$C_4H_8^{\bullet+}$ [8a]

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fast ions[11c] has the further disadvantage of low sensitivity.

An alternative approach is to take advantage of the higher isomerization barrier of neutrals by the use of neutralization–reionization mass spectrometry (NRMS).[12] We have recently shown[13] that mass-selected fast distonic ions such as $^{\bullet}CH_2CH_2CH_2N^{+}H_3$, which readily isomerize to $CH_3CH_2CH_2NH_2^{\bullet+}$, can be distinguished from their isomeric molecular ions by neutralization to yield an unstable hypervalent neutral which dissociates without appreciable isomerization. The resulting fast neutral products are reionized and characterized[12,13] by a second mass analysis (MS/MS).[14] In this study NRMS is applied to the more common situation in which the neutrals are more stable with respect to dissociation than their precursor ions, such as the $C_4H_8^{\bullet+}$ isomers (Figure 2). Two approaches for dissociating these fast neutrals are explored: (i) subjecting them to a separate process of collisionally activated dissociation,[15] or (ii) using a neutralization target of low ionization energy to form excited neutrals.[16,17] The latter technique, plus kinetic energy release measurements, has been used by Porter and co-workers[16] for energy state and structural characterization of the small ions $C_2H_5^+$,[16b] $C_2H_3^+$, and $C_2H_2^{\bullet+}$.[16c] In the present study method ii reionization to negative[18] as well as to positive ions is more useful for characterization of the five $C_4H_8^{\bullet+}$ positional isomers. Method i is used in a separate study to characterize four $C_4H_4^{\bullet+}$ isomers.[19]

Experimental Section

The MS/MS instrument, described elsewhere,[15b] utilizes a Hitachi RMH-2 double-focusing mass spectrometer as the first mass analyzer (MS-I) and an electrostatic analyzer (ESA) as the second (MS-II). Primary ions are formed by electron ionization, accelerated to 10-keV energy, mass-analyzed by MS-I, and neutralized by a target gas (Hg, Cs, or Na vapor) in a differentially pumped collision chamber (Cls-I). Any remaining ions are removed by the first deflection electrode (Dfl-I) located immediately after Cls-I. The resulting beam of fast neutrals is subjected to collisions with a second target gas in the second differentially pumped chamber (Cls-II). These collisions are used to dissociate and/or reionize the neutrals; for only dissociation, any ions formed are deflected by Dfl-II and the neutrals reionized in Cls-III. Mass spectra are measured in MS-II under computer control, averaging 6–15 1-min scans. For cross-section values the ionic precursor intensity I_0 was measured before and after the spectra scans.

Four general types of spectra were measured: (1) $^{+}NCR^{+,-}$ (neutralization of the primary positive ions, CAD of the resulting neutrals, and reionization to either positive or negative secondary ions) under experimental conditions such as Hg (30% T)/He (10% T)/O_2 (80% T), which is neutralization with Hg at a pressure giving 30% transmittance of the primary ions, deflection of the remaining ions (indicated by the slash), He CAD, ion deflection, and O_2 cationization; (2) $^{+}NCR^{+}$, Hg (90% T)/He (30% T), in which multiple collisions in Cls-II are used for both CAD and reionization of the neutrals; (3) $^{+}NR^{-}$, Na (80% T)/C_6H_6 (30% T), in which sodium neutralization produces neutrals which spontaneously dissociate to give products anionized by benzene; (4) $^{+}NR^{-}$, Na (30% T), in which Na produces neutrals that can be reionized to negative ions by a second Na collision.[18] The high sodium pressure causes high detector noise; reproducibility was partially restored (to ±3%, absolute) by using a discrete dynode multiplier, by placing a copper shield at the β'-slit in front of the detector, and by allowing the detector to stabilize for ~10 min after achieving the operating Na pressure. Using Na, reproducibility of cross-section measurements is only ±50%. He is used for reionization because O_2 gradually oxidizes the Na condensed in the instrument, causing charging problems.

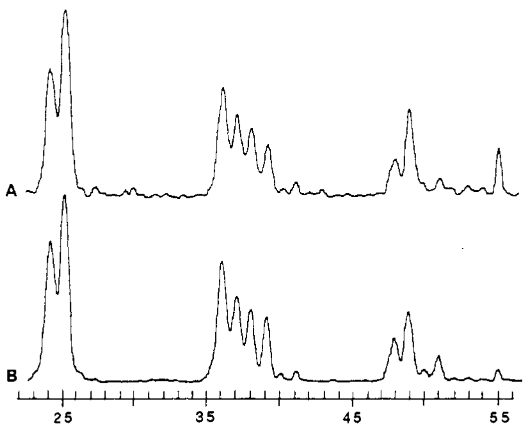

Figure 3. $^{+}NR^{-}$ spectra of (A) 1-$C_4H_8^{\bullet+}$ and (B) 2-$C_4H_8^{\bullet+}$ using benzene (30% T. $[36^{-}–39^{-}]/I_0$ values: (A) 1.6×10^{-6}; (B) 3.3×10^{-6}.

β-Valerolactone was prepared[20] by the $BF_3{\cdot}Et_2O$ catalyzed addition of ketene[21] to propanal. The other chemicals, obtained commercially, showed no significant impurities in their mass spectra. The trans isomer was used for the spectra designated as 2-butene, but remeasurement with the cis isomer gave the same spectra within experimental error.

Results and Discussion

Collisionally Activated Neutral Dissociation. The isomers 1- and 2-$C_4H_8^{\bullet+}$ were studied initially, as these are particularly difficult to distinguish using their EI or CAD (Figure 1A,B) mass spectra.[8,9] In the absence of rearrangement, methyl loss should be much less favorable for 2-$C_4H_8^{\bullet+}$ than for 1-$C_4H_8^{\bullet+}$ (Figure 2, Table I), yet the $[C_3H_5^+]/[C_4H_7^+]$ values of 1.3 and 1.2, respectively, from CAD are not significantly different. However, the CAD cross sections, $[products^+]/[C_4H_8^{\bullet+}]$ (not measured in the earlier studies),[8] do indicate a substantially higher tendency for dissociation of 1-$C_4H_8^{\bullet+}$, consistent with its higher heat of formation. Neutralization followed by reionization to cations (a normal $^{+}NR^{+}$ spectrum) also gives quite similar spectra (Figure 1C,D), with $[C_3H_5^+]/[C_4H_7^+] = 2.2$ for 1-$C_4H_8^{\bullet+}$ and 1.7 for 2-$C_4H_8^{\bullet+}$, and a substantially higher dissociation extent for 1-$C_4H_8^{\bullet+}$; both are consistent with most of the dissociation occurring after reionization. These neutrals should be formed with relatively low internal energy, as Hg has a higher ionization energy (IE = 10.4 eV) than the C_4H_8 isomers.[16,17]

In an attempt to dissociate separately the C_4H_8 neutrals, under the same NR conditions the neutral beam was collisionally activated with a relatively high pressure (30% transmittance) of He target gas, and any resulting ions deflected, before the resulting neutral products were reionized (Figure 1E,F). Although secondary products such as C_2H_2 and C_3H_3 increased and 1-$C_4H_8^{\bullet+}$ again showed the higher dissociation extent, the $[C_3H_5^+]/[C_4H_7^+]$ values of 2.2 for 1-$C_4H_8^{\bullet+}$ and 1.8 for 2-$C_4H_8^{\bullet+}$ were not appreciably different from those without CAD. Oxygen reionization with a helium pressure giving 10% transmittance of the neutrals led to very similar results, producing $[C_3H_5^+]/[C_4H_7^+] = {\sim}2.1$ for both isomers. For the $^{+}NCR^{+}$, Hg (80% T)/He/O_2 (90% T) spectra, values for $[C_4H_8^{\bullet+}\ (\text{reionized})]/[\sum\text{ions}]$ for He (100%, 30%, 10% T) are respectively 23, 13, and 9% for 1-$C_4H_8^{\bullet+}$ and 44, 24, and 15% for 2-$C_4H_8^{\bullet+}$. This corresponds to values of 34 and 32% for 1-C_4H_8, and 26 and 29% for 2-C_4H_8, precursor dissociation per collision, based on the average number of scattering collisions per precursor for 30% T and 10% T of 1.5 and 3.1, respectively.[22] Based on the average of these values, exceeding

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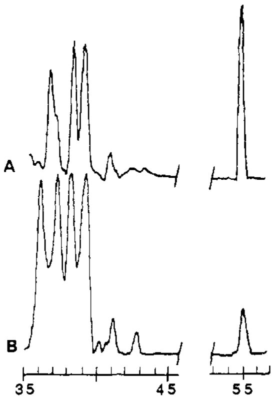

Figure 4. Partial $^+NR^-$ spectra of (A) 1-$C_4H_8{}^{\bullet+}$ and (B) 2-$C_4H_8{}^{\bullet+}$ using Cs (30% T). $[36^- - 39^-]/I_0$ values: (A) 0.54×10^{-4}; (B) 1.3×10^{-4}.

the 3.3-eV dissociation threshold for 50% of C_4H_8 requires ~1.9 collisions; this indicates that the CAD energy deposition values for fast neutrals are comparable, but possibly somewhat less, than those for CAD of ions[23] (all C_4H_8 neutrals undergoing CAD are also probably not in their ground state). However, CAD has still apparently supplied sufficient energy for dissociation, especially with the collisions at 10% transmittance. The stepwise CAD addition of energy offers a possible explanation; a collision exciting the C_4H_8 neutral above the rearrangement threshold (Figure 2) may often not deposit sufficient energy to make dissociation occur first, while the time between collisions ($>10^{-8}$ s) is sufficient to allow rearrangement before more energy is added. Increasing the number of collisions may have the negative effect of dissociating the $C_3H_5{}^\bullet$ and the $C_4H_7{}^\bullet$ products needed for characterization, or increasing their internal energy so that they dissociate more easily on reionization (vide infra).

Negative Ion Dissociation. Reionization of the same neutral beam to negative ions[18] with benzene (IE = 9.2 eV) does show significant differences in $[C_3H_5{}^-]$ and $[C_4H_7{}^-]$ for the $^+NR^-$, Hg (80% T)/benzene (80% T) spectra of 1-$C_4H_8{}^{\bullet+}$ and 2-$C_4H_8{}^{\bullet+}$, although H loss is now greater from the 1-isomer. Similar results were obtained for $^+NR^-$, Hg (30% T), and $^+NR^-$, benzene (30% T) (Figure 3A,B) spectra, in which both neutralization and anionization are effected in the same collision chamber. These differences indicate that a substantial proportion of the $C_4H_8{}^{\bullet+}$ ions reaching the neutralization region have internal energies less than that required for isomerization. However, the extensive dissociation shown by peaks such as $C_2{}^-$, C_2H^-, and $C_3{}^-$, which probably originate[18b] from excited $C_4H_8{}^{\bullet-}$, and the order of magnitude lower cross section indicate that such $^+NR^-$ spectra should be of marginal utility for isomer identification. Thus, for reionization to anions, complete dissociation of C_4H_8 would avoid its interfering reionization to the unstable $C_4H_8{}^{\bullet-}$.

Excited Neutral Formation Using a Cesium Target. When the ionization energy of the target is less than that of the neutralized primary ion, the difference can appear as excitation energy in the charge-transfer products.[16,17] Thus, a Cs target (IE = 3.9 eV) should produce C_4H_8 neutrals of internal energies well above that required for dissociation (Figure 2). The $^+NR^-$, Cs (30% T), spectra (Figure 4A,B) do indicate that more $C_4H_7{}^\bullet$ neutrals have been formed than with Hg or benzene neutralization (Figure 3A,B), but $[C_3H_5{}^-]/[C_4H_7{}^-]$ is much lower for the 1-$C_4H_8{}^{\bullet+}$ than the 2-$C_4H_8{}^{\bullet+}$ precursors.[24] This is consistent with 1-$C_4H_8{}^*$ being produced (Figure 2) ~56 kcal mol^{-1} above its lowest dissociation limit (versus ~37 kcal mol^{-1} for 2-$C_4H_8{}^*$), so that the 1-$C_4H_8{}^*$ yields $^\bullet CH_2CH{=}CH_2$ with sufficient internal energy to dissociate further (Figure 2). Irrespective of the basis for the spectra in Figure 4A,B, formation of $C_4H_8{}^*$ with less internal energy appears desirable.

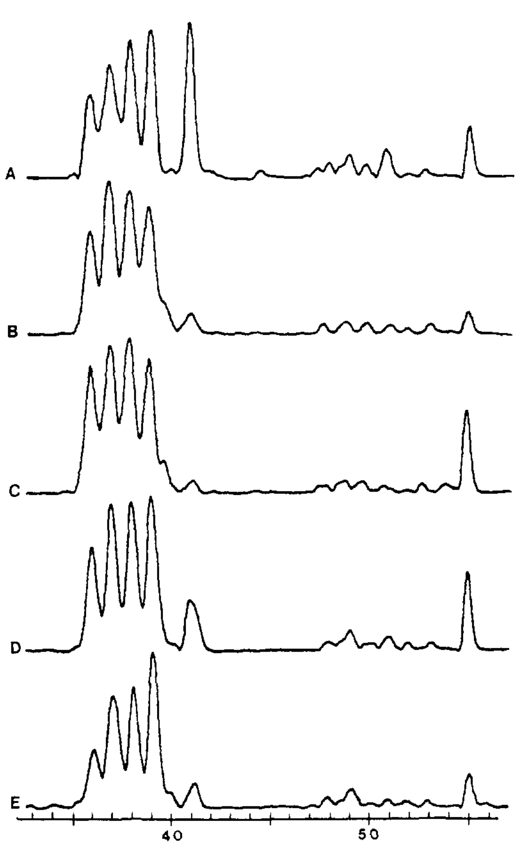

Figure 5. Partial $^+NR^-$ spectra, Na (30% T), of (A) 1-$C_4H_8{}^{\bullet+}$, (B) 2-$C_4H_8{}^{\bullet+}$, (C) *i*-$C_4H_8{}^{\bullet+}$, (D) c-$C_3H_5CH_3{}^{\bullet+}$, and (E) c-$C_4H_8{}^{\bullet+}$. None of the omitted lower mass peaks has an abundance >15% of $[36^- - 39^-]$. $[36^- - 39^-]/I_0$ values: (A) 1.4×10^{-4}; (B) 1.7×10^{-4}; (C) 1.3×10^{-4}; (D) 0.83×10^{-4}; (E) 0.68×10^{-4}.

Excited Neutral Formation Using a Sodium Target. The internal energy of the neutralized C_4H_8 should be ~1.2 eV less using Na (IE = 5.1 eV) versus Cs as the charge-exchange target. Gratifyingly, the $^+NR^-$, Na (30% T), spectra show $[C_3H_5{}^-]/[C_4H_7{}^-]$ much greater for 1-$C_4H_8{}^{\bullet+}$ than for 2-$C_4H_8{}^{\bullet+}$ (Figure 5A,B), as predicted by the reaction enthalpies of the C_4H_8 neutrals. Further, the values for *i*-$C_4H_8{}^{\bullet+}$ and c-$C_3H_5CH_3$ are similarly consistent; c-C_4H_8 can only lose CH_3 by a rearrangement process. The $C_3H_5{}^\bullet$ formed on neutralization of 1-$C_4H_8{}^{\bullet+}$ should now on average have 1.2 eV of internal energy, substantially below the dissociation limit (Figure 2). Further, this will provide a corresponding increase in the electron affinity of the $C_3H_5{}^\bullet$, increasing the cross section for electron transfer from Na.

Reionization to positive ions ($^+NR^+$, Na (80% T)/He (80% T), spectra, Figure 6) provides further data for isomeric differentiation. The absence of $C_4H_8{}^{\bullet+}$ ions in the $^+NR^+$ spectrum shows that essentially all neutrals formed with Na have excitation energies above the dissociation barrier. Now $[C_3H_5{}^+]/[C_4H_7{}^+]$ is less for 1-$C_4H_8{}^{\bullet+}$ than for 2-$C_4H_8{}^{\bullet+}$; Na neutralization of 2-$C_4H_8{}^{\bullet+}$ followed by dissociation should lead to essentially ground-state $C_3H_5{}^\bullet$ (Figure 2), so it is possible that reionization of $C_3H_5{}^\bullet$ of 1.2 eV internal energy formed from 1-C_4H_8 gives $C_3H_5{}^{+*}$ undergoing much more extensive further dissociation than $C_3H_5{}^+$ from precursor 2-$C_4H_8{}^{\bullet+}$. The most characteristic values for these Na neutralization spectra ($^+NR^+$ and $^+NR^-$) are given in Table II. The near identity of the $^+NR^+$ spectra for c-$C_3H_5CH_3{}^{\bullet+}$ and c-$C_4H_8{}^{\bullet+}$ suggest that substantial isomerization between these could have occurred before neutralization (barriers of 13 and 16 kcal mol^{-1}, Table I).

Structural Characterization of $C_4H_8{}^{\bullet+}$ Products. These $^+NR^+$ and $^+NR^-$ mass spectra appear to be relatively insensitive to precursor ion internal energy. Spectra of 1-$C_4H_8{}^{\bullet+}$, 2-$C_4H_8{}^{\bullet+}$, and *i*-$C_4H_8{}^{\bullet+}$ ions formed by 17-eV electron ionization are identical

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[23] Kim, M. S.; McLafferty, F. W. *J. Am. Chem.* **1978**, *100*, 3279. Lee, S. H.; Kim, M. S.; Beynon, J. H. *Int. J. Mass Spectrom. Ion Processes* **1987**, *75*, 83–89.

[24] Reionization efficiencies can differ by more than an order of magnitude, so that product ion abundances do not necessarily reflect the abundances of the neutrals formed. Wesdemiotis, C.; Feng, R.; Williams, E. R.; McLafferty, F. W. *Org. Mass Spectrom.* **1986**, *21*, 689–695.

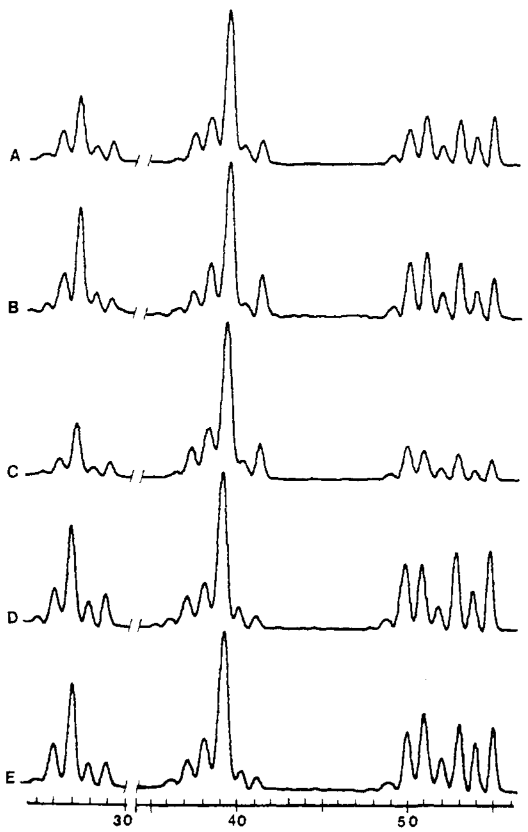

Figure 6. $^+NR^+$ spectra, Na (80% T)/He (80% T), of (A) 1-$C_4H_8^{\bullet+}$, (B) 2-$C_4H_8^{\bullet+}$, (C) *i*-$C_4H_8^{\bullet+}$, (D) c-$C_3H_5CH_3^{\bullet+}$, and (E) c-$C_4H_8^{\bullet+}$. $[39^+]/I_0$ values: (A) 1.4×10^{-4}; (B) 1.2×10^{-4}; (C) 1.8×10^{-4}; (D) 0.90×10^{-4}; (E) 1.2×10^{-4}.

Table II. $^+NR^+$ and $^+NR^-$ Spectral Data (%) for $C_4H_8^{\bullet+}$ Ions from Various Precursors[a]

precursor	$[41^+]/[39^+]$	$[55^+]/[39^+]$	$[41^-]/[36^-–39^-]$	$[55^-]/[36^-–39^-]$	structure
1-C_4H_8	17 ± 2	34 ± 2	33 ± 3	16 ± 3	1-$C_4H_8^{\bullet+}$
1-C_4H_8 (17 eV)[b]	16	34	30	17	1-$C_4H_8^{\bullet+}$
2-C_4H_8	23	22	5	6	2-$C_4H_8^{\bullet+}$
2-C_4H_8 (17 eV)[b]	22	24	5	5	2-$C_4H_8^{\bullet+}$
i-C_4H_8	21	14	2	18	*i*-$C_4H_8^{\bullet+}$
i-C_4H_8 (17 eV)[b]	21	15	5	22	*i*-$C_4H_8^{\bullet+}$
c-$C_3H_5CH_3$	8	51	9	13	c-$C_3H_5CH_3^{\bullet+}$
c-C_4H_8	7	48	4	6	c-$C_4H_8^{\bullet+}$
β-valerolactone	16	33	33	15	1-$C_4H_8^{\bullet+}$
n-butyl acetate	20	26	7	8	2-$C_4H_8^{\bullet+}$[c]
sec-butyl acetate	19	21	7	7	2-$C_4H_8^{\bullet+}$
isobutyl acetate	21	15	7	21	*i*-$C_4H_8^{\bullet+}$
tert-butyl acetate	23	14	5	18	*i*-$C_4H_8^{\bullet+}$
γ-valerolactone	9	49	10	3	c-$C_3H_5CH_3^{\bullet+}$[c]
methylcyclopentane	16	27	1	1	2-$C_4H_8^{\bullet+}$[c]
cyclohexane	15	43	5	7	c-$C_4H_8^{\bullet+}$[c]
n-BuOH	8	45	1	2	c-$C_4H_8^{\bullet+}$

[a] Ionizing electron energy 70 eV, unless noted otherwise. [b] Electron energy at which the primary $C_4H_8^{\bullet+}$ abundance is reduced to 10% of the 70-eV value. [c] Major isomer; see text.

within experimental error with those of the corresponding precursor ions formed with 70-eV electrons (Table II). This is also true for fragment $C_4H_8^{\bullet+}$ formed by accepted mechanisms of unimolecular ion decomposition.[2] Loss of CO_2 from *β*-valerolactone molecular ions should produce 1-$C_4H_8^{\bullet+}$, consistent with its $^+NR^{+,-}$ spectra (Table II). Similarly, *sec*-butyl acetate ions produce 2-$C_4H_8^{\bullet+}$, and its *i*-Bu and *t*-Bu isomers produce *i*-$C_4H_8^{\bullet+}$, as predicted by the classical γ-hydrogen rearrangement[2] (the previous CAD results[8a] had been interpreted as 1- and/or 2-$C_4H_8^{\bullet+}$ from *sec*-butyl acetate, and *i*- and 2-$C_4H_8^{\bullet+}$ from *iso*- and *tert*-butyl acetate). γ-Radiolysis of *iso*- and *tert*-butyl acetate in 77 K matrices also produces *i*-$C_4H_8^{\bullet+}$, as shown by ESR.[5] However, the $^+NR^{+,-}$ spectra of $C_4H_8^{\bullet+}$ from *n*-butyl acetate indicate that these ions have primarily the 2-$C_4H_8^{\bullet+}$ structure, with little of the 1-isomer expected from the γ-hydrogen rearrangement mechanism. For *n*-butyl acetate ions Terlouw, Schwarz, and co-workers noted recently[25] that the abundance of $C_4H_8^{\bullet+}$ became large relative to that of the charge-competitive product $C_2H_4O_2^{\bullet+}$ for *low-energy* (long lifetime) dissociations. Their postulated mechanism involving a long-lived ion/dipole or hydrogen-bridged intermediate which facilitates rearrangement to the more stable 2-$C_4H_8^{\bullet+}$ is also consistent with the $^+NR^{+,-}$ data. These data show additionally that only a small proportion of the higher energy $C_4H_9OCOCH_3^{\bullet+}$ ions formed by 70-eV electron ionization dissociate by the classical γ-H rearrangement to form 1-$C_4H_8^{\bullet+}$.

The $^+NR^{+,-}$ spectra of $C_4H_8^{\bullet+}$ from 1-butanol indicate that these ions are mainly the same isomer(s) as produced by c-C_4H_8 ionization. In repeat runs $[C_3H_5^-]$ and $[C_4H_7^-]$ still appear lower than expected for c-$C_4H_8^{\bullet+}$; possibly some of the open-chain isomers such as $^\bullet CH_2CH_2CH_2CH_2^+$ or $CH_3{}^\bullet CHCH_2CH_2^+$ are present (in this case the CAD assignment[8a] was also c-$C_4H_8^{\bullet+}$). This isomer (or the distonic ions) has long been the postulated product,[2] but definitive evidence has not been reported previously;[26] recent ab initio calculations suggest that primary cations, such as $^\bullet CH_2CH_2CH_2^+$, are unstable[27] (an alternative possibility conceivably consistent with the Table II data is that c-C_4H_8 ionization forms some molecular ions with internal energies above the isomerization barrier, so that higher purity c-$C_4H_8^{\bullet+}$ ions are formed from 1-butanol).

The cyclohexane $^+NR^{+,-}$ spectra are consistent with the formation of c-$C_4H_8^{\bullet+}$, as expected[2] (but not indicated by CAD);[8a] in addition the product appears to contain a substantial proportion of 2-$C_4H_8^{\bullet+}$ (other combinations of isomeric products could also fit the data within experimental error). Ring opening of the cyclohexane molecular ion followed by hydrogen rearrangement before C_2H_4 loss could reasonably lead to formation of the stable 2-$C_4H_8^{\bullet+}$ isomer.

Loss of CO_2 from γ-valerolactone$^{\bullet+}$ should yield c-$C_3H_5CH_3^{\bullet+}$. This is consistent with the corresponding $^+NR^{+,-}$ spectra, except that the $[C_4H_7^-]/[C_3^-–C_3H_3^-]$ value is 3% instead of the expected 13%. Remeasurement indicates that this difference is outside experimental error; this could possibly be due to the presence of $^\bullet CH_2CH_2CH^+CH_3$, the open-chain form of c-$C_3H_5CH_3^{\bullet+}$.[27] This is also the only apparent explanation for the very low values for the $^+NR^-$ spectrum (Table II) of $C_4H_8^{\bullet+}$ from methylcyclopentane (formation of additional isomers except c-$C_4H_8^{\bullet+}$ in the ionization of c-$C_3H_5CH_3$ is not consistent with the Table II data), which is otherwise consistent with c-$C_3H_5CH_3^{\bullet+}$ and 2-$C_4H_8^{\bullet+}$ as major products. These unexpectedly low values for the $^+NR^-$ spectra could also arise from internal energy differences, but (vide supra) a higher energy c-$CH_3C_3H_5$ neutral from methylcyclopentane should yield more abundant $C_3H_5^-$ and $C_4H_7^-$ ions. We are investigating other possible sources of reference c-$C_4H_8^{\bullet+}$, c-$CH_3C_3H_5^{\bullet+}$, $^\bullet CH_2CH_2CH_2CH_2^+$, and $^\bullet CH_2CH_2CH^+CH_3$ isomers to resolve these inconsistencies.

Conclusions

The isomeric $C_4H_8^{\bullet+}$ ions can be characterized, despite their ready isomerization tendency, by dissociating the corresponding less isomerizable neutrals. Application of this NRMS technique requires a method to add enough energy to the neutral for its dissociation with minimum rearrangement (for C_4H_8, CAD gave poor differentiation), but not so much that the more characteristic primary products dissociate further (Cs neutralization added too

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much energy). In reionizing these primary products, their excess internal energy may produce unstable cations, but this may increase the cross section for anion formation by increasing the electron affinity. With such selection of experimental conditions this technique is useful for the structural characterization of $C_4H_8^{\bullet+}$ isomers from a variety of sources.

Acknowledgment. The authors thank R. F. Porter, B. Leyh, and F. Turecek for helpful discussions, and K. D. Henry for data processing. Generous financial support was provided by the National Science Foundation and instrumentation by the National Institutes of Health.

Registry No. Cs, 7440-46-2; Na, 7440-23-5; Hg, 7439-97-6; 1-C_4H_8, 106-98-9; 2-C_4H_8, 107-01-7; *i*-C_4H_8, 115-11-7; c-$C_6H_5CH_3$, 594-11-6; c-C_4H_8, 287-23-0; *n*-BuOH, 71-36-3; 1-$C_4H_8^{\bullet+}$, 34467-39-5; 2-$C_4H_8^{\bullet+}$, 34526-42-6; *i*-$C_4H_8^{\bullet+}$, 34526-44-8; c-$C_3H_5CH_3^{\bullet+}$, 56306-64-0; c-$C_4H_8^{\bullet+}$, 34474-99-2; benzene, 71-43-2; β-valerolactone, 15890-55-8; *n*-butyl acetate, 123-86-4; *sec*-butyl acetate, 105-46-4; isobutyl acetate, 110-19-0; *tert*-butyl acetate, 540-88-5; γ-valeroacetone, 108-29-2; methylcyclopentane, 96-37-7; cyclohexane, 110-82-7.

Product Kinetic Energy Release Distributions as a Probe of the Energetics and Mechanisms of Organometallic Reactions Involving the Formation of Metallacyclobutanes in the Gas Phase

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Abstract: Product kinetic energy release distributions and collision-induced dissociation studies are used to probe the energetics and mechanisms of several gas-phase organometallic reactions involving the formation of metallacyclobutanes. Reaction of atomic cobalt ions with 1-pentene yields $Co(C_2H_4)^+$. Loss of C_3H_6 in this process exhibits a *bimodal* kinetic energy release distribution. The low-energy portion can be modeled using statistical phase space theory by assuming that propylene is eliminated. The high-energy portion of the distribution is similar to that observed for the decarbonylation of cyclobutanone by Co^+ to yield $Co(CO)^+$. It is inferred for both systems that cyclopropane elimination is being observed with a tight transition state and a reverse activation energy. The characteristically broad kinetic energy release distributions cannot be described by statistical theories. Similar results are observed with Fe^+ as a reactant. In this case, however, the reaction with 1-pentene leads to a broadened rather than a bimodal distribution. These arguments are substantiated using product distributions measured in collision-induced dissociation studies of various adducts which might have structures analogous to those invoked for the reactions of Co^+ and Fe^+ with cyclobutanone. Metastable loss of CO is also observed in these reactions. Fitting the statistical phase space theory to the measured distribution yields a heat of formation for the cobaltacyclobutane ion of 274 ± 5 kcal/mol. The heat of formation (0 K) of the ferracyclobutane ion is less well determined but is approximately 268 kcal/mol. These are substantially higher (by 27 and 16 kcal/mol, respectively) than those for the corresponding isomeric propylene complexes. From these measurements, we estimate strain energies of cobaltacyclobutane and ferracyclobutane to be 22 and 18 kcal/mol, respectively, to be compared with 26 kcal/mol for cyclobutane.

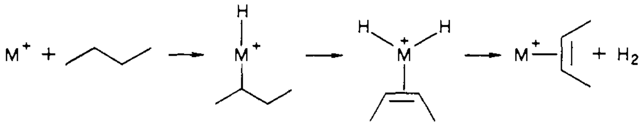
An intriguing aspect of transition metal–ion chemistry is the facility with which gas-phase atomic metal ions induce skeletal rearrangements of hydrocarbons.[1-8] For example, transition metal ions react exothermically with hydrocarbons to eliminate hydrogen, alkanes, or alkenes by processes which involve both bond cleavage and formation.

This is particularly apparent for the first-row transition metal ions Fe^+, Co^+, and Ni^+ where C–C bond cleavage and formation are pervasive. Elucidating the mechanism of these reactions has proven to be a challenge for the available experimental techniques for studying ionic processes in the gas phase. The dehydrogenation of *n*-butane, process 1, by Co^+ represents an example. Initially,

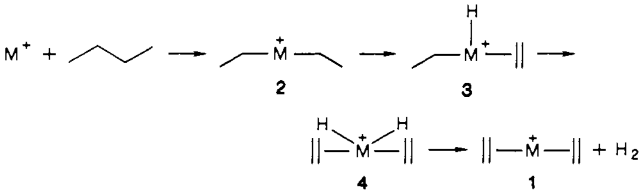
$$Co^+ + n\text{-butane} \rightarrow Co(C_4H_8)^+ + H_2 \tag{1}$$

this reaction was believed to proceed by a simple C–H bond insertion followed by β-hydrogen elimination process as depicted in Scheme I.[9] Detailed structural studies on the product of reaction 1, however, revealed that it comprises, not a 2-butene–metal ion complex, but rather a bisethylene complex **1**.[10] A

Scheme I



Scheme II



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