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THE DIRECT OBSERVATION OF ENERGY RELEASE IN CARBONIUM ION REARRANGEMENTS

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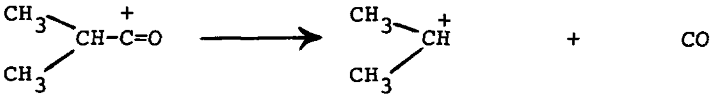
The metastable peaks appearing in a mass spectrum give a direct measure of the kinetic energy released in the dissociation of an ion.[1] Such dissociations normally occur with excess energies in the transition state comparable to those for solution reactions.[2]

Simple, one-step bond-breaking which is continuously endothermic as dissociation occurs must give rise to a relatively narrow metastable peak, since there is no reverse activation energy available to pass into repulsion of products (kinetic energy release). This situation is typified by carbon monoxide loss from the acylium ion <u>1</u> to give the isopropyl cation. From known or estimated heats of formation of reactant and products, the activation energy for this reaction (assuming no reverse activation energy) should be <u>ca</u> 36 kcal mol^{-1}. An approximate experimental determination of the activation energy (by appearance potential measurements) gives <u>ca</u> 29 kcal mol^{-1}, in satisfactory agreement. There is indeed little kinetic energy released in this dissociation (an average of 0.1 kcal mol^{-1}, Table 1), the metastable peak being narrow (Fig. 1a).[3]



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However, carbon monoxide loss from 2 releases much more kinetic energy (Table 1 and Fig. 1b). Clearly, the dissociation is proceeding in a manner different to that of 1 and indeed, the experimental activation energy for dissociation of 2 is *ca* 38 kcal mol^{-1} - appreciably less than that (*ca* 52 kcal mol^{-1}) required to produce $CH_3CH_2CH_2^+$ together with CO. We conclude that after extension of the C-C bond which is to be broken (3), the incipient *n*-propyl ion isomerises to the *iso*propyl ion prior to final departure of CO; some of the potential energy released in the exothermic isomerisation (*ca* 16 kcal mol^{-1})[4] can then fluctuate into the reaction co-ordinate and appear as kinetic energy.

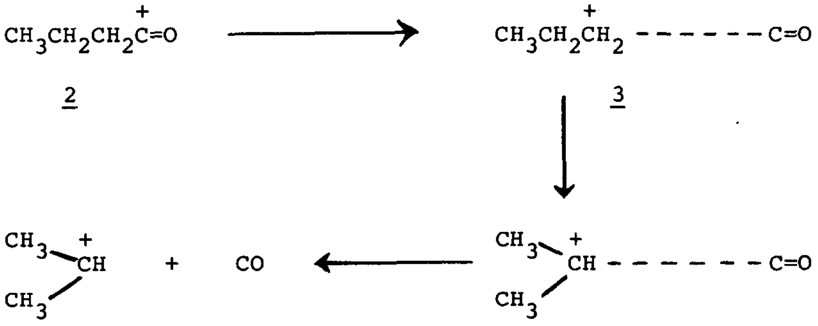
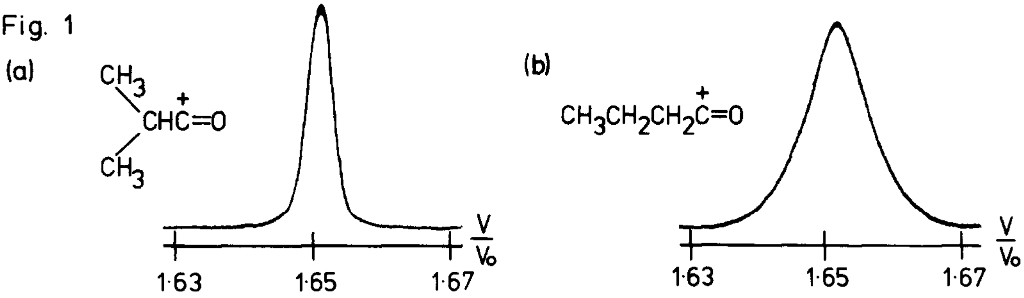
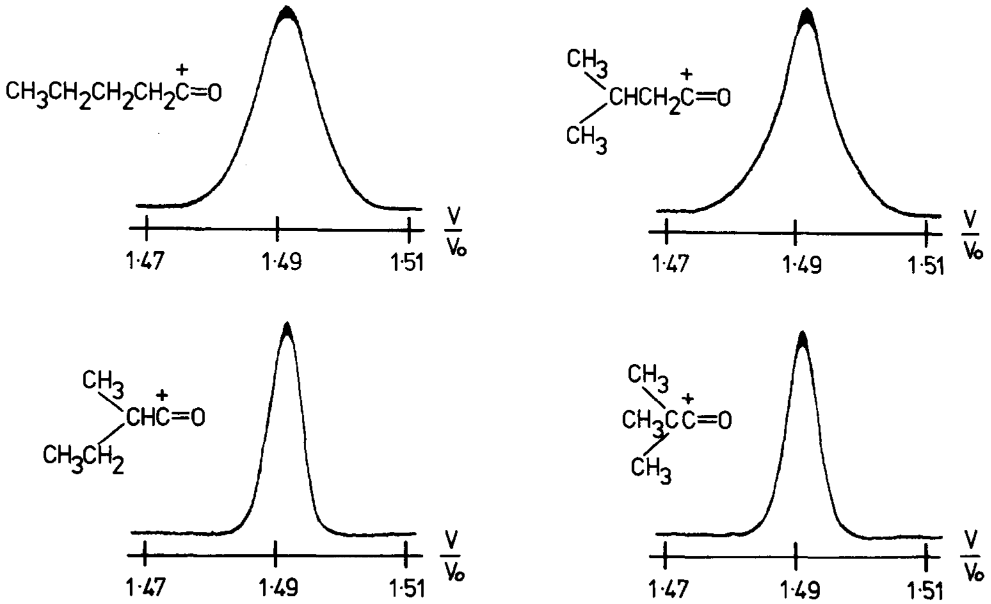


Fig. 1



If the above conclusions are correct, then the expectation is that analogous reactions leading to the homologous butyl ions should occur with little kinetic energy release from $(CH_3)_3C\overset{+}{C}{=}O$ and $CH_3CH_2(CH_3)CH\overset{+}{C}{=}O$ (*t*-C_4H_9 and *sec*-$C_4H_9^+$ cations being stable cations, existing in potential wells); but with a larger kinetic energy release from $CH_3(CH_2)_3\overset{+}{C}{=}O$ and $(CH_3)_2CHCH_2\overset{+}{C}{=}O$, *n*-$C_4H_9^+$ isomerising to *sec*-$C_4H_9^+$ before CO departure and *iso*-$C_4H_9^+$ isomerising to *t*-$C_4H_9^+$ and/or *sec*-$C_4H_9^+$ before CO departure. The peak shapes (Fig. 2)[3] and average kinetic energy releases (Table 1) are in accord with this interpretation. The peak shape for dissociation of $(CH_3)_2CHCH_2\overset{+}{C}{=}O$ is particularly intriguing since it is clearly different to that for dissociation of $CH_3(CH_2)_3\overset{+}{C}{=}O$ (Fig. 2), and shows clear evidence for a broad component superimposed on an even broader component. Such a situation would arise if a 1,2-hydride shift in weakly co-ordinated $(CH_3)_2CH\overset{+}{C}H_2$ were competitive with a 1,2-methyl shift: the former would release ca 32 kcal mol^{-1} of potential energy and the latter ca 16 kcal mol^{-1}.[4]

Fig. 2



Finally, the phenomenon should be general in higher incipient alkyl cations, and possibly occur with leaving groups other than CO. This is seen to be the case for the incipient C_5 cations in Table 1, and also where $Br^{\cdot}$ is the leaving group.

The following points are particularly noteworthy: (i) among those compounds where X is attached to a $-CH_2-$ group, only when R is CH_3CH_2 does a relatively narrow peak result from loss of X, since here isomerisation to a more stable cation is not possible (ii) only when R^+ formally corresponds to $CH_3\overset{+}{C}HCH(CH_3)_2$ is a kinetic energy release > 0.35 kcal mol^{-1} observed for those cases which lead to secondary cations in the absence of rearrangement; only in this case can a secondary ion isomerise to a tertiary via a 1,2-shift without first passing through a higher energy (and hence inaccessible) primary ion.

Table 1

Kinetic Energy Release (kcal mol^{-1}) Associated with Loss of X from RX Ions

R^+	X = CO[a]		X = Br·[a]	
	1FFR	2FFR	1FFR	2FFR
$CH_3CH_2^+$	0.1	0.1	-	-
$CH_3CH_2CH_2^+$	0.8	0.7	0.5	0.5
$CH_3\overset{+}{C}HCH_3$	0.1	0.1	0.1	0.3[b]
$CH_3CH_2CH_2CH_2^+$	1.0	1.0	0.5	0.4
$CH_3CH_2\overset{+}{C}HCH_3$	0.3	0.2	0.1(5)	-
$(CH_3)_2CH\overset{+}{C}H_2$	0.8	1.1	1.0[c]	1.8[c]
$(CH_3)_3C^+$	0.3	0.2	-	-
$CH_3CH_2CH_2CH_2CH_2^+$	1.1	0.9	0.5	0.4
$CH_3CH_2CH_2\overset{+}{C}HCH_3$	0.3(5)	0.3	-	-
$CH_3CH_2\overset{+}{C}HCH_2CH_3$	0.3	0.3	-	-
$(CH_3)_2CHCH_2\overset{+}{C}H_2$	2.0	-	0.9[c]	1.5[c]
$(CH_3)_3C\overset{+}{C}H_2$	1.1	-	0.5	0.8[b]
$(CH_3)_2\overset{+}{C}CH_2CH_3$	0.3	0.3	-	-
$CH_3CH_2(CH_3)CH\overset{+}{C}H_2$	2.1	-	-	-
$CH_3\overset{+}{C}HCH(CH_3)_2$	0.5	-	-	-

[a] 1FFR and 2FFR denote values obtained in the first and second field-free regions, respectively; the values given correspond to the kinetic energy release at half-height.

[b] Weak signal, data less reliable.

[c] Overlapping isotope peaks; the value given is a lower limit for the KE release.

References and Footnotes

1. J.H. Beynon and A.E. Fontaine, Z. Naturforsch. A, 1967, 22, 334.
2. See, for example, D. H. Williams, Accts. Chem. Res., 1977, 10, 280.
3. First field-free region metastable peaks; the abscissae are in units of V/V_O, where V_O is the accelerating voltage used to transmit the main beam, and V the corresponding voltage required to transmit alkyl cations formed in the first field-free region.
4. F. P. Lossing and G.P. Semeluk, Canad. J. Chem., 1970, 48, 955.