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Ion-Neutral Complexes as Intermediates in the Decompositions of $C_5H_{10}O_2^{\cdot +}$ Isomers

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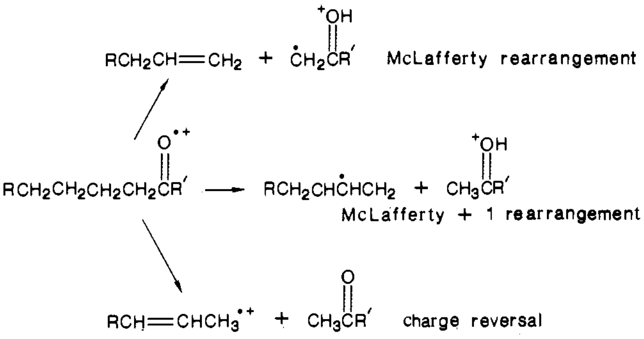
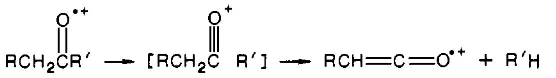
Abstract: Ionized pentanoic acid, 3-methylbutanoic acid, and the enol isomer of ionized isopropyl acetate are shown to pass in part through common intermediates before decomposing to $CH_3\dot{C}HC(OH)_2^+$ (7) and the "McLafferty + 1" ion $CH_3C(OH)_2^+$ (**10**). The H transfer to form the methyl of $CH_3C(OH)_2^+$ and the joining of two CH_2 groups to form the C–C bond in the ethylene eliminated to produce $CH_3\dot{C}HC(OH)_2^+$ are both attributed to reactions of the ion–neutral complex [$CH_3CH{=}CH_2$ $\dot{C}H_2C(OH)_2^+$]. The McLafferty + 1 ion is also formed, especially from ionized esters, by another pathway in which complexes may or may not be intermediates. The intermediacy of the ion–neutral complexes is supported by energetic considerations, isotope effects, and the decomposition patterns of labeled ions. The latter correlate with a preference for hydrogen transfer from the end carbons of the C_3 partner in other reactions proposed to be complex-mediated. Unification of the McLafferty rearrangement, the McLafferty + 1 rearrangement, and the McLafferty rearrangement with charge reversal by a common initial γ-hydrogen rearrangement followed by dissociation or isomerization in ion-neutral complexes is proposed. Group migration by 1,2-shifts, possibly by dissociation to form a double bond in one partner in an ion-neutral complex followed by addition at the opposite end of the double bond, is shown to be a general reaction of ions in the gas phase.

"McLafferty + 1" ions are formed in the mass spectrometer by double hydrogen transfers accompanied by β-cleavage in ionized esters,[1] acids,[2] ketones,[3] and other ions.[4] These ions are formed



in parallel with the McLafferty rearrangement and the McLafferty rearrangement with charge reversal. Despite much study,[1-4] satisfactory mechanisms for formation of many McLafferty + 1 ions have never been proposed. Issues have included whether the two hydrogen transfers are stepwise or simultaneous,[1c,d] and, if stepwise, which hydrogen is transferred first.[2a] However, the most significant question is: how do bonds to itinerant hydrogens from alkyl chains replace the C–C bonds cleaved in the decompositions? Alkane eliminations from ions in the gas phase, which also involve replacement of a C–C by a C–H bond, probably achieve this by cleavage to ion–neutral complexes followed by hydrogen abstraction:[5]



$$RCH_2\overset{O^{\cdot +}}{\overset{\|}{C}}R' \longrightarrow [RCH_2\overset{O^{+}}{\overset{|||}{C}}\ R'] \longrightarrow RCH{=}C{=}O^{\cdot +} + R'H$$

Similar steps have been suggested for formation of McLafferty + 1 ions.[5b] Passage through electrostatically bound complexes has been proposed[6] to rationalize products of many other ionic decompositions in the gas phase. Audier and Sozzi[7] have shown that ionized 3-methylbutanoic acid (**2**) produces the McLafferty + 1 ion $CH_3C(OH)_2^+$ containing C1 and C2, and $C_3H_6O_2^{\cdot +}$ containing C1, C3, and a C4. This suggested[8] a mechanism for $CH_3C(OH)_2^+$ formation involving the complex [$CH_3CH{=}CH_2$ $\dot{C}H_2C(OH)_2^+$] that could be tested by characterizing the parallel formation of $C_3H_6O_2^{\cdot +}$ (see Scheme I). This mechanism would also have to apply to $CH_3C(OH)_2^+$ and $CH_3\dot{C}HC(OH)_2^{\cdot +}$ formation from ionized pentanoic acid (**1**), as **1** and **2** reach those products through common intermediates.[9] We will conclude that ion–neutral complexes are intermediates in the formation of McLafferty + 1 ions and then show that a variety of ionic decompositions can be rationalized by related mechanisms. A similar mechanism has been recently proposed to account for formation of acetic acid plus ionized 2-butene from ionized hexanoic acid.[10]

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(1) (a) Sharkey, A. G.; Schultz, J. L.; Friedel, R. A. *Anal. Chem.* **1959**, *31*, 87–94. (b) Beynon, J. H.; Saunders, R. A.; Williams, A. E. *Ibid.* **1961**, *33*, 221–225. (c) Godbole, E. W.; Kebarle, P. *Trans. Faraday Soc.* **1962**, *58*, 1897–1904. (d) Djerassi, C.; Fenselau, C. *J. Am. Chem. Soc.* **1965**, *87*, 5756–5762. (e) McFadden, W. H.; Boggs, L. E.; Buttery, R. G. *J. Phys. Chem.* **1966**, *70*, 3516–3523. (f) Benoit, F. M.; Harrison, A. G.; Lossing, F. P. *Org. Mass Spectrom.* **1977**, *12*, 78–82. (g) Borchers, F.; Levsen, K. *Int. J. Mass Spectrom. Ion Phys.* **1979**, *31*, 247–256.

(2) (a) Weber, R.; Levsen, K.; Wesdemiotis, C.; Weiske, T.; Schwarz, H. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *43*, 131–155. (b) Halim, H.; Schwarz, H.; Terlouw, J. K.; Levsen, K. *Org. Mass Spectrom.* **1983**, *18*, 147–149.

(3) (a) Carpenter, W.; Duffield, A. M.; Djerassi, C. *J. Am. Chem. Soc.* **1968**, *90*, 160–164. (b) Bente, P. F.; McLafferty, F. W.; McAdoo, D. J.; Lifshitz, C. *J. Phys. Chem.* **1975**, *79*, 713–721.

(4) McLafferty, F. W. *Chem. Ind.* (*London*) **1958**, 1366–1367.

(5) (a) Wendelboe, J. F.; Bowen, R. D.; Williams, D. H. *J. Am. Chem. Soc.* **1981**, *103*, 2333–2339. (b) Hudson, C. E.; McAdoo, D. J. *Int. J. Mass Spectrom. Ion Processes* **1984**, *59*, 325–332. (c) Traeger, J. C.; Hudson, C. E.; McAdoo, D. J. *J. Phys. Chem.*, in press. (d) McAdoo, D. J.; Traeger, J. C.; Hudson, C. E.; Griffin, L. L. *J. Phys. Chem.*, in press.

(6) (a) Bowen, R. D.; Stapleton, B. J.; Williams, D. H. *Chem. Commun.* **1978**, 24–26. (b) Bowen, R. D.; Williams, D. H. *Int. J. Mass Spectrom. Ion Phys.* **1979**, *29*, 47–55. (c) Morton, T. H. *J. Am. Chem. Soc.* **1980**, *102*, 1596–1602. (d) Hall, D. G.; Morton, T. H. *Ibid.* **1980**, *102*, 5688–5691. (e) Longevialle, P. *Chem. Commun.* **1980**, 823–825. (f) Schwarz, H.; Stahl, D. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *36*, 285–289. (g) Biermann, H. W.; Freeman, W. P.; Morton, T. H. *J. Am. Chem. Soc.* **1982**, *104*, 2307–2308. (h) Morton, T. H. *Tetrahedron* **1982**, *38*, 3195–3243. (i) Longevialle, P.; Botter, R. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *47*, 179–182. (j) Tumas, W.; Foster, R. F.; Brauman, J. I. *J. Am. Chem. Soc.* **1984**, *106*, 4053–4054. (k) Holmes, J. L.; Mommers, A. A.; Szulejko, J. E.; Terlouw, J. K. *Chem. Commun.* **1984**, 165–167. (l) Longevialle, P. *Org. Mass Spectrom.* **1985**, *20*, 644–645. (m) Bather, W.; Grutzmacher, H. *Int. J. Mass Spectrom. Ion Processes* **1985**, *64*, 193–212.

(7) Audier, H. E.; Sozzi, G. *Org. Mass Spectrom.* **1984**, *19*, 150–151.

(8) (a) McAdoo, D. J.; Hudson, C. E. *Adv. Mass Spectrom.* **1985**, 823. (b) Hudson, C. E., Griffin, L. L.; Broido, E.; Skyiepal, M. D.; McAdoo, D. J. *Proc. 34th Annu. Conf. Mass Spectrom. Allied Top.* **1986**, 983–984.

(9) (a) Audier, H.; Milliet, A.; Sozzi, G. *Bull. Soc. Chim. Fr.* **1985**, 833. (b) Audier, H.; Sozzi, G. *Nouv. J. Chim.*, in press.

(10) van Baar, B. L. M.; Terlouw, J. K.; Akkok, S.; Zummack, K. W.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes*, in press.

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Scheme I

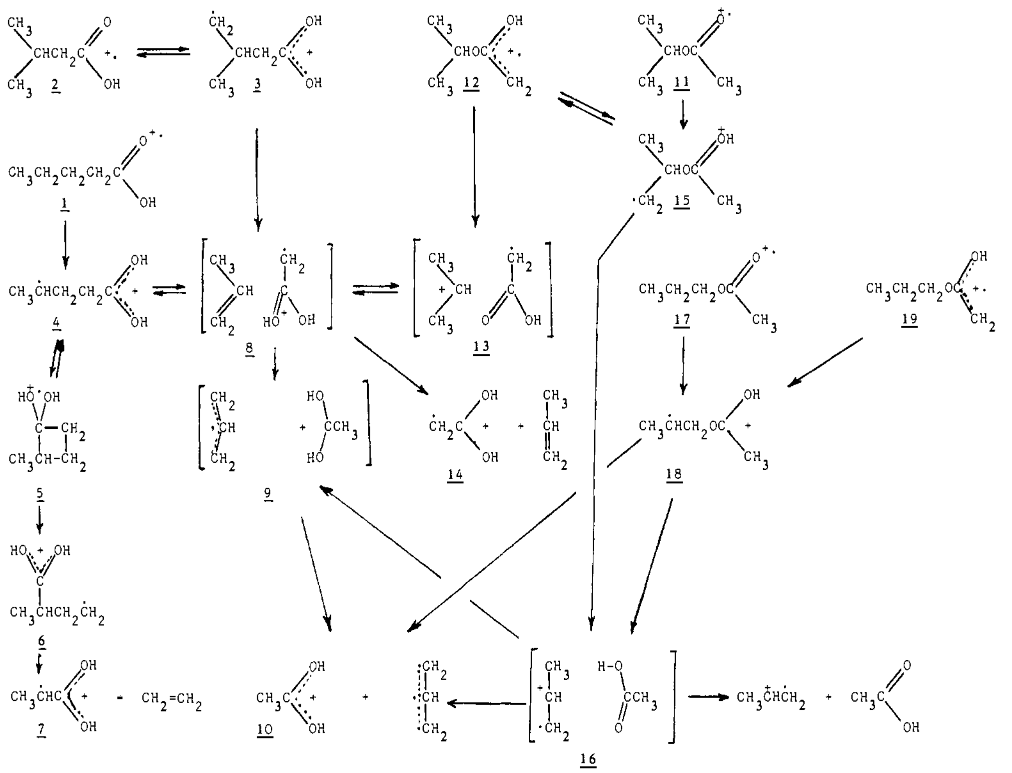


Table I. Decomposition Patterns of Metastable $C_5H_{10}O_2^{\bullet+}$ Ions

ion	product				
	$\dot{C}H_2C(OH)_2^+$	$CH_3C(OH)_2^+$	$CH_2{=}CHC(OH)_2^+$	$CH_3\dot{C}HC(OH)_2^+$	$C_4H_7O_2^+$
$CH_3CH_2CH_2CH_2CO_2H^{\bullet+}$	3	94	100	39	50
$CH_3CH_2CH_2\dot{C}HC(OH)_2^+$		0.6	100	0.3	2
$(CH_3)_2CHCH_2CO_2H^{\bullet+}$	2	100	2	63	51
$(CH_3)_2CH\dot{C}HC(OH)_2^+$			9		100
$CH_3CH_2CH(CH_3)CO_2H^{\bullet+}$		2		1	100
$CH_3CH_2\dot{C}(CH_3)C(OH)_2^+$			49	0.3	100
$CH_3CO_2^{\bullet+}CH(CH_3)_2$		100		2	0.4
$\dot{C}H_2C(OH)OCH(CH_3)^+$	3	100		8	
$CH_3CO_2^{\bullet+}CH_2CH_3CH_3$		100			5
$\dot{C}H_2C(OH)OCH_2CH_2CH_3^+$	1	100			4

Table II. Decomposition Patterns of $^{13}CC_4H_{10}O_2^{\bullet+}$ Ions

ion	product[a]						
	$CH_3C(OH)_2^+$	$^{13}CH_3C(OH)_2^+$	m/z 73	m/z 74	$^{13}CC_2H_6O_2^{\bullet+}$	$C_4H_7O_2^+$	$^{13}CC_3H_7O_2^+$
$CH_3CH_2{}^{13}CH_2CH_2CO_2H^{\bullet+}$	100		42	81	15[b] (17)	1	25
$CH_3{}^{13}CH_2CH_2CH_2CO_2H^{\bullet+}$	100		47	51	31 (32)		51
$^{13}CH_3CH_2CH_2CH_2CO_2^{\bullet+}H$	100	2	37	68	32[c] (18)	36	31
$\dot{C}H_2C(^+OH)O^{13}CH(CH_3)_2$	100	2		0.6	12		

[a] Values in parentheses were obtained from decompositions in the first field-free region of a DuPont 21-491 mass spectrometer. [b] First field-free region = 9. [c] First field-free region = 10.

Table III. $C_2(H,D)_5O_2^{+\bullet}$ Patterns from Metastable $C_5(H,D)_{10}O_2^{\bullet+}$ Ions Derived from Acids

ion	product[a]			
	$C_2H_5O_2^+$	$C_2H_4DO_2^+$	$C_2H_3D_2O_2^+$	$C_2H_2D_3O^+$
$CH_3CH_2CH_2CH_2CO_2D^{\bullet+}$	88	56		
$CH_3CH_2CH_2CD_2CO_2H^{\bullet+}$	8	10	69	
$CH_3CH_2CD_2CH_2CO_2H^{\bullet+}$	33	37	4	
$CH_3CD_2CH_2CH_2CO_2H^{\bullet+}$	100	70	3	
$CD_3CH_2CH_2CH_2CO_2H^{\bullet+}$	31	92	39	1
$(CH_3)_2CHCH_2CO_2D^{\bullet+}$	100	75		
$CH_3CH(CD_3)CH_2CO_2H^{\bullet+}$	26	100	41	
$(CH_3)_2CHCD_2CO_2H^{\bullet+}$		5	100	

[a] Each value is normalized to the most intense peak in the spectrum = 100. This intensity may appear in Table IV, or may be due to $C_4(H,D)_7O_2^+$ formation.

Table IV. $C_3(H,D)_5O_2^+ + C_3(H,D)_6O_2^{\bullet+}$ Patterns from Metastable $C_5(H,D)_{10}O_2^{\bullet+}$ Ions Derived from Acids

ion	product m/z[a]				
	73	74	75	76	77
$CH_3CH_2CH_2CH_2CO_2D^{\bullet+}$	4	100	96		
$CH_3CH_2CH_2CD_2CO_2H^{\bullet+}$	56	56	100	2	
$CH_3CH_2CD_2CH_2CO_2H^{\bullet+}$	31	16	100	25	
$CH_3CD_2CH_2CH_2CO_2H^{\bullet+}$	79	3	100	62	
$CD_3CH_2CH_2CH_2CO_2H^{\bullet+}$	54	68	57	59	64
$(CH_3)_2CHCH_2CO_2D^{\bullet+}$	3	25	71		
$CH_3CH(CD_3)CH_2CO_2H^{\bullet+}$			27	43	47
$(CH_3)_2CHCD_2CO_2H^{\bullet+}$		60			

[a] Values normalized as in Table III.

Results and Discussion

Similarity of the Decompositions of $CH_3CH_2CH_2CH_2CO_2H^{\bullet+}$, $(CH_3)_2CHCH_2CO_2H^{\bullet+}$, and $\dot{C}H_2C(^+OH)OCH(CH_3)_2$. Metastable decomposition patterns of assorted $C_5H_{10}O_2^{\bullet+}$ isomers and labeled forms thereof are given in Tables I–VI. The $C_5H_{10}O_2^{\bullet+}$ spectra divide roughly into those dominated by $CH_3C(OH)_2^+$ and $C_3H_6O_2^{\bullet+}$ formation and those dominated by $C_3H_5O_2^+$ and/or

Table V. $C_2(H,D)_5O_2^+$ Products of Metastable $C_5(H,D)_{10}O_2^{\cdot +}$ Ester Ions

	product[b]				
ion	$C_2H_5O_2^{\cdot +}$	$C_2H_4DO_2^+$	$C_2H_3D_2O_2^+$	$C_2H_3D_2O_2^+$	$C_2HD_4O_2^+$
$\dot{C}D_2C(^+OH)OCH(CH_3)_2$		10	100		
$CD_3CO_2^{\cdot +}CH(CH_3)_2$				100	
$\dot{C}H_2C(^+OH)OCD(CH_3)_2$	100	3.1			
$CH_3CO_2^{\cdot +}CD(CH_3)_2$	100	3			
$\dot{C}H_2C(^+OH)OCH(CD_3)_2$	9[a]	14	100	22	
$\dot{C}H_2C(^*OH)OCH(CD_3)CH_3$	3	100			
$CH_3CO_2^{\cdot +}CH(CD_3)_2$	1.5[a]	1.5	100	3	0.7
$CH_3CO_2^{\cdot +}CH(CD_3)CH_3$	2	100	3		
$CD_3CO_2^{\cdot +}CH_2CH_2CH_3$			4	100	
$CH_3CO_2^{\cdot +}CD_2CH_2CH_3$	100	19			
$CH_3CO_2^{\cdot +}CH_2CD_2CH_3$	2	100			
$CH_3CO_2^{\cdot +}CH_2CH_2CD_3$	1	100	2		
$\dot{C}H_2C(^+OH)OCD_2CH_2CH_3$	100	11			
$\dot{C}H_2C(^+OH)OCH_2CD_2CH_3$	1	100[c]			
$\dot{C}H_2C(^+OH)OCH_2CH_2CD_3$		100[d]	2		

[a] $C_2H_3DO_2^{\cdot +}$. [b] Values normalized similarly to those in Table III. [c,d] Water losses in the CAD spectra of products of metastable decomposition demonstrate near exclusive formation of [c]$CH_2DC(OH)_2^+$ and [d]$CH_3C(OD)OH^+$.

Table VI. $C_3(H,D)_6O_2^{\cdot +}$ Products of Metastable $C_5(H,D)_{10}O_2^{\cdot +}$ Ester Ions

	product[a]					
ion	$C_3H_6O_2^{\cdot +}$	$C_3H_5DO_2^{\cdot +}$	$C_3H_4D_2O_2^{\cdot +}$	$C_3H_3D_3O_2^{\cdot +}$	$C_3H_2D_4O_2^{\cdot +}$	$C_3HD_5O_2^{\cdot +}$
$\dot{C}D_2C(^+OH)OCH(CH_3)_2$	16	1.1	1.8			
$CD_3CO_2^{\cdot +}CH(CH_3)_2$						
$\dot{C}H_2C(^+OH)OCD(CH_3)_2$	≤0.2					
$CH_3CO_2^{\cdot +}CD(CH_3)_2$	1.2	2.4				
$\dot{C}H_2C(^+OH)OCH(CD_3)_2$				<0.2	54	15
$\dot{C}H_2C(^+OH)OCH(CD_3)CH_3$		0.5	0.5	1		
$CH_3CO_2^{\cdot +}CH(CD_3)_2$				0.7	2.2	1.5
$CH_3CO_2^{\cdot +}CH(CD_3)CH_3$			1	2		

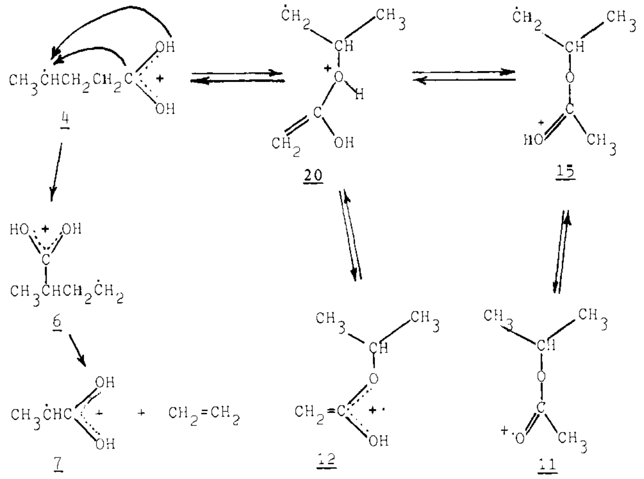
[a] Values normalized similarly to those in Tables III and IV.

$C_4H_7O_2^+$ formation. Thus, as with ionized butanoic acid and its isomers,[11] metastable $C_5H_{10}O_2^{\cdot +}$ ions decompose from rather isolated subregions of their potential surface. The reactions of the enol isomers of the ionized acids have been discussed by others.[9a,b,12] The structure $CH_3C(OH)_2^+$ (**10**) has been established[2b] for McLafferty + 1 products of ionized acids and the structure $CH_3\dot{C}HC(OH)_2^+$ (**7**) for the accompanying $C_3H_6O_2^{\cdot +}$ ions.[7] Scheme I summarizes mechanisms to be considered and assigns numerical designations to most proposed reactants.

Our main purpose was to determine whether the H transfer forming the methyl of **10** and the joining of C2 and C4 in **2** to form the ethylene lost upon formation of **7** (and the corresponding reaction of other ions) both occur, providing evidence for formation of the ion–neutral complex $[CH_3CH{=}CH_2\ \dot{C}H_2C(OH)_2^+]$. This predicts formation of **10** containing C2 and elimination of ethylene containing C2 together with (a) a C4 carbon from ionized 3-methylbutanoic acid, (b) carbon 3 or 5 of ionized pentanoic acid, and (c) a carbon from one of the isopropyl methyls of **12**.

Audier and co-workers[7,9a,b] have established that **2** produces **10** containing C2 and loses ethylene containing C2 and a C4. Therefore, **2** fulfills the predictions of Scheme I. That group also established by ^{13}C-labeling that C2 is quantitatively eliminated in the formation of $C_3H_6O_2^{\cdot +}$ from **1**.[9b] This is confirmed by our observation that C_2H_4 is eliminated from **1**-*2,2-d*$_2$ (Table IV) only about 5% as often as from the unlabeled ion, indicating predominant elimination of $C_2H_2D_2$ and/or C_2H_3D from **1**-*2,2-d*$_2$. The model predicts formation of $^{13}CC_2H_6O_2^{\cdot +}$ in the ratio 1:2:1 from **1**-3-, **1**-4-, and **1**-5-^{13}C if sufficient hydrogen exchange occurs in the complex. This is within experimental uncertainty of the results obtained on one mass spectrometer, consistent with the results of Audier and co-workers,[9b] and with observations in the first field-free region of the MS 50TA mass spectrometer. However, less loss of ethylene containing C5 than C3 was consistently observed in the third field-free region of the MS 50TA. The longer-lived, presumably lower energy ions observed in the third field-free region of the MS 50TA are either less able to dissociate to **8** or to undergo the hydrogen transfer **8** → **13**. The dominant formation of **10**-*d*$_2$ from **1**-*2,2-d*$_2$ establishes retention of C2 in **10** formed from **1**.

Scheme II



Scheme I predicts that the enol isomer of isopropyl acetate (**12**) will eliminate ethylene containing 100% of the enolic carbon and 100% of a carbon from one of the isopropyl methyls. $C_3H_6O_2^{\cdot +}$ made up 84% of the $C_3(H,D)_6O_2^{\cdot +}$ products from $\dot{C}D_2C(^+OH)OCH(CH_3)_2$, so most of these ions fulfill the first part of the prediction. Deuteration of the methyl groups in **12** led predominantly to $C_3H_2D_4O_2^{\cdot +}$, again as expected. $\dot{C}H_2C(^+OH)O^{13}CH(CH_3)_2$ lost C_2H_4 20 times as often as it lost $^{13}CCH_4$, fulfilling the second part of the prediction.

In summary, our evidence requires the presence of an intermediate in which methylene containing C2 and a second carbon

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(11) (a) McAdoo, D. J.; Hudson, C. E. *J. Am. Chem. Soc.* **1981**, *103*, 7710–7713. (b) McAdoo, D. J.; Hudson, C. E.; Zwinselman, J. J.; Nibbering, N. M. M. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1703–1709. (d) McAdoo, D. J.; Hudson, C. E. *Int. J. Mass Spectrom. Ion Processes* **1986**, *70*, 57–65.

(12) (a) Weiske, T.; Halim, H.; Schwarz, H. *Chem. Ber.* **1985**, *118*, 495–509. (b) Weiske, T.; Schwarz, H. *Tetrahedron* **1986**, *42*, 6245–6251.

Table VII. Heats of Formation Relevant to $C_5H_{10}O_2^{\bullet+}$ Decompositions

species	ΔH_f (kJ mol^{-1})
$CH_3CH_2CH_2CH_2CO_2H^{\bullet+}$ (**1**)	485^{13a}
$(CH_3)_2CHCH_2CO_2H^{\bullet+}$ (**2**)	481^{13a}
$CH_3CO_2^{\bullet+}CH_2CH_2CH_3$ (**17**)	484^{1f}
$CH_3CO_2^{\bullet+}CH(CH_3)_2$ (**11**)	479^{1f}
$\dot{C}H_2C(^+OH)OCH_2CH_2CH_3$	379^{a}
$\dot{C}H_2C(^+OH)OCH(CH_3)_2$ (**12**)	374^{b}
$CH_3C(OH)_2^+$ (**10**)	315^{1e}
$C_3H_5^{\bullet}$	165^{13c}
$\dot{C}H_2C(OH)_2^+$ (**14**)	502^{13d}
$CH_3CO_2H^{\bullet+}$	594^{13d}
$CH_3CH{=}CH_2$	20^{13e}
$CH_3\dot{C}HC(OH)_2^+$ (**7**)	439^{13b}
$CH_2{=}CH_2$	52^{13e}
$CH_3O^+H\dot{C}H_2$	960^{13e}
CH_3CO_2H	-432^{13e}
$CH_3C^+HCH_3$	800^{13c}
$CH_3CH_2O^+H_2$	868^{13e}
$\dot{C}H_2CO_2H$	-265^{c}
$\cdot CH_3$	143.9^{13g}

[a] Estimated from $\Delta H_f(CH_3\dot{C}HC(^+OH)OCH_2CH_3)$ = 435 kJ mol^{-1},[13b] $\Delta H_f(CH_3CH_2C(O^{\bullet+})OCH_2CH_3)$ = 540 kJ mol^{-1}, and $\Delta H_f(CH_3CO_2^{\bullet+}CH_2CH_2CH_3)$. [b] Estimated from $\Delta H_f(CH_3CO_2^{\bullet+}CH(CH_3)_2)$ as in footnote *a*. [c] $\Delta H_f(CH_2CO_2H) = \Delta H_f(CH_3CO_2H) - \Delta H_f(H^{\bullet})$ + dissociation energy, DE(C–H) = −432 kJ mol^{-1} − 218 kJ mol^{-1} + 385 kJ mol^{-1}. DE(C–H) was taken to equal the homolytic bond dissociation energies for $H{-}CH_2CHO$ and $H{-}CH_2C({=}O)CH_3$.[13f]

can be joined prior to the formation of **7** from **12**, **2**, and in part **1**, and a close relationship between the formation of this species and decomposition to **10**. These requirements are nicely met by complex **8**. However, there is another pathway to **10** which will be discussed below.

Energetic Considerations. The conventional reactions presented in Scheme II provide a possible alternative rationalization of our observations. (We refer to non-complex-mediated reactions as conventional reactions.) Energetic requirements will determine whether the ion–neutral complexes in Scheme I or the reactions in Scheme II actually occur. Table VII gives needed thermochemical information. Appearance energies[9a] for the formation of **10** + $C_3H_5^{\bullet}$ place the highest barrier on the way from **2** to those products at about 495 kJ mol^{-1} and at about 505 kJ mol^{-1} from **1**. Product stabilities are $\Delta H_f(\mathbf{10} + C_3H_5^{\bullet})$ = 480 kJ mol^{-1} and $\Delta H_f(\mathbf{7} + CH_2{=}CH_2)$ = 491 kJ mol^{-1}. $CH_3C(OH)_2^+$ is formed from **11** and **17** at 480–485 kJ mol^{-1},[1f] so all precursors decompose to **7** and **10** quite close to the thermochemical thresholds for those reactions.

The apparent binding energy of the complex $[(CH_3)_2CHCO^+\ \dot{C}H(CH_3)_2]$, 35 kJ mol^{-1},[5c] should be a reasonable estimate of the electrostatic attractions between ions and C3 hydrocarbon moieties. Combining this with information in Table VII gives $\Delta H_f(\mathbf{8})$ = 487 kJ mol^{-1} and $\Delta H_f(\mathbf{9})$ = 445 kJ mol^{-1}. CH_3CO_2H and $^{\bullet}CH_2CO_2H$ should both have relatively large permanent dipoles, so we take their binding energy to be that of $[\dot{C}H_2C^+H_2\ OH_2]$, close to 79 kJ mol^{-1}.[14] This gives $\Delta H_f(\mathbf{13})$ = 456 kJ mol^{-1} and $\Delta H_f(\mathbf{16})$ = 449 kJ mol^{-1}. Thus, unless the stabilities of the complexes are overestimated by more than 30 kJ mol^{-1}, **8**, **9**, **13**, and **16** are all energetically plausible intermediates in $C_5H_{10}O_2^{\bullet+}$ reactions.

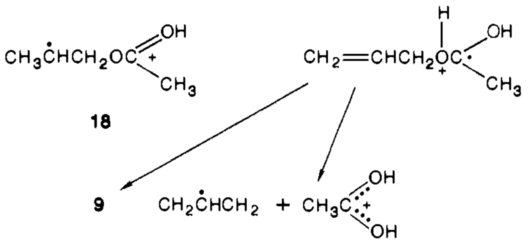
Disruption of the resonance of the protonated carboxyl group would make **20** (Scheme II) a high-energy ion. Computations[2b] give $\Delta H_f(\mathbf{10})$ = 307 kJ mol^{-1} and $\Delta H_f(CH_2{=}C(OH)_2H^+)$ = 644 kJ mol^{-1}. Adding the difference between these values to $\Delta H_f(\mathbf{12})$ (Table VII) gives 701 kJ mol^{-1} for $\Delta H_f(\mathbf{19})$. Although this is an extremely crude estimate, it indicates that **19** should be much less stable than the complexes in Scheme I and much higher in energy than measured thresholds for the decompositions studied. Anticipated high activation energies for four-membered ring H-transfers[11b,15] also make unlikely several steps in Scheme II. Thus the proposed ion–neutral complexes are the energetically more reasonable intermediates for explaining our observations.

Isotope Effects. Six times more **7** was formed from $\dot{C}H_2C(^+OH)OCH(CD_3)_2$ than from the unlabeled form of that ion. This large isotope effect demonstrates that complex **13** can readily become prominent in the decompositions of **12**. Any isotope effects on

$$\dot{C}H_2C(^+OH)OCH(CD_3)_2 \rightarrow [\dot{C}H_2CO_2H\ ^+CH(CD_3)_2] \rightarrow [\dot{C}H_2C(OH)OD^+\ CD_2{=}CHCD_3]$$

will influence formations of **7** and **10** equally, but subsequent $[\dot{C}H_2C(OH)OD^+\ CD_3CH{=}CD_2] \rightarrow CH_2DC(OH)OD^+ + \bar{C}\bar{D}_2\bar{C}\bar{H}\bar{C}D_2$ will be strongly inhibited relative to **8** → **4**. That there is a strong isotope effect on **8** → **9** → **10** is demonstrated by a 15-fold increase in the ratio of **14** to **10** from **2**-*O*,*4*,*4*,*4*,*4*,*'4*,*'4*-*'d*$_7$ in comparison to unlabeled **2**.[9a] Isotope effects on conventional H transfers in unimolecular gas-phase ionic reactions seldom exceed 2–3,[16] but can be as high as 7.[12a] Isotope effects observed in competing, complex-mediated dissociations can be many times larger.[5b–d] Thus the large isotope effect is consistent with formation of **10** from **2** predominantly via **8** → **9** → **10** rather than by **8** → **13** → **12** → **15** → **16** → **9** → **10**.

$CH_3C(OH)_2^+$ Formation from Acetates and $\dot{C}H_2C(^+OH)OCH_2CH_2CH_3$. The very specific formation of **10**-*d*$_3$ from $CD_3CO_2^{\bullet+}CH(CH_3)_2$ and $CD_3CO_2^{\bullet+}CH_2CH_2CH_3$ demonstrate that very little **10** is formed from **11** and **17** via **12** → **13** → **8**; i.e., **10** is not formed from **11** and **17** through the main pathway to **10** from **1** and **2**. Hydrogen is transferred from C2 to the enolic carbon and from C3 to an oxygen of **19**. This suggests that **17** and **19** isomerize to **18** and then decompose as shown in eq 1. It



(1)

is not possible to determine whether decomposition of **18** to products is simultaneous with or immediately follows H transfer, or whether one or both of the indicated intermediates are formed. The complex **9** seems quite plausible energetically; perhaps there is too much energy in the system to permit its formation following **19** → **18**. The formation of significant $C_2H_4DO_2^+$ from ionized *n*-propyl-*1*,*1*-*d*$_2$ acetate is consistent with some **9** → **16** occurring following formation of **18** by the pathway **17** → **18**, probably a slightly lower energy pathway than **19** → **18**.[17] Complex formation in other systems disappears completely at energies of 20–30 kJ mol^{-1} in excess of the dissociation threshold.[5b–d]

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(13) (a) Holmes, J. L.; Fingas, M.; Lossing, F. P. *Can. J. Chem.* **1981**, 59, 80–93. (b) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1980**, *102*, 1591–1595. (c) Traeger, J. C. *Int. J. Mass Spectrom. Ion Processes* **1984**, *58*, 259–271. (d) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1980**, *102*, 3732–3735. (e) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, Suppl. 1. (f) Holmes, J. L.; Lossing, F. P.; Terlouw, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 1086–1087. (g) Traeger, J. C.; McLoughlin, R. G. *Ibid.* **1981**, *103*, 3647–3652.

(14) (a) Bouma, W. J.; Nobes, R. H.; Radom, L. *J. Am. Chem. Soc.* **1983**, *105*, 1743–1746. (b) Postma, R.; Ruttink, P. J. A.; Van Baar, B.; Terlouw, J. K.; Holmes, J. L.; Burgers, P. C. *Chem. Phys. Lett.* **1986**, *123*, 409–415.

(15) (a) Lifshitz, C. *J. Phys. Chem.* **1983**, *87*, 2304–2313. (b) De Koster, C. G.; Terlouw, J. K.; Levsen, K.; Halim, H.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1984**, *61*, 87–95.

(16) (a) McLafferty, F. W.; McAdoo, D. J.; Smith, J. S.; Kornfeld, R. *J. Am. Chem. Soc.* **1971**, *93*, 3720–3730. (b) Schwarz, H.; Williams, D. H.; Wesdemiotis, C. *Ibid.* **1978**, *100*, 7052–7055. (c) Hemberger, P. H.; Kleingeld, J. C.; Levsen, K; Mainzer, N.; Mandelbaum, A.; Nibbering, N. M. M.; Schwarz, H.; Weber, R.; Weisz, A.; Wesdemiotis, C. *Ibid.* **1980**, *102*, 3736–3745. (d) McAdoo, D. J.; Hudson, C. E.; Griffin, L. L. *J. Phys. Chem.* **1984**, *88*, 1481–1485.

(17) (a) McAdoo, D. J.; McLafferty, F. W.; Parks, T. E. *J. Am. Chem. Soc.* **1972**, *94*, 1601–1609. (b) Griffin, L. L.; Holden, K.; Hudson, C. E.; McAdoo, D. J. *Org. Mass Spectrom.* **1986**, *21*, 175–182. (c) Hudson, C. E.; Lin, T.; McAdoo, D. J. *Ibid.* **1987**, *22*, 311–315.

Table VIII. Sources of H-Transfer Preceding Eliminations of C_3 Fragments from Assorted *n*-Propyl-Containing Ions

ion	position in C_3 fragment		
	1	2	3
$CH_3CH_2CH_2CH_2CO_2H^{\cdot+a}$	31	24	45
$CH_3CH_2CH_2CH_2CO_2H^{\cdot+b}$	30	20	50
$C_6H_5OC_3H_7^{\cdot+c}$	28	19	53
$C_6H_5OHC_3H_7^{+d}$	30	20	50
$CH_3C(OH)OC_3H_7^{+e}$	24	24	52
$C_6H_5C(OH)OC_3H_7^{+e}$	30	22	48
$[C_6H_5C_3H_7]H^{+f}$	30	22	48

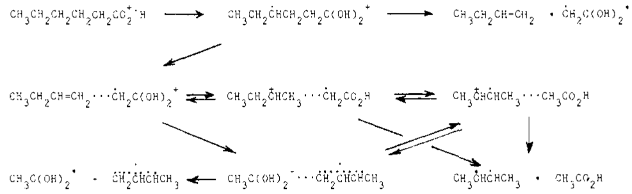
[a] Based on number of D's transferred from each position derived from data in Table III. The percentages of deuteriums in the product $C_2(H,D)_5O_2^+$ ions from each precursor (d_2 ions counted twice, d_3 ions counted three times) were calculated and then the percent of the transfer from each position computed to produce the numbers presented in the Table. [b] Reference 9a. [c] Metastable decomposition data from reference 22a. [d] Methane chemical ionization, reference 22a. [e] Chemical ionization, reference 22b. [f] Reference 22c.

Shift of the Protonated Carboxyl Group. The postulated 1,3-protonated carboxyl shift **4** → **6** in Scheme I parallels the proposal that loss of $^2CH_2{=}^3CH_2$ from metastable butanoic acid ions takes place through a cyclobutanediol intermediate or transition state.[18] Audier and co-workers have demonstrated that the analogous reaction of **3** does not occur, as that would yield some **10**-d_0 from **2**-*2,2*-d_2, contrary to observations.[9a] We attribute the disparate behavior of **3** and **4** to an inability of cyclization of **3** to compete with **3** → **8** and **3** → **14**. Protonated carboxyl groups are also transferred through ionized cyclopropanediol[11b,12] and cyclopentanediol[9b,19] intermediates or transition states, demonstrating that such reactions occur through a series of ring sizes.

Hydrogen Exchange in the Complexes. Audier and Sozzi[7] established by labeling that **2** extensively interchanges its methyl and carboxyl hydrogens. This hydrogen exchange might occur by conventional mechanisms and/or in the ion–neutral complexes. $CD_3CH_2CH_2CH_2CO_2H^{\cdot+}$ and **2**-*4,4,4*-d_3 produce very similar $C_2(H,D)_5O_2^+$ patterns (Table III), suggesting exchange after those two ions reach a common point on the reaction surface. Little **10**-d_2 is formed from **1**-*4,4*-d_2 (ref 9a and Table III), indicating that **1** ⇄ **4** is minor. This is supported by the weak formation of **10**-d_1 from **2**-*3*-d_1 and $\dot{C}H_2C(^+OH)OCD(CH_3)_2$ (ref 9a and Table V). As **1** → **4** should be the most facile conventional exchange process, **1** ⇄ $CH_3CH_2\dot{C}HCH_2C(OH_2)^+$ and **1** ⇄ $\dot{C}H_2CH_2CH_2CH_2C(OH)_2^+$ are also unlikely to be important. A plausible conventional mechanism for the observed hydrogen exchange is **2** ⇄ **3**. We assume that cyclization of **3** should be as facile as that of **4**, so the absence of cyclization of **3** suggests that **3** → **2** is at most infrequent. Thus conventional intermediates may be unimportant in the observed hydrogen exchanges.

Hydrogen exchange between partners in ion–neutral complexes is well-established for bimolecular ion–molecule reactions,[20] and has been proposed to account for extensive exchange associated with several unimolecular decompositions.[6,21] Hydrogen exchange, if complex mediated, is more extensive at the ends than the middle of the C3 partners in complexes formed from **1**, **2**, and **12**. Preferential hydrogen transfer from C1 and C3 is observed for eliminations of propene from a variety of *n*-propyl-containing ions (Table VIII). Complex-mediated isomerization to isopropyl followed by hydrogen transfer and decomposition has been proposed for ionized phenyl *n*-propyl ether[6c] and seems likely for the other processes in Table VIII. However, in contrast to the exchange that occurs in the present system, most of the other ions in Table VIII probably undergo undirectional H-transfer from an isopropyl methyl.[6c] The present patterns could be due to transfer of a hydrogen from the middle carbon followed by extensive exchange between the ends of C3 fragments and their partners in complexes. However, similar patterns could also result from reactions such as **2** ⇄ **3**. Exchange exclusively at the methyls is observed in single collisions of isopropyl ions with neutrals of proton affinities very close to that of propene,[23] exchanges that must involve an ion–neutral complex. This correlates with the patterns of **2** and **12**. In contrast, hydrogen exchange is more frequent at the middle than at the end carbons of C4 partners.[1d,2a,3a,6c] The more rapid exchange of the middle hydrogens of C4 partners is expected from the greater stability of secondary than primary carbonium ions. Earlier workers[6c,24] have concluded that, taken together, the hydrogen transfer patterns of C3 and C4 groups are indicative of ion–neutral complex intermediates.

Scheme III



H-transfer ring sizes in conventional mechanisms are prefered in the order 6 > 3 > 5 > 4.[12b,17b,c] Therefore, a unified interpretation of the exchange patterns with C3 and C4 moieties utilizing conventional mechanisms is impossible, as, depending on the nature of the rest of the ion, three- and five-membered ring H-transfers would have to be dominant with some C3 partners (e.g., aromatic ethers[5c]), six-membered ring H-transfers with others (e.g., **2**), and five- and seven-membered ring H-transfers with still others (e.g., **1**). Similar problems exist when considering exchange involving C4 partners.

In summary, we conclude that ion–neutral complexes are important in the low-energy decompositions of $C_5H_{10}O_2^{\cdot+}$ isomers. This is based on the correlation of the formation of **10** with formation of **7**, the requirement for reactive methylenes in each reaction, theoretical descriptions[14] of reactions analogous to the conversion of **2** to **4**, predicted energetics of ion–neutral complex vs. conventional intermediates, and arguments that complex-mediated processes are probably more important than conventional rearrangements in the observed hydrogen exchange. While there are uncertainties about each type of evidence, we believe that the consistency of the conclusions from each of these lines of reasoning makes a compelling case for the intermediacy of ion–neutral complexes in low-energy reactions of $C_5H_{10}O_2^{\cdot+}$ isomers.

Unification of the McLafferty Rearrangement, McLafferty Rearrangement with Charge Reversal, and the McLafferty + 1 Rearrangement. Despite study for nearly 30 years,[1,4,25] the relationship between these reactions is not completely defined. We propose that these three processes are related as illustrated in Scheme III. This scheme rationalizes all observations, including the formation of methyls in species such as **10**, the apparently

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(18) McAdoo, D. J.; Witiak, D. N.; McLafferty, F. W.; Dill, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 6639–6643.

(19) (a) Weiske, T.; Schwarz, H. *Chem. Ber.* **1983**, *116*, 323–347. (b) Schwarz, H.; Weiske, T.; Levsen, K.; Maquestiau, A.; Flammang, R. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *45*, 367–375.

(20) (a) Squires, R. R.; DePuy, C. H.; Bierbaum, V. M. *J. am. Chem. Soc.* **1981**, *103*, 4256–4258. (b) Ausloos, P.; Lias, S. G. *Ibid.* **1981**, *103*, 3641–3647. (c) Kleingeld, J. C.; Nibbering, N. M. M. *Tetrahedron* **1983**, *39*, 4193–4199. (d) Squires, R. R.; Bierbaum, V. M.; Grabowski, J. J.; DePuy, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 5185–5192. (e) Grabowski, J. J.; DePuy, C. H.; Van Doren, J. M.; Bierbaum, V. M. *Ibid.* **1985**, *107*, 7384–7389.

(21) McAdoo, D. J.; Hudson, C E. *Org. Mass Spectrom.* **1987**, *22*, 615–621.

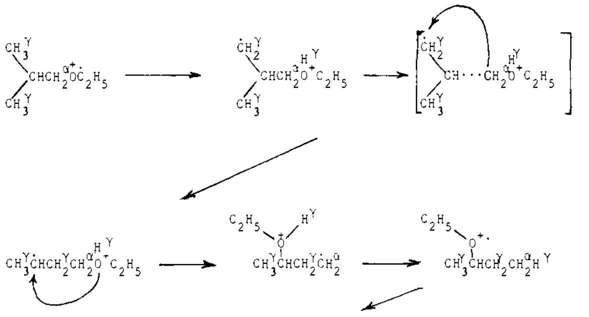
(22) (a) Benoit, F. M.; Harrison, A. G. *Org. Mass Spectrom.* **1976**, *11*, 599–608. (b) Benoit, F. M.; Harrison, A. G. *Ibid.* **1978**, *13*, 128–132. (c) Leung, H. W.; Harrison, A. G. *Ibid.* **1977**, *12*, 582–588.

(23) McAdoo, D. J.; McLafferty, F. W.; Bente, P. F. *J. Am. Chem. Soc.* **1972**, *94*, 2027–2033.

(24) (a) Bowen, R. D.; Williams, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 2752–2756. (b) Herman, J. A.; Harrison, A. G. *Org. Mass Spectrom.* **1981**, *16*, 423–427.

(25) (a) McLafferty, F. W. *Anal. Chem.* **1959**, *31*, 82–86. (b) Budzikiewicz, H.; Djerassi, C.; Williams, D. H. *Mass Spectrometry of Organic Compounds*; Holden-Day: San Francisco, 1967; pp 155–162. (c) McLafferty, F. W. *Interpretation of Mass Spectra*, 3rd ed.; University Science Books: Mill Valley, CA, 1980; pp 65, 158–159.

Scheme IV



nonspecific hydrogen transfers which usually accompany the McLafferty rearrangement with charge reversal,[21,25c,26] and the formation of McLafferty + 1 ions.[1c,d,2a,3a,7] It also accounts for the formation of $CH_3CHO + CH_3C^+H\dot{C}HCH_3$ from ionized hexanal[26,27] and of $CH_3CO_2H + CH_3C^+H\dot{C}HCH_3$ from ionized hexanoic acid,[10] an impossibility by conventional stepwise processes and an improbability by various concerted schemes that might be concocted.

Related Reactions. Double hydrogen transfers are also observed in the decompositions of some ionized alcohols,[28] ethers,[29] and amines.[29] These decompositions have in common with the present system the production of allylic neutrals and ions that can be generated by protonation of small neutral molecules, for example, the formation of $CH_3OH_2^+$ + $\bar{C}\bar{H}_2\dot{\bar{C}}\bar{H}\bar{C}\bar{H}_2$ from ionized 2-methylpropanol.[28] Like 3-methylbutanoic acid, this ion exchanges the original methyl and hydroxyl hydrogens extensively prior to fragmenting, but leaves the hydrogens on its first and second carbons largely undisturbed.[28a] Bowen and Williams[28b] have proposed that exchange and decomposition take place by

$$[CH_3OH\ \dot{C}H_2\overset{+}{C}HCH_3] \rightleftarrows [CH_3\overset{+}{O}H_2\ \bar{C}\bar{H}_2\dot{\bar{C}}\bar{H}\bar{C}\bar{H}_2] \rightarrow CH_3\overset{+}{O}H_2 + \bar{C}\bar{H}_2\dot{\bar{C}}\bar{H}\bar{C}\bar{H}_2$$

However, this conclusion has been criticized.[30]

A less obviously related reaction that can be explained by mechanisms paralleling those in Scheme I is the loss of ethyl containing 2- and 3-hydrogens from ionized ethyl isobutyl ether,[31] as illustrated in Scheme IV. The proposal that $C_2H_5O{=}CH_2^+$ migrates in a complex is our only modification of the picture presented by Audier and co-workers.[31] They found that $C_2H_5O^+HCH_2CH_2\dot{C}HCH_3$ did not return to $C_2H_5O^+HCH_2CH(\dot{C}H_2)CH_3$, which they attributed to the greater stability of a secondary than that of a primary radical. Conventional shifts between adjacent carbons in alkyl radicals are very high-energy reactions,[32] occurring only in the absence of competing processes, if at all,[32] so shift of $CH_3CH_2O{=}CH_2^+$ by a free radical-like reaction seems highly improbable. Systems characterized or discussed here establish that migration by a 1,2-shift across an incipient double bond is a common gas-phase ionic reaction. The theoretically[14,33] and experimentally[34] characterized 1,2-shifts of H_2O and NH_3 in $\dot{C}H_2CH_2O^+H_2$ and $\dot{C}H_2CH_2N^+H_3$ are the archetypal examples of this reaction. Other likely processes are the chain straightening that must precede loss of ethyl from ionized 3-methylbutanal[35] and interconversions of ionized ketone isomers.[36]

Present and other recent work[5,6] indicates that ion–neutral complex-mediated reactions are common in gas-phase ion chemistry. The rationalization of many reactions for which concerted mechanisms might be drawn as being complex-mediated is consistent with the idea[17,37] that bond makings and breakings do not usually occur simultaneously in gas-phase ions.

Experimental Section

Data were acquired except where otherwise indicated on a Kratos MS 50TA mass spectrometer[38] by focussing the precursor ion of interest on the collector and scanning the voltage on the second electric sector.

$CH_3CH_2{}^{13}CH_2CH_2CO_2H$ was prepared by addition of $^{13}CO_2$ to C_2H_5MgBr, destruction of the excess Grignard with CH_3OH and $LiAlH_4$ reduction of the resulting magnesium salts, followed by acidification to produce $CH_3CH_2{}^{13}CH_2OH$. This alcohol was converted to the bromide with HBr/H_2SO_4 and then to pentanoic acid by the malonic ester synthesis. $CH_3{}^{13}CH_2CH_2CH_2CO_2H$ was prepared starting with reduction of $CH_3{}^{13}CO_2H$ with $LiAlH_4$,[34] conversion to the bromide with HBr/H_2SO_4, $CuBr{\cdot}(CH_3)_2S$-catalyzed conjugate addition of the Grignard reagent to methyl acrylate, and hydrolysis of the resulting $CH_3{}^{13}CH_2CH_2CH_2CO_2CH_3$. $CH_3CH_2CH_2CO_2{}^{13}CH(CH_3)_2$ was prepared by reduction of $(CH_3)_2{}^{13}C{=}O$ with $LiAlH_4$[39] followed by esterification with butanoic anhydride/H_2SO_4. $CH_3CH_2CH_2CD_2CO_2H$ was prepared by $LiAlD_4$ reduction of butanoic acid, conversion to the bromide with HBr/H_2SO_4, and carbonation of the Grignard reagent. $CH_3CH_2CD_2CH_2CO_2H$ was prepared by $LiAlD_4$ reduction of propanoic anhydride, conversion to the bromide with HBr/H_2SO_4, and conversion to the acid by the malonic ester synthesis. $CH_3CD_2CH_2CH_2CO_2H$ and $CD_3CH_2CH_2CH_2CO_2H$ were prepared by the $CuBr{\cdot}(CH_3)_2S$-catalyzed conjugate addition of the appropriately labeled Grignard reagent to methyl acrylate followed by hydrolysis. CD_3CH_2Br was prepared by reduction of CD_3CO_2D[37] with $LiAlH_4$ and reaction with HBr/H_2SO_4. CH_3CD_2Br was similarly prepared starting with reduction of acetic anhydride with $LiAlD_4$.

$CD_3CH(CH_3)CH_2CO_2H$ was prepared by addition of CD_3MgI with catalysis by $CuBr{\cdot}(CH_3)_2S$ to $CH_3CH{=}CHCO_2CH_3$ and hydrolysis of the resulting ester. $(CH_3)_2CHCD_2CO_2H$ was prepared by reduction of 2-methylpropanoic acid with $LiAlD_4$, conversion to the bromide with PBr_3, and carbonation of the Grignard reagent. $CH_3CH_2CD_2CO_2CH(CH_3)_2$ was prepared from $CH_3CH_2CD_2Br$ (prepared as above) by carbonation of the Grignard reagent and esterification with 2-propanol. $CD_3CO_2CH(CH_3)_2$ was prepared from CD_3CO_2D by conversion to the acid chloride with PCl_5 and esterification with 2-propanol. $CD_3CO_2CH_2CH_2CH_3$ was prepared similarly. $(CH_3)_2CDOH$ was prepared by $LiAlD_4$ reduction of acetone. It was converted to esters by reactions with acetic and butanoic anhydride in the presence of H_2SO_4. $(CD_3)_2CHOH$ was prepared by $LiAlH_4$ reduction of acetone-d_6.[6] It was converted to esters by reaction with acid anhydride/H_2SO_4.

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(26) (a) Morgan, R. P.; Derrick, P. J. *Chem. Commun.* **1974**, 836–837. (b) Morgan, R. P.; Derrick, P. J.; Loudon, A. G. *J. Chem. Soc., Perkin Trans. 2* **1980**, 306–312. (c) Audier, H. E.; Milliet, A. *Org. Mass Spectrom.* **1980**, *15*, 477–482.

(27) Derrick, P. J.; Falick, A. M.; Lewis, S.; Burlingame, A. L. *J. Phys. Chem.* **1979**, *83*, 1567–1573.

(28) (a) Tajima, S.; van der Greef, J.; Nibbering, N. M. M. *Org. Mass Spectrom.* **1978**, *13*, 551–555. (b) Bowen, R. D.; Williams, D. H. *Chem. Commun.* **1981**, 836–838.

(29) Bowen, R. D.; Maccoll, A. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1005–1007.

(30) Hammerum, S.; Derrick, P. J. *J. Chem. Soc. Perkin Trans. 2* **1986**, 1577–1580.

(31) Audier, H. E.; Bouchoux, G.; Hoppilliard, Y.; Milliet, A. *Org. Mass Spectrom.* **1982**, *17*, 382–385.

(32) (a) Walling, C. In *Molecular Rearrangements*; de Mayo, P., Ed.; Interscience: New York, 1963; pp 407–455. (b) Gordon, A. S.; Tardy, D. C.; Ireton, R. *J. Phys. Chem.* **1976**, *80*, 1400–1404.

(33) Golding, B. T.; Radom, L. *J. Am. Chem. Soc.* **1976**, *98*, 6331–6338.

(34) (a) Hammerum, S.; Kuck, D.; Derrick, P. J. *Tetrahedron Lett.* **1984**, *25*, 893–896. (b) McAdoo, D. J.; Hudson, C. E. *Org. Mass Spectrom.* **1986**, *21*, 779–780.

(35) Hudson, C. E.; McAdoo, D. J. *Org. Mass Spectrom.* **1984**, *19*, 1–6.

(36) Masur, M.; Sprafke, A.; Grutzmacher, H. F. *Org. Mass Spectrom.* **1987**, *22*, 307–310.

(37) McAdoo, D. J.; Hudson, C. E. *Int. J. Mass Spectrom. Ion Processes* **1984**, *62*, 269–276.

(38) Gross, M. L.; Chess, E. K.; Lyon, P. A.; Crow, F. W.; Evans, S.; Tudge, H. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *42*, 243–254.

(39) Friedman, L.; Jurewicz, A. T. *J. Org. Chem.* **1968**, *33*, 1254–1255.