The residue from the trap-to-trap distillation of the filtrate was extracted with 150 ml of boiling cyclohexane. From the extracts triphenylphosphine oxide, mp 156–157°, could be isolated as white needles in 38% yield.

Reaction of Phenyl(1,1-dihalo-2,2,2-trifluoromethyl)mercury Compounds with Sodium Iodide in 1,2-Dimethoxyethane in the Presence of Cyclohexene. (a) $PhHgCCl_2CF_3$. The standard apparatus was charged with a solution containing 30.0 mmol of the mercury reagent, 10 ml of cyclohexene, and 50 ml of DME. The solution was heated to reflux and 4.82 g (32.2 mmol) of sodium iodide (powdered and dried for 24 hr at 110° and 0.05 mm) in 35 ml of DME was added slowly over 35 min. The reaction mixture became slightly yellow and cloudy during the addition; it was heated at reflux for an additional 4 hr and stirred at room temperature overnight. Filtration was followed by trap-to-trap distillation (0.1 mm, pot temperature to 35°, closed system) into a receiver at −78°. Glc analysis showed the presence of a single low-boiling product in addition to cyclohexene and solvent. In particular, 7-chloro-7-trifluoromethylnorcarane was not present. The product was isolated *via* distillation through a Widmer column (receiver cooled to −78°). The product obtained was identified as 1,1-dichloro-2,2-difluoroethylene by comparison of its gas phase infrared spectrum with that recorded in the literature: 1747 vs, 1326 vs, 1031 vs, and 991 cm^{-1} vs (bands broadened due to rotational structure) (lit.[35] 1749, 1327, 1032, 993 cm^{-1}). The yield of $CCl_2{=}CF_2$ (*via* glc, column A, 55°) was 60%.

(b) $PhHgCClBrCF_3$. Essentially the same procedure was used in the reaction of 14.0 mmol of the mercurial with 15.6 mmol of sodium iodide in 25 ml of DME in the presence of 5.0 ml of cyclohexene. Redistillation of the trap-to-trap distillate gave a fraction at 39–67° from which the product could be isolated by glc (column D, 75°). It was identified as 1-bromo-1-chloro-2,2-difluoroethylene by means of its infrared spectrum: (gas cell) 1730 vs, 1319 vs, 1021 vs, and 943 cm^{-1} vs (lit.[36] 1731, 1314, 1022, 945 cm^{-1}, major bands only). Glc (column I, 100°) established that $CClBr{=}CF_2$ had been formed in 68% yield. None of the 7-chloro-7-trifluoronorcarane was present.

Acknowledgments. The authors are grateful to the U. S. Air Force Office of Scientific Research (SRC)-OAR for generous support of this work (USAF Grant AFOSR-68-1350) and to the Ayerst Laboratories for a gift of "Fluothane."

(35) D. E. Mann, L. Fano, J. H. Meal, and T. Shimanouchi, *J. Chem. Phys.*, 27, 51 (1957).

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The Enolic $C_3H_6O\cdot^+$ Ion Formed from Aliphatic Ketones[1-3]

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Abstract: Contrary to previous postulations, the ubiquitous enolic $C_3H_6O\cdot^+$ ion found in ketone mass spectra decomposes mainly by rearrangement to an unstable acetone ion, **2** → **8**, not by simple cleavage loss of the methyl group, **2** → **7**. A methyl hydrogen can also rearrange through a four-membered ring intermediate to the methylene group, **2** → **11**, and both reactions exhibit substantial primary isotope effects. All six hydrogen atoms show nearly equivalent secondary isotope effects on the relative rates for the losses of the two methyl groups, consistent with their loss from the intermediate acetone ion. An unusual observation is that the two methyl groups are lost from this intermediate acetone ion at unequal rates; we suggest that this is due to incomplete randomization of energy before decomposition. Apparently this is the first case reported in which ion fragmentation is not independent of initial preparation. The fragmentations of isotopically labeled $C_3H_6O\cdot^+$ ions formed by the double hydrogen rearrangement of alkanones closely resemble the behavior of the enolic $C_3H_6O\cdot^+$ ions. This provides independent verification of the recent ion cyclotron resonance evidence of Djerassi and coworkers which shows that these double rearrangement ions have the enolic structure, in contrast to the oxonium ion structure postulated originally.

The odd-electron $C_3H_6O\cdot^+$ ion and its higher homologs are well known as characteristic peaks in the mass spectra of aliphatic ketones, arising from the rearrangement of a γ-hydrogen atom, **1** → **2**, or the sequential rearrangement of γ- and γ′-hydrogen atoms, **3** → **4** → **2** (Scheme I).[5-7] This ion is also the most abundant peak in the spectrum of 1-methylcyclobutanol (**5**).[8] Although these alkanone rearrangements have been among the most thoroughly studied of all electron-impact reactions,[5-10] there are many aspects of the unimolecular reactions of these enolic ions that are poorly understood. It was established only recently that the characteristic olefin loss from the enolic ion **4** proceeded mainly through rearrangement of hydrogen to the methylene group, **4** → **2**, not to the hydroxyl group, **4** → **6**.[2,9,10] Further, most reported reactions of such enolic ions are typical of reactions of the olefinic functionality, not of the hydroxyl group;[6,9] particular note has been made of the absence of any evidence for tautomerization of an enolic ion to the ketonic structure.[6,9,11]

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(1) Metastable Ions Characteristics. XVIII. XVII: I. Howe and F. W. McLafferty, *J. Amer. Chem. Soc.*, **93**, 99 (1971).

(2) (a) For a preliminary report of this work, see D. J. McAdoo, F. W. McLafferty, and J. S. Smith, *ibid.*, **92**, 6343 (1970); (b) further details are given in the Ph.D. Thesis of D. J. McAdoo, Cornell University, 1971.

(3) The generous financial support of the Army Research Office, Durham, and the National Institutes of Health, GM16609, is gratefully acknowledged.

(4) National Institutes of Health Predoctoral Fellow, 1969–1970.

(5) F. W. McLafferty, *Anal. Chem.*, 31, 82 (1959).

(6) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Ions," Holden-Day, San Francisco, Calif., 1967, Chapter 3.

(7) (a) W. Carpenter, A. M. Duffield, and C. Djerassi, *J. Amer. Chem. Soc.*, 90, 160 (1968); (b) G. Eadon and C. Djerassi, *ibid.*, **92**, 3084 (1970), and references cited therein.

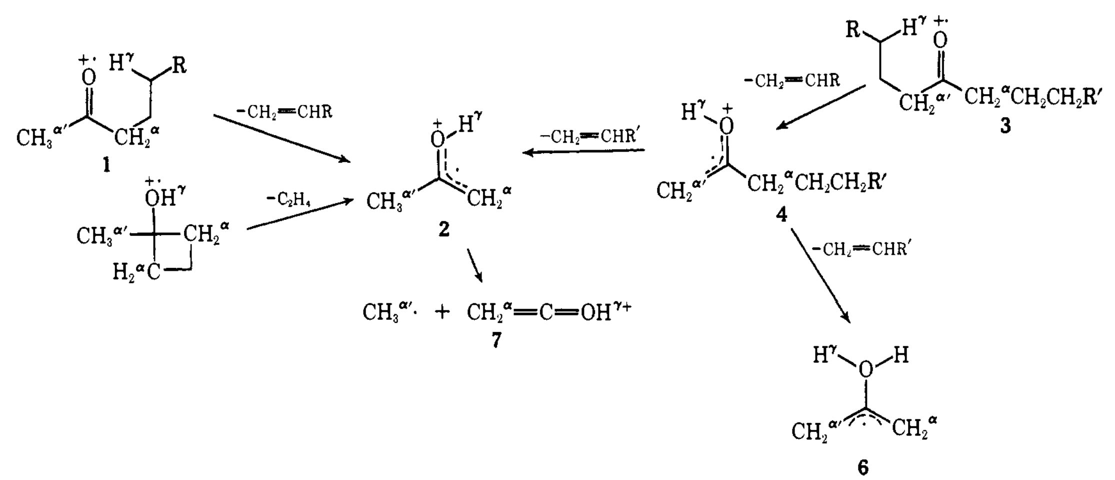
(8) P. Ausloos and R. E. Rebbert, *ibid.*, **83**, 4897 (1961).

(9) J. Diekman, J. K. MacLeod, C. Djerassi, and J. D. Baldeschwieler, *ibid.*, 91, 2069 (1969).

(10) G. Eadon, J. Diekman, and C. Djerassi, *ibid.*, 91, 3986 (1969); **92**, 6205 (1970). We are indebted to Professor Djerassi for preprints of these manuscripts.

(11) S. Meyerson and E. K. Fields, *Org. Mass Spectrom.*, 2, 1309 (1969).

Scheme I



For example, recent work[11] cites the absence of $C_2H_2DO^+$ in the mass spectrum of $CH_3COCH_2CH_2CD_2CH_3$ as evidence that the enolic ion, in this case $CH_3C(OD)=CH_2\cdot^+$, does not revert to the ketonic form, $CH_3COCH_2D\cdot^+$, before decomposing. Also, direct cleavage of the vinylic bond of the enolic ions $CH_3C(OH)=CH_2\cdot^+$ (**2**)[7a] and $CH_3CH_2C(OH)=CH_2\cdot^+$[9] has been postulated to explain the loss of the $CH_3\cdot$ and $CH_3CH_2\cdot$ radicals, respectively. Vinylic cleavage in other systems is known to be a relatively unfavorable process, although such an alkyl loss might be viewed as analogous to the well-known decomposition of alkanones. However, in a preliminary communication[2a] we presented evidence that the major decomposition pathways of both the enolic $C_3H_6O\cdot^+$ and $C_4H_8O\cdot^+$ ions involve rearrangement to a ketonic intermediate.

The numerous studies of alkanone mass spectra which have utilized deuterium labeling have shown many instances in which there is substantial scrambling of hydrogen atoms between various positions in the molecule before decomposition, especially in the decomposition of metastable and other low energy ions.[6,7,12–14] This often makes it difficult to interpret the data for elucidation of other reaction pathways. A better understanding of the mechanisms by which such scrambling can take place is obviously desirable.[7] Suggested mechanisms include reciprocal hydrogen transfer,[7a] concerted exchange of hydrogens between two positions,[13] or a stepwise hydrogen migration to a site of lowered electron density.[15] Little is known of the effect of the ring size of the transition state involved in scrambling; any exchange of hydrogen atoms between the positions of the enolic ion **2** must involve a transition state with no larger than a four-membered ring.

Most deuterium-labeling studies have assumed that isotope effects are negligible;[7,11] however, such effects can be large, especially for low energy processes such as metastable ion transitions.[1,16] For example, the metastable transition for the loss of hydrogen from toluene ions shows $k_H/k_D = 2.8$;[1] the existence of such an isotope effect in the enolic ion system would cause the rate of ketonization of $CH_3C(OD)=CH_2\cdot^+$ to be substantially slower than that of $CH_3C(OH)=CH_2\cdot^+$. To avoid any ambiguity of this type in the present study complementary labeling was employed for the $C_3(H,D)_6O\cdot^+$ ions used.

Results

Table I summarizes the results for the normal and metastable ions formed by unimolecular decompositions of the $C_3(H,D)_6O\cdot^+$ ions examined in this study. It is assumed that nearly all of the $C_3(H,D)_6O\cdot^+$ ions formed from the three types of precursors, **1**, **3**, and **5**, have the enolic structure, **2**, although this point will be substantiated further in later discussion.

Isotopic Integrity in the $C_3(H,D)_6O\cdot^+$ Ions. Isotopic isomerization before or during formation of the $C_3H_6O\cdot^+$ ions would make the data on their decompositions much more difficult to interpret; fortunately, the extent of this isomerization appears to be quite small. Formation of the normal enol ions from alkanones by either the single or double hydrogen rearrangement proceeds with negligible scrambling of the hydrogen atoms between the separating parts of the molecular ion, as shown by the high specificity for γ-H transfer.[6] The isotopic purity of the $C_3(H,D)_6O\cdot^+$ ions from 1-methyl-d_3-cyclobutanol (**5a**) also appears to be equivalent to the isotopic purity of its molecular ion, although determination of the latter is of lower accuracy because of the low molecular ion abundance. Note that these $C_3(H,D)_6O\cdot^+$ ions which are observed in the normal spectrum must be of *lower* energy than those which serve as precursors for the normal or metastable formation of $C_2(H,D)_3O^+$ ions, and so the latter higher energy $C_3(H,D)_6O\cdot^+$ ions should exhibit even less isotopic scrambling when formed.[12,13,17]

It has been shown that the hydrogen rearrangement reaction which yields **2** from ketones has a substantially higher appearance potential and *looser* activated complex than have many other rearrangement reactions;[14]

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(12) F. W. McLafferty and R. B. Fairweather, *J. Amer. Chem. Soc.*, 90, 5915 (1968).

(13) A. N. H. Yeo and D. H. Williams, *ibid.*, 91, 3582 (1969).

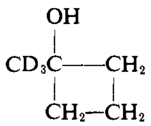
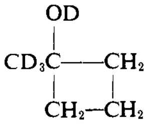
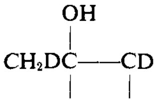
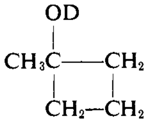
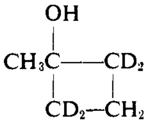
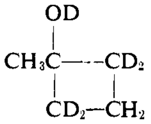
(14) F. W. McLafferty, D. J. McAdoo, and J. S. Smith, *ibid.*, 91, 5400 (1969).

(15) F. P. Boer, T. W. Shannon, and F. W. McLafferty, *ibid.*, 90, 7239 (1968), and references cited therein.

(16) C. Lifshitz and R. Sternberg, *J. Mass Spectrom. Ion Phys.*, 2, 303 (1969); M. Vestal and J. H. Futrell, *J. Chem. Phys.*, 52, 978 (1970).

(17) Note, however, that the metastables corresponding to the *formation* of $C_3(H,D)_6O\cdot^+$ from the molecular ion would have a higher probability for scrambling than either the normal $C_3(H,D)_6O\cdot^+$ ions or the metastables corresponding to their *decomposition*. Also note that this preservation of isotopic integrity in the initially formed $C_3(H,D)_6O\cdot^+$ ions is in sharp contrast to the behavior of other decomposition modes; for example, scrambling is indicated in the spectrum of **5a** by the presence of $(M\cdot^+ - CH_3)$ and $(M\cdot^+ - CH_2D)$ ions in an abundance which is 15% of that of $(M\cdot^+ - CD_3)$.

Table I. Metastable[c] (and Normal[d]) Ion Abundances Corresponding to Decomposition of $C_3(H,D)_6O^+$ Ions

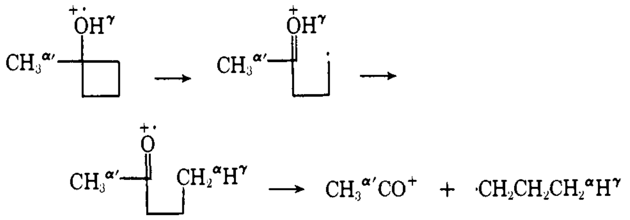
Precursor molecule		$C_3(H,D)_6O^+$	$\Sigma[C_2(H,D)_3O^+]$[a,b]/ $[C_3(H,D)_6O^+]$	Product ions			
				$C_2H_3O^+$	$C_2H_2DO^+$	$C_2HD_2O^+$	$C_2D_3O^+$
	**5a**	$CD_3C(OH){=}CH_2\cdot^+$	0.0064 (0.69 ± 0.03)[b]	54 ± 4 (32)[d]	8 ± 3 (21)	7 ± 3 (20)	100 (100)
$CD_3COC_4H_9$	**1a**	$CD_3C(OH){=}CH_2\cdot^+$		54 ± 4	22 ± 3	20 ± 3	100
$CD_3CH_2CH_2$-$COCD_2C_3H_7$	**3a**	$CD_3C(OH){=}CH_2\cdot^+$		54 ± 4	19 ± 3	18 ± 3	100
	**5b**	$CD_3C(OD){=}CH_2\cdot^+$	0.0059 (0.40 ± 0.03)		60 ± 3 (47)	9 ± 2 (21)	100 (100)
$CD_3COCD_2C_2H_5$[e]	**1c**	$CD_3C(OH){=}CD_2\cdot^+$				66 ± 4	100
$CD_3COCD_2C_3H_7$	**1c′**	$CD_3C(OH){=}CD_2\cdot^+$				66 ± 4	100
$CD_3COCD_2C_5H_{11}$	**1c″**	$CD_3C(OH){=}CD_2\cdot^+$				67 ± 4	100
$CD_3CH_2CD_2COCD_2$-C_3H_7	**3c**	$CD_3C(OH){=}CD_2\cdot^+$				71 ± 3	100
$C_2H_5CD_2COCD_2C_2H_5$[f]	**3d**	$CHD_2C(OH){=}CD_2\cdot^+$			4 ± 2	100	4 ± 2
$C_2H_5CD_2COCD_2C_3H_7$	**3d′**	$CHD_2C(OH){=}CD_2\cdot^+$			4 ± 2	100	5 ± 2
$C_3H_7CD_2COCD_2C_3H_7$	**3d″**	$CHD_2C(OH){=}CD_2\cdot^+$			3 ± 2	100	5 ± 2
	**5e**	$CH_2DC(OH){=}CD_2\cdot^+$	0.0069	2 ± 1	100	86 ± 4	3 ± 1
$C_2H_5CHDCOC_4H_9$	**3f**	$CH_3C(OH){=}CHD\cdot^+$		97 ± 3	100		
	**5g**	$CH_3C(OD){=}CH_2\cdot^+$	0.0047 (0.43 ± 0.03)	100 (100)	78 ± 5 (68)		
	**5h**	$CH_3C(OH){=}CD_2\cdot^+$	0.0069 (0.64 ± 0.03)	100	4 ± 2	90 ± 3	
$CH_3COCD_2C_3H_7$	**1h**	$CH_3C(OH){=}CD_2\cdot^+$		100	5 ± 2	87 ± 3	
	**5i**	$CH_3C(OD){=}CD_2\cdot^+$	0.0050	99 ± 4 (100)	53 ± 4 (67)	62 ± 6 (50)	100 (75)

[a] The sum of the intensities of all of the metastables arising from the $C_3(H,D)_6O\cdot^+$ ion divided by its intensity. [b] Values in parentheses are the sum of the intensities, corrected for contributions from $C_3(H,D)_6O\cdot^+$ isotopic impurities, of all the normal $C_2(H,D)_3O^+$ ions divided by the intensity of the $C_3(H,D)_6O\cdot^+$ ion; this value for undeuterated 1-methylcyclobutanol is 0.64 ± 0.03. [c] The intensity of the metastable relative to the intensity of the most abundant metastable arising from the $C_3(H,D)_6O\cdot^+$ ion. [d] Relative intensities of the corresponding $C_2(H,D)_3O^+$ ions in the normal spectra. Sufficiently high resolution was employed to eliminate hydrocarbon contributions to these ions. [e] Similar values were also obtained for $CD_3COCD_2C_4H_9$. [f] Similar values were also obtained for $C_2H_5CD_2COCD_2C_4H_9$, $C_2H_5CD_2COCD_2$-C_5H_{11}, $C_2H_5CD_2COCD_2CH_2CH(CH_3)_2$, and $C_3H_7CD_2COCD_2C_5H_{11}$.

this suggests that the rate constant for formation of $C_3(H,D)_6O\cdot^+$ rises much faster with increasing ion internal energy than competing reactions which produce scrambling in the molecular ions, $M\cdot^+$, so that there is little overlap of the energy region of $M\cdot^+$ which produces $C_3(H,D)_6O\cdot^+$ ions with those which give isotopic scrambling. Data of Table I bear this out; the metastables corresponding to the loss of CD_3 and CH_2D from $CHD_2C(OH){=}CD_2\cdot^+$ originating from **3d** represent only 7% of the total metastable abundance due to methyl loss, and this small amount appears to arise by isomerization *after* the $C_3H_2D_4O\cdot^+$ ion is formed (*vide infra*).

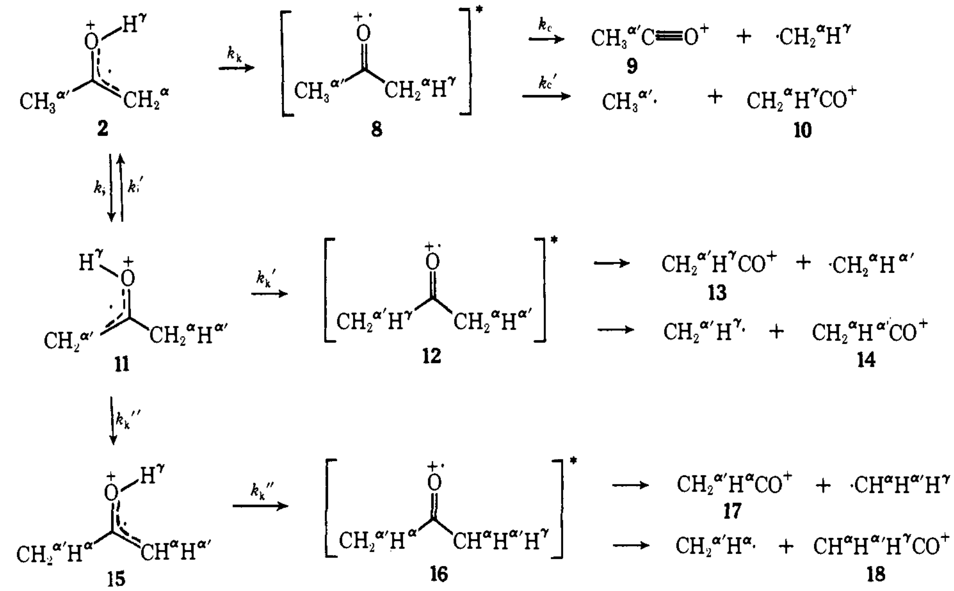
In the case of the two 4-octanone-*1*-d_3 compounds, **3a** and **3c**, there should be a small amount of initial migration of a primary γ-D atom to the oxygen in competition with migration of a secondary γ-H atom, as indicated by the normal ion abundances in **3a** of $[M\cdot^+ - C_2H_2D_2)]/[(M\cdot^+ - C_3H_6)] = 0.04$. The second hydrogen rearrangement from $(M\cdot^+ - C_2H_2D_2)$ would produce $CH_3C(OD){=}CD_2\cdot^+$ as an impurity in the double rearrangement product, $CD_3C(OH){=}CH_2\cdot^+$. However, ICR evidence puts an upper limit of 5% on the proportion of the $C_3H_6O^+$ that is formed by this alternative double rearrangement in 4-nonanone.[10]

Most of the normal $C_2H_3O^+$ ions in the spectrum of **5** should arise from the decomposition of $C_3H_6O\cdot^+$.[9] Ionization efficiency curves of $C_2H_3O^+$ and m*($C_3H_6O^+$ → $C_2H_3O^+$) indicate a small amount of $C_2H_3O^+$ is formed by a separate low energy pathway



A variety of alternate pathways of $C_2H_3O^+$ formation

Scheme II



are possible in the alkanone spectra, and so their normal ion data are not considered for the studies of the $C_3H_6O\cdot^+ \rightarrow C_2H_3O^+$ reaction.

For some compounds only partial deuteration of a particular position was achieved, but this generally is not a serious disadvantage. The metastable data define the isotopic compositions of both the precursor $C_3(H,D)_6O\cdot^+$ ion and the product $C_2(H,D)_3O^+$ ion, so there is no serious cross-contribution to the metastable being measured by products from a precursor of different isotopic composition, in contrast to the ambiguity that this can cause in the measurement of normal ion data. For example, it was difficult to achieve complete deuteration of the hydroxyl group of **5** with D_2O in the inlet system; however, the only contribution of the -OH species to the metastable ion of the corresponding -OD species should be the 3.3% contribution due to the ^{13}C content.

The most serious possible ambiguity in the isotopic integrity of the $C_3(H,D)_6O\cdot^+$ ions used in this study appears to be isomerization of the H and D atoms of the ketones which has occurred *before* ionization, either during preparation or in storage. This is indicated by the presence of isotopic impurities of higher deuterium content, such as those observed in **1a** and **3a**. In these cases the isotopic impurities appear to have arisen through intermolecular interchange of H and D atoms between the α positions, and these impurities were noted to increase markedly on storage, even under refrigeration. Note, however, that the isotopic impurities of higher than expected deuterium content for **1a** and **3a** are far greater than for any other compounds used in the study, suggesting that errors in metastable abundances from this cause are relatively small for compounds other than **1a** and **3a**. We have noticed no isotopic scrambling of this type in the 1-methylcyclobutanols, even after extended periods of storage; all available evidence indicates that the $C_3(H,D)_6O\cdot^+$ ions from these precursors are of high isotopic integrity.

Discussion

Evidence for Ketonization Prior to Decomposition. The mechanism shown in Scheme II is proposed to account for the main pathways of decomposition of the enolic $C_3H_6O\cdot^+$ **2**.[2a] Decomposition through rearrangement to an unstable acetone ion, **8**, and not through the direct cleavage loss of methyl, **2** → **7**, is indicated by several pieces of experimental evidence. In the ion $CH_3C(OD)CD_2\cdot^+$ (**2i**) the metastables m*(**2** → $C_2D_3O^+$), corresponding to **2** → **7** and/or **2** → **10**, and m*(**2** → $C_2H_3O^+$), corresponding to **2** → **9**, exhibit appearance potential values (Figure 1) that are the same within experimental error (±0.2 eV), consistent with the formation of these products through decomposition of an unstable common intermediate, **8**. The appearance potentials of **9** and **10** are 2.0 eV above the value for the formation of the $C_3(H,D)_6O\cdot^+$ ion, indicating that acetone ion intermediate is formed with *ca.* 33 kcal of excess internal energy.[2b]

The rate of a direct cleavage reaction such as **2** → **7** should increase much more rapidly with increasing energy than the rate of a rearrangement reaction such as **2** → **8** → **9**.[12,13] Yet the higher energy normal ions do not show the behavior predicted for a direct cleavage; for the 1-methylcyclobutanols, $[C_2H_2{}^{\alpha}H^{\gamma}O^+]/[C_2H_3{}^{\alpha'}O^+]$ has *decreased* in comparison to the corresponding metastable transitions.[18] The ionization efficiency curves of m*(**2** → $C_2H_3O^+$) and m*(**2** → $C_2D_3O^+$) from $CH_3C(OD)CD_2\cdot^+$ (**2i**) are also identical (Figure 1), but experimentally this is not a sensitive test for differences in mechanisms. Collision-induced metastables should also represent decompositions of higher energy ions;[19] these data show no appreciable increase in $[m^*(\mathbf{2} \rightarrow C_2H_2{}^{\alpha}H^{\gamma}O^+)]/[m^*(\mathbf{2} \rightarrow C_2H_3{}^{\alpha'}O^+)]$ in comparison to this ratio for normal metastable transitions, again inconsistent with an appreciable contribution of the direct cleavage reaction **2** → **7** to the formation of the $CH_2{}^{\alpha}H^{\gamma}CO^+$ ion. As will be shown below, isotope effects indicate that less than 10% of the $C_3H_6O\cdot^+$ ions decompose by reaction **2** → **7**.[20]

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(18) For the metastable and normal ions formed by the decomposition of **2a** this ratio is 0.54 and 0.32, respectively. However, as discussed above, some of the $CH_3{}^{\alpha'}CO^+$ normal ions may be formed by a competing decomposition of the molecular ion, **5a**.

(19) (a) F. W. McLafferty and H. D. R. Shuddemage, *J. Amer. Chem. Soc.*, **91**, 1866 (1969); (b) F. W. McLafferty, I. Howe, R. Kornfeld, H. D. R. Schuddemage, and S.-C. Tsai, in preparation.

(20) Other enol ions which apparently ketonize instead of undergoing direct cleavage include $CH_3CH_2C(OH){=}CH_2\cdot^{+\,2a}$ and $C_6H_5C(OH){=}$

The ion cyclotron resonance experiments of Djerassi and coworkers[9] conclude that no appreciable amount of the ketonic isomer **8** is present. Thus, if Scheme II is correct, decomposition after ketonization must be rapid; further supporting evidence for this will be presented below.

Primary Isotope Effects. Before the data of Table I can be used to determine the relative rates of the various ketonization, k_k, isomerization, k_i, and cleavage, k_c, reactions, an evaluation of any isotope effects which influence these rates must be made.

In the ketonization reaction a hydrogen atom, H^{γ}, is transferred from oxygen to carbon, so that a primary isotope effect should be expected on replacement of this hydrogen by deuterium, as ketonization is the rate-controlling step in the decomposition of the enolic ion (*vide infra*). Note that the identity of the isotope at H^{γ} is not changed by isomerization of **2** to structures **11** or **15**, so that k_k, k_k', and k_k'' will be identical for any particular precursor enolic ion **2** of a specific internal energy except for secondary isotope effects; this rate will be reflected by the total products formed relative to the precursor ion. For the 1-methylcyclobutanols the values (Table I) of the sum of the $C_2(H,D)_3O^+$ ion intensities relative to the intensity of the $C_3(H,D)_6O\cdot^+$ ion are 0.64 and 0.69 for OH, and 0.40 and 0.43 for OD; the values of the sum of the metastable ion intensities relative to the normal $C_3(H,D)_6O\cdot^+$ ion intensity are 0.0064, 0.0069, and 0.0069 for OH, and 0.0050, 0.0047, and 0.0059 for OD. This indicates that the ketonization is appreciably slowed by the substitution of deuterium on the hydroxyl group, but that substitution at other positions has no effect that is discernible.

It should be noted that the effect of the deuterium is actually to shift $k(E)$, which describes the value of the rate constant as a function of the ion internal energy, so that an ion of a particular internal energy value will exhibit a lower rate constant. The lifetime of metastable ions which decompose in the field-free drift region is determined by the mass of the ion and by instrument parameters.[21] The lifetimes of observed metastables fall within a relatively narrow range, which defines the range of reaction rates giving these metastables. Thus the experimentally observed isotope effect on a metastable intensity is not to change these rates, but to change the ion internal energy required to produce these rates. Replacing OH by OD shifts the $k(E)$ function to lower rate constants for the same internal energies; these same ions will thus exhibit higher rates for any competing reactions whose $k(E)$ functions have not been changed.[22]

The isotope effect on $k_i(E)$ of the isomerization reaction should be reflected in the abundance of the products, [**11**] and [**15**], relative to [**2**]. Of course **2**, **11**, and **15** are indistinguishable in the mass spectrum, so that their abundances must be inferred from the abundances of their cleavage products, *e.g.*, [**11**] is reflected by [**13**] + [**14**]. Thus to use these ion product sums to measure the isotope effects on k_i, one must compensate for the isotope effect on k_k. Unfortunately, the value for k_k measured from $\Sigma[m^*]/[C_3(H,D)_6O\cdot^+]$ cannot be used for this.[22] Further, there is no possible combination of isotopic $C_3(H,D)_6O\cdot^+$ isomers which will serve to distinguish the primary isotope effects on k_i and k_k in these experiments, as when the same isotope is involved in both the ketonization and isomerization reactions, the products **9** and **14**, and **10** and **13**, must be identical.[23] The relative abundances of **13**, **14**, **17**, and **18** can be used, however, to compare the effect of H migration on k_i for ions of the higher internal energy required for D transfer in the ketonization reaction with the effect of D migration on k_i for ions of the lower internal energy required for H transfer in the ketonization reaction; thus the values obtained reflect the combined isotope effect on all of the applicable $k_k(E)$ and $k_i(E)$ functions.

The kinetic picture is complicated by the dependence of the metastable ion abundances on a number of rate constants (Scheme II). The combined primary isotope effect (secondary isotope effects were ignored) on $k_k(E)$ and $k_i(E)$ was calculated[24] from the metastable ion data for $CD_3C(OH)CH_2\cdot^+$ (**2a**) and $CH_3C(OD)CD_2\cdot^+$ (**2i**). The results indicate that in 39% of the original **2i** ions an H atom will have rearranged, **2** → **11**, before the decomposition involving ketonization through transfer of a D atom, while in only 9% of the original **2a** ions will a D atom have rearranged before the decomposition involving transfer of an H atom. Thus the combined isotope effect k_H/k_D for $k_k(E)$ and $k_i(E)$ is approximately 4.3.

To check these calculated rates they can be applied to predict the metastable intensities from the decomposition of other $C_3(H,D)_6O^+$ ions in which the isotopic distribution allows the appropriate reaction products to be distinguished. For example, in $CH_2DC(OH)CD_2\cdot^+$ (**2e**), isomerization of a D atom should proceed at a rate which is one-third (on a statistical basis) of that found for $CD_3C(OH)CH_2\cdot^+$ (**2a**) as both ions transfer H in ketonization; thus **2e** should yield an abundance of $1/3 \times 0.09 = 0.03$ of $CD_3C(OH)CH_2\cdot^+$ (**2a**) before ketonization; this value will be lowered slightly (*ca.* 0.001) by isomerization of **2a** before ke-

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$CD_2\cdot^+$ (F. W. McLafferty and T. Wachs, *J. Amer. Chem. Soc.*, **89**, 5043 (1967), and unpublished work).

(21) W. A. Chupka, *J. Chem. Phys.*, 30, 191 (1959); F. W. McLafferty in "Topics in Organic Mass Spectrometry," A. L. Burlingame, Ed., Interscience, New York, N. Y., 1970.

(22) However, the relative magnitude of the isotope effect on $\Sigma[m^*]/[C_3(H,D)_6O\cdot^+]$ depends also on the distribution of internal energies of the precursor $C_3(H,D)_6O\cdot^+$ ions, which are unknown, and so this value cannot be used to determine the magnitude of the isotope effect on the rate constant at a particular internal energy.

(23) For example, $CH_3C(OH)CD_2\cdot^+$ (**2h**) yields CH_3CO^+ and CHD_2CO^+ as **9** and **10**, respectively. Isomerization of **2h** produces $CHD_2C(OH)CH_2\cdot^+$, which yields CHD_2CO^+ and CH_3CO^+ as **13** and **14**, respectively.

(24) The equation describing this system was derived using the procedure recommended by Benson.[25,26] However, the complexity of the equation was such that an exact solution for a particular system would be very laborious; we felt that the experimental accuracy of the data did not justify the effort required. Instead, an approximate kinetic treatment was used in which the time scale was divided into ten equal segments, and the product distribution in each successive segment was calculated from the distribution in the preceding segment by means of the general expression governing unimolecular kinetics, $I/I_0 = e^{-kt}$, where I_0 and I are the original and final amounts of the ions undergoing isomerization. By successive approximations a value was found for the rate constant, k, which would yield the observed product ratio. Thus for $CH_3C(OD){=}CD_2\cdot^+$ from **5i** a rate constant corresponding to isomerization of 39.1% of the original ions, **2**, before metastable decomposition was found to yield the final observed value of isomerized ions **11**, of 36.6%, the difference representing the **11** ions which had been formed and isomerized back to **2** before decomposing in the metastable drift region.

(25) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, pp 39–42.

(26) We are indebted to P. F. Bente for the derivation of this equation and helpful discussions of these problems.

Table II. Primary Isotope Effects on Hydrogen Rearrangements (**2** → **8** and **2** → **11**) and Secondary Isotope Effects on the Loss of Methyl Groups (**2** → **9** and **2** → **10**) involving $C_3(H,D)_6O^+$ Ions

Ion	Precursor	([m*(**11** → **13**)] + [m*(**11** → **14**)])/Σ[m*] × 100		[m*(**2** → **10**)]/(m*(**2** → **9**)] × 100	
		Calcd	Exptl	Calcd	Exptl
$CD_3C(OH)CH_2$	**5a**	(9)	9 ± 2	(54)	54 ± 4
$CD_3C(OD)CH_2$	**5b**	2.5	5 ± 1	68[a]	60 ± 3
$CHD_2C(OD)CH_2$	**5i**			69[b]	85 ± 10
$CD_3C(OH)CD_2$	**1c**			65	66 ± 4
$CHD_2C(OH)CD_2$	**3d**	5.7	8 ± 3		
$CH_2DC(OH)CD_2$	**5e**	2.9[c]	3 ± 1	87[a]	86 ± 4
$CH_3C(OH)CHD$	**3f**			92[a]	97 ± 3
$CH_3C(OD)CH_2$	**5g**			79	78 ± 5
$CH_3C(OH)CD_2$	**5h**	0.5	2 ± 1	99[a]	90 ± 3
$CH_3C(OD)CD_2$	**5i**	(37)	37	96	101 ± 4

[a] Value is less accurate as it includes calculated contributions of m*(**11** → **13**) and m*(**11** → **14**). [b] Value is less accurate, as it is calculated for [m*(**11** → **13**)]/[m*(**11** → **14**)], including contributions of m*(**15** → **17**) and m* (**15** → **18**). [c] {[m*(**2** → $C_2H_3O^+$)]+ [m*(**2** → $C_2D_3O^+$]}/Σ[m*] × 100.

tonization. The final calculated value agrees with the observed value within experimental error. Similar calculations on the extent of isomerization of D in $CHD_2C(OH)CD_2\cdot^+$ (**2d**) were made; the results are shown in Table II.

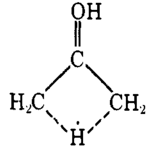
Calculations for the ions $CD_3C(OD)CH_2\cdot^+$ (**2b**) and $CH_3C(OH)CD_2\cdot^+$ (**2h**) which should produce $CHD_2C(OD)CHD\cdot^+$ and $CH_2DC(OH)CHD\cdot^+$, respectively, by the consecutive isomerizations **2** → **11** → **15**, are complicated by the fact that the first step, **2** → **11**, involves transfer of the same isotope in both ketonization and isomerization. For reasons which will be discussed below, it was assumed that the isotope effects on k_k and k_i are equal; thus approximately 19% isomerization involving D from CD_3 should occur in **2b** before the ketonization which involves D, and 19% isomerization involving H from CH_3 should occur in **2h** before the ketonization which involves H. These assumptions give values for the various isotopic ions as shown in Table III.

Table III. Values for Per Cent of Isomerization, **2** → **11**, before Metastable Decomposition by Ketonization **2** → **9** + **10** for $CH_3{}^{\alpha'}C(OH^{\gamma}){=}CH_2{}^{\alpha+}\cdot$ Ions

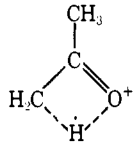
α′-Methyl	-OH ions isotope isomerized		-OD ions isotope isomerized	
	D	H	D	H
CH_3		19		39
CH_2D	3	13	6	26
CHD_2	6	6	13	13
CD_3	9		19	

Despite the approximations necessary in these calculations, the values found (Table II) are within or nearly within the experimental error, the differences observed being consistent with a relatively small amount of isotopic impurity. Further tests of the postulated primary isotope effects of Table III will be described below in connection with the evaluation of secondary isotope effects on k_c/k_c'.

Although these results do not show the relative importance of the k_k and k_i isotope effects on this overall effect, a large isotope effect for the isomerization is consistent with that expected for a symmetrical transition state[27] such as **19**, for which other canonical forms could be written. A radical site mechanism can be invoked to justify lowering the transition state energy in a manner similar to that proposed for other hydrogen rearrangement reactions.[15] Note that the transition state for the ketonization reaction **20** is isoelectronic with **19**, and so the reactions might be expected to exhibit similar isotope effects. The reaction **2** → **8** is similar to the reverse (except for ring size) of the γ-H rearrangement in ketones.[15] The slightly lower (*ca.* 0.3 eV) appearance potential of this rearrangement in comparison to that of **2** → **11** (Figure 1) is consistent with the higher migratory aptitude usually found for the rearrangement of a hydroxyl hydrogen atom in comparison to that of a methyl hydrogen atom.[5,6]



19



20

Secondary Isotope Effects on the Ketone Ion Decomposition. If the loss of the methyl groups from the symmetrical acetone ion, **8**, occurs as proposed (Scheme II), the possible products, **9** and **10**, should be formed in equal abundances, except for secondary isotope effects. Such effects have been noted in mass spectra.[28] For example, Stevenson[29] found that $C_2H_4D^+$ is 1.2 times as intense as $C_2H_5{}^+$ in the mass spectrum of propane-*1*-d_1. He concluded that the deuterated ion was favored because of its slightly lower zero point energy. The data of Table I indicate that the loss of methyl parallels this behavior, with replacement of hydrogen by deuterium on a methyl group making loss of that methyl less favored. The largest difference should be found in comparing the behavior of $CD_3C(OH)CH_2\cdot^+$ (**2a**) with that of $CH_3C(OD)CD_2\cdot^+$ (**2i**); this is indeed the case, with [m*(**2** → **10**)]/[m*(**2** → **9**)] = 0.54 and 1.01, respectively. Intermediate values should be obtained by replacing one or more of the 3 H atoms of one methyl with D, or one or more of the 3 D atoms on the other methyl with H; thus a total of six replacement steps are possible. For the ion $CD_3C(OH)CD_2\cdot^+$

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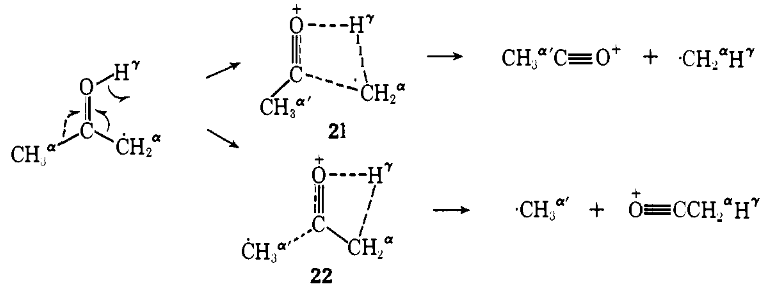
(27) K. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, pp 351-363.

(28) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957, pp 204-217.

(29) D. P. Stevenson, *Disc. Faraday Soc.*, 10, 35 (1951).



(**2c**), [m*(**2** → **10**)]/[m*(**2** → **9**)] = 0.66; a value of 0.65 would be predicted assuming that each of the replacement steps, on either methyl group, has an equal relative effect, equivalent to k_H/k_D of 1.10.[30] In the same way the experimental and predicted values for $CH_3C(OD){=}CH_2\cdot^+$ (**2g**) are 0.78 and 0.77, respectively. Values calculated for other $C_3(H,D)_6O\cdot^+$ ions are shown in Table II.[31] Although substantial experimental errors are involved, the agreement found is fairly satisfactory.

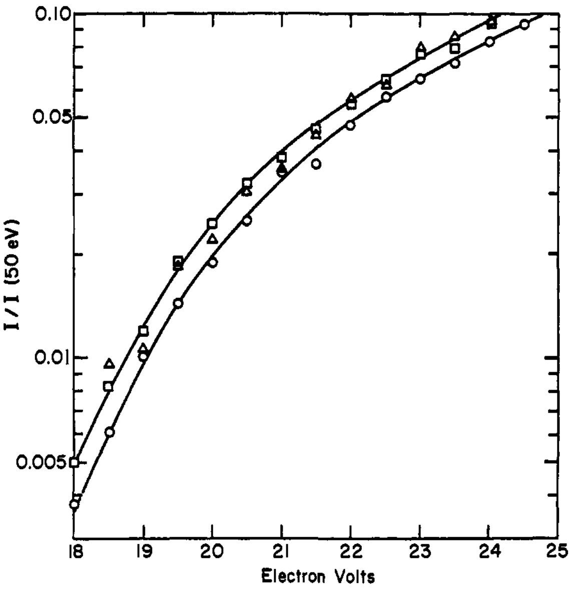


Figure 1. Ionization efficiency curves for metastable ions in the mass spectrum of 1-methylcyclobutan-α,α,α′,α′-d_4-ol-d_1 (**5i**): □, $m^*(C_3H_3D_3O\cdot^+ \rightarrow C_2D_3O^+)$; △, $m^*(C_3H_3D_3O\cdot^+ \rightarrow C_2H_3O^+)$; ○, $m^*(C_3H_3D_3O\cdot^+ \rightarrow C_2HD_2O^+)$.

The replacement of an isotope in any one of the three different positions (α, α′, or γ) of the enol ion has nearly the same effect as any other. Note in particular that the OD isomers appear to give as consistent an agreement between calculated and experimental values as do the OH isomers. A contribution from the direct cleavage reaction **2** → **7** should lead to different values for the OH and OD isomers, so that these data indicate that <10% $m^*(C_3H_6O\cdot^+ \rightarrow C_2H_3O^+)$ can arise from this pathway.[32]

Note that the secondary isotope effect of a hydrogen on a bond dissociation at an sp^3-hybridized carbon atom which proceeds through an sp^2-hybridized transition state, such as $CH_3X \rightarrow CH_3^+ + X^-$, is generally k_H/k_D = 1.1–1.2,[33] again consistent with the postulated dissociations of the acetone ion, **8** → **9** and **8** → **10**.

ICR Evidence for the Ketonization of Enolic $C_3H_6O\cdot^+$. The elegant ion cyclotron resonance (ICR) study of the $C_3H_6O\cdot^+$ ions by Djerassi and coworkers[6] also provides data on the decomposition of the $CD_3C(OH){=}CH_2\cdot^+$ ion formed from **5a**. The normal ion abundances presented are consistent with those of Table I, although the products are formulated as the protonated ketene ion, $CH_2{=}C{=}O^+H$, and the acetyl ion, $CD_3C{\equiv}O^+$. The general mechanism proposed in Scheme II would predict that all of the possible product ions ($C_2H_3O^+$, $C_2H_2DO^+$, $C_2HD_2O^+$, and $C_2D_3O^+$) should have the acetyl structure. This ICR study[9] points out that isomeric ions, such as the keto and enol forms of $C_3H_6O\cdot^+$, can show markedly different behavior in ion molecule reactions. It is gratifying to note for the reaction of $C_2(H,D)_3O^+$ with **5a** to yield acetic acid and the methyl-d_3-cyclobutyl ion that "the pulsed double resonance spectrum indicates that all four of these ions (*m/e* 43–46) contribute to the formation of the methylcyclobutyl cation,"[9] a behavior which is consistent with the identical structures postulated by Scheme II.

The evidence of Meyerson and Fields[11] should also be reexamined. They reported the presence of $CH_3C(OD){=}CH_2\cdot^+$ (**2g**) but not $C_2H_2DO^+$, in the mass spectrum of $CH_3COCH_2CH_2CD_2CH_3$ (**1g**). Table I shows that decomposition of **2g** does yield CH_2DCO^+, but because of isotope effects and lack of energy equilibration the ion CH_3CO^+ is produced in nearly 50% greater abundance. A substantial abundance of CH_3CO^+ would also be expected by direct cleavage of **1g**, so that [CH_2DCO^+] is probably small relative to [CH_3CO]$^+$ in the spectrum of **1g**. We find that [CHD_2CO^+]/[CH_3CO^+] = 0.035 in the spectrum of $CH_3COCD_2C_3H_7$ (**1h**).

Incomplete Energy Randomization in the Keto Ion. The data of Table II are not consistent, however, with this intermediacy of the keto form in an important way; if **2** is isotopically *symmetrical*, the value of [m*(**2** → **10**)]/[m*(**2** → **9**)] is 0.72,[30] not the expected value of 1.00. Thus, when isotope effects are eliminated, *a substantially higher proportion of the metastable transitions must be proceeding through the loss of* $CH_2^{\alpha}H^{\gamma}$ *than through the loss of* $CH_3^{\alpha'}$.[34] A possible explanation is that

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[30] The predicted values for the replacement steps are thus (0) 0.54; (1) 0.59; (2) 0.65; (3) 0.72; (4) 0.79; (5) 0.87; and (6) 0.96.

[31] For the $C_3(H,D)_6O\cdot^+$ ions formed by isomerization, the primary isotope effects of Table III were used in the calculation; the predicted values should be of lower accuracy than those for ions 2a, 2c, 2g, and 2i, for which such corrections are not necessary.

[32] Thus if 10% $m^*(2 \rightarrow C_2H_2^{\alpha}H^{\gamma}O^+)$ for an OH isomer is due to 2 → 7, for the higher energy ions giving metastables from the OD isomer an increase by a factor of *ca.* 2.2 would be expected in the rate of 2 → 7 relative to the rate of 2 → 8 (there should be no primary isotope effect on 2 → 7). This would yield a 12% increase in the relative abundance of $m^*(2 \rightarrow C_2H_2^{\alpha}H^{\gamma}O^+)$ for OD isomers, which should cause substantially greater deviations than those found in the data (Table II).

[33] A. A. Zavitsas and S. Seltzer, *J. Amer. Chem. Soc.*, **86**, 3836 (1964); K. Humski, R. Malojcic, S. Borcic, and D. E. Sunko, *ibid.*, **92**, 6534 (1970).

[34] Note that if any of $m^*(2 - CH_3^{\alpha'})$ is due to 2 → 7, the true value of [m*(2 → 10)]/[m*(2 → 9)] will be even lower than 0.72.

there is an important pathway in addition to that of Scheme II for the formation of $CH_3^{\alpha'}CO^+$, such as one in which there is a concerted rearrangement of hydrogen and elimination of methyl through a transition state such as **21**. For this explanation the data require that approximately 16% of the $C_3H_6O\cdot^+ \rightarrow C_2H_3O^+$ reactions proceed through such a pathway. This appears improbable, however, as any such reaction would not only have to have the same appearance potential as **2** → **9**, but would also have to exhibit isotope effects which are comparable to that found for **2** → **8** and **8** → **9**, *i.e.*, the hydroxyl hydrogen (γ-H) must exhibit a primary isotope effect (k_H/k_D) of approximately 2, and the γ-H and both α-H atoms must exhibit secondary isotope effects of *ca.* 1.1.[35] Further, for this additional pathway to be a distinctly different reaction, **21** should be distinguishable from the vibrationally excited acetone ion proposed as the intermediate of the main reaction. For this it would appear that in **21** the $C-CH_2^{\alpha}$ bond should be stretched considerably beyond its normal length before the $CH_2^{\alpha}-H^{\gamma}$ bond approaches a normal length; yet such a transition state should exhibit different isotope effects for H^{α} and H^{γ} (k_H/k_D for H^{α} might be <1.0[33] and H^{γ} would show a primary isotope effect) and would appear to involve less favorable steric and energy requirements (the $C-CH_2^{\alpha}$ bond cleaved has partial vinylic character) than the pathway involving the excited acetone intermediate.

A further alternative is that the unstable acetone ion intermediate is not involved, and that separate transition states such as **21** and **22** lead to the products **9** and **10**, respectively,[36] by concerted reactions that somehow bypass the acetone energy valley. Again the isotope effects of H^{α}, H^{β}, and H^{γ} should be different. The energy and possibly the steric requirements would not only appear to be different for **21** and **22**, but should actually *favor* the formation of **10**, in contrast to the observed data.

In summary, it is difficult to formulate a distinctly different reaction pathway whose transition state exhibits the same activation energy and the same isotope effects as the transition state for the proposed reaction path **2** → **8** → **9**. It thus appears that all of the $CH_3^{\alpha'}CO^+$ ions are formed through the same reaction pathway, **2** → **8** → **9**, and that the methyl groups are lost from the intermediate acetone ion, **8**, at unequal rates.

The most logical explanation for this behavior appears to be that it is due to *incomplete randomization of the internal energy* of the keto intermediate, **8**. Reaction **2** → **8** should have a tight activated complex in which the incipient $CH_2^{\alpha}H^{\gamma}$ group has a substantially different configuration and average vibrational energy than the $CH_3^{\alpha'}$ group. The average lifetime of the keto ion, **8**, must then be less than the time required for equilibration of this energy.[37] A possible explanation for the increase in $[C_3H_6O\cdot^+ - CH_2^{\alpha}H^{\gamma}]/[C_3H_6O\cdot^+ - CH_3^{\alpha'}]$ for the normal ions relative to the metastables is that the higher energy ions have less time to equilibrate the energy from the ketonization reaction before they decompose.

A basic assumption of the quasi-equilibrium theory[38] is that energy randomization is fast in comparison to the rate of any decomposition reaction, and thus that the fragmentation pathways, (*i.e.*, the $k(E)$ functions) are independent of the method of ion preparation. Apparently this is the first exception to this rule which has been observed.[39] It has also been difficult to find neutral systems in which incomplete energy randomization can be demonstrated unequivocally;[40] perhaps reaction systems analogous to the present case would provide a fruitful approach.

The Structure of the $C_3H_6O\cdot^+$ Ion Produced by Double Hydrogen Rearrangement. An important objective of this research was to differentiate between the possible pathways **3** → **4** → **2** and **3** → **4** → **6** for the double hydrogen rearrangement of alkanones, especially in view of the conflicting conclusions that had been reached.[2,9,10,15,41] Our original postulation[41] of structure **6** was based on the observation of different metastable ion abundance ratios, $[m^*(C_3H_6O\cdot^+ \rightarrow C_2H_3O^+)]/[m^*(C_3H_6O\cdot^+ \rightarrow CH_3^+)]$, for $C_3H_6O\cdot^+$ ions produced by single and double rearrangements. Occolowitz[42] has raised valid criticisms of this evidence, as variations in this ratio can be caused by different energy distributions of the molecular ions and different rates of formation of the metastable precursor ions. We have confirmed his general findings in an independent study of other systems.[43]

In investigating this point, we repeated the earlier measurements[41] utilizing the higher sensitivity of the Barber-Elliott-Major defocusing technique.[44] Unfortunately, we were unable to reproduce these data; $[m^*(C_3H_6O\cdot^+ \rightarrow C_2H_3O^+)]/[m^*C_3H_6O\cdot^+ \rightarrow CH_3^+)] > 2000$, instead of the values of 110 and 280 found for **1** and **3**, respectively.[45] Thus these metastable abundance data should not be considered as valid evidence for the formation of the oxonium ion structure, **6**.

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[35] If the isotope effect of the γ-hydrogen atom on the rate of this alternative reaction for loss of $CH_2^{\alpha}H^{\gamma}$ were substantially different (higher or lower) than the γ-H isotope effect on the ketonization reaction **2** → **8**, the ratio of these reaction rates would be substantially different for –OD ions than for –OH ions. This would cause a deviation in the secondary isotope effect correlation of Table II, in the same way that the direct cleavage **2** → **7** would cause such a deviation.[32] In a similar manner if the secondary isotope effect of the α-H atoms on this alternative reaction for loss of $CH_2^{\alpha}H^{\gamma}$ were substantially different than that on **8** → **9**, a deviation on the secondary isotope effect correlation of Table II should also be observable.

[36] We thank a referee for this suggestion.

[37] Careful examination of these metastables reveals no evidence of any "flat-top" character; thus no substantial part of the excess energy is localized in the translational coordinate of the reaction.

[38] H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Nat. Acad. Sci. U. S.*, **38**, 667 (1952).

[39] H. M. Rosenstock, *Advan. Mass Spectrom.*, **4**, 523 (1968); see p 542.

[40] L. D. Spicer and B. S. Rabinovitch, *Annu. Rev. Phys. Chem.*, **21**, 349 (1970); J. D. Rynbrandt and B. S. Rabinovitch, *J. Phys. Chem.*, **74**, 4175 (1970).

[41] F. W. McLafferty and W. T. Pike, *J. Amer. Chem. Soc.*, **89**, 5953 (1967).

[42] J. L. Occolowitz, *ibid.*, **91**, 5202 (1969).

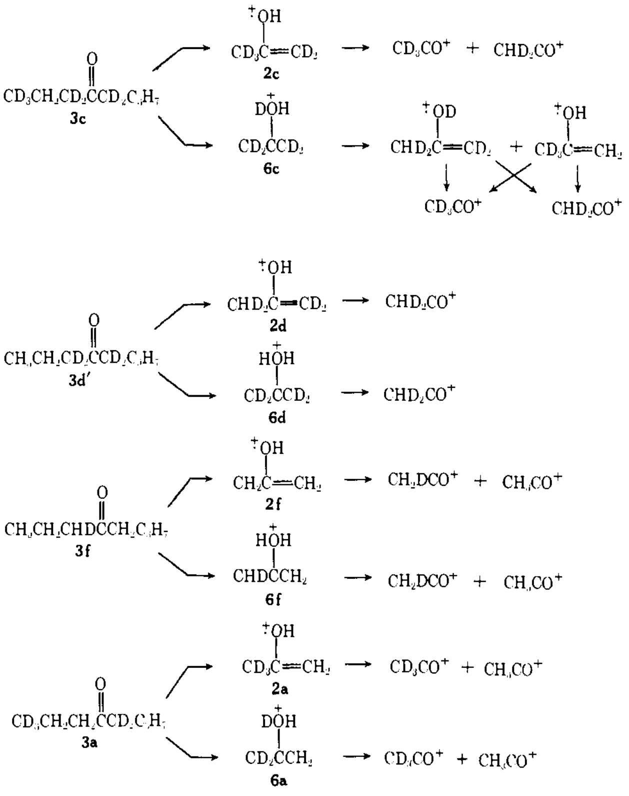
[43] D. J. McAdoo, F. W. McLafferty, P. F. Bente, C. Lifshitz, and M. L. Gross, in preparation.

[44] M. Barber and R. M. Elliott, ASTM E14 Conference on Mass Spectrometry, Montreal, June 1964; F. W. McLafferty, J. Okamoto, H. Tsuyama, Y. Nakajima, T. Noda, and H. W. Major, *Org. Mass Spectrom.*, **2**, 751 (1969).

[45] It would be surprising if the geometries and operating parameters of the single-focusing Hitachi RMU-6D used previously are sufficiently different from those of the double-focusing RMU-7 used in the present study to be the cause of this discrepancy. (It is not possible to remeasure the data under the original conditions, as the former instrument is no longer available to us.) The previous data in general show poor signal-noise ratios, and an incorrect metastable identification could have been made ($m^* = 15^2/58 = 3.88$). It is possible that the observed metastables were collision induced, although no effect of pressure was observed on these data. We have found[19b] that $[m^*(C_3H_6O\cdot^+ \rightarrow C_2H_3O^+)]/[m^*(C_3H_6O\cdot^+ \rightarrow CH_3^+)] = 14$ and 13 for 2- and 4-nonanone, respectively, at 3×10^{-4} Torr.

On the other hand, the present data give strong additional evidence that the decomposing $C_3H_6O^{\cdot+}$ ions produced by both the single and double hydrogen rearrangements, as well as by the decomposition of **5**, have the same structure. Data on four different isotopic $C_3(H,D)_6O^{\cdot+}$ species resulting from the double rearrangement are given in Table I; all of these data are consistent within experimental error with the predicted behavior of the enolic $C_3(H,D)_6O^{\cdot+}$ ion **2**. For three of these species, those formed from **3c**, **3d**, and **3f**, the oxonium ion could possibly yield products whose identities would be consistent with those found, as shown in Scheme IV; thus small amounts of **6** would be difficult to detect without knowledge of its fragmentation.[46] For ions from **3d**, both the enol and oxonium structures should yield only $m^*(C_3H_2D_4^{\cdot+} \rightarrow C_2HD_2O^+)$; note, however, that the small amounts of $m^*(C_3H_2D_4O^{\cdot+} \rightarrow C_2H_2DO^+)$ and $m^*(C_3H_2D_4O^{\cdot+} \rightarrow C_2D_3O^{\cdot+})$ agree with the value calculated for the isomerization of the enolic ion (Table II).

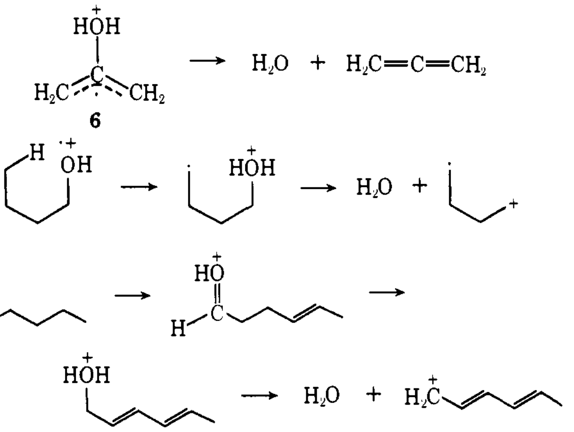
Scheme IV



Data on the $C_3H_3D_3O^{\cdot+}$ ions from **3a** provide much more definitive evidence for the absence of the oxonium ion, however. These ions yield the same ratio of $[m^*(C_3H_3D_3O^{\cdot+} \rightarrow C_2H_3O^+)]/[m^*(C_3H_3D_3O^{\cdot+} \rightarrow C_2D_3O^+)]$ when formed from **1a**, **3a**, or **5a**. The oxonium ion, **6a**, which would be formed from **3a**, would have the structure $CD_2C(OHD)CH_2^{\cdot+}$, and should thus exhibit all four of the possible metastable transitions for methyl loss (Scheme IV). These metastables would occur in equal abundances if there were no isotope effects. An isotope effect would be expected, but note that it should not cause *both* $m^*(C_3H_3D_3O^{\cdot+} \rightarrow C_2D_3O^+)$ and $m^*(C_3H_3D_3O^{\cdot+} \rightarrow C_2H_3O^+)$ to be favored over *both* $m^*(C_3H_3D_3O^{\cdot+} \rightarrow C_2HD_2O^+)$ and $m^*(C_3H_3D_3O^{\cdot+} \rightarrow C_2H_2DO^+)$.[47] It was not possible to prepare the ketone precursors in high purity, unfortunately, so that the $CD_3C(OH){=}CH_2^{\cdot+}$ ions from **1a** and **3a** probably also contain $CHD_2C(OH){=}CHD^{\cdot+}$ as an impurity (*vide supra*). The metastable abundances $[m^*(C_3H_3D_3O^{\cdot+} \rightarrow C_2HD_2O^+)] + [m^*(C_3H_3D_3O^{\cdot+} \rightarrow C_2H_2DO^+)]$ from **3a** which are in excess of the amount found from **5a** can be accounted for by the presence of 23% of the oxonium ion, **6a**, or by 12% $CHD_2C(OH){=}CHD^{\cdot+}$, or a combination of both. Note that the **2a** ions produced by single hydrogen rearrangement from **1a** (which contain 18% of an impurity with one extra deuterium atom) show metastable abundances indicative of 14% $CHD_2C(OH){=}CHD^{\cdot+}$; **3a** contains 12% of an impurity with one extra deuterium atom, which is strong evidence that most of the excess metastable abundance is due to the impurity, *not* to the oxonium ion.

Little is known of the types of unimolecular decompositions which would be expected for ions of the oxonium structure, **6**.[46] However, the loss of a stable H_2O molecule would appear to be an obvious possibility, and similar reactions have been postulated for oxonium ions formed from alcohol[48] and acylium[7a] ion precursors (Scheme V); both of the latter reactions exhibit unimolecular metastables. The $C_3H_6O^{\cdot+}$ ions formed from **3** by double hydrogen rearrangement show $[m^*(C_3H_6O^{\cdot+} \rightarrow C_3H_4^{\cdot+})]/[m^*(C_3H_6O^{\cdot+} \rightarrow C_2H_3O^+)] < 0.01$ for unimolecular metastables. For collision-induced metastables this value is 0.04 for 4-nonanone, which compares to a value of 0.03 for $C_3H_6O^{\cdot+}$ ions formed by single hydrogen rearrangement in 2-nona-

Scheme V



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(46) A possible mechanism for methyl loss from **6** would involve initial enolization; any $CD_2C(OHD)CD_2^{\cdot+}$ ions from **3c** should then form $CHD_2C(OD){=}CD_2^{\cdot+}$ and $CD_3C(OH){=}CD_2^{\cdot+}$ (**2c**). The former enolic ion should be in higher abundance because of the isotope effect on enolization, and it should exhibit $[m^*(C_3HD_5O^{\cdot+} \rightarrow C_2D_3O^+)]/[m^*(C_3HD_5O^{\cdot+} \rightarrow C_2HD_2O^+)] = 0.79$.[30] Thus though the data of Table I for **3c** are consistent with the formation of only the enol ion, **2c** (for which the calculated metastable ratio is 0.65), a substantial amount of the oxonium ion **6c** mght cause a relatively small change in the ratio. Similarly, for the $C_3H_5DO^+$ ions from **3f** the metastable abundance data are consistent with either the enol or the oxonium structures.

(47) If methyl loss from these oxonium ions involves prior formation of **2**,[43] the rearrangement of hydrogen on the oxygen atom should be favored over the rearrangement of deuterium to form **2**; thus **6a** should rearrange to yield a greater abundance of $CH_3C(OD){=}CD_2^{\cdot+}$ and $CHD_2C(OD){=}CH_2^{\cdot+}$ than of $CH_2DC(OH){=}CD_2^{\cdot+}$ and $CD_3C(OH){=}CH_2^{\cdot+}$. From the expected decomposition of these enol ions (Table II), an isotope effect, k_H/k_D, of 1.1 would produce $[m^*(C_3H_3D_3O^{\cdot+} \rightarrow C_2HD_3O^+)]/[m^*(C_3H_3D_3O^{\cdot+} \rightarrow C_2H_3O^+)] = 1.2$. However, the value $\{[m^*(C_3H_3D_3O^{\cdot+} \rightarrow C_2HD_2O^+)] + [m^*(C_3H_3D_3O^{\cdot+} \rightarrow C_2H_2DO^+)]\}/\{[m^*(C_3H_3D_3O^+ \rightarrow C_2D_3O^+)] + [m^*(C_3H_3D_3O^{\cdot+} \rightarrow C_2H_3O^+)]\}$ should be nearly unity and almost independent of the isotope effect.

(48) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, New York, N. Y., 1966, p 132.

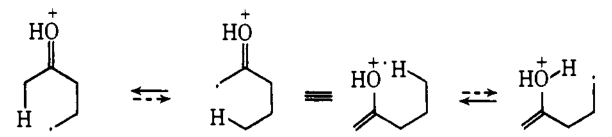
none.[19b] Although the loss of H_2O from **6** involves cleavage of a vinylic bond, loss of H_2O from the enol ion **2** should be even less favorable, so that these data also are consistent with the predominant formation of the enolic $C_3H_6O\cdot^+$ ion from the double hydrogen rearrangement of ketones.[2,9,10]

Note that these data provide information on $C_3H_6O\cdot^+$ ions formed with a variety of internal energies. If any oxonium $C_3H_6O\cdot^+$ ions, **6**, are present in the normal spectrum, these must have internal energies below that required for decomposition in 10^{-6} sec. The ICR studies[9,10] found no bimolecular reactions attributable to oxonium ions; however, experimental conditions require that the ions studied have internal energies below that required for decomposition in approximately 10^{-3} sec. The unimolecular metastable data presented above show that the quantity of **6** ions with intermediate internal energies (*i.e.*, energies required for decomposition in *ca.* 10^{-5} sec) is also low.

An appreciable quantity of the oxonium $C_3H_6O\cdot^+$ ions, **6**, could have gone undetected in the ICR studies[9,10] if these ions are not reactive toward any of the reagents used.[49] For the oxonium ions to have also gone undetected in the unimolecular metastable studies reported here requires that the rate constant increase rapidly with internal energy in the energy region required for metastable decomposition; this should occur only for a reaction with a loose activated complex, such as a direct cleavage reaction, not a rearrangement.[12,13] The only logical reaction of this kind appears to be the loss of H_2O; evidence against this from collision-induced metastables was cited above. The oxonium ions would also have gone undetected in the unimolecular metastable studies if they are formed with insufficient internal energy to decompose in 10^{-5} sec. However, such ions should still have been observed in the collision-induced metastable study, as the addition of energy on collision[19b] would raise substantially the probability of decomposition.

In summary, the original evidence for the formation of the oxonium ion, **6**, by double hydrogen rearrangement appears to have been based on erroneous experimental data; ICR,[9,10] unimolecular metastable, and collision-induced metastable data give no evidence for the formation of the oxonium ion, but instead appear to be explicable only in terms of formation of the enolic $C_3H_6O\cdot^+$ ion (**2**).

Effects of Structure on the Relative Rates of Hydrogen Rearrangement. Thus the rearrangement of the γ-hydrogen in the enolic intermediate, **4**, occurs to the CH_2 group, not to the OH group. The steric requirements of these competing reactions should be nearly equivalent, as both involve six-membered ring transition states. A possible rationalization for this behavior is found in the reverse of the reactions for formation of the oxonium and enolic $C_3H_6O\cdot^+$ ions. Hydrogen migration is usually preferred *from* a hydroxyl group rather than *from* a methyl group;[6,50] this tendency should be reversed for reactions proceeding in the opposite direction.[51]



Experimental Section

All data were obtained on a Hitachi RMU-7 double focusing mass spectrometer using 70 eV electron energy, 3.6 kV accelerating voltage, and a 10 V repeller potential. Metastable ion intensities were recorded by the Major modification of the Barber-Elliott defocusing technique.[44,52] Ionization efficiency curves of metastable ions were obtained by the 50 eV normalization–semilog plot method of Lossing and coworkers.[53]

2-Hexanone-*1,1,1*-d_3 **(1a).** 1-Bromobutane was added under nitrogen to magnesium turnings in ether and refluxed for 1 hr; 20% excess of anhydrous $CdCl_2$ was added at 0° and refluxed for 30 min. A 20% excess of acetyl-d_3 chloride was added at 0°, the mixture was refluxed and poured onto ice, and enough 20% H_2SO_4 was added to clarify the solution. Ether extracts of the aqueous solution were washed, dried over $MgSO_4$, and distilled to yield the desired 2-hexanone-*1,1,1*-d_3 (18% d_4, 63% d_3, 19% d_2).

2-Hexanone-*3,3*-d_2 **(1h).** 1-Butanol-*1,1*-d_2 was prepared by the reduction of butanoic acid with $LiAlD_4$ in ether. This was converted to 1-bromobutane-*1,1*-d_2 by means of 49% HBr and concentrated H_2SO_4. 2-Hexanone-*3,3*-d_2 was prepared from this bromide by the organocadmium synthesis described above (94.1% d_2, 5.9% d_1).

4-Octanone-*1,1,1,5,5*-d_5 **(3a).** Pentanoic acid-*2,2*-d_2 was obtained from 1-bromobutane-*1,1*-d_2 (see above) by preparation of the Grignard reagent and pouring the reaction mixture onto crushed Dry Ice. The resulting acid was converted to the acid chloride with $SOCl_2$. This and 1-bromopropane-*3,3,3*-d_3 (Merck Sharp and Dohme) were used in the organocadmium synthesis described above to prepare 4-octanone-*1,1,1,5,5*-d_5 (12% d_6, 73% d_5, 17% d_1).

4-Octanone-*3*-d_1 **(3b).** 1-Propanal-*1*-d_1 was prepared by the reduction of propanol with $LiAlD_4$ and converted to 1-bromopropane-*1*-d_1. This was used with pentanoyl chloride in the organocadmium synthesis to prepare 4-octanone-*3*-d_1 (92% d_1, 8% d_0).

2-Hexanone-*1,1,1,3,3*-d_5 **(1c′)** was the gift of Dr. James Tou and L. B. Westover, the Dow Chemical Co., Midland, Mich. (95.2% d_5, 4.6% d_4, 0.2% d_3).

4-Heptanone-*3,3,5,5*-d_4 **(3d)** was prepared by exchange with D_2O over potassium carbonate[54] (91.5% d_4, 8.1% d_3, 0.3% d_2).

The following compounds were prepared by passage through a 10% Carbowax 20M 10% KOD gas chromatography column:[55] **2-pentanone-***1,1,1,3,3*-d_5 **(1c)** (49% d_5, 37% d_4, 12% d_3, 2% d_2); **2-octanone-***1,1,1,3,3*-d_5 **(1c′)** (72% d_5, 25% d_4, 3% d_3); **4-octanone-***1,1,1,3,3,5,5*-d_7 **(3c)** from 4-octanone-1,1,1,5,5-d_5 (54% d_7, 36% d_6, 10% d_5); **4-octanone-***3,3,5,5*-d_4 **(3d′)** (65% d_4, 29% d_3, 6% d_2); **5-nonanone-***4,4,6,6*-d_4 **(3d′′)** (77% d_4, 20% d_3, 3% d_2); **1-methylcyclobutanol** (cyclobutanone was added to the Grignard reagent of methyl iodide, the solution was refluxed and poured onto ice, and enough 20% H_2SO_4 was added to clarify the solution; ether extracts of the solution were washed with aqueous $NaHCO_3$, dried over $MgSO_4$, and distilled); **1-methyl-**d_3**-cyclobutanol (5a)** was prepared as above using CD_3I (94% d_3, 6% d_2 based on $[C_3H_3D_3O\cdot^+]/[C_3H_4D_2O\cdot^+]$); **cyclobutanone-***2,2,4,4*-d_4 (5 g of cyclobutanone was refluxed in D_3PO_4–DCl solution prepared by adding 2 cm^3 of PCl_5 to 80 g of D_2O and refluxing for 24 hr; the deuterated cyclobutanone was recovered by ether extraction, the ether distilled off, and the deuteration procedure repeated; the final recovery was 20% (87% d_4, 12% d_3, 0.6% d_2); **1-methylcyclobutanol-***2,2,4,4*-d_4 **(5h)** was prepared from cyclobutanone-*2,2,4,4*-d_4 (79% d_4, 17% d_3, 4% d_2).

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(49) However, some of these reagents did react with protonated isopropyl alcohol,[10] a saturated even-electron oxonium ion.

(50) Note that this is borne out even in the four-membered ring rearrangements of the enolic $C_3H_6O\cdot^+$; transfer of hydrogen from the hydroxyl group to the CH_2 group, **2** → **8**, is favored over the transfer of a methyl H, **2** → **11**.

(51) This assumes that the oxonium ion will exhibit at least as great a tendency to donate a hydrogen atom as the hydroxyl group.

(52) The relative magnitudes of the measured metastable abundances are sensitive to instrumental conditions, and care was taken to ensure the reproducibility of the data. For example, changing the position of the magnet and collector slit could cause more than an order of magnitude in $[m^*(C_4H_8O\cdot^+ \rightarrow C_2H_3O^+)]/[m^*(C_4H_8O\cdot^+ \rightarrow C_3H_5O^+)]$ for both the normal and defocused metastables.

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The following 1-methylcyclobutanols were prepared by exchange with D_2O in the mass spectrometer inlet system: **1-methylcyclobutanol-*O-d* (5g)** (75% d_1, 25% d_0); **1-methylcyclobutanol-*2,2,4,4-d*$_4$-*O-d* (5i)** (41% d_5, 55% d_4, 3.6% d_3); **1-methyl-d_3-cyclobutanol-*O-d* (5b)** (73% d_4, 22% d_3, 5% d_2).

Acknowledgment. Helpful discussions with S. H. Bauer, G. G. Hammes, R. Hoffmann, B. L. Murr, H. D. R. Schuddemage, and B. Widom are gratefully acknowledged.

Vinyl Radicals. V. The Relative Reactivity of the 2-Methylpropenyl Radical

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Received October 22, 1970

Abstract: The thermal decompositions of 3-ethyl-2-pentenoyl and 3-methyl-2-butenoyl peroxides and *tert*-butyl peresters have been studied as possible sources of 2-ethyl-1-butenyl and 2-methylpropenyl radicals. Intermediate acyloxy radicals are formed which partition between intramolecular H abstraction and decarboxylation. 2-Methyl-2-butenoyl peroxide is shown to be a useful source of 2-methylpropenyl radicals for experiments competing benzylic hydrogen donors (k_H) *vs.* carbon tetrachloride (k_{Cl}) at 78°. The relative reactivity of the 2-methylpropenyl radical toward benzylic hydrogens is primary : secondary : tertiary 1.0 : 3.9 : 8.6, with a marked preference for chlorine abstraction, k_H/k_{Cl} for toluene = 0.048. The effects of para substituents on the reactivities of substituted toluenes toward 2-methylpropenyl radicals are small.

Vinyl radicals are readily available from the thermal and photochemical decompositions of the corresponding α,β-unsaturated peresters and diacyl peroxides[1-3] and as intermediates in free radical additions to alkynes.[4-8] The details of these reactions and the behavior of the vinyl radicals have been studied in some detail. The vinyl systems show typical radical reactions such as displacement on hydrogen,[1-2] halogen,[3] and sulfur,[9] and addition to aromatic rings.[10] Because vinyl radicals represent a fundamental structural type of carbon radical, it seemed worthwhile to seek quantitative data on their chemical behavior. This paper reports a study of the relative reactivity of the 2-methylpropenyl radical toward a series of benzylic hydrogen donors and carbon tetrachloride. Similar reactivity studies are already available for a large number of other types of free radicals.[11-20] The experimental technique involves a competition between H donor (reaction 1) and Cl donor (reaction 2) for the vinyl radical (V·). Under favorable circumstances,[14] the ratio of the yields of products is related to the ratio of rate constants of the competing reactions (3). The assumptions involved in

$$V\cdot + RH \xrightarrow{k_H} VH \tag{1}$$

$$V\cdot + CCl_4 \xrightarrow{k_{Cl}} VCl \tag{2}$$

$$\frac{k_H}{k_{Cl}} = \frac{[VH][CCl_4]}{[VCl][RH]} \tag{3}$$

the use of eq 3 will be examined in connection with the pertinent experimental data.

The Decomposition of 3-Methyl-2-butenoyl Peroxide (I). Product Studies. The peroxide is readily obtained by the reaction of 3-methyl-2-butenoyl chloride with urea peroxide.[21] The purified material is a crystalline solid and the nmr spectrum reveals no trace of the β,γ isomer. The peroxide in cumene at 110° gives CO_2 (45%),[22] dicumyl, and an acidic fraction whose weight accounts for 59% of the weight of the starting peroxide. Decomposition in carbon tetrachloride at 110° also gives an acidic fraction as the major reaction product (67% of the weight of the starting peroxide). The yields of vinyl radical products from the peroxide at 78 and 110° in cumene and carbon tetrachloride are given in Tables I and II, respectively.

It is clear from the data that the decomposition of peroxide I involves more than simple oxygen–oxygen homolysis and subsequent decarboxylation of the acyloxy radicals to give vinyl radicals. Most striking are the low yields of carbon dioxide and vinyl radical prod-

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