Chemical Ionisation Mass Spectra of Selected C_4H_8O Compounds

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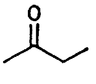
The chemical ionisation mass spectra of six isomers of C_4H_8O (butanone, isobutyraldehyde, butyraldehyde, 2-methyloxetan, 3-methyloxetan, and tetrahydrofuran) with a variety of reagent gases (H_2, H_2–N_2, H_2–CO_2, H_2–CO, and D_2) are reported. The behaviour of the resultant $C_4H_9O^+$ ions is compared with that reported previously for $C_4H_9O^+$ ions generated by electron-impact induced ionisation and fragmentation. Deuterium labelling results are also given and interpreted. The effect of changing the exothermicity of protonation on the relative abundance of the various decomposition routes is presented and discussed.

CONSIDERABLE progress has been made in recent years towards the development of a better understanding of the unimolecular reactions of isolated organic ions. In particular, the use of a potential energy profile approach, in conjunction with a careful consideration of the plausible mechanisms for reaction, frequently affords great insight into the chemistry of the ions under investigation. The approach is especially successful for relatively small organic ions, particularly when the slow (k 10^4—10^6) reactions of such species are considered.[1-3]

Most earlier work in this field employed mainly or exclusively electron-impact induced ionisation as a means of generating the ions of interest. More recent studies have applied alternative ionisation techniques, notably chemical ionisation. Although it is well known that the extent to which ions produced by chemical ionisation fragment decreases as the exothermicity of protonation decreases, very little work has been performed in order to set this generalisation on a quantitative basis. A recent study[4] of $C_3H_7O^+$ ions, formed by protonation of C_3H_6O isomers by various reagent ions, indicates that most of the theoretical heat of protonation is retained by the $C_3H_7O^+$ ion; however, significant collisional deactivation precedes decomposition. This study also showed that the reactions of $C_3H_7O^+$, generated in this way, were similar to those observed in metastable transitions following electron impact. Moreover, the observed behaviour of these $C_3H_7O^+$ ions could be interpreted in terms of the previously published potential energy profile derived from earlier electron impact investigations.[5] The present work concerns the reactions of $C_4H_9O^+$ ions, generated by protonation of selected isomers (1)—(6) of C_4H_8O. Since $C_4H_9O^+$ isomers have been the subject of studies employing the potential energy profile approach,[6] it ought to be possible to compare the behaviour of ions generated by electron impact and chemical ionisation.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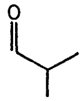
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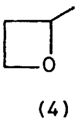
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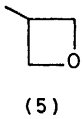
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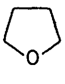
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RESULTS AND DISCUSSION

The chemical ionisation (CI) spectra of six isomers of C_4H_8O with five different reagent gases are given in Tables 1—5. These data are best discussed under three headings.

TABLE 1

H_2-CI Mass spectra of C_4H_8O compounds

	Compound					
m/z	(1)	(2)	(3)	(4)	(5)	(6)
73	47.5	23.5	11.5	4	13	14.5
72	1	1	1	2.5	2.5	3.5
71	0.5	3.5	3.5	23.5	30	53.5
70	0	0	0	0	0	0
69	0	0	0	0.5	0	0
59	0.5	1	0.5	4.5	1	0.5
58	0	0	0	1	0	0
57	6.5	1	2	16.5	6	0.5
56	4.5	4	4	3	3	3
55	100	100	95.5	57.5	49	72
47	0	0	0	0	0	0
46	0.5	0.5	0	0.5	0.5	0
45	21	25	9	15.5	21	11.5
44	1	1.5	3.5	3.5	4	3
43	29	43.5	100	100	98	100
42	0	0.5	0.5	3.5	13	7.5
41	2	4.5	5.5	15.5	23	8
34	0	0	0	0	2	0
33	0.5	0	0.5	4.5	73	1
32	0	0	0	0.5	2.5	0
31	7.5	11.5	31.5	47.5	100	29.5
30	0	0	0	0	1	0
29	85	7.5	19	23	43	11

(a) *The Site of Protonation.*—A comparison of the CI spectra with H_2 and D_2 reagent gases (H_3^+ and D_3^+ reagent ions, respectively) indicates that the C_4H_8O isomers are protonated predominantly, if not exclusively, on oxygen. In the case of H_3^+ as reagent ion, the main reactions are loss of H_2O (to give m/z 55), loss of C_2H_4 (to give m/z 45), loss of CH_2O (to give m/z 43), and loss of C_3H_6 (to give m/z 31); other reactions are relatively low in abundance and are discussed separately. When D_3^+ is substituted for H_3^+, the deuterium label is retained essentially exclusively in the oxygen-containing frag-

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TABLE 2

D_2-CI Mass spectra of C_4H_8O compounds

m/z	Compound (1)	(2)	(3)	(4)	(5)	(6)
74	36	25.5	12.5	4.5	15	12
73	13.5	11.5	18.5	11	20	21.5
72	1.5	2.5	2	4	3.5	5.5
71	0	4.5	4	29.5	47.5	64
70	0	0	0	0	0	0
59	0	0	1	1	0.5	0.5
58	0.5	1	1	1	1.5	1
57	4.5	3	27	27	6.5	4
56	13	11	7.5	7.5	6.5	7
55	100	100	78.5	78.5	72.5	91.5
47	0.5	0	0	0	1	0.5
46	13	23.5	8.5	14.5	21	10
45	1	1	3	4	3.5	4
44	24	29.5	85.5	100	90	100
43	8.5	10	8.5	12	10.5	10.5
42	0	1	1	10	23	8
41	0	2.5	2	6	12	4.5
34	0	0	0	2	56.5	1
33	0	0	0.5	1	6	0.5
32	5.5	10	29.5	51	100	33.5
31	1	1	2.5	5	10.5	3.5
30	2.5	4.5	4.5	9.5	8	5

TABLE 3

N_2–H_2-CI Mass spectra of C_4H_8O compounds

m/z	Compound (1)	(2)	(3)	(4)	(5)	(6)
73	100	100	36	26	75	53.5
72	3.5	4	2.5	5	2	5.5
71	2	6	3	1.5	22.5	32
70	0	0	0	0	0	0
69	1	0	0	0	0	0
59	1.5	2	1	8	1.5	0.5
58	0	0	0	0.5	1	0
57	3.5	2	1	10.5	3	1
56	1	3.5	4.5	4.5	4	4.5
55	24.5	70.5	100	100	90	100
47	0.5	0	0	0	0	0
46	0.5	0.5	0.5	0.5	0	0
45	3	8	2	6	11.5	3
44	0.5	1	3	2.5	3.5	2
43	6	20	49.5	81.5	100	54.5
42	1.5	1	1	2.5	14.5	5.5
41	0.5	2.5	2	2.5	7.5	3
34	0	0	0	0	7	0
33	0	0	0	2	66.5	0.5
32	7	4	3	3.5	6	3
31	1.5	2.5	12	19	58	7.5
30	12	6	6	4	9.5	4

m/z 29 is obscured by the reagent ion peak.

TABLE 4

H_2–CO_2-CI Mass spectra of C_4H_8O compounds

m/z	Compound (1)	(2)	(3)	(4)	(5)	(6)
73	100	100	45	18	55	58.5
72	1.5	2	2	1.5	1	2
71	0	3	2	6.5	8	17
70	0	0	0	0	0	0
69	0	0	0	0	0	0
59						
58						
57	1	0.5	1.5	4	2.5	1
56	0	0.5	2	4.5	5	4.5
55	3.5	14.5	100	100	100	100
47						
46						
44	0.5	1	2.5	2.5	3.5	1.5
43	2.5	4	23.5	31.5	68	23
42	0	0	0	1	8.5	4
41	0	0.5	1	0.5	3	1
34	0					
33	0	0	0	1	57.5	0
31	0	0	3	6	29	2.5
30	0	0	0	0.5	15	2.5

m/z 29, 32, and 45 are obscured by reagent ion peaks.

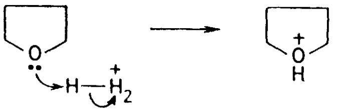
TABLE 5

H_2–CO-CI Mass spectra of C_4H_8O compounds

m/z	Compound (1)	(2)	(3)	(4)	(5)	(6)
73	100	100	69.5	16	87	100
72	2	2	1.5	1.5	1	4.5
71	0	2.5	3.5	4.5	10	27.5
70	0	0	0	0	0	0
69	0	0	0	0	0	0
59	0.5	0.5	0.5	4	0.5	0
58	0	0	0	0	0	0
57	2	0.5	1.5	1.5	2	0.5
56	0	0.5	4.5	2.5	4.5	4.5
55	4.5	10	100	100	100	94.5
47	0.5	0.5	0.5	0.5	0.5	0
46	0	0	0	0	0	0
45	1	1.5	1	2	4	1
44	0	0	3	1	2	0.5
43	5.5	5.5	12.5	21	49.5	19
42	0	0	0	1.5	12	6.5
41	1.5	2.5	2.5	2	7.5	3.5
34	0	0	0	0	3	0
33	0	0	0	1	42.5	0.5
32	0.5	0.5	0.5	3	2.5	1.5
31	0.5	1	3	6.5	24	3
30	2.5	1.5	3	3.5	4.5	2.5

m/z 29 is obscured by reagent ion peak.

ment produced by elimination of water, ethene, and propene. This is consistent with protonation on oxygen. Only in the case of formaldehyde loss does the added deuteron appear in the fragment not containing the oxygen atom; thus *m/z* 43 ($C_3H_7^+$) in the H_2 spectra shifts to *m/z* 44 ($C_3H_6D^+$) in the D_2 spectra. This result could be taken as indicative of some protonation on carbon. However, such an occurrence seems intuitively implausible for at least some of the isomers of C_4H_8O. Thus, for example, protonation of tetrahydrofuran is considered in equations (1) and (2). Protonation on oxygen [equation (1)] requires no rearrangement, whereas protonation on carbon [equation (2)] must involve opening the five-membered ring, if a plausible structure of $C_4H_9O^+$ is to be produced. As such, protonation on oxygen must be kinetically preferable. In addition, energy data[7] reveal that protonation on oxygen yields an exceptionally stable daughter ion [heat of formation (ΔH_f) 530 kJ mol^{-1}]. In contrast, equation (2) gives rise to a less stable daughter ion (ΔH_f 580 kJ mol^{-1}).[6] Consequently, protonation on oxygen is also thermodynamically more favourable than protonation on carbon. Similar arguments apply for other C_4H_8O isomers. Moreover, the reaction involving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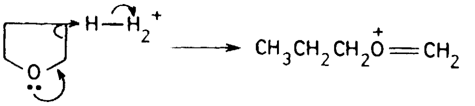
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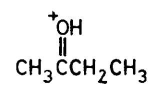
formaldehyde loss can be interpreted in terms of the appropriate potential energy profile on the assumption that protonation occurs on oxygen. It is logical, therefore, to proceed with this hypothesis, which is supported by results from protonation and self-protonation studies on C_3H_6O isomers.[8] As will be seen, all the experimental data can be accommodated in this fashion.

(b) *The Reactions of* C_4H_8O *Species after Interaction with the Reagent Ions*.—These may be classified into two broad sections, reactions of the MH^+ species produced by protonation of C_4H_8O, and reactions occurring other than by protonation of the C_4H_8O compounds. The latter class comprises hydride (and possibly methide) abstraction from C_4H_8O to give *m/z* 71 (and perhaps *m/z* 57). These processes would correspond to H_2 and CH_4 elimination from $C_4H_9O^+$; as such, they are not observed in metastable transitions of $C_4H_9O^+$ generated by electron impact (EI).[6,9] Loss of H_2 and CH_4 are frequently high-energy processes, especially in the case of concerted suprafacial 1,2-eliminations;[10,11] moreover, in the present context, there are four reasons for ascribing *m/z* 71 and 57 to processes other than H_2 and CH_4 loss from $C_4H_9O^+$. First, hydride and methide abstractions are known to occur in CI spectra,[12] particularly when vigorous protonating agents (H_3^+ in H_2-CI) are employed.[13] Reference to Tables 1—5 reveals that *m/z* 71 and 57 are of appreciable abundance only for H_2-, D_2-, and N_2-H_2-CI. In the other spectra, *m/z* 71 and 57 can usually be explained in terms of $H^\cdot$ and $CH_3^\cdot$ loss from $C_4H_8O^{+\cdot}$, as established by control EI experiments on the appropriate compound. Only in the cases of 3-methyloxetan and tetrahydrofuran does it appear that *m/z* 71 and 57 are significantly greater than would be expected on this basis.

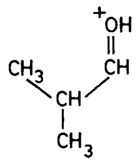
Secondly, a comparison of the H_2- and D_2-CI spectra shows that *m/z* 71 and 57 are of similar abundance, for a given compound, in both spectra. This is consistent with hydride or methide abstraction being the origin of these peaks. Thirdly, the abundances of *m/z* 71 and 57 reflect the expected stabilities of the ions that would be produced by hydride and methide abstraction from the various C_4H_8O isomers. Thus, the only species that shows a negligible *m/z* 71 peak is butanone, for which the associated carbonium ions (for example $CH_3CO\overset{+}{C}HCH_3$) must be of high energy. In contrast, all the other isomers investigated exhibit significant *m/z* 71 peaks, in keeping with the expected increased stability of the derived carbonium ions. The effect is especially pronounced for the cyclic compounds and can be interpreted in terms of the relatively stable carbonium ions [$\overline{CH_2CH_2(CH_3)C{=}O}^+$ from $\overline{CH_2CH_2(CH_3)CHO}$, $\overline{CH_2(CH_3)CHCH{=}O}^+$ from $\overline{CH_2(CH_3)CHCH_2O}$, and $\overline{CH_2CH_2CH_2CH{=}O}^+$ from $\overline{CH_2CH_2CH_2CH_2O}$] which are produced by hydride abstraction. An analogous trend can be discerned for *m/z* 57, which occurs in moderate abundance (*ca.* 20% of the base peak) for 2-methyloxetan but is scarcely significant in the spectra of the other isomers. Only in the case of 2-methyloxetan does methide abstraction give rise to a relatively stable daughter ion ($\overline{CH_2CH_2CH{=}O}^+$). Finally, the results of ^{2}H-labelling studies support the contention that *m/z* 71 and 57 arise by hydride abstraction. Thus, the H_2-CI spectra of $CH_3CH_2CD_2CHO$ and $(CH_3)_2CDCHO$ have negligible peaks (0.5% of the base peak abundance) at *m/z* 72 and 71, respectively, but small peaks (8 and 4% of the base peak abundance) at *m/z* 73 and 72. These data are consistent with abstraction of the aldehyde hydride to form the relatively stable acylium ions $CH_3CH_2CD_2\overset{+}{C}O$ and $(CH_3)CD\overset{+}{C}O$, respectively, in which all the deuterium label is retained in the daughter ion. More cogent evidence is furnished by $\overline{CH_2(CH_3)CHCD_2O}$, which exhibits approximately equally abundant *m/z* 73 and 72 ions (18.5 and 15%, respectively, of base peak abundance in H_2-CI, and 16 and 13%, respectively, of base peak abundance in D_2-CI). This observation can be understood on the basis of hydride and deuteride abstractions occurring in nearly equal amounts from the CH_2 and CD_2 groups of $\overline{CH_2(CH_3)CHCD_2O}$, as would be expected statistically.

The bulk of the ion current due to fragment ions in the CI spectra can be interpreted in terms of protonation on oxygen followed by decomposition. Four reactions of this type are of high abundance for some or all isomers; these are elimination of H_2O (*m/z* 55), C_2H_4 (*m/z* 45), CH_2O (*m/z* 43), and C_3H_6 (*m/z* 31). Three of these processes, H_2O, C_2H_4, and CH_2O losses, are observed from metastable $C_4H_9O^+$ ions, containing the $>C{=}\overset{+}{O}H$ group, generated by EI;[6,9] however, C_3H_6 loss is a higher energy process and only occurs for $C_4H_9O^+$ ions of high internal energy. The occurrence of significant C_3H_4 loss (*m/z* 33) in the CI spectra of 3-methyloxetan is interesting. This process, which gives rise to protonated methanol as the daughter ion, has a very high activation energy and is only detected in metastable transitions of one isomer [$(CH_3)_2C{=}\overset{+}{O}CH_3$] of $C_4H_9O^+$ under EI conditions.[6]

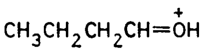
(i) *Water loss.* Of the eight possible onium isomers of $C_4H_9O^+$, five are known to eliminate mainly H_2O in metastable transitions. This trend is particularly pronounced for the three isomers (1′)—(3′) that arise by protonation of C_4H_8O carbonyl compounds (Table 6).[9]


$CH_3\overset{\overset{+}{O}H}{\overset{\|}{C}}CH_2CH_3$

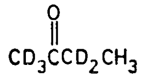
(1′)



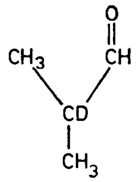
(2′)


$CH_3CH_2CH_2CH=\overset{+}{O}H$

(3′)


$CD_3\overset{O}{\overset{\|}{C}}CD_2CH_3$

(1D)



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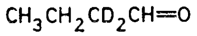

$CH_3CH_2CD_2CH=O$

(3D)

Table 6

Slow unimolecular reactions of metastable $C_4H_9O^+$ ions

Ion	Neutral species lost[a] H_2O	C_2H_4	CH_2O
$CH_3CH_2(CH_3)C=\overset{+}{O}H$	89	3	8
$(CH_3)_2CHCH=\overset{+}{O}H$	90	3	7
$CH_3CH_2CH_2CH=\overset{+}{O}H$	99	1	0

[a] Abundances normalised to a total metastable ion current of 100 units (first field-free region) from *m/z* 73 and taken from ref. 9.

Table 7

CI Mass spectra of $CH_3CD_2(CD_3)C=O$

m/z	Reagent gas H_2	D_2	H_2–N_2	H_2–CO_2	H_2–CO
79		100			
78	100	20	100	100	100
77	8	3	8	6.5	7.5
76	0.5	0.5	0	0	0
75	0	0	0	0	0
74	0	0.5	0	0	0
62	0.5	0.5	0	0	0
61	3	7.5	0	0	0
60	64	69	9	1.0	2
59	57.5	57	7	1.5	2.5
58	4	2.5	0.5	0	0
50		5.5			
49	6	8			
48	6.5	13.5	0.5	*a*	0
47	13	15.5	1	*a*	(0.5)
46	22	13	6	*a*	5
45	1	0.5	0.5	*a*	0.5
44	0.5	0	0	*a*	0
34	0	3	0	*a*	0
33	2.5	3	0	*a*	0
32	2.5	2.5	2.5	*a*	0.5
31	2	2	0.5	*a*	0.5
30	0.5	*b*	0	*a*	2

[a] Peak not significantly greater than in pure reagent gas spectrum. [b] Peak obscured by N_2D^+ peak.

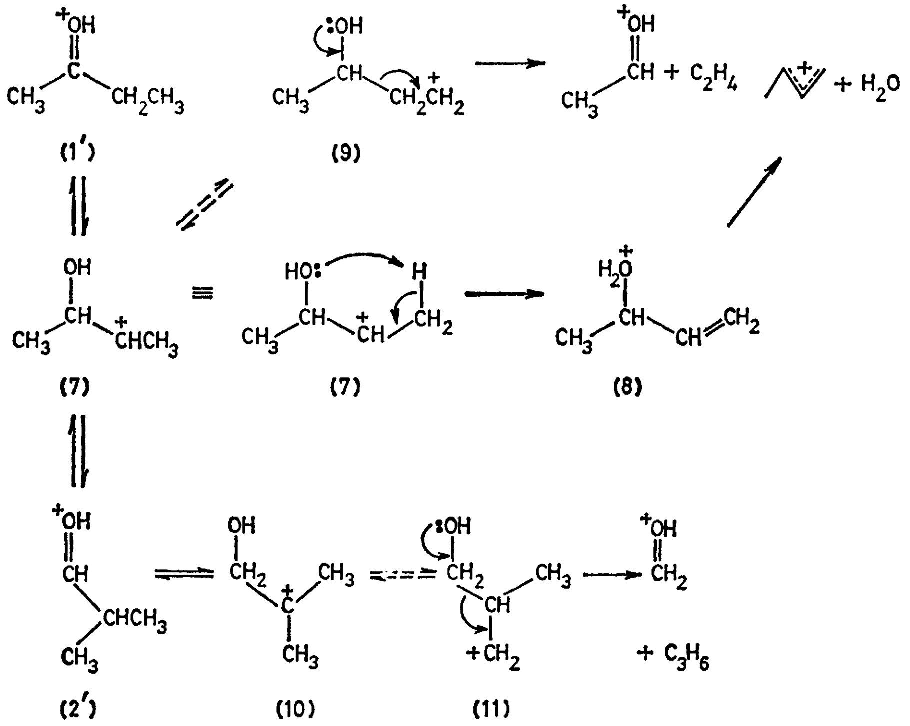
Table 8

CI Mass spectra of $(CH_3)_2CDCHO$

m/z	Reagent gas H_2	D_2	H_2–N_2	H_2–CO_2	H_2–CO
76					
75		27.5			
74	33.5	14	100	100	100
73	3.5	2	10	8	8.5
72	4	3.5	3	1.5	2
71	0.5	0.5	0	0.5	0.5
60	0	0		0	0
59	0.5	0.5		0	0
58	0.5	1	0	0	0.5
57	5	10.5	4.5	1	0.5
56	100	100	61	13	8.5
55	8.5	8	5	3	1
47	0	8		2	0
46	7.5	14.5		4	0.5
45	13	16	2	*a*	0.5
44	24	17	5.5	3.5	4.5
43	13.5	2	12	1	1
42	1.5	1.5	6	0.5	1.5
41	1	0.5	1	0	0.5
35	0	0		*a*	0
34	0	0.5		*a*	0
33	0.5	3	0	*a*	0
32	3	5.5	2.5	*a*	0.5
31	4.5	0.5	1	*a*	0.5
30	3.5				1.5

[a] Peak not significantly greater than in pure reagent gas spectrum.

Potential energy profiles have been constructed for (1′)—(3′) and related ions.[6] As expected from the dominance of H_2O loss from these ions, CH_2O and C_2H_4 eliminations have higher energy requirements.[9] It is, therefore, not surprising that H_2O loss also occurs in high abundance when (1′)—(3′) are produced by protonation of butanone, isobutyraldehyde, and butyraldehyde. Moreover, the observation of predominantly HDO loss from C_4H_8-DO^+ species, generated in D_2-CI, is consistent with earlier EI results and supports the hypothesis that water loss from (1′) and (2′) involves preferential retention of the original hydrogen attached to oxygen in the expelled water. Further insight is furnished by studies on the three deuterium labelled analogues, (1D)—(3D) which exhibit the CI spectra recorded in Tables 7—9, respectively. The H_2-CI spectra of (1D)—(3D) indicate that the derived protonated species eliminate H_2O and HOD in the respective ratios of *ca.* 1 : 1, 11 : 1, and 10 : 1; similar conclusions follow from the CI spectra with other reagent gases. The previously proposed [6] mechanisms for water loss from (1′)—(3′) are summarised in Schemes 1 and 2. The CI data support the conclusion reached from earlier EI work that (1′) and (2′) interconvert prior to dissociation in metastable transitions. Given that this occurs, the two methyl groups in (1D) are rendered equivalent by the reversible methyl shifts, but the hydrogen atoms of the methylene group remain distinct. Hydrogen transfer to oxygen eventually occurs from a methyl group, on an irreversible basis, followed by water loss. Since there is an equal probability that a CH_3 or CD_3 group will be involved in this step [(7) ⟶ (8)], the observation of approximately equal amounts of



Scheme 1

Table 9

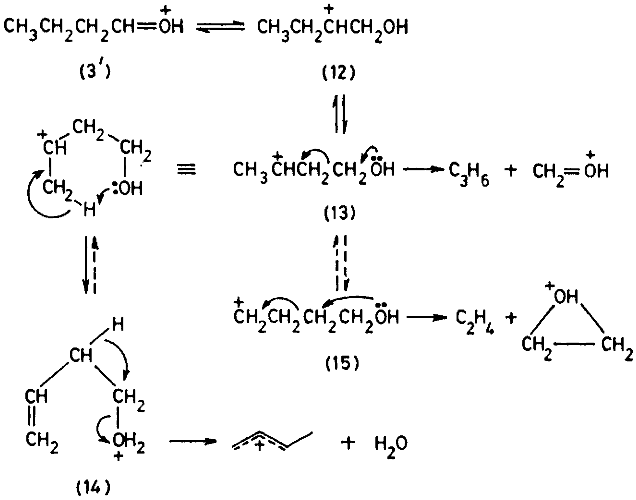
CI Mass spectra of $CH_3CH_2CD_2CHO$

m/z	Reagent gas H_2	D_2	H_2–N_2	H_2–CO_2	H_2–CO
76		10.5			
75	26	12	42.5	38	80.5
74	3.5	1.5	3	3	7
73	8	3.5	3	3	8
72	0.5	0	0	0	0.5
71	0	0	0	0	0.5
60	0	1.5	0	0	0
59	2	1	1	1	1.5
58	4.5	9.5	4	4	4.5
57	100	100	100	100	100
56	9	6	4	4	5
55	0.5	1.5	0	1	1
47	4	2.5	1	1.5	0.5
46	5	17.5	4	4	3.5
45	27.5	60	1	*a*	5
44	50	12.5	29	11	6.5
43	12.5	1.5	7.5	3	3
42	1.5	1	1	0	1
41	1	0.5	0.5	0	0.5
35	0	0	0	*a*	0
34	0	3.5	0	*a*	0
33	3	17	2	*a*	0.5
32	13.5	7	8.5	*a*	15
31	4.5	3	2.5	*a*	1
30	1	3.5	4.5	*a*	2

[a] Peak not significantly greater than in pure reagent gas spectrum.

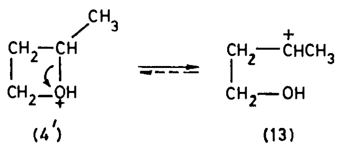
H_2O and HOD loss from $CH_3CD_2(CD_3)C{=}OH^+$ can be explained. Moreover, the poor competition of HOD loss from $(CH_3)_2CDCH{=}OH^+$ can also be understood because it is difficult to incorporate the deuterium atom into the methyl groups; similar remarks apply to $CH_3CH_2CD_2$-$CH{=}OH^+$.

Loss of water is also a major reaction in the H_2-CI spectra of the cyclic ethers; however, it does not become the dominant reaction (base peak) until weaker protonating agents are employed. The most likely course for H_2O loss from (4′)—(6′) is *via* ring opening to form an open-chain carbonium ion, followed by isomerisation to intermediates involved in Schemes 1 and 2; equations (3)—(5) depict the most likely pathways. There are two sources of evidence that support this view. First, the D_2-CI spectra are consistent with protonation on oxygen, followed by proton transfer, on an essentially irreversible basis, from carbon to oxygen, before eventual water loss; Schemes 1 and 2, together with equations (3)—(5),

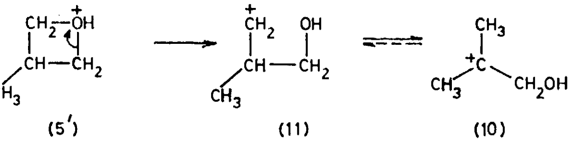


Scheme 2

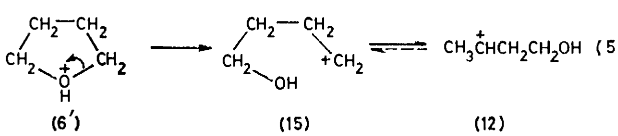
explain this observation. Secondly, the cyclic compounds undergo a greater amount of the higher energy reactions such as C_2H_4, C_3H_6, and CH_2O loss, than do the carbonyl isomers, relative to water elimination. This is explicable, in terms of Schemes 1 and 2 and equations (3)—(5), because the open-chain carbonium ions (13) and (15), *en route* to the intermediates in Schemes 1 and 2, are high energy species and can readily undergo other reactions. Water loss from (4′)—(6′) requires extensive rearrangement and could easily be pre-empted by faster bond cleavage reactions at high internal energies.



(3)



(4)

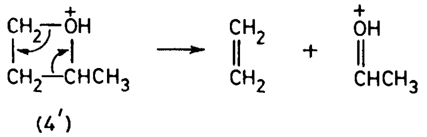


(5)

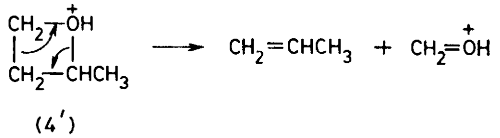
(ii) *Ethene loss.* Earlier EI work on metastable $C_4H_9O^+$ ions reveals that C_2H_4 loss is a rather high-energy process, requiring significantly more internal energy than H_2O loss from (1) and (2) and much more internal energy than H_2O loss from (3). This is reflected by the poor competition (1—5% relative to H_2O loss) of C_2H_4 elimination in slow reactions. The most plausible routes for C_2H_4 loss from (1′)—(3′) are given in Schemes 1 and 2. The H_2-CI spectra of butanone, isobutyraldehyde, and butyraldehyde show a significant peak at *m/z* 45, due to C_2H_4 loss from $C_4H_9O^+$, corresponding to more effective competition of the higher energy process in the CI spectra than occurs when the analogous $C_4H_9O^+$ decay in metastable transitions. This supports the similar results obtained in a study on the lower homologues, $C_3H_7O^+$,[4] for which the reactions detected in CI experiments parallel those for the analogous species decomposing in metastable transitions following EI generation. In the case of the ions (1′)—(3′), the abundance of C_2H_4 loss, relative to H_2O elimination, decreases as the exothermicity of protonation is reduced. This trend is discussed in more detail subsequently.

Deuterium labelling studies lend support to the mechanisms proposed in Schemes 1 and 2. Thus, when D_2-CI spectra are obtained, a significant shift of *m/z* 45 to 46 takes place; this shows that the oxygen-bound hydrogen atom is predominantly retained in the daughter ion. Moreover, the loss of both C_2H_4 and C_2H_3D from $(CH_3)_2CDCH=\overset{+}{O}H$ is also compatible with Scheme 1.

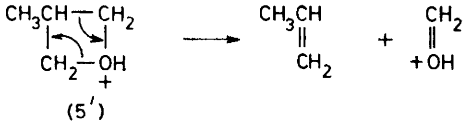
Ethene loss from the cyclic isomers also occurs to a significant degree and can be interpreted as occurring *via* rearrangement to give common intermediates to those postulated in Schemes 1 and 2 [equations (3)—(5)]. It is instructive to note that (5′) eliminates C_2H_4; this proves that alkene elimination from (4′) and (5′) can proceed by mechanisms other than the 2 + 2 cycloreversions [equations (6)—(8)]. Were the cycloreversion mechanism the only feasible pathway for alkene loss, (5′) could not eliminate C_2H_4. The occurrence of C_2H_4 loss from (5′) demonstrates that it prefers to undergo ring opening, to yield (11), than to eliminate C_3H_6; such a conclusion might have been expected on the grounds of orbital symmetry arguments.[14] The most probable mechanism for C_2H_4 loss from (5′) is *via* the sequence $(5') \longrightarrow (11) \longrightarrow (10) \longrightarrow (2') \longrightarrow (7) \longrightarrow (9) \longrightarrow C_2H_4 + CH_3CH=OH^+$ (Scheme 1); such a series of rearrangements is less likely than direct dissociation of (11) to give $C_3H_6 + CH_2=OH^+$. This interpretation is consistent with the observation that (5′) eliminates C_3H_6 in greater abundance than C_2H_4.



(6)



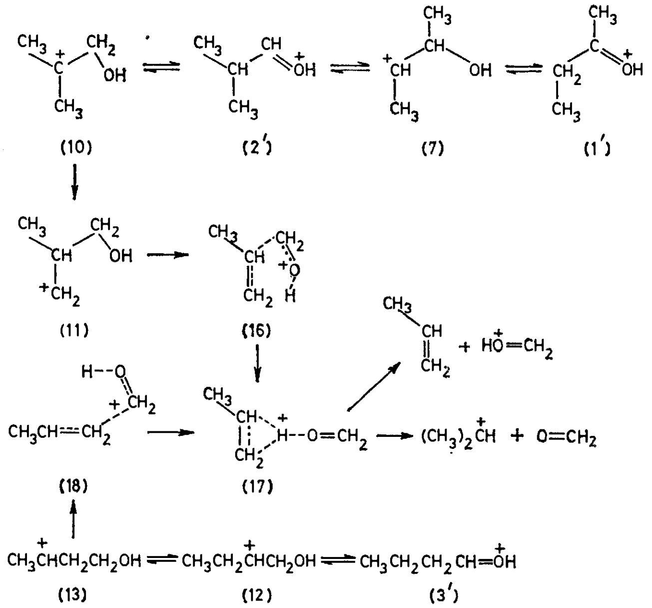
(7)



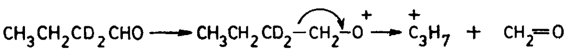
(8)

(iii) *Formaldehyde loss.* Apart from H_2O and C_2H_4 loss, metastable ions of structure (3′) undergo no other reactions; the isomeric ions, (1′) and (2′), however, eliminate a small percentage (7—8%) of CH_2O. It is clear from Tables 1—5 that formaldehyde loss is of greater significance than this for (1′) and (2′) generated by CI; indeed, CH_2O loss is also observed from (3′) produced by CI and constitutes the major reaction when H_3^+ is the protonating species. Moreover, there is the anomaly, referred to earlier, that D_2-CI spectra exhibit a shift of *m/z* 43 to 44; it is in fact difficult to envisage a mechanism, at first sight, whereby CH_2O can be eliminated from (1′)—(3′). A mechanism has been proposed, however, which explains the facts available for $C_4H_9O^+$ metastable ions;[6] it is summarised in Scheme **3**. The central intermediate in Scheme **3** is (17), in which formaldehyde and propene are both co-ordinated to a common proton. This species ought to be more stable than either products ($CH_2=\overset{+}{O}H + C_3H_6$ or $CH_2=O + C_3H_7^+$). Application of mechanisms containing species such as (17) has been of considerable use in explaining the unimolecular reactions of numerous organic ions.[2,3,5,6,15-17]

In the present context, Scheme 3 can be utilised to interpret the behaviour of (1')—(3') generated by CI. The complex (17) is accessible from (1') and (2'), or from (3'), *via* species (11) and (13), respectively, *en route* to C_3H_6 loss. As the final steps proceed [(11) ⟶ (16) ⟶ products and (13) ⟶ (18) ⟶ products], slight rearrangement can lead from (16) or (18) to (17). The observation that formaldehyde loss from $C_4H_8DO^+$ species produced by D_2-CI gives rise to $C_3H_6D^+$ and CH_2O can be understood in terms of Scheme 3. Although protonation occurs on oxygen, this proton eventually becomes the common proton in (17); therefore, when (17) dissociates *via* formaldehyde loss, this proton is retained in the resultant isopropyl cation. Consequently, when D_2-CI spectra are recorded, CH_2O alone is lost and *m/z* 44 is the daughter ion. Further support for the mechanism stems from the appearance of *m/z* 43, 44, and 45 in the H_2-CI spectrum of $CH_3CH_2CD_2CHO$. This may be explained in terms of partial equilibration of (3'), (12), and (13), prior to rearrangement to (18). Were CH_2O to arise by protonation on the carbonyl carbon [equation (9)] exclusive CH_2O (daughter ion *m/z* 45) would be anticipated. Similar remarks apply to the decomposition of $(CH_3)_2CDCHO$ which clearly cannot proceed by simple protonation on the carbonyl carbon atom.



SCHEME 3



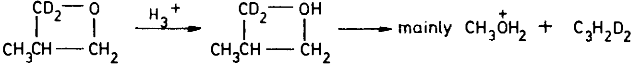
$$CH_3CH_2CD_2CHO \longrightarrow CH_3CH_2CD_2{-}CH_2{-}\overset{+}{O} \longrightarrow \overset{+}{C}_3H_7 + CH_2{=}O \qquad (9)$$

Formaldehyde loss also takes place from the cyclic isomers (4')—(6'). As with H_2O and C_2H_4 loss, this reaction is most plausibly interpreted as occurring *via* ring opening and isomerisation to intermediates shown in Scheme 3. This explanation avoids the necessity of postulating protonation on carbon in order to rationalise the D_2-CI spectra.

(iv) *Propene loss*. This reaction does not occur for metastable ions of structures (1')—(3');[9] the inability of C_3H_6 loss to compete has been ascribed to the relatively high energy of the products.[6] In contrast to this EI work, when (1')—(3') are generated by H_2-CI, elimination of C_3H_6 occurs in fair to moderate abundance. This process could take place either by direct cleavage of (11) [Scheme 1, for (1') and (2')] or (13) [Scheme 2, for (3')], or after rearrangement of (11) or (13) to (17); it is not possible to distinguish between these two alternatives on the basis of ^{2}H-labelling studies. However, it is evident that the earlier classification of C_3H_6 loss from $C_4H_9O^+$ as a high energy process is correct; thus, C_3H_6 loss rapidly becomes of negligible abundance when relatively weak protonating agents are employed.

The cyclic isomers (4')—(6') lose C_3H_6 in greater abundance, compared to H_2O loss, than is observed for (1')—(3'). This trend is especially noticeable for (5') which continues to eliminate significant amounts (24% of base peak) of C_3H_6 even for H_2–CO-CI; with such a weak protonating agent, $H\overset{+}{C}O$, none of the other isomers lose significant amounts of C_3H_6. These observations can be understood in terms of ring opening followed by isomerisation to intermediates shown in Schemes 1—3. Since the ring opening of (5') must proceed *via* the high-energy carbonium ion (11), which is ideally arranged to eliminate C_3H_6 by simple cleavage, the persistence of C_3H_6 loss from (5') can be explained. In all cases, D_2-CI spectra indicate that the added proton is retained in the $CH_2{=}OH^+$ daughter ion, as expected if protonation occurs on oxygen.

(v) C_3H_4 *loss*. This curious reaction occurs in high abundance in the CI spectra of 3-methyloxetan. It must be a high energy process because the products (presumably $CH_3OH_2^+$ and $CH_3C{\equiv}CH$ or $CH_2{=}C{=}CH_2$) have a high total (765 kJ mol^{-1}) heat of formation.[7,18] No such process occurs for metastable $C_4H_9O^+$ ions, except to an extremely small (*ca.* 0.5%) degree from $(CH_3)_2C{=}\overset{+}{O}CH_3$.[6] Moreover, no other isomers of C_4H_8O exhibit a significant *m/z* 33 peak in their CI spectra. Comparison of the H_2- and D_2-CI spectra of 3-methyloxetan reveals that the added proton is retained in the $CH_3OH_2^+$ fragment. Further insight is afforded by the behaviour of the ^{2}H-labelled analogue (19); the CI spectra of this compound are presented in Table 10. It is clear from these data that the exocyclic methyl group is predominantly retained in the $CH_3OH_2^+$ daughter ion. Moreover, some contribution is observed for CH_3OHD^+ (or $CH_2DOH_2^+$) as the ionic fragment; however, *m/z* 35 ($CD_2HOH_2^+$, or isomers) is of negligible abundance. These results suggest that the protonated methanol is derived as follows: the CH_3 group originates from the exocyclic methyl group, one oxygen-bound hydrogen is



(19) (20)

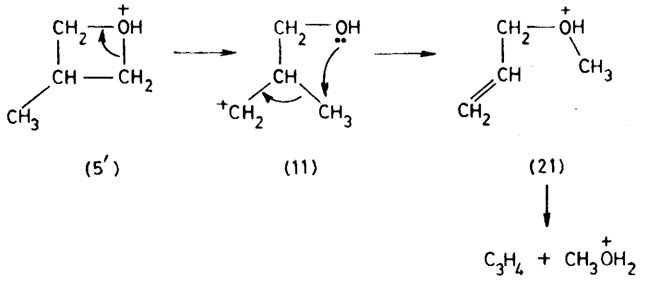
TABLE 10

CI Mass spectra of $\overline{CH_2CH(CH_3)CD_2O}$

m/z	Reagent gas H_2	D_2	H_2–N_2	H_2–CO_2	H_2–CO
76		16			
75	12.5	17.5	45.5	34	80
74	1.5	2	2	2	4
73	18.5	16	6	9	6
72	15	13	4	2	3
71	0	0.5	0	1.5	1
60	0.5	3.5	4	0.5	0.5
59	4	1.5	2	4.5	6.5
58	2.5	7	42	3	3.5
57	48.5	49.5	3.5	60	95
56	4.5	4.5	0	6.5	7
55	1	2	17.5	8.5	2
47	4	6.5		4	2
46	5.5	25		1	1.5
45	29.5	15	17.5	*a*	20
44	21	24	13.5	12.5	18.5
43	26	6	13.5	13.5	17
42	6.5	7.5	3	3	6.5
41	6	4.5	1.5	1	3
35	1	27.5		0.5	0.5
34	15.5	100	11	18	11.5
33	100	18.5	100	100	100
32	10.5	30.5	4	*a*	5
31	37	13.5	13	10	10.5
30	2.5	5.5	3.5		7

[a] Peak obscured by reagent ion peak.

that added in the CI process, and the final hydrogen is selected from those on the ring carbon atoms. This hypothesis is summarised in Scheme 4. Some steps required by this mechanism are energetically very demanding [for example, (11) ⟶ (21)]; however, the high energy of the eventual products indicates that C_3H_4 loss could involve high energy intermediates and transition states.



SCHEME 4

(c) *The Effect of Changing the Exothermicity of Protonation on the Relative Abundances of Competing Dissociations.*—Energy parameters are often of great importance in determining the relative abundances of competing reactions of isolated ions, especially when ions of low internal energy are investigated.[19] Moreover, when a population of ions can undergo two or more competing dissociations, a reduction in the average internal energy of the ions favours the decay route requiring the least energy.[20] This trend has been observed for numerous ions generated by EI and is well known. However, in a study of $C_3H_7O^+$ generated by protonation of C_3H_6O isomers, only a marginal effect on the relative abundance of competing decomposition channels was observed when the exothermicity of protonation was decreased.[4] It is, therefore, pertinent to examine the effect of variation of the exothermicity of protonation on the reactions of $C_4H_9O^+$.

The results of earlier EI work, which may be summarised by appropriate potential energy profiles,[6] allow the energies needed to cause H_2O, C_2H_4, CH_2O, and C_3H_6 losses from (1′)—(3′) to be established. Moreover, the theoretical heats of protonation ΔH_p when the C_4H_8O carbonyl compounds interact with H_3^+, N_2H^+, CO_2H^+, and HCO^+ can be calculated from the proton affinities (420, 490, 540, and 590 kJ mol^{-1}, respectively) of H_2, N_2, CO_2 and CO,[21] together with those of butanone, isobutyraldehyde, and butyraldehyde[7] (825, 800, and 795 kJ mol^{-1}, respectively). These energy data are summarised in Table 11. The relative abundances of H_2O, C_2H_4, CH_2O, and C_3H_6 losses from (1′)—(3′), formed with various reagent ions, are given in Table 12. It is clear from these data that the competition between the various decomposition channels is systematically dependent on the exothermicity of protonation. The process having the lowest energy requirement, H_2O elimination, dominates increasingly as weaker protonating agents are employed. This effect is most dramatic for protonated butyraldehyde, for which the differences in energy requirement for H_2O loss and the other processes is greatest. A similar trend can be discerned for the cyclic $C_4H_9O^+$ ions, but is not discussed further since the energy data pertaining to these ions are less clearly established than those of (1′)—(3′). However, even with the weakest proton protonating agent (HCO^+), C_2H_4, CH_2O, and C_3H_6 losses compete more effectively with H_2O loss than is the case for the corresponding metastable ions generated by EI.[9] This indicates that $C_4H_9O^+$ ions generated by CI have similar, but somewhat greater, internal energies than those of the corresponding metastable ions formed by EI; a similar conclusion has been reached for the homologous $C_3H_7O^+$ ions.[4]

TABLE 11

Energy data relevant to the decomposition of $C_4H_9O^+$ ions

	Energy requirement for loss of [a]				ΔH_p [a]			
Ion	H_2O	C_2H_4	CH_2O	C_3H_6	H_3	$N_2\overset{+}{H}$	CO_2H^+	$H\overset{+}{C}O$
$CH_3CH_2(CH_3)C{=}\overset{+}{O}H$	210	220	220	240	405	335	285	235
$(CH_3)_2CHCH{=}\overset{+}{O}H$	170	185	185	200	380	310	260	210
$CH_3CH_2CH_2CH{=}\overset{+}{O}H$	110	195	170	190	375	305	255	205

[a] All values in kJ mol^{-1}.

TABLE 12

Relative abundances of competing dissociations of $C_4H_9O^+$ ions formed by protonation of C_4H_8O isomers with various reagent ions

	$CH_3CH_2(CH_3)C{=}\overset{+}{O}H$ [a]				$(CH_3)_2CHCH{=}\overset{+}{O}H$ [a]				$CH_3CH_2CH_2CH{=}\overset{+}{O}H$ [a]			
Reagent ion	H_2O	C_2H_4	CH_2O	C_3H_6	H_2O	C_2H_4	CH_2O	C_3H_6	H_2O	C_2H_4	CH_2O	C_3H_6
H_3^+	1	0.21	0.29	0.08	1	0.25	0.44	0.12	0.94	0.09	1	0.32
N_2H^+	1	0.12	0.25	0.06	1	0.11	0.20	0.04	1	0.02	0.50	0.12
CO_2H^+	b				b				1	c	0.24	0.03
HCO^+	b				b				1	0.01	0.13	0.03

[a] Abundances are assigned relative to a value of 1 for the most abundant reaction. [b] These data are not significant on account of negligible decomposition induced by protonation with these reagent ions. [c] Reagent ion peak interferes with this reaction.

Conclusions.—The reactions of six isomers of $C_4H_9O^+$ produced by CI of C_4H_8O compounds with H_3^+, N_2H^+, CO_2H^+, and HCO^+ reagent ions can be interpreted as occurring after protonation on oxygen. As the exothermicity of protonation is reduced, the overall degree of fragmentation decreases; moreover, there is a greater relative preference for undergoing the dissociation with the lowest energy requirement (H_2O loss) as weaker protonating agents are employed. The reactions undergone by the $C_4H_9O^+$ ions generated by CI are similar to those observed for the corresponding metastable ions formed after EI; however, the ions produced by CI appear to possess a greater average internal energy than the metastable ions generated by EI.

EXPERIMENTAL

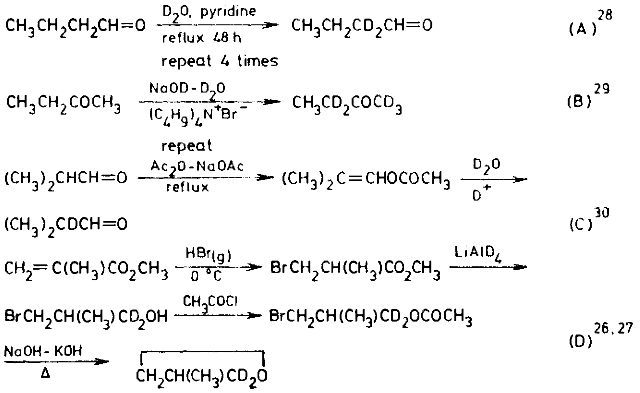
The chemical ionisation mass spectra were obtained using a Dupont 21–490 mass spectrometer equipped with a high pressure chemical ionisation source. An ionising electron energy of 70 eV was employed, with the ion repellers maintained at cage potential. The source temperature was kept as low as possible (*ca.* 60 °C) to minimise any thermal decomposition of the samples, which were introduced through a heated inlet system at *ca.* 100 °C. The reagent ions H_3^+ and D_3^+ were produced by electron impact ionisation of H_2 and D_2, respectively, at source pressures of *ca.* 0.3 Torr. The remaining reagent ions XH^+ ($X = N_2, CO_2, CO$) were produced by electron impact ionisation of mixtures of *ca.* 10% X in H_2. Under these conditions, the required species NH^+ accounted for >95% of the total reagent ion signal at source pressures of *ca.* 0.2 Torr. The sequence of reactions generating XH^+ is shown in Scheme 5. All these reactions are known from previous studies to occur quite rapidly.[22-24]

$$\begin{aligned}
H_2^{+\cdot} + H_2 &\longrightarrow H_3^+ + H^\cdot \\
H_3^+ + X &\longrightarrow XH^+ + H_2 \\
H_2^{+\cdot} + X &\longrightarrow XH^+ + H^\cdot \\
X^{+\cdot} + H_2 &\longrightarrow XH^+ + H^\cdot
\end{aligned}$$

SCHEME 5

The reagent gases were commercial samples of high purity and were used directly, with the exception of D_2 which was passed through a heated palladium thimble prior to use.

The unlabelled C_4H_8O compounds were either commercially available (butanone, isobutyraldehyde, butyraldehyde, and tetrahydrofuran) or synthesised by literature procedures (2-methyloxetan [25,26] and 3-methyloxetan [26,27]). The ^2H-labelled compounds were obtained by the routes in Scheme 6.



SCHEME 6

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