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INTRINSIC ALKYL RADICAL PROPERTIES INFERRED FROM THE STUDY OF UNIMOLECULAR DISSOCIATIONS OF GASEOUS CARBOXYLIC ACID CATION RADICALS†

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Abstract—The study of metastable carboxylic acid cation radicals (lifetime 10^{-5} s) in the gas phase provides a detailed insight into a chemistry which is best described in terms of "free radical chemistry". In addition to the well-known 1,*n*-hydrogen migrations ($n = 4,5$) of radicals evidence is presented that even the long-sought 1,2-hydrogen migration may take place in appropriate cases. Examples for 1,*n*-migrations of protonated carboxyl groups ($n = 2,4,5$) are also discussed, while (1,*n*) alkyl migrations do not occur. For all n-alkyl elimination processes studied, ene-1,1-diol cation radicals were identified as the essential intermediates; the mechanism of dissociation is the exact counterpart to the addition of nucleophilic alkyl radicals to deactivated double bonds. The study of metastable carboxylic acids in the gas phase provides the following ordering of relative leaving group abilities for n-alkyl radicals: $C_2H_5 \gg C_3H_7 > C_4H_9 > C_5H_{11} > C_6H_{13} > C_7H_{15} > C_8H_{17} \ggg CH_3$

INTRODUCTION

In this contribution we will present an overview of our recent work on the gas phase chemistry of carboxylic acid cation radicals, employing sophisticated mass spectrometric methodologies, such as MSMS,[1] combined with time-honoured labelling experiments and aided by moleular orbital calculations. We aim to provide evidence that many of the intriguing features of isolated alkyl radicals can be conveniently studied by analyzing the unimolecular dissociation reactions of ionized carboxylic acids generated upon 70 eV electron impact ionization of appropriate neutrals. In particular, we should like to make the following points.

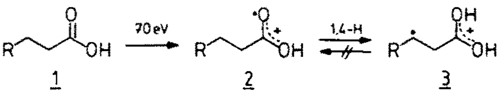
(1) In all C—C bond cleavages observed, the alkyl radical is eventually eliminated from the cation radical of an ene-1,1-diol. Neither direct C—C bond cleavage nor $S_R i$-type reactions play a role in the chemistry of metastable $RCO_2H^{+\cdot}$ (lifetime $t \geq 10^{-5}$ s). Dissociation of the ionized enediols constitutes the reversal of the addition of nucleophilic alkyl radicals to electronic deficient C═C bonds. From the gas phase study of decomposing cation radicals a relative leaving group ability of n-alkyl radicals is derived, showing that methyl is the poorest and ethyl is the best alkyl radical leaving group.

(2) Insight into the mechanisms of homolytic (1,*n*)-rearrangements ($n = 2$–5), in which the migrating substituents could be either H, alkyl or protonated carboxyl groups, is also provided by the gas phase study of ionized carboxylic acids. Evidence is presented for the occurrence of the long-sought 1,2-migrations of both hydrogen and $\overset{+}{C}(OH)_2$; 1,2-migrations involving alkyl groups are unlikely to compete with the former ones. The operation of the remarkable 1,2-hydrogen shift is, however, limited to those cases in which a methyl radical is subseqently eliminated. For systems, in which a better leaving group, e.g. $C_2H_5^{\cdot}$, can be split off from the parent cation radical, 1,2-hydrogen migration does not play any role. The overall chemistry reflects that typical for free n-alkykl radicals.

A detailed account of all experimental aspects—instrumentation, labelling data, product analysis by collisional activation (CA) mass spectrometry[2]—will not be given here; instead, the reader will be referred to the original references where appropriate. Before turning to the discussion of selected examples, the generation of the cation radicals and their principal isomerization modes are mentioned briefly.

GENERATION AND ISOMERIZATION OF CATION RADICALS

As already mentioned, ionization in the gas phase is brought about by electron impact (**1** → **2**); for those species **2** which eventually decompose via loss of alkyl radicals (≥ 90% of all metastable ions) the initial ionization of the carboxyl group is followed by an irreversible 1,4-hydrogen migration (**2** → **3**); from the study of deuterated isotopomers it was concluded[3] that the 1,4-hydrogen shift **2** → **3** is associated with a significant kinetic isotope effect, $k_H/k_D > 1$. For example, pivalic acid showed an isotope effect of $k_H/k_D = 7.0$.



(I)

Whereas the ionization of carboxylic acids is a convenient way to generate cation radicals of type **3**, it should be mentioned that much higher yields of radical ions are provided by a McLafferty-type process[4] (**4** → **5**), in which a cation radical expels a closed-shell neutral, usually an alkene, in a stepwise elimination to generate the enediol cation radical **5**. As will be shown later, the non-conjugated intermediate **3** will

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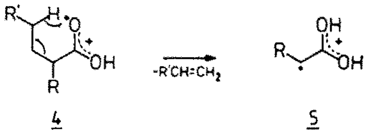
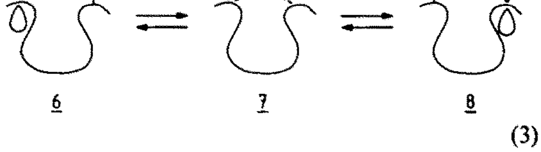
†Dedicated to Professor Ferdinand Bohlmann on the occasion of his 65th birthday.

rearrange to the conjugated one (5) prior to dissociation.



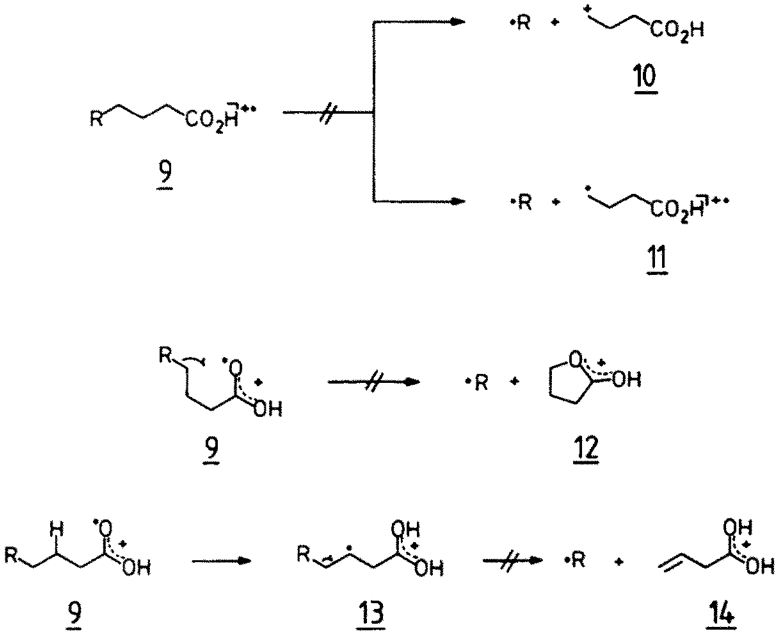
(2)

With regard to the isomerization modes of alkyl radicals carrying a protonated carboxyl group e.g. 6, we observe migration of both hydrogen and the C(OH)$_2^{+\cdot}$ group. The probability of hydrogen migration decreases in the order of ring size, $6 > 5 > 3$. There is no evidence that four-membered transition states play a role. The observed dependence of the hydrogen migration upon ring size is in line with the analogous trend in the gas phase chemistry of neutral alkyl radicals.[5] However, there is no compelling example of a 1,2-hydrogen migration in alkyl radicals. It should also be mentioned that the 1,2-hydrogen migration $\mathbf{6} \rightleftarrows \mathbf{7} \rightleftarrows \mathbf{8}$ is confined to those cases, in which the $\overset{+}{C}(OH)_2$ group is adjacent to the radical centre. With regard to the migration of the $\overset{+}{C}(OH)_2$ group, we observe that in line with predictions of *ab initio* calculations[6] and semi-empirical MO studies[3] the 1,2-migration of $\overset{+}{C}(OH)_2$ is more facile than that of a hydrogen. Quantitative data for a comparison of (1,*n*)-migrations of X = H, $\overset{+}{C}(OH)_2$ are not available as yet.


(3)

PRINCIPAL DECOMPOSITION PROCESSES

Metastable carboxylic acid cation radicals are characterized by the fact that their gas phase behaviour is entirely governed by the formation of n-alkyl radicals, which depending on the substrates, are formed in 80–99% yield. What is the structure of the products formed, by which mechanism is the n-alkyl radical expelled? Determination of the product ion structure by means of CA mass spectrometry clearly rules out simple direct C—C cleavages, such as **9** → **10** or **9** → **11**. Similarly, there is no evidence that the dealkylated cationic products have either cyclic (**12**) or non-conjugated (**14**) structures. Consequently, the S$_R$*i*-type reaction (**9** → **12**) can be ruled out as can the hidden hydrogen migration[7] induced process **9** → **13** → **14**.

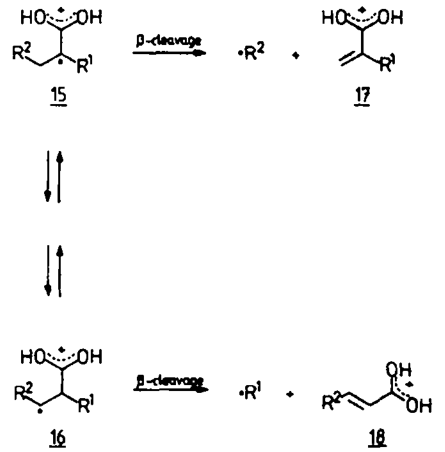

(4)

Instead, multi-step processes take place which comprises combinations of hydrogen rearrangements within the alkyl radical chain and migrations of the C(OH)$_2^+$ group leading to species of the general structure **15**. Ion **15**, an enol cation radical, serves as the actual precursor for the C—C cleavage,[3,8] from which **17** is eventually generated. We never observed C—C cleavage for the cation radical **16** which is isomeric with **15**. In line with MO calculations,[3,9] the fragmentation **16** → **18** has a higher barrier than the multi-step process **16** → **15** → **17**. In fact, species generated initially as **16** rearrange to **15** prior to dissociation, although the product ions formed are not always the thermodynamically most favoured ones. For example, cation **18** with substitutuents R^2 = CH$_3$ is calculated to be 1.4 kcal mol^{-1} more stable than the corresponding cation **17** (R^1 = CH$_3$);[10] nevertheless, **17** is the only cation formed from **16**.

The solution to this seemingly puzzling result is surprisingly trivial when one analyzes the reverse process, i.e. the addition of alkyl radicals to deactivated double bonds. Addition of (nucleophilic)[5a,11] alkyl radicals R˙ will undoubtedly prefer attack at C(*β*) and

Table 1. Relative leaving group abilities (LGA) of n-alkyl radicals $R^{\cdot}$

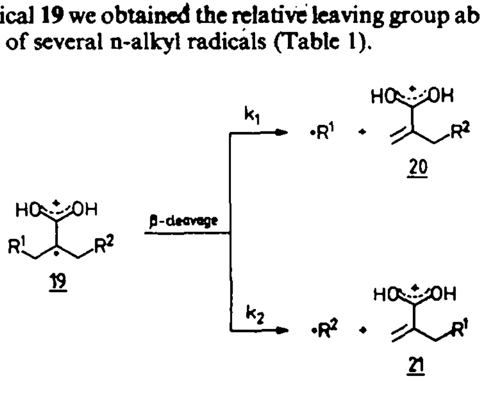
$R^{\cdot}$	CH_3	C_2H_5	C_3H_7	C_4H_9	C_5H_{11}	C_6H_{13}	C_7H_{15}	C_8H_{17}
LGA	0.022	1.000	0.709	0.658	0.551	0.463	0.393	0.348



(5)

not at C(α),[12] simply because of the fact that the transition state to generate **15** from **17** will be lower in energy than that for the formation of **16** from **18**. Conversely, and applying the principle of microscopic reversibility, dissociation of the enol cation radical **15** is kinetically favoured over that of **16** in line with all experimental and theoretical findings we are going to present below.

A quantitative assessment of the relative leaving group abilities of n-alkyl radicals was obtained by studying the unimolecular dissociation of a series of enediol cation radicals, **19**, which can lose either of two different groups, R^1 or R^2, from two equivalent carbon atoms.[13] The ratio of the rates, k_1/k_2, corresponds to the ratio of the signal intensities of the ions **20** and **21**. The resulting ions do not decompose further and their structures were independently determined by using CA mass spectrometry. By systematic variation of the substituents, R^1 and R^2, in cation radical **19** we obtained the relative leaving group abilities of several n-alkyl radicals (Table 1).



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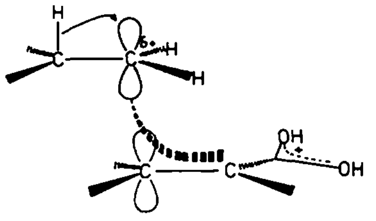

Fig. 1. Transition structure for loss of an alkyl group from an ene-1,1-diol cation radical.

The significant difference between the LGAs of $CH_3^{\cdot}$ and $C_2H_5^{\cdot}$ can be explained readily in terms of β-CH hyperconjugation of the incipient positively charged carbon centre in the transition state (Fig. 1) for loss of $R^{\cdot}$ from the enol cation radical. As $CH_3^{\cdot}$ cannot be stabilized by C—H hyperconjugation, the transition state for loss of $CH_3^{\cdot}$ is less favourable by a factor of *ca.* 50 than the corresponding transition state for loss of $C_2H_5^{\cdot}$ (Fig. 1). However, β-CH hyperconjugation cannot account exclusively for the stabilization of the transition structure. Otherwise, one would predict comparable LGA-values for all n-C_nH_{2n+1} radicals ($n \geq 3$).† Inspection of our data (Table 1) reveals, however, that from $n = 3$ to 8 the relative leaving group abilities diminish by a factor of two. It remains to be established whether this decrease in LGA with increasing chain length can be accounted for by size effects.

The low leaving group ability of $CH_3^{\cdot}$ is associated with a quite substantial activation energy for the dissociation step, enediol$^{+\cdot}$ → $CH_3^{\cdot}$ + product cation. As a consequence, dissociation is often preceded by high-energy rearrangement processes, like the above mentioned 1,2-hydrogen migration. Moreover, unimolecular loss of $CH_3^{\cdot}$ is limited to relatively small-sized carboxylic acids ($\leq C_5$). For larger systems elimination of $CH_3^{\cdot}$ cannot compete with loss of higher alkyl radicals and is frequently difficult to observe at all.[13a] In the following section we will discuss specific examples to illustrate the diversity of processes depending on the size of the starting carboxylic acid cation radical.

IONIZED C(6) CARBOXYLIC ACIDS[4a, 13a]

It has already been stated that the gas phase properties of metastable cation radicals can be described in terms of alkyl radicals in which one hydrogen is replaced by the protonated carboxyl group. The latter serves three functions:

(a) it carries the species through the mass spectrometer,

(b) the $\overset{+}{C}(OH)_2$ function participates actively as a migrating group in (1,*n*) rearrangements, and

(c) the dissociation step involves an intermediate,

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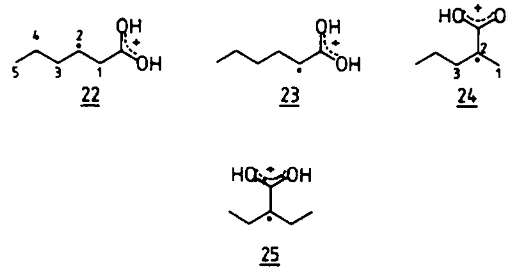
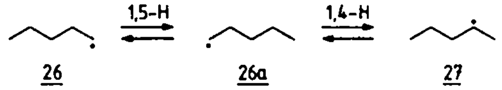
†Recent ESR studies[14] indicate that C-H hyperconjugation may be more important than C—C hyperconjugation. This contradicts theoretical interpretations of carbocation stabilities in terms of preferential C—C hyperconjugation.[15]

in which the radical site is located α to the $\overset{+}{C}(OH)_2$ group (enediol cation radical).



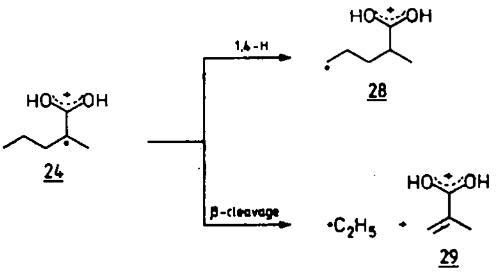
(7)

Mono-substitution of $\overset{+}{C}(OH)_2$ for hydrogen in an n-pentyl radical results in several isomers, four of which (**22**–**25**) are of interest in the present context. Isomer **22** is available via ionization of hexanoic acid, following the sequence outlined in Eq. (1); the remaining cation radicals were generated via McLafferty-type rearrangements according to Eq. (2). From the chemistry of free n-pentyl radicals **26** it is known[5] that they undergo the degenerate isomerization **26** ⇄ **26a** via 1,5-hydrogen migration, and to a smaller extent isomerization to the thermochemically more stable 2-pentyl radical **27**. 1,2- or 1,3-Hydrogen migrations have not been observed. In view of the fact that the hydrogen and the $C(OH)_2^{+\cdot}$ group have, to a first approximation, comparable migratory aptitudes in cation radicals,[3,8a,d,h,9,13] it was not surprising to learn that **22**–**24** prior to dissociation form a common intermediate, i.e. **24**. This is evidenced by a nearly complete positional loss of hydrogens attached to C-1, C-2, C-4 and C-5, but *not* of C-3 and the carboxyl group of **22** and **23**. Complete H scrambling is prevented by the fact that loss of $C_2H_5^\cdot$ (**24** → **29**) from the enediol cation radical **24** competes efficiently with intramolecular hydrogen migration which would transform **24** to the less stable cation radical **28**.



(8)

Furthermore, ^{13}C labelling indicates that the $C(OH)_2^{+\cdot}$ group originally bound to C-1 (**22**) "freely" migrates between C-1, C-2, C-4 and C-5.



(9)

It is interesting to note that greater than 90% of metastable **22** and 99% of metastable **23** and **24** undergo loss of $C_2H_5^\cdot$ to yield **29** while loss of a $C_3H_7^\cdot$ radical from **23** is less favourable on two grounds:

(a) $C_3H_7^\cdot$ is a less efficient leaving group than $C_2H_5^\cdot$ (Table 1), and

(b) $C_3H_7^\cdot$ loss from **23** would generate a product (**17**, $R^1 = H$) which is significantly less stable than **29**.

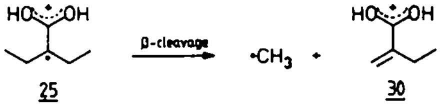
This thermochemical argument does, however, not apply to higher homologues of **17** ($R^1 \geqslant CH_3$), since their stabilities seem to be of minor importance for the actual dissociation pattern. The conclusion that loss of $C_2H_5^\cdot$ from **22**–**24** is preceded by the radical-like reactions described above is clearly evidenced by the result of a comprehensive ^{13}C-labelling study.[8a] Two conclusions can be derived from these results:

(a) the $C_2H_5^\cdot$ radicals eliminated from **22** and **23** originate to approximately the same extent as C(4)/C(5) and as C(1)/C(2); and

(b) the two carbon atoms remain bonded together in the overall rearrangement/dissociation process.

The enediol cation radical **24** behaves exceptionally in that it is prone to split off the C(4)/C(5) unit directly (> 95%) and undergoes rearrangement to **28** only to a minor extent (< 5%).

The gas phase chemistry behaviour of **25** is fundamentally different from that of the isomeric cation radicals **22**–**24**.[8a] As (1,*n*)-isomerizations via low-lying transition states are precluded on structural grounds, the only options available to **25** are the unfavourable 1,2- or 1,3-migrations or elimination of the poor leaving group $CH_3^\cdot$. Our results unambiguously show that CH_3 loss is the favoured route in that greater than 93% of metastable **25** dissociates to $CH_3^\cdot$ and **30**. Labelling experiments[8a,13a] clearly demonstrate that there is no hydrogen exchange within the alkyl chain preceding the dissociation **25** → **30**. Obviously, **25** is separated by substantial barriers from **22** to **24** and also from species which would be formed via 1,2- or 1,3-hydrogen migrations.



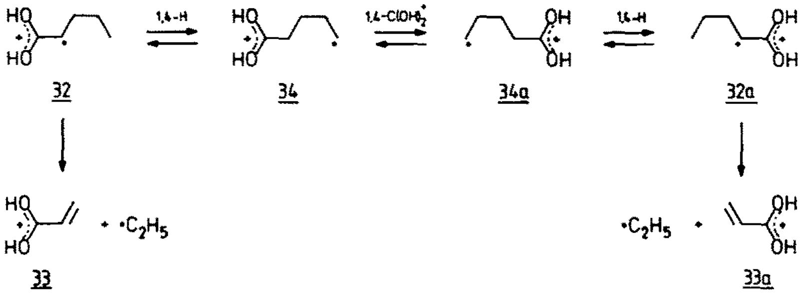
(10)

CATION RADICALS OF n-PENTANOIC ACID[8a,13a]

For 1-butyl radicals the only feasible isomerization is that of a degenerate 1,4-hydrogen migration (**31** ⇄ **31a**).

(11)

What is the situation for the corresponding $\overset{+}{C}(OH)_2$-substituted cation radical **32**, which is accessible via McLafferty rearrangement? More than 99% of these radical cations eliminate $C_2H_5^\cdot$ under formation of protonated acrylic acid as the only ionic product (**33**).[8a,13a] ^{13}C-Labelling reveals[8a,13a] that the $C_2H_5^\cdot$ radical comprises the original C(3)/C(4) position to 59%, and C(1)/C(2) to 41%. Deuteration of either C(2) or C(3) leads to specific losses of $CH_3CD_2^\cdot$, thus precluding exchange of these positions with C(1) and C(4). The latter, however, undergo a partial loss of positional identity prior to dissociation. The complete analysis of all labelling data[8a,13a] suggests that *ca* 19% of **32** decomposes directly, while 81% undergoes a degenerate isomerization **32** ⇄ **32a** prior to formation of **33**. Isotope effects were found[8a,13a] to be operative in the dissociation step: for the deuterated compounds secondary isotope effects, k_H/k_D, of 1.33–1.65 were observed, which are mainly due to re-hybridization $sp^3 \rightarrow sp^2$ in the course of ethyl radical formation.

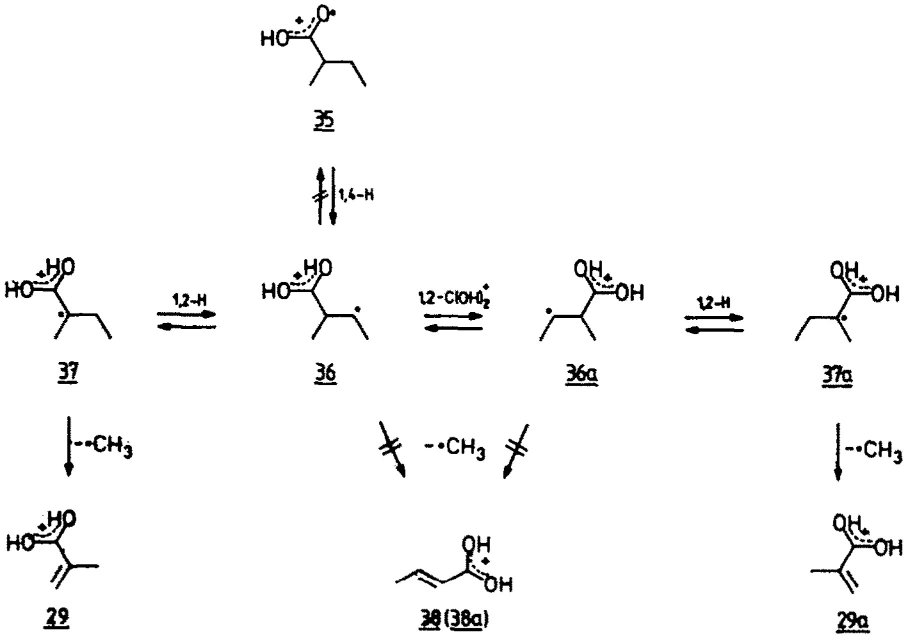


(12)

CATION RADICALS OF 2-METHYL BUTANOIC AND PIVALIC ACID[3,13]

The examples discussed so far involved transition state sizes of rearrangements characterized by the operation of 1,4- and 1,5-hydrogen migrations, while for the $C(OH)_2^{+}$ group evidence was presented that in addition to these familiar ring sizes 1,2-migration is also operative. The following examples were chosen to indicate that under certain circumstances even 1,2-hydrogen migrations to a radical centre do occur.

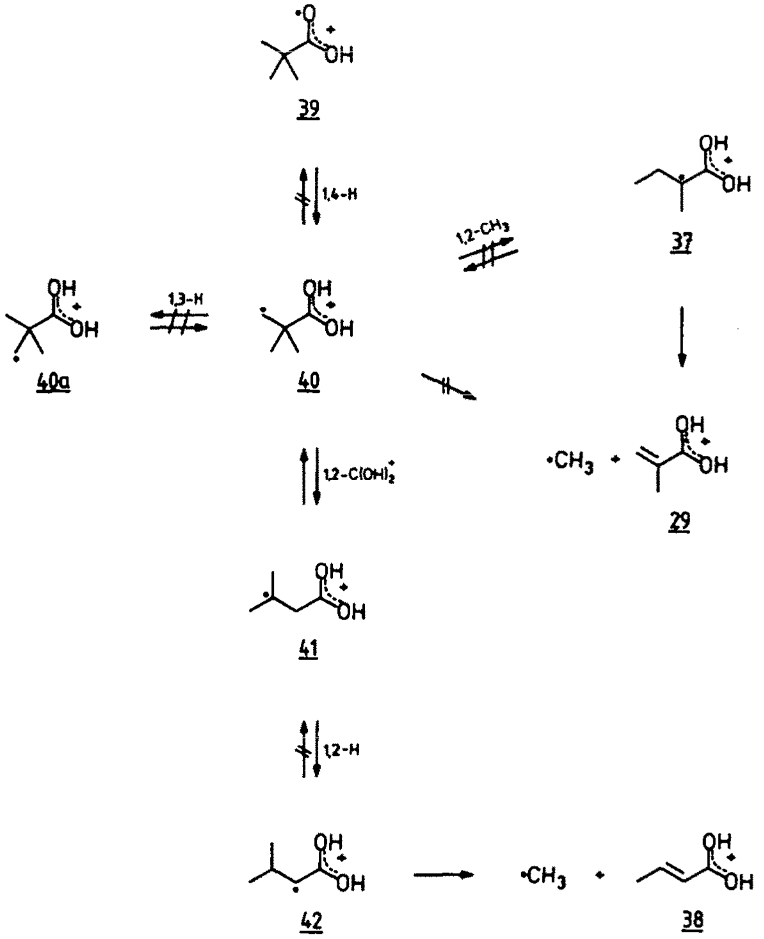
The metastable 2-methyl butanoic acid cation radicals dissociate almost exclusively (98%) to $CH_3^{\cdot}$ and protonated methacrylic acid (**29**). The thermochemically more stable isomer **38** is not formed. Extensive ^{13}C- and ^{2}H-labelling experiments prove that both original CH_3 groups of **35** are eliminated to the same extent without prior hydrogen exchange with the CH and CH_2 group. The labelling data also provide evidence that the overall reaction commences with hydrogen transfer from the methylene group to the ionized carboxyl function (**35** → **36**). Ion **36**, which is not an enediol cation radical, does not dissociate to **38**, but rather undergoes 1,2-migration of both hydrogen and $\overset{+}{C}(OH)_2$. The former leads to the ionized enediol **37** and the latter brings about the degenerate isomerization (**36** ⇄ **36a**) which accounts for the involvement of both original CH_3 group in the dissociation step **37** → **29**. Enediol **37** can also be generated directly via McLafferty rearrangement, and labelling studies indicate that the ion generated in this fashion is indistinguishable from the one formed via the sequence **35** → **36** → **37**. This observation makes it mandatory to assume that the barrier for the dissociation step **37** → **29** is as high (if not higher) as the one for the 1,2-hydrogen migration; MNDO calculations,[3] indeed, indicate this to be the case: for the reaction **37** → **29** a barrier of *ca* 50 kcal mol^{-1} is calculated, while the process **37** → **36** is associated with a barrier of *ca* 48 kcal mol^{-1}. As entropy factors in general favour dissociation over rearrangement reactions it is not surprising that **36**, generated directly, splits off the methyl group C(4) to 94%, and only 6% are provided by the methyl group, attached to C(2). As stated above, however, complete positional loss of the two CH_3 groups is observed for **35**.



(13)

It should be emphasized that the process **36** → **37** is the first proven case for the operation of an unimolecular, uncatalyzed 1,2-hydrogen migration to a radical centre.†[16,17] The reported hydrogen-scrambling of gaseous $C_2H_5^{\cdot}$ which originally[16] had been attributed to a 1,2-hydrogen migration, was later interpreted[18] as a surface catalyzed reaction.

The gas phase chemistry of ionized pivalic acid (**39**) has also been studied in great detail.[3,13a] Metastable **39** is found to dissociate to 89% to $CH_3^{\cdot}$ and protonated crotonic acid (**38**). Again, extensive ^{13}C- and ^{2}H-labelling in conjunction with CA studies allow the following conclusions to be drawn: The initial hydrogen transfer step, **39** → **40**, is rate-determining and irreversible. This reaction has a kinetic isotope effect, $k_H/k_D = 7.0$. Consecutive 1,2-migrations of the $C(OH)_2^+$ group (**40** → **41**) and hydrogen (**41** → **42**) generate the enediol cation radical **42**, from which the dissociation takes place. The fact that the formation of **42** is irreversible is particularly noteworthy, because the isomeric cation radicals **36**, **37** and **36a**, **37a** derived from methylbutanoic acid are readily interconverted. In contrast, ion **42**, once formed, dissociates without rearranging back to **41**.[19] This is demonstrated convincingly by directly generating **42** via McLafferty rearrangement. The enediol cation radical formed in this fashion dissociates to **38** without having interchanged the hydrogens attached to C(2)/C(3). It is worth recalling that neither the degenerate isomerization **40** ⇄ **40a**, nor isomerization **40** → **37**, nor dissociation **40** → **29** were found to occur. Thus, 1,3-hydrogen rearrangement (**40** → **40a**), 1,2-alkyl migration (**40** → **37**)‡ and dissociation from a non-enolic cation radical intermediate (**40** → **29**) must have energy requirements substantially higher than that for the 1,2-migration of a protonated CO_2H group.



(14)

The results described in this article for the gas phase chemistry of ionized carboxylic acids are not confined to alkyl groups bearing the carboxyl functionality. Preliminary studies[13a] clearly show that groups, like

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† A referee has argued that the 1,2-hydrogen migration **36** ⇄ **37** should not be viewed as an example for a "pure" radical reaction because considerable positive charge had been calculated for the radical centres C(3) and C(4) in the ions $CH_3CH_2\dot{C}H\overset{+}{C}(OH)CH_3$ and $CH_3\dot{C}HCH_2\overset{+}{C}(OH)CH_3$, which are also found[17] to undergo 1,2-hydrogen migration prior to dissociation. However, for the system **36** ⇄ **37** MNDO calculations (H. Halim and H. Schwarz, unpublished results) clearly show that there is no positive charge located at the respective radical centres; for **36** we obtain a value of −0.16 for C(3), and for **37** a value of −0.03 has been calculated for C(2). The positive charge resides mainly at the carbon and hydrogen atoms of the carboxyl group.

‡ Note, however, that cation radicals of polycyclic hydrocarbons upon photoexcitation may undergo 1,2-alkyl migration.[20] See also Ref. 21.

—C(OH)X ($X = OCH_3$, NH_2, alkyl) and the 1,3-dioxolanyl substituent, exert effects comparable to that of $C(OH)_2^+$.

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