

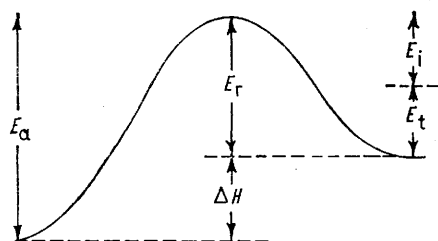
## Partitioning of Reverse Activation Energy between Kinetic and Internal Energy in Reactions of Some Simple Organic Ions

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Nine unimolecular reactions, in which simple organic cations lose molecular hydrogen, have been studied. For each reaction, the structures of the products are either unambiguous, or may be plausibly inferred. From appearance potential measurements, and metastable peak widths, it is possible to evaluate the forward and reverse activation energies, and the partitioning of reverse activation energy between kinetic and internal energy.

Mass spectrometers are convenient devices for producing a beam of positive ions, such that some of them are sufficiently energized to undergo unimolecular decomposition. If the unimolecular decompositions are monitored as reactions occurring after a few  $\mu\text{s}$  (as metastable peaks), then reaction is occurring only after some  $10^8$  vibrations of the energized ion and as a consequence does so with relatively little non-field energy in the transition state. The relatively large isotope effects for C-D versus C-H bond stretching in the transition state (isotope effects frequently comparable with,<sup>1</sup> or much larger than,<sup>2</sup> those observed in solution chemistry near ambient temperatures) attest to the relatively small amount of energy present in activated complexes appropriate to metastable transitions.

Thus, the metastable transition observed from a given precursor ion identifies its lowest activation energy unimolecular decomposition, and the activation energy



Energy diagram for metastable transitions

( $E_a$ ) for the decomposition can, in a reasonable approximation, be determined from appearance potential measurements. The reaction may also be associated with a reverse activation energy ( $E_r$ ) which, in the case of the forward reaction may be partitioned between translational (kinetic) ( $E_t$ ) and internal energy ( $E_i$ ) of the products. For the reasons above, any excess energy present in the activated complex is neglected for our present purposes, and the situation summarised as shown in the Figure. Some years ago, Beynon and his co-workers<sup>3,4</sup> showed that the width of a flat-topped or dished metastable peak can be used to evaluate the translational energy release ( $E_t$ ) in these relatively slow unimolecular reactions. Thus, if the heats of formation of the products of the unimolecular decomposition are

<sup>1</sup> I. Howe and F. W. McLafferty, *J. Amer. Chem. Soc.*, 1971, **93**, 99.

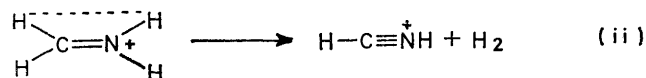
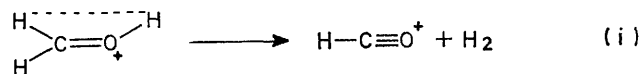
<sup>2</sup> U. Löhle and Ch. Ottinger, *J. Chem. Phys.*, 1969, **51**, 3097.

<sup>3</sup> J. H. Beynon, R. A. Saunders, and A. E. Williams, *Z. Naturforsch.*, 1965, **20a**, 180.

<sup>4</sup> J. H. Beynon and A. E. Fontaine, *Z. Naturforsch.*, 1967, **22a**, 334.

known,  $E_r$  is known and the partitioning of this reverse activation energy between translational energy and internal energy can be investigated.<sup>5</sup>

Recently, we have examined a number of concerted 1,2-eliminations of molecular hydrogen from simple positive organic ions<sup>6</sup> in terms of orbital symmetry,<sup>7</sup> and concluded that these reactions occur through symmetry forbidden pathways. In the actual reaction pathways, it appears that an intended crossing of two levels is foiled since the energies involved are insufficient to produce the products of dissociation in excited states. However, there is a symmetry imposed barrier to reaction and correlation diagrams reveal that, subsequent to the surface crossing, a molecular orbital is occupied which is characterized by a mutual repulsion between the products.<sup>6,8</sup> The symmetry forbidden nature of the reverse reaction is most easily seen in its description as a [2 + 2] addition.<sup>7</sup> Therefore, such symmetry forbidden dissociations will occur with the release of translational energy,<sup>6</sup> and the (hypothetical) reverse [2 + 2] additions would require relative translational energy of the reactants in order to bring about reaction. Conversely, concerted symmetry allowed dissociations can in principle occur without the release of translational energy, although the release of translational energy which originates from other sources may occur. Thus, a reaction occurring with a relatively large and precise release of kinetic energy (flat-topped or dished metastable peak) may be, but is not necessarily, a symmetry forbidden dissociation. A reaction occurring without a significant release of kinetic energy (gaussian metastable peak with steeply sloping sides) cannot be a concerted symmetry forbidden process of the type described. Two typical symmetry forbidden dissociations to be discussed subsequently in greater detail are reactions (i)<sup>6,8</sup> and (ii).<sup>6</sup>



<sup>5</sup> For a summary of much of the earlier work in this area, see R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, 'Metastable Ions,' Elsevier, Amsterdam, 1973.

<sup>6</sup> D. H. Williams and G. Hvistendahl, *J. Amer. Chem. Soc.*, 1974, **96**, 6753.

<sup>7</sup> R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Verlag Chemie, Weinheim, 1970.










<sup>8</sup> K. C. Smyth and T. W. Shannon, *J. Chem. Phys.*, 1969, **51**, 4633.

The stage is therefore set to study the unimolecular dissociation of some simple organic cations and cation-radicals in terms of energy partitioning measurements and orbital symmetry considerations. The present paper deals mainly with the unimolecular dissociation of ionised ethane and ethylene, and some simple organic cations.

## RESULTS AND DISCUSSION

All heats of formation of neutrals and ions utilised in this study are given in Table 1. Unless otherwise

TABLE 1  
Heat of formation ( $\Delta H_f$ ) (kJ mol<sup>-1</sup>)

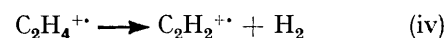
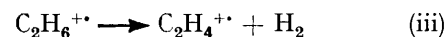
Compound	Neutral		Positive ion			
	$\Delta H_f$	Ref.	$\Delta H_f$	Method <sup>a</sup>	Ref.	Our results
CH <sub>3</sub> CH <sub>3</sub>	-84	9	1024	PI	10	
CH <sub>2</sub> =CH <sub>2</sub>	50	10	1058	S	10	
HC≡CH	225	10	1325	PI	10	
CH <sub>3</sub> CH <sub>2</sub> *	104	10	916	PI	10	
CH <sub>2</sub> =CH*	251	11	1112	EM	11	
CH <sub>3</sub> ĊHCH <sub>3</sub>	75	12	803	EM	13	803 <sup>b</sup>
CH <sub>2</sub> =ĊH-CH <sub>2</sub>	167	11	945	EM	11	
HC≡C-ĊH <sub>2</sub>	339	14	1175	EM	15	
			1071	EM	15	
	108	16	907	RPD	17	
	108	16	945	RPD	17	
			932	EVD	17	961 <sup>c</sup>
			945	EVD	17	
			1191	SL,PI	10	
	{ 92	18	932	VC	18	
			1028	SL	18	
			966	SL	18	870 <sup>d</sup>
			874	S	10	
* CH <sub>2</sub> OH	-4	19	710	RPD	19	
* HC=O	33	19	823	PI	20	
* CH <sub>2</sub> NH <sub>2</sub>			744	PI	10	
* HC=NH			1057	EVD	10	

\* Site of radical or positive charge.

<sup>a</sup> PI = Photo-ionisation, EM = electron monochromator (also used for Lossing's electron energy selector), S = spectroscopic, RPD = retarding potential difference, EVD = extrapolated voltage difference, VC = vanishing current, SL = semi-log plot. <sup>b</sup> From hydrogen radical loss from the propane molecular ion. <sup>c</sup> From hydrogen radical loss from the molecular ion of cyclohexa-1,3-diene. <sup>d</sup> From hydrogen radical loss from the molecular ion of cyclohepta-1,3-diene.

stated, all activation energies and energy partitioning data were obtained in the present study.

*Ethane and Ethylene.*—The unimolecular reactions observed following ionisation of ethane and ethylene are elimination of molecular hydrogen [(iii) and (iv)]. The



relevant data for these reactions are summarised in Table 2.

TABLE 2  
 $\Delta H$ ,  $E_a$ ,  $E_t$ ,  $E_r$ , and  $E_i$  (kJ mol<sup>-1</sup>) for reaction of  $\text{C}_2\text{H}_6^{+\cdot}$  and  $\text{C}_2\text{H}_4^{+\cdot}$

Reaction	$\Delta H$	$E_a$	$E_r$	$E_t$	$E_i$
(iii)	34	53	19	18	1
(iv)	267	234	≤38	0	≤38
		(305) <sup>a</sup>			

<sup>a</sup> Values in parentheses obtained from the *m/e* 26 daughter ion.

The energetics of reaction (iii) have previously been considered by Vestal<sup>21</sup> who used an experimental activation energy of 96 kJ mol<sup>-1</sup>. Our measured activation may be appreciably lower because our determination was carried out on metastable ions (as opposed to daughter ions). Several workers<sup>22,23</sup> have obtained lower appearance potentials from measurements on metastable peaks as opposed to daughter ions. A possible interpretation is that a significantly larger excess of energy is necessary to bring about reactions in the source than as metastable transitions, the latter reactions being associated with somewhat lower rate constants. This interpretation of the differences has recently been questioned,<sup>24</sup> and it appears more likely that measurements on metastable peaks give lower values due to the arbitrary nature of the normalisation procedure in semi-log plots. However, most importantly in the present context, the conclusion of both the present and

<sup>9</sup> D. A. Pittam and G. Pilcher, *J.C.S. Faraday I*, 1972, **68**, 2224.

<sup>10</sup> J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, and K. Draxl, 'Ionisation Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions,' NSRDS-NBS-26, National Bureau of Standards, Washington, 1969.

<sup>11</sup> F. P. Lossing, *Canad. J. Chem.*, 1971, **49**, 357.

<sup>12</sup> J. A. Kerr, *Chem. Rev.*, 1966, **66**, 465.

<sup>13</sup> F. P. Lossing and G. P. Semeluk, *Canad. J. Chem.*, 1970, **48**, 955.

<sup>14</sup> W. Tsang, *Internat. J. Chem. Kinetics*, 1970, **2**, 23.

<sup>15</sup> F. P. Lossing, *Canad. J. Chem.*, 1972, **50**, 3973.

<sup>16</sup> J. L. Franklin, *Ind. Eng. Chem.*, 1949, **41**, 1070.

<sup>17</sup> J. L. Franklin and S. R. Carroll, *J. Amer. Chem. Soc.*, 1969, **91**, 6564.

<sup>18</sup> C. Lifshitz and S. H. Bauer, *J. Phys. Chem.*, 1963, **67**, 1629.

<sup>19</sup> M. A. Haney and J. L. Franklin, *Trans. Faraday Soc.*, 1969, **65**, 1794.

<sup>20</sup> C. S. Matthews and P. Warneck, *J. Chem. Phys.*, 1969, **51**, 854.

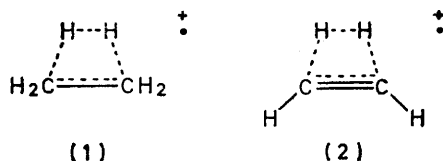
<sup>21</sup> M. L. Vestal in 'Fundamental Processes in Radiation Chemistry,' ed. P. Ausloos, Wiley-Interscience, New York, 1968, ch. 2.

<sup>22</sup> I. Hertel and C. Ottinger, *Z. Naturforsch.*, 1967, **22a**, 40.

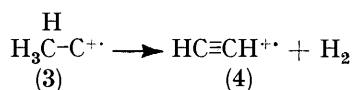
<sup>23</sup> J. H. Beynon, J. A. Hopkinson, and G. R. Lester, *J. Mass Spectrometry Ion Phys.*, 1969, **2**, 291.

<sup>24</sup> T. W. Bentley, R. A. W. Johnstone, and B. N. McMaster, *J.C.S. Chem. Comm.*, 1973, 510.

the earlier study<sup>21</sup> is that much of the reverse activation energy appears as translational energy of the products. Deuterium labelling establishes reaction (iii) to occur via 1,2-elimination,<sup>2,25</sup> and the translational energy release is in accord with a symmetry forbidden reaction occurring through a transition state (1).<sup>6</sup>



The reaction for loss of H<sub>2</sub> from C<sub>2</sub>H<sub>4</sub><sup>+</sup> is in marked contrast to the above case, no significant translational energy being released and the reverse activation energy (if any; see later) being retained as internal energy of the products (Table 2). Isotope effects show this reaction to be concerted,<sup>26</sup> but the absence of translational energy release precludes a concerted 1,2-elimination (2). In a preliminary communication<sup>27</sup> we have therefore formulated this reaction as 1,1-elimination of H<sub>2</sub> through a linear cheletropic pathway<sup>7</sup> from the ionised carbene, resulting in the formation of ionised acetylene (3) → (4).



The orbital analysis of such a pathway has been given previously<sup>27</sup> and is mentioned again subsequently in this paper [e.g., see (7) and (8)]. However, measurements on the metastable peak for the transition *m/e* 28 → 26 consistently give an activation energy which is 33 kJ mol<sup>-1</sup> less than the endothermicity of the reaction on the assumption that the reaction product is ionised acetylene. This discrepancy remains when the measurements have been carried out at various pressures and extrapolated to zero pressure to eliminate any possible collision-induced component. Since the Δ*H*<sub>f</sub> values of ionised ethylene and acetylene are accurately known (Table 1), we conclude that either there is a consistent experimental error in the appearance potential determination or that there is another configuration of the C<sub>2</sub>H<sub>2</sub><sup>+</sup> ion which has a lower heat of formation than ionised acetylene. The former interpretation seems more likely.<sup>24</sup> Appearance potential measurements on the *m/e* 26 daughter ion give an activation energy for reaction that gives an internal energy of 38 kJ mol<sup>-1</sup> to an acetylene ion and hydrogen as products.

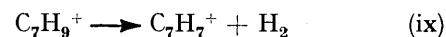
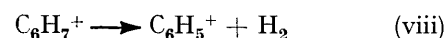
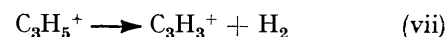
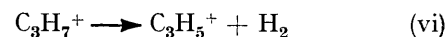
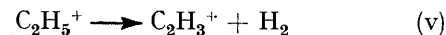
The 1,2-hydrogen shift required to produce (3) from the ethylene ion is in accord with the loss of identity of H and D in specifically deuteriated ethylenes,<sup>28</sup> and is in marked contrast with the specific loss of HD from CH<sub>3</sub>CD<sub>3</sub>.<sup>2,25</sup>

**Molecular Hydrogen Loss from Some Simple Cations.**—The activation energies and energy partitioning data

<sup>25</sup> C. Lifshitz and R. Sternberg, *Int. J. Mass Spectrometry Ion Phys.*, 1969, **2**, 303.

<sup>26</sup> G. Hvistendahl and D. H. Williams, *J.C.S. Chem. Comm.*, 1975, 4.

for reactions (v)—(ix) discussed in this section are given in Table 3.



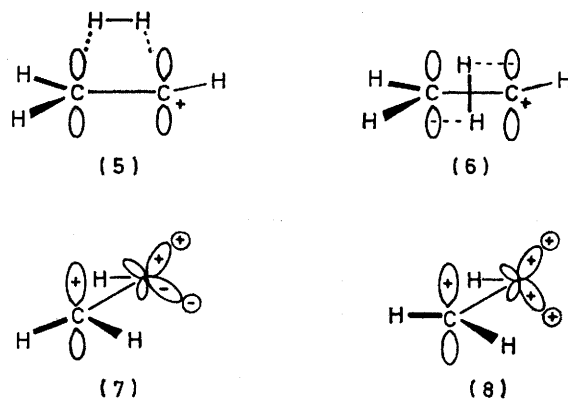
The energy partitioning data for reaction (v) are based on the assumption that the only plausible structure for the product is the vinylium ion. The most

TABLE 3

Reaction	Δ <i>H</i>	<i>E</i> <sub>a</sub>	<i>E</i> <sub>r</sub>	<i>E</i> <sub>t</sub>	<i>E</i> <sub>i</sub>
(v)	196 (200)	280 (230)	84 (30)	~0 (~0)	84 (30)
(vi)	142 (138)	192 (196)	50 (58)	34 (41)	17 (17)
(vii)	{ 230 126	{ 272 272	{ 42 146	{ 13 71	{ 29 75
(viii)	230	272	42	~0	42
(ix)	4	242	238	79	159

<sup>a</sup> Values in parentheses refer to data previously obtained by Vestal.<sup>21</sup>

characteristic feature of the reaction is that it occurs without a significant release of translational energy, and therefore a symmetry forbidden path in which the transition state for reverse reaction is attained through a concerted [2 + 2] suprafacial addition of H<sub>2</sub> to the vinylium ion (5) is excluded. Although it has been emphasized that the vinylium ion is constituted *par excellence* for participation as a π<sub>2a</sub> component in a [π<sub>2s</sub> + π<sub>2a</sub>] cycloaddition,<sup>7</sup> no examples of a σ-bond participating in antarafacial addition to a π-bond appear to have been reported, and the transition state (6) appears unlikely because of the extremely poor orbital overlap between the σ-bond of incipient H<sub>2</sub> and the π-system of an incipient vinylium ion. However, 1,1-elimination of H<sub>2</sub> from the ethyl cation through a linear pathway is an



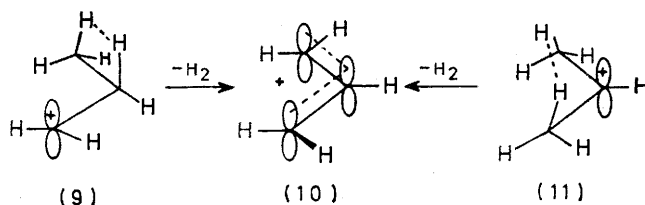
allowed cheletropic reaction, and in accord with the experimental facts may proceed without translational energy release. The product ion is again the vinylium

<sup>27</sup> D. H. Williams and G. Hvistendahl, *J. Amer. Chem. Soc.*, 1974, **96**, 6755.

<sup>28</sup> I. Baumel, R. Hagemann, and R. Botter, 19th Annual Conference on Mass Spectrometry and Allied Topics, Committee E.14, ASTM, Atlanta, 1971.

ion. The 1,1-elimination allows two electrons from the antisymmetric  $\sigma$ -orbital (7) to pass into the  $\pi$ -orbital of the vinylum ion, while two electrons from the symmetric  $\sigma$ -orbital (8) pass into the  $\sigma$ -bond of  $H_2$ .<sup>27</sup>

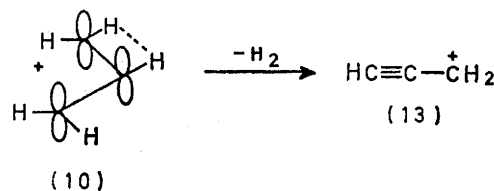
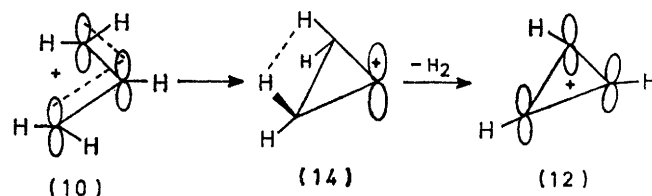
The data for the loss of  $H_2$  from  $C_3H_7^+$  are referred to the ground state of the secondary  $C_3H_7^+$  cation as the starting point for reaction. In contrast to the loss of  $H_2$  from the ethyl cation, the reaction on the  $C_3$  manifold is characterised by (a) a markedly lower activation energy (192 versus 280 kJ mol<sup>-1</sup>) and a translational energy release (34 versus 0 kJ mol<sup>-1</sup>). It might be anticipated that the nature of the potential surface would fundamentally change on passing from reaction (v) to (vi) since in the decomposition of the higher homologue, there is the possibility of producing the allyl ion as a product, rather than a vinylum ion. Energetic considerations show that even with the allyl ion as product (the most stable species on the  $C_3H_5^+$  manifold<sup>29</sup>) the available energy only allows 17 kJ mol<sup>-1</sup> of internal energy of products (Table 3). In the light of these considerations, and the release of 33 kJ mol<sup>-1</sup> of kinetic energy in the reaction, it is formulated as a concerted,<sup>26,27</sup> symmetry forbidden 1,2- or 1,3-elimination from the n-propyl or s-propyl cation, respectively [(9)  $\rightarrow$  (10) or (11)  $\rightarrow$  (10)].



The loss of  $H_2$  from  $C_3H_5^+$  [reaction (vii)] is particularly interesting because the metastable peak for this process is a composite one, establishing that two potential surfaces are involved; one reaction occurs with the release of 71 kJ mol<sup>-1</sup> of translational energy and the other with release of 13 kJ mol<sup>-1</sup>.<sup>30</sup> Our own measurements establish that in metastable transitions these processes compete in the same ratio over a wide range of electron beam energies, and even down to electron beam energies near to the thresholds for the two reactions. In addition, the ionisation efficiency curve for the  $m/e$  42  $\rightarrow$  39 metastable transition shows no break. We conclude that the two reactions have very similar activation energies (272 kJ mol<sup>-1</sup>, referenced to the allyl ion as the most stable species on the  $C_3H_5^+$  manifold). We assume that the possible products of reaction which are most worthy of consideration are the cyclopropenyl cation (12) and the propargyl cation (13) ( $\Delta H_f^\circ$  values given in Table 1). The total energy content of the products formed with release of 71 kJ mol<sup>-1</sup> is 1145 kJ mol<sup>-1</sup>, insufficient to allow the generation of (13) ( $\Delta H_f^\circ$  1175 kJ mol<sup>-1</sup>). Thus energetic considerations suggest that the only possible product of the reaction occurring with a large release of kinetic energy is (12), the most stable structure on the  $C_3H_3^+$  manifold. Starting

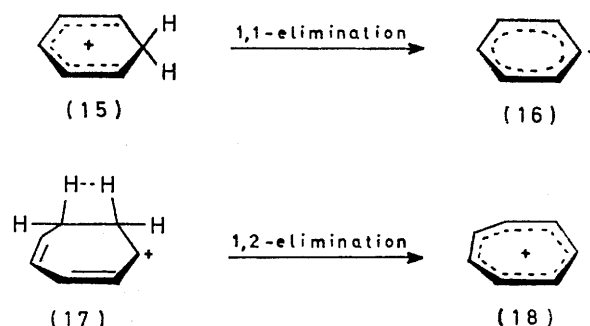
<sup>29</sup> L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1973, **95**, 6531.

from the allyl ion, the reaction may proceed through conrotatory closure to the cyclopropyl cation (14), followed by symmetry forbidden 1,2-elimination of  $H_2$ , occurring as required<sup>6</sup> with a large release of kinetic energy.



The second reaction if assumed to result in the production of (13) (as in Table 3) may be formulated in terms of 1,2-elimination from the allyl cation [(10)  $\rightarrow$  (13)]. Such a pathway would require the release of translational energy,<sup>6</sup> as observed (13 kJ mol<sup>-1</sup>).

Reactions (viii) and (ix) have been formulated in terms of (15)  $\rightarrow$  (16) and (17)  $\rightarrow$  (18) [1,3-elimination of  $H_2$  is a viable alternative in the production of (18)] for reasons outlined in our preliminary communication.<sup>27</sup> The complete energy partitioning data (Table 3) show that (17)  $\rightarrow$  (18) is approximately thermoneutral, and the reverse activation energy large, so that (18), and  $H_2$  are produced with considerable internal energy, despite the large kinetic energy release associated with reaction.



*Molecular Hydrogen Loss from Protonated Formaldehyde and Protonated Methyleneimine.*—These reactions are given in equations (i) and (ii), and it has previously been inferred that the proven concerted 1,2-eliminations are symmetry forbidden reactions.<sup>6</sup> We now give the energy partitioning data for these two reactions (Table 4). It is apparent that the hypothetical reverse reactions occurring through the same channels require much more internal energy for the

<sup>30</sup> P. Goldberg, J. A. Hopkinson, A. Mathias, and A. E. Williams, *Org. Mass Spectrometry*, 1970, 1009.

addition of H<sub>2</sub> to formyl ion than to protonated HCN, while both reactions require a relatively large amount of translational energy.

TABLE 4

$\Delta H$ ,  $E_a$ ,  $E_r$ ,  $E_t$ , and  $E_i$  (kJ mol<sup>-1</sup>) for reactions (i) and (ii)

Reaction	$\Delta H$	$E_a$	$E_r$	$E_t$	$E_i$
(i)	113	335	222	138	84
(ii)	313	405	92	84	8

Although many ion-molecule reactions occur with a small or negligible activation energy,<sup>31</sup> it is evident from the data given in Tables 3 and 4 that a number of the dissociations considered in this work have large reverse activation energies. Particularly noteworthy in this respect is the addition of H<sub>2</sub> to the formyl ion requiring 222 kJ mol<sup>-1</sup> and the addition of H<sub>2</sub> to the (assumed) tropylium ion requiring 238 kJ mol<sup>-1</sup>.

#### EXPERIMENTAL

All measurements were carried out on an AEI MS9 mass spectrometer fitted with a variable monitor slit,<sup>32</sup> and metastable refocusing unit to allow observation of metastable transitions occurring in front of the electric sector (first field-free region metastable peaks).<sup>33</sup>

The ionisation efficiency (IE) curves of metastable peaks were recorded from decomposition occurring in the first field-free regions. Simple modification of the existing metastable refocusing unit allowed the electric sector analyser voltage to be lowered while keeping the acceler-

<sup>31</sup> See, for example, P. F. Knewstubb, 'Mass Spectrometry and Ion-Molecule Reactions,' Cambridge University Press, Cambridge, 1969.

<sup>32</sup> J. H. Beynon, W. E. Baitinger, J. W. Amy, and T. Komatsu, *J. Mass Spectrometry Ion Phys.*, 1969, **3**, 47.

ating voltage constant at 8 kV. Under these conditions, an appropriate lowering of the electric sector analyser voltage allows observation of the first field-free region metastable transition for a selected reaction;<sup>34</sup> the intensity of the metastable peak increased by about an order of magnitude compared to the corresponding transition in the second field-free region (in front of the magnetic analyser) at the same multiplier voltage. To obtain maximum sensitivity the monitor slit was kept wide open for the IE curve measurements, and the trap current was at 100  $\mu$ A. During measurement of the ionisation potentials (IP), the trap current was set to 20  $\mu$ A.

Due to the high sensitivity for the detection of metastable peaks, the source pressure could be kept at reasonably low values ( $2 \times 10^{-6}$  Torr), thus minimising possible collision induced processes. No significant increase in the analyser pressure was detected. Furthermore, where comparison is possible, appearance potentials determined in the present work agree well with literature values (except where noted as otherwise in the text). Contributions from collision induced reactions are therefore considered to be unimportant.

The IE curves were interpreted by the semi-log plot method.<sup>35</sup> All curves were parallel with those of the reference compound, argon, and reproducibility of the results was good (normally  $< \pm 0.1$  eV;  $\pm 10$  kJ mol<sup>-1</sup>).

All translational energy releases were computed from second field-free region metastable transitions.

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<sup>33</sup> K. R. Jennings, *J. Chem. Phys.*, 1965, **43**, 4176.

<sup>34</sup> F. W. McLafferty, J. Okamoto, H. Tsuyama, Y. Nakajima, T. Noda, and H. W. Major, *Org. Mass Spectrometry*, 1969, **2**, 751.

<sup>35</sup> F. P. Lossing, A. W. Tickner, and W. A. Bryce, *J. Chem. Phys.*, 1951, **19**, 1254.