Ion–Dipole Complexes in the Unimolecular Reactions of Isolated Organic Ions. Effect of *N*-Methylation on Olefin and Amine Loss from Protonated Aliphatic Amines

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The slow unimolecular fragmentation reactions of 18 gaseous protonated aliphatic amines of general formula $R^1NH^+R^2R^3$ (R^1 = Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, or Bu^t; R^2,R^3 = H,CH_3) are reported and discussed. Two decomposition routes are observed for metastable ions $R^1NH^+R^2R^3$. The first involves elimination of a neutral amine, R^2R^3NH, and formation of a carbocation, R^{1+}, *via* a mechanism involving an incipient cation bound to the developing amine by an ion–dipole attraction. Rearrangement of the cation, to give thermodynamically more stable isomers, is feasible in these ion–dipole complexes. Further reorganization of the complexes leads to a species in which an incipient olefin [R^1 − H] and an amine [R^2R^3NH] are co-ordinated to a common proton. Dissociation of these proton-bound complexes, with retention of the proton by the developing amine, results in olefin loss, which is the second reaction undergone by metastable ions $R^1NH^+R^2R^3$. The relative abundance of amine expulsion is greater for protonated amines containing a primary alkyl group, R^1, than is the case for isomeric ions containing secondary or tertiary alkyl groups. Progressive methylation of the nitrogen atom decreases the relative abundance of amine loss from $R^1NH^+R^2R^3$, regardless of the nature of the principal alkyl group. These two trends are explained in terms of the energetics of the intermediates and products involved in the decomposition of the protonated amines.

The reactions of isolated organic ions can be investigated conveniently using mass spectrometers.[1] Particularly useful information may be acquired from the study of metastable ions, which undergo dissociation under relatively well defined conditions, with excess energies in the transition state similar to those involved in solution experiments.[2,3] As a result the relative rates of competing fragmentation reactions are determined primarily by relative reaction critical energies, and the results often can be understood in terms of potential-energy profiles.[3] Recent work has revealed that complexes comprising an incipient cation and a neutral species, held together by an ion–dipole attraction, sometimes play a central role in the chemistry of isolated ions.[4–15] Much of the earlier work on these ion–dipole complexes developed from analysis of the behaviour of closed-shell 'onium' ions, generated by dissociative electron ionization of alcohols, ethers, and amines.[4–8] More recently, ion–dipole complexes have been shown to be involved in the decomposition of closed-shell species produced by bimolecular ion/molecule reactions.[10–15] In addition, similar species, also known as ionized ylides, have been shown to be of crucial significance in the chemistry of open-shell radical cations.[16]

Despite these studies there have been relatively few examinations of the role of ion–dipole complexes in the low-energy fragmentation reactions of the ions produced by protonation of simple amines, ethers, and alcohols. Ion–dipole complexes have been implicated as intermediates in the dissociation of some small protonated alcohols.[10] More recently, the low-energy unimolecular fragmentation reactions of a number of protonated monoalkylamines have been reported;[17] theoretical calculations of the potential energy profile for a typical example, protonated isopropylamine, showed the involvement of ion–dipole complexes and proton-bound complexes in the fragmentation reactions. The effect of progressive methylation of the nitrogen atom in these ammonium cations is of interest; this paper reports the reactions of eighteen metastable ammonium ions of general structure $R^1NH^+R^2R^3$ (R^1 = Pr or Bu; R^2,R^3 = H,CH_3) and illustrates the role of ion–dipole complexes in the fragmentation of these species.

Results and Discussion

The unimolecular reactions of metastable ions $R^1NH^+R^2R^3$ produced by protonation of the parent amine with Bu^{t+} or $CH_5^+/C_2H_5^+$ under chemical ionization conditions are shown in Table 1. Pertinent data concerning the thermochemistry of reactant ions and likely combinations of product ions and neutral species are given in Table 2. Two general trends are immediately apparent in the data of Table 1.

First, the relative abundance of alkyl ion products arising by amine loss from $R^1NH^+R^2R^3$ is greater for protonated amines in which the principal alkyl group, R^1, has a primary structure than for those protonated amines containing isomeric secondary or tertiary alkyl groups. Indeed, amine elimination is of only minor or negligible importance for the protonated amines containing isopropyl, s-butyl, or t-butyl substituents. This trend is the opposite of that which would be expected on energetic grounds assuming that amine expulsion proceeded by simple cleavage of the C–N σ-bond. Such an analysis would lead to the conclusion that amine loss should compete more effectively with alkene elimination in systems containing secondary or tertiary alkyl groups, simply because more stable cations would be produced (Table 2). A more attractive mechanism, which involves rearrangement of the incipient primary cations, is illustrated in the Scheme for the isomeric ions $C_3H_7NH^+R^2R^3$.

Stretching of the C–N σ-bond in the protonated isopropylamine (**1**) leads to (**1a**), which may be described as a complex containing an incipient isopropyl cation co-ordinated to the amine R^2R^3NH. Further lengthening of this weakened bond yields the products Pr^{i+} and R^2R^3NH. Alternatively, hydrogen transfer between the developing products leads to C_3H_6 and $R^2R^3NH_2^+$, probably *via* an intermediate (**3**) in which propene and the incipient amine are bound to a common proton. The species (**1a**) should be stabilized quite substantially by ion–dipole attraction;[4] in this system the stabilization is estimated to be *ca.* 50 kJ mol^{-1}, relative to the separated products Pr^{i+} and R^2R^3NH. As already noted there is considerable evidence for the intermediacy of complexes such as (**1a**) in the chemistry of isolated ions[4—15] and, in cases where the developing neutral species has a large dipole moment, stabilization by 100 kJ mol^{-1} or more has been found.[4] It is clear from the thermochemical data in Table 2 that, provided reorganization of (**1a**) to (**3**) requires less energy than that (*ca.* 50 kJ mol^{-1}) needed to cause dissociation of (**1a**) to Pr^{i+} plus R^2R^3NH, olefin elimination should be the dominant reaction of (**1**). Regardless of the identity of R^2 and R^3, olefin elimination is the thermochemically preferred decomposition route of all protonated amines. Amine loss requires significantly more energy and, therefore, is of minor or negligible importance for protonated amines containing secondary or tertiary alkyl groups.

Table 1. Reactions of metastable ions $R^1NH^+R^2R^3$

			Relative abundance of products[a]	
R^1	R^2	R^3	R^{1+} + R^2R^3NH	$[R^1 - H]$ + $R^2R^3NH_2^+$
$CH_3CH_2CH_2$	H	H	19	81
	CH_3	H	7	93
	CH_3	CH_3	0	100
$(CH_3)_2CH$	H	H	1	99
	CH_3	H	0	100
	CH_3	CH_3	0	100
$CH_3CH_2CH_2CH_2$	H	H	73	27
	CH_3	H	26	74
	CH_3	CH_3	22	78
$(CH_3)_2CHCH_2$	H	H	86	14
	CH_3	H	47	53
	CH_3	CH_3	28	72
$CH_3CH_2(CH_3)CH$	H	H	5	95
	CH_3	H	2	98
	CH_3	CH_3	0	100
$(CH_3)_3C$	H	H	5	95
	CH_3	H	0	100
	CH_3	CH_3	0	100

[a] Values measured by metastable peak areas, as determined using the MIKES techniques (D. H. Aue and M. T. Bowers, 'Gas Phase Ion Chemistry,' ed. M. T. Bowers, Academic Press, New York, 1979, vol. 2), and normalized to a total metastable ion current of 100 units.

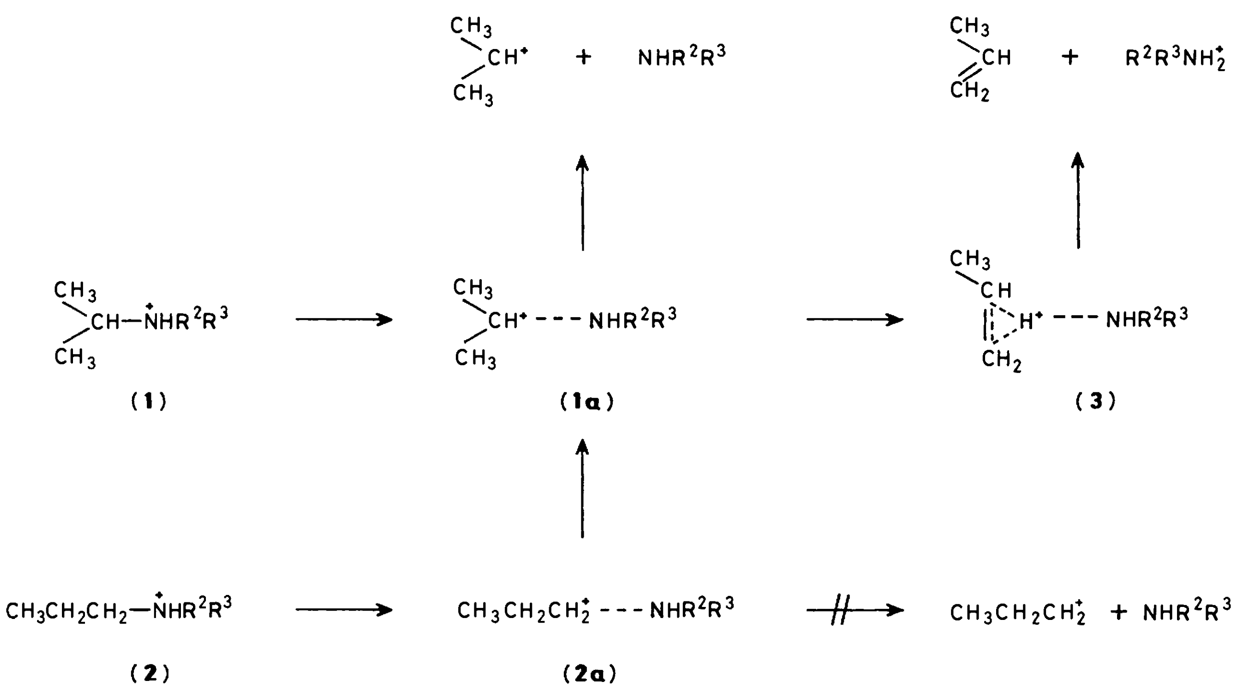
However, a second factor comes into play in the dissociation of protonated amines such as (**2**) where R^1 is a primary alkyl group. After formation of (**2a**), rearrangement of the incipient n-propyl cation leads to (**1a**) and releases *ca.* 65 kJ mol^{-1} of potential energy. The excited complex (**1a**) thus formed decomposes relatively rapidly and, since its energy is above the threshold for formation of Pr^{i+} plus R^2R^3NH, there is an enhanced tendency for (**1a**), produced from (**2a**), to separate from these products, rather than undergo further rearrangement to give C_3H_6 and $R^2R^3NH_2^+$. A similar mechanism, involving isomerization of the incipient n-butyl ion to the s-butyl structure and isomerization of the incipient isobutyl ion to the t-butyl structure, rationalizes the enhanced extent of amine elimination in these systems. It is likely that, in all these cases, isomerization of the incipient cation constitutes the rate-determining step. The increase in the relative yield of higher-energy processes in the reactions of ions which have undergone rate-determining rearrangements is well established.[18]

Thus, the mechanism of the Scheme explains the greater relative importance of amine loss for ions $R^1NH^+R^2R^3$ containing primary alkyl groups. Moreover, the behaviour[17] of the isomeric ions $C_5H_{11}NH_3^+$ also can be understood. Those ions containing C_5H_{11} groups that correspond to stable cations (t-pentyl, 1-methylbutyl, and 1-ethylpropyl) undergo predominantly (94—99%) C_5H_{10} loss. In contrast, those species in which the incipient cation would be expected to rearrange to more stable isomers show a diminished (17—71%) yield of olefin loss and a corresponding increase in ammonia loss. The case of $(CH_3)_2CH(CH_3)CHNH_3^+$ is especially informative. Although the incipient cation [$(CH_3)_2CHCH^+CH_3$, ΔH_f = 732 kJ mol^{-1} (ref. 19)] here possesses a secondary structure, a 1,2-hydride shift leads to the thermochemically more stable isomer

Table 2. Thermochemical data relevant to decomposition of $R^1NH^+R^2R^3$

			[ΔH_f/kJ mol^{-1} [a]]						
R^1	R^2	R^3	$R^1NH^+R^2R^3$	R^{1+} [b]	R^2R^3NH [c]	Σ	$[R^1 - H]$ [c]	$R^2R^3NH_2^+$ [d]	Σ
$CH_3CH_2CH_2$	H	H	551[d]	870	−46	824	21	632	653
	CH_3	H	523[e]	870	−23	847	21	613	634
	CH_3	CH_3	511[e]	870	−18	852	21	590	611
$(CH_3)_2CH$	H	H	534[d]	803	−46	757	21	632	653
	CH_3	H	506[e]	803	−23	780	21	613	634
	CH_3	CH_3	494[e]	803	−18	785	21	590	611
$CH_3CH_2CH_2CH_2$	H	H	524[d]	841	−46	795	−1[f]	632	631
	CH_3	H	496[e]	841	−23	818	−1[f]	613	612
	CH_3	CH_3	485[e]	841	−18	823	−1[f]	590	589
$(CH_3)CHCH_2$	H	H	520[d]	833	−46	787	−18[g]	632	614
	CH_3	H	492[e]	833	−23	810	−18[g]	613	595
	CH_3	CH_3	480[e]	833	−18	815	−18[g]	590	572
$CH_3CH_2(CH_3)CH$	H	H	507[d]	766	−46	720	−8[h]	632	624
	CH_3	H	479[e]	766	−23	743	−8[h]	613	605
	CH_3	CH_3	467[e]	766	−18	748	−8[h]	590	582
$(CH_3)_3C$	H	H	489[d]	695	−46	649	−18[g]	632	614
	CH_3	H	461[e]	695	−23	672	−18[g]	613	595
	CH_3	CH_3	449[e]	695	−18	677	−18[g]	590	572

[a] Uncertainty estimated to be ±5 kJ mol^{-1}. [b] F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, 1970, **48**, 955. [c] Ref. 24. [d] Value obtained from proton affinity (D. H. Aue and M. T. Bowers, 'Gas Phase Ion Chemistry,' ed. M. T. Bowers, Academic Press, New York, vol. 2) and enthalpy of formation[24] of parent amine. [e] Proton affinity estimated from those of homologous and analogous amines (ref. in footnote *d*) and enthalpy of formation estimated from those[24] of homologous species. [f] Value for but-1-ene. [g] Value for 2-methylpropene. [h] Value average of those for *cis*- and *trans*-but-2-ene.



Scheme.

[$(CH_3)_2C^+CH_2CH_3$, $\Delta H_f = 674$ kJ mol^{-1} (ref. 20)] and releases *ca.* 58 kJ mol^{-1} of potential energy. This is sufficient to exceed the barrier for formation of t-pentyl cation plus NH_3 and, accordingly, a significant yield (29%) of $C_5H_{11}^+$ is observed. Such an exothermic rearrangement is not available for the 1-methylbutyl and 1-ethylpropyl ions and, consequently, little $C_5H_{11}^+$ is formed. A similar effect has been reported[21] in the chemistry of $(CH_3)_2CH(CH_3)CHBr^{+\cdot}$ and $(CH_3)_2CH(CH_3)CHCO^+$, both of which behave differently from their 1-methylbutyl and 1-ethylpropyl isomers.

The second trend in the general behaviour of ions $R^1NH^+R^2R^3$ is that amine elimination is reduced in importance in metastable ion fragmentation reactions by progressive methylation on nitrogen, regardless of the nature of the principal alkyl group, R^1. When R^1 is a secondary or tertiary alkyl group, for which amine loss is unfavourable even when $R^2 = R^3 = H$, this further discrimination is sufficiently pronounced to suppress amine loss completely for $R^2 = R^3 = CH_3$. The effect also operates, albeit less emphatically, in those those systems in which the incipient cation rearranges to a more stable isomer. Thus, for $(CH_3)_2CHCH_2NH^+R^2R^3$, the relative abundance of R^{1+} decreases from 86% for $R^2 = R^3 = H$, through 47% for $R^2 = CH_3$, $R^3 = H$, to 28% for $R^2 = R^3 = CH_3$. This trend is consistent with the mechanism of the Scheme and the relative energetics of the two fragmentation reactions of the activated ions. The details are best discussed in relation to approximate potential energy profiles and the Figure presents such profiles for the isomeric ions $Bu^iNH^+R^2R^3$ and $Bu^tNH^+R^2R^3$.

In these profiles the ion–dipole stabilizations in the alkyl ion complexes with ammonia, methylamine, and dimethylamine are estimated to be 50, 45, and 35 kJ mol^{-1}, respectively, relative to the separated products. The reduction in these stabilizations on progressing from ammonia to dimethylamine reflects the diminution in the permanent electric dipole moments of the amines (1.47 D for ammonia, 1.31 D for methylamine, and 1.03 D for dimethylamine).[22]

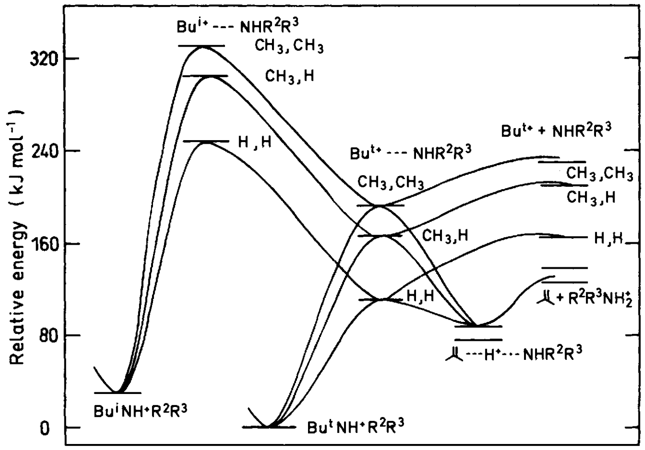


Figure. Potential-energy profiles for fragmentation of $Bu^iNH^+R^2R^3$ and $Bu^tNH^+R^2R^3$

For $Bu^tNH^+R^2R^3$ the ΔH for reaction (1) remains essentially

$$Bu^tNH^+R^2R^3 \longrightarrow R^2R^3NH_2^+ + (CH_3)_2C{=}CH_2 \quad (1)$$

constant with increasing methyl substitution on nitrogen. In essence, as the data of Table 2 show, increasing methyl substitution stabilizes the reactant ion and product ion to the same extent. On the other hand the enthalpy change for reaction (2) increases substantially with increasing methyl substitution

$$Bu^tNH^+R^2R^3 \longrightarrow Bu^{t+} + R^2R^3NH \quad (2)$$

on nitrogen. As a result, reaction (1) becomes increasingly favoured thermochemically, leading to a decrease in importance of the already unimportant amine elimination channel with increasing methyl substitution.

In a similar fashion the enthalpy of Bu^{i+} plus R^2R^3NH, relative to the ground-state-protonated amines, increases with increasing methyl substitution on nitrogen. It is clear that rearrangement and fragmentation of this activated species to $R^2R^3NH_2^+$ plus 2-methylpropene becomes increasingly exothermic while the exothermicity for fragmentation to Bu^{t+} plus

R^2R^3NH remains approximately the same as the methyl substitution increases. As predicted by phase space theory[23] the channel to form $R^2R^3NH_2^+$ plus 2-methylpropene increases in importance with methyl substitution as this reaction channel becomes, relatively speaking, more exothermic.

An additional parameter which probes the details of the potential-energy profiles is the kinetic energy release in the metastable ion fragmentation reaction.[2] Table 3 records the kinetic energy releases, evaluated as $T_{\frac{1}{2}}$,[1] for fragmentation to $R^2R^3NH_2^+$ of the twelve $BuNH^+R^2R^3$ isomers studied. Of particular note are the $T_{\frac{1}{2}}$ values measured for $Bu^tNH^+R^2R^3$, which are 10.8 meV for $R^2 = R^3 = H$, 20.9 meV for $R^2 = CH_3$, $R^3 = H$, and 22.8 meV for $R^2 = R^3 = CH_3$. The potential-energy diagram of the Figure shows that the incipient ion–dipole complex $Bu^t \cdots NH_3$ is lower in energy than the separated products NH_4^+ plus 2-methylpropene. Consequently, a small kinetic energy release would be expected. By contrast the energies $Bu^{t+} \cdots NH_2CH_3$ and $Bu^{t+} \cdots NH(CH_3)_2$ are both greater than the energy of the final protonated amine plus 2-methylpropene products. A portion of the exothermicity of this final rearrangement fragmentation step appears as kinetic energy of the separating products leading to the higher $T_{\frac{1}{2}}$ values observed. As the Figure shows, the energies of the $Bu^{i+} \cdots NHR^2R^3$ complexes all are considerable higher in energy than those of the $Bu^{t+} \cdots NHR^2R^3$ complexes. As expected, a greater kinetic energy release is observed in fragmentation of the isobutyl isomers.

The potential-energy profile for fragmentation of the $Bu^sNH^+R^2R^3$ and related $Bu^nNH^+R^2R^3$ isomers, analogous to the Figure, shows that in all cases the energy of the $Bu^{s+} \cdots NHR^2R^3$ complex is greater than that of the $R^2R^3NH_2^+$ plus but-2-ene products. Hence, fragmentation of this complex is exothermic in all cases and increases in exothermicity with increasing methyl substitution; this is reflected in the $T_{\frac{1}{2}}$ values observed. Again, the rate-determining isomerization of the incipient n-butyl cation to the s-butyl structure leads to the $Bu^{s+} \cdots NHR^2R^3$ species of even higher energy and a consequent increase in the kinetic energy release in the final fragmentation process.

Finally, it is significant that losses of molecular hydrogen and alkanes are not observed in slow low-energy reactions of protonated amines. These processes would give rise to very stable products; for example, reaction (3) has $\Delta H = 9$ kJ mol^{-1}

$$(CH_3)_2CHNH_2^+CH_3 \longrightarrow (CH_3)_2C{=}NH_2^+ + CH_4 \quad (3)$$

$\{\Delta H_f[CH_4] = -75$ kJ mol^{-1},[24] $\Delta H_f[(CH_3)_2C{=}NH_2^+] = 590$ kJ mol^{-1},[25]$\}$, *ca.* 118 kJ mol^{-1} lower than the observed fragmentation reaction of propene expulsion. Clearly there must be a substantial reverse critical energy for 1,2-elimination of alkanes from protonated amines. *Ab initio* calculations[17] have estimated this reverse critical energy to be *ca.* 340 kJ mol^{-1} for methane elimination from protonated isopropylamine. Large energy barriers towards 1,2-eliminations have been uncovered in many other systems.[26]

Conclusion

Metastable ions of general structure $R^1NH^+R^2R^3$ dissociate by losing an olefin $[R^1 - H]$ or by elimination of R^2R^3NH. Ion–dipole complexes are of importance in the reactions of these protonated amines. Loss of R^2R^3NH usually requires more energy than olefin expulsion, which is favoured when R^1 is a secondary or tertiary alkyl group; progressive methylation on nitrogen ($R^2 = R^3 = CH_3$) also increases the relative abundance of olefin loss.

Table 3. Kinetic energy release ($T_{\frac{1}{2}}$ meV ± 0.5) for production of $R^2R^3NH_2^+$ from $BuNH^+R^2R^3$

R^2,R^3	Bu^n	Bu^s	Bu^i	Bu^t
H,H	29.3	24.3	25.0	10.8
CH_3,H	34.0	30.4	27.8	20.9
CH_3,CH_3	33.6	29.8	27.7	22.4

Experimental

The amines required for this work were commercial samples of high purity in the case of the series R^1NH_2. The monomethylamines, R^1NHCH_3, and the dimethylamines, $R^1N(CH_3)_2$, were prepared by routes (4) and (5); after careful fractional distillation, the mass spectra or ^1H n.m.r. spectra of the synthetic amines showed no impurities.

$$R^1NH_2 \xrightarrow[\text{pyridine, 0 °C}]{ClCO_2Et} R^1NHCO_2Et \xrightarrow[Et_2O]{LiAlH_4} R^1NHCH_3 \quad (4)$$

$$R^1NH_2 \xrightarrow[\text{heat}]{CH_2O/HCO_2H} R^1N(CH_3)_2 \quad (5)$$

The unimolecular fragmentation reactions of the protonated amines, which occur in the metastable ion time-frame, were investigated by the MIKES technique[2] using a VG Analytical ZAB-2FQ mass spectrometer.[27] The protonated amines were prepared by chemical ionization methods in a combined EI/CI source, operating in the CI mode, using isobutane as reagent gas for measurement of relative fragment ion intensities and methane as reagent gas when kinetic energy release measurements were made. The ion source was operated at *ca.* 200 °C with 50 eV electron-ionizing energy and 8 kV ion-accelerating potential. The kinetic energy releases are recorded as $T_{\frac{1}{2}}$ values evaluated from the metastable ion peak widths at half-height after correction for the main beam width according to the relation (6),[28] where $W_{\text{met.}}$ is the measured width of the meta-

$$W_{\text{corr.}} = (W_{\text{met.}}^2 - W_{\text{mb}}^2)^{\frac{1}{2}} \quad (6)$$

stable ion signal and W_{mb} is the measured width of the main ion beam for ions formed in the ion source.

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