94. Temperature Dependence of the Isobutane Chemical Ionization Mass Spectra of Open-chain and Cyclic Alcohols; Structural, Stereochemical and Molecular-Size Effects. A Reevaluation of the Isobutane Chemical Ionization of Alcohols

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Summary

The temperature dependence of the isobutane chemical ionization (CI.) mass spectra of 54 open-chain, cyclic and unsaturated C_5- to C_{10}-alcohols was studied at temperatures ranging from 60 to 250°, and enthalpy changes were calculated for the corresponding main reactions of typical alcohols.

The CI. reactivity is controlled by the temperature and the substrate structure as usual, and in addition, by the molecular size. The combination of thermal, structural and substrate-size effects leads to the following main conclusions.

At low-reactivity conditions, *i.e.* at 150° or less, the alcohols with less than 11 C-atoms give four distinct types of spectra, with $(M-OH)^+$ usually as the base peak. The characteristic ions are $MC_4H_9^+$ and $(M-H)^+$ for primary, MH^+ and $(MC_4H_9-H_2O)^+$ for secondary, $(MC_4H_9-H_2O)^+$ for tertiary and allyl-type alcohols. Configurational assignments of stereoisomeric alcohols are also possible, by means of steric compression and shielding effects. The $MH^+/(M-OH)^+$ ratio in the spectra of epimeric methylcyclohexanols is at least 3 to 4 times higher for the isomers with mainly *axial* OH-group conformation compared to the *equatorial* isomers. Stereospecific $(M-H)^+$ ions are apparently formed from *trans*-2-methylcyclopentanol and *endo*-norbornan-2-ol by a favorable abstraction of the unshielded H(*a*)-atoms *versus* normal behavior of the other epimers.

While the spectra recorded at 200° show almost exclusively $(M-OH)^+$ ions, those at 250° give nevertheless some C-skeleton information through the temperature dependent decomposition of the $(M-OH)^+$ ions.

Introduction. – Chemical ionization mass spectrometry [1] [2] is a versatile method for analytical and structural investigations of alcohols. After initial studies

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[3] [4] with methane as the reagent gas, the first comprehensive work in this area was done by *Field* in 1970 [5] using the more adequate isobutane reagent gas. Closer studies of tertiary [6] and secondary [7] alcohols were reported by *Field et al.* and by *Munson et al.* subsequently. Further relevant articles deal with gas phase intermolecular and internal substitutions of protonated alcohols [8–10] and benzyl alcohol *t*-butyl complex ions [11], exothermicity effects on alkanol protonation [12], *ab initio* calculations for CI. reactions [13–16] and alcohol analysis by ammonia [17], negative ion [18] [19] and nitric oxide [20] CI. spectra.

The ion source temperature can strongly influence the relative ion abundances in CI. spectra [21–25], as demonstrated for cyclohexanol [7]. As a substrate-inherent parameter, the size of the alcohol can also control the fragmentation [5] [26]. In this paper we describe and discuss the results of systematic measurements on the temperature dependence of isobutane CI. mass spectra of a variety of alcohols, underlining molecular-size [26], stereochemical [16] [27] and structural aspects. A parallel ammonia CI. study is in progress [26] [27]. Isobutane CI. mass spectra of the monoalcohols **1** to **18**, including open-chain and cyclic species were measured at ion source temperatures of 60, 100, 150, 200 and 250°.

Scheme. *Gas-phase ion chemistry of alcohols in isobutane CI. spectra*

Lewis *acid addition*	$ROH + C(CH_3)_3^+ \rightarrow R{-}\overset{+}{O}H{-}C(CH_3)_3$	(Ia)
Brønsted *acid addition*	$ROH + H^+ \cdots H_2C{=}C(CH_3)_2 \rightarrow R(OH) \cdots H^+ \cdots H_2C{=}C(CH_3)_2$	(Ib)
Dehydration of $MC_4H_9^+$	$ROH + C(CH_3)_3^+ \rightarrow R{-}CH_2{-}\overset{+}{C}(CH_3)_2 + H_2O$	(II)
Proton transfer	$ROH + C(CH_3)_3^+ \rightarrow ROH_2^+ + i\text{-}C_4H_8$	(III)
Hydride abstraction	$R'R''CHOH + C(CH_3)_3^+ \rightarrow R'R''C{=}OH^+ + i\text{-}C_4H_{10}$	(IVa)
Dehydrogenation of MH^+	$R'R''CHOH_2^+ \rightarrow R'R''C{=}OH^+ + H_2$	(IVb)
Hydroxy group abstraction	$ROH + C(CH_3)_3^+ \rightarrow R^+ + HOC(CH_3)_3$	(Va)
Dehydration of MH^+	$ROH_2^+ \rightarrow R^+ + H_2O$	(Vb)
Alkene loss from R^+	$R^+ \rightarrow (R \text{ minus } C_nH_{2n})^+ + C_nH_{2n}$	(VI)
Rearrangement of $MC_4H_9^+$	prim/sec- $ROH \cdot C_4H_9^+ \rightarrow$ tert-$ROH{-}C_4H_9^+$	(VIIa)
Rearrangement of MH^+	prim/sec-$ROH_2^+ \rightarrow$ tert-ROH_2^+	(VIIb)

Thermochemical aspects. – The major types of reactions and fragmentations of alcohols under isobutane CI. conditions [1] [5–7] [11] are summarized in the *Scheme. Table 1* shows the corresponding thermochemical data and the estimated enthalpy changes of these reactions for a number of selected alcohols. No calculations are given for *Eqn. VI* and *VII* which include C,C-bond cleavages and rearrangement reactions. Finally, *Figure 1* gives a synopsis of the energetics of *reactions I* to *V* in the primary, secondary and tertiary alkanols **1**, **4** and **12**.

Table 1. *Thermochemical values and estimated enthalpy changes for the isobutane CI. reactions* Ia *to* Vb *of selected alcohols* (see *Figure 1*)

ROH	ΔH_f^0(ROH)[b]	PA(ROH)[c]	ΔH_f^0(R^+)[d]	ΔH_r(Ia)	ΔH_r(II)	ΔH_r(III)	ΔH_r(IVa)	ΔH_r(IVb)	ΔH_r(Va)	ΔH_r(Vb)
Pentan-1-ol (**1**)	−296	807	821	−104	−64	17	−32	69	109	145
Decan-1-ol (3)	−397	812	720	−108	−63	13	−40	65	109	149
Pentan-2-ol (**4**)	−315	812	744	−105	−54	12	−75	31	51	92
Cyclopentanol (**5**)	−243	812	830	−105	−82	12	−80	26	65	105
Cyclohexanol (**6**)	−286	814	781	−107	−59	10	−68	39	59	102
cis-3-Methylcyclohexanol (*c*-**6a**)	−316	815	751	−108	−72	9	−78	31	59	103
trans-3-Methylcyclohexanol (*t*-**6a**)	−313	815	751	−108	−72	9	−80	28	56	100
Adamant-2-ol (**10**)	−325	818	682	−111	−72	6	−81	30	0	46
Norbornan-2*endo*-ol (*endo*-**11**)	−219	816	783	−109	−72	8	−79	30	−5	39
Norbornan-2*exo*-ol (*exo*-**11**)	−218	816	783	−109	−72	8	−80	29	−7	38
2-Methylbutan-2-ol (**12**)	−331	820	669	−100	−52	4	-	-	−8	41
1-Methylcyclopentanol (**13**)	−280	823	703	−102	−52	2	-	-	−24	27
1-Methylcyclohexanol (**14**)	−338	823	657	−103	−52	1	-	-	−13	39
Adamant-1-ol (**15**)	−335	825	666	−105	−52	−1	-	-	−7	47
Pent-1-en-3-ol (**16a**)	−182	804	825	− 83	−72	21	−64	33	0	32
Benzyl alcohol (**18**)	−100	807	909	− 84	−53	17	−67	33	−2	38

[a] All values are given in kJ/mol. Heats of reaction ΔH_r were calculated with reported or estimated values of proton affinities (PA.) and heats of formation were calculated with data from [28–31]. For ΔH_r (*Ib*) see legend of *Fig. 1*. PA.(NH_3) = 858 kJ/mol. PA.(i-C_4H_8) = 824 kJ/mol.

[b] Reported [30] or estimated (**6a**, **10**, **11**, **13**, **14**, **15**, **16a**) by *Benson's* increments [31].

[c] These values have been calculated or estimated from data given in [28].

[d] Reported in [28] [32] or estimated by isodesmic substitution [29].

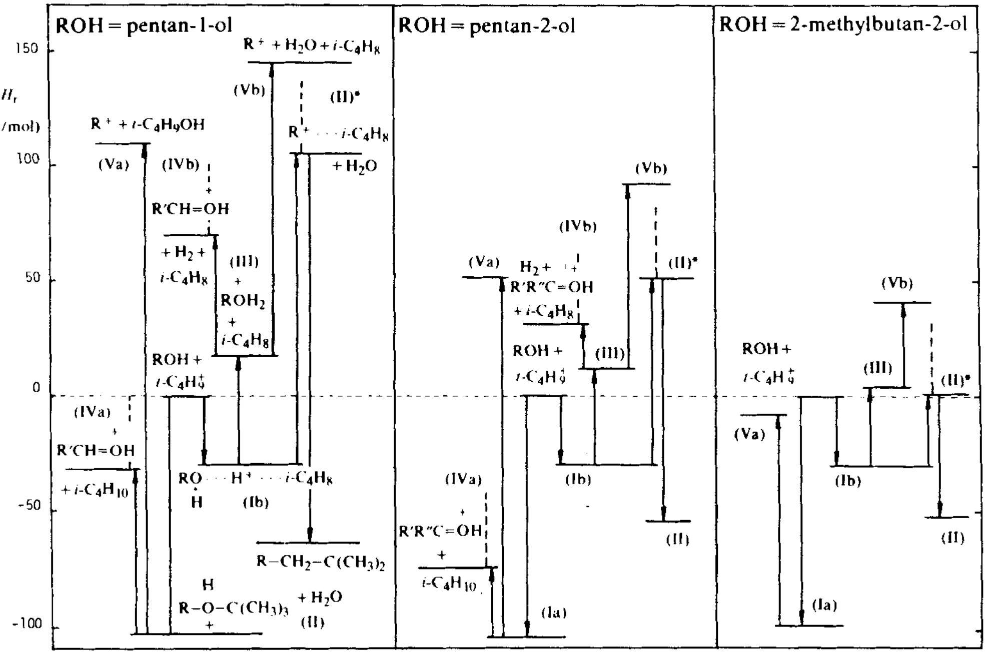

Fig. 1. *Energy diagram of isobutane CI. reactions of primary, secondary and tertiary alcohols.* Enthalpy changes are taken from *Table 1.* Estimated solvation energies of 30 and 40 kJ/mol for *reactions Ib* and *II**. The dotted vertical barriers indicate the large entropy term of the elimination *reactions II, IVa* and *IVb* with tight transition states in contrast to the simple bond cleavage *reactions III, Va* and *Vb.* The important entropy barriers of the adduct formation *processes Ia* and *Ib* are not shown.

In isobutane spectra of alcohols, the nature of the initial $MC_4H_9^+$ collision complex and the contributions of competing pathways to common fragment ions are rather intriguing. The covalently bonded *Lewis* adduct *(reaction Ia)* is strongly exothermic by approximately 100 kJ/mol, whereas the *Brønsted* proton-bound species is less exothermic *(reaction Ib)*. These two well defined adducts, and further nominal $MC_4H_9^+$ intermediates, show interconversion, dissociation and fragmentation, depending on the initial internal energy and on energy exchange during collision. For primary and secondary alcohols with minor rearrangement tendencies *(VIIa, VIIb)*, thermochemistry is in favor of the *IVa* and *Va Lewis* acid reaction channels. The need of thermal activation of these alcohols for the fragmentation, except *IVa*, should lead to strong temperature effects. No protonated dimers M_2H^+ [1] are observed in our spectra, due to the low sample concentration.

Results and discussion. – *Primary alcohols.* The isobutane CI. spectra of seven primary alcohols (**1**–**3**, **1a**–**1c**, **2a**), recorded at 60 to 250° (*Fig. 2* and *Table 2*) show substantial changes as a function of temperature, in line with known general rules [2] [21–25]. The previously reported spectra of **1**, **2** and **3** at 180° [5] can be located within our data in the 100–120° range, and thus demonstrate the influence of experimental conditions.

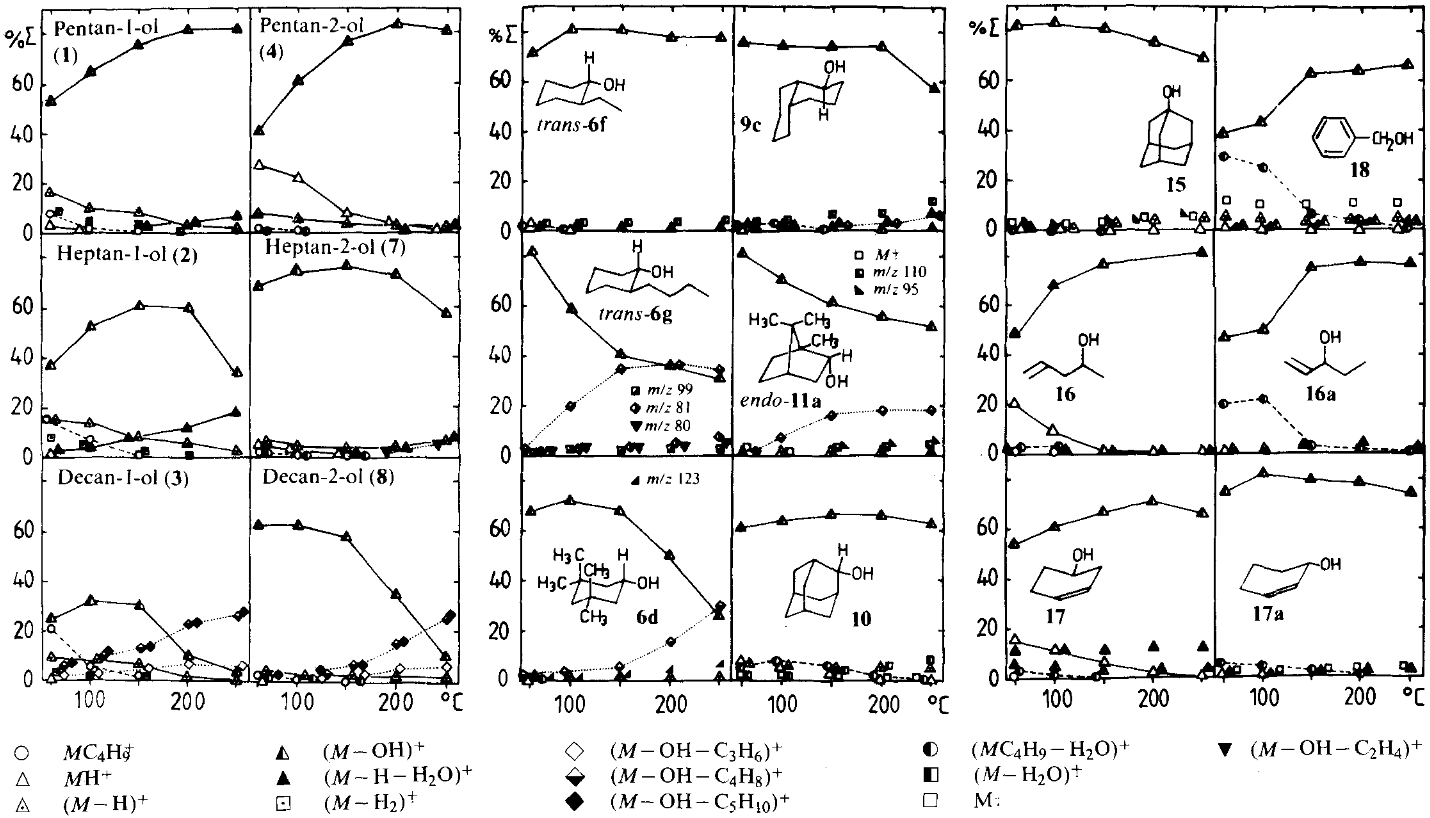

Fig. 2. *Effect of the temperature on the relative abundances of key ions in the isobutane CI. mass spectra of alcohols*

Table 2. *Temperature dependence of isobutane CI. mass spectra of branched primary alcohols, unbranched secondary alcohols and* cis-*3-methylcyclopentanol*

Ion source nominal temperature (°)	60	100	150	200	250	60	100	150	200	250
Ion	Relative abundances (% Σ60)[a]					Relative abundances (% Σ60)				
	2-Methylbutan-1-ol (**1a**)					3-Methylbutan-1-ol (**1b**)				
$MC_4H_9^+$	8	4	0.4	-	-	8[b])	3	0.6	-	-
MH^+	0.7	0.3	-	-	-	3	2	1	0.3	0.03
$(M-H)^+$	14	11	6	4	3	15	9	7	3	2
$(M-H_2)^+$	2	2	1	1	0.4	6	3	2	1	0.1
$(M-OH)^+$	64	71	83	86	88	53	69	78	84	83
$(M-H_2O)^+$	8	6	5	4	3	8	8	5	4	5
$(M-H-H_2O)^+$	0.5	1	1	1	1	1	2	2	3	5
	2,2-Dimethylpropanol (**1c**)					Cyclohexanemethanol (**2a**)[c])				
$MC_4H_9^+$		6[b])	-	-	-	13	4	0.6	0.05	-
MH^+		0.8	-	-	-	1	0.3	0.1	0.05	0.02
$(M-H)^+$		17	8	3	3	19	11	6	4	2
$(M-H_2)^+$		-	-	-	-	2	1	1	0.4	0.2
$(M-OH)^+$		70	67	82	86	44	60	58	70	72
$(M-H_2O)^+$		-	-	-	-	6	6	5	5	5
$(M-H-H_2O)^+$		-	-	-	-	5	8	9	9	8
	Pentan-3-ol (**4a**)[d])					Cyclopentanol (**5**)[d])[e])				
$MC_4H_9^+$	0.7	0.5	-	-	-	-	0.2	-	-	-
$(MC_4H_9-H_2O)^+$	2	1	-	-	-	4	6	2	0.8	0.3
MH^+	43	16	0.9	1	0.6	45	21	9	7	5
$(M-H)^+$	5	5	2	2	2	20	14	10	7	5
$(M-OH)^+$	36	72	86	89	82	3	44	66	72	74
$(M-H-H_2O)^+$	1	-	1	-	2	4	3	3	3	4
	Cyclohexanol (**6**)[d])					*cis*-3-Methylcyclopentanol (**5a**)[d])				
$MC_4H_9^+$	0.5	1	0.9	0.4	0.1	0.3	0.1	-	-	-
$(MC_4H_9-H_2O)^+$	0.1	1	2	1	1	3	3	0.5	0.2	-
MH^+	40	40	32	23	16	-	-	-	-	-
$(M-H)^+$	8	9	8	7	6	7	7	4	3	2
$(M-OH)^+$	33	37	46	57	65	66	75	81	82	83
$(M-H-H_2O)^+$	2	2	2	2	2	4	4	3	3	3

[a]) Rel. abundances higher than 1% have been rounded off. [b]) $(MC_4H_9-H_2O)^+ = 0.2\%$. [c]) *m/z* 83 and *m/z* 81 = 1-2%. [d]) $(M-H_2O)^+ = 2\%$. [e]) $M^+ = 2$-3%.

The alkyl ions R^+ or $(M-OH)^+$, which dominate the spectra of the primary alkanols **1**, **1a**, **1b** and **1c**, show an intensity increase from 50 to 80% in the 60-250° temperature range (%Σ60). The hydride abstraction ions $(M-H)^+$ form the second largest peak at low temperatures. However, due to the tight transition states of *reactions IVa* and *IVb*, the corresponding abundances of 18% at 60° decrease to approximately 2% at 250°. A negative temperature slope is also found for the weaker peaks of the ions $MC_4H_9^+$, MH^+ and $(M-H_2)^+$. Finally, the subsequent fragments $(M-H-H_2O)^+$ or $(M-OH-H_2)^+$ increase with the temperature. These observations are largely in line with the expected temperature influences and entropy requirement differences [33-35]. Larger molecules or ions can accomodate higher amounts of thermal energy than smaller ones at a given temperature accordding to the number of degrees of freedom (modes of vibrational motions) in the respective species. This molecular-size effect shows two different consequences in the isobutane CI. spectra of the homologous C_5-, C_7- and C_{10}-alkanols **1**–**3** discussed here. The exothermicity of the $MC_4H_9^+$ adduct formation is nearly independent of the substrate size for the larger alcohols. However, the $MC_4H_9^+$ peaks distinctly increase at 60° and similarly up to 150° within the homologous series of the alkanols **1**, **2** and **3** and their isomers. Thus, larger molecules are more efficient sinks for the distribution of the complex formation energy.

In addition, a strong enhancement of subsequent fragmentations is also found with rising C-atom numbers. At 250°, the $(M-OH-H_2)^+/(M-OH)^+$ ratio increases from 7/82 (**1**) to 18/34 (**2**) and 4/0.2 (**3**). For **3** the respective peaks are nearly extincted by alkene eliminations which give 28% $C_5H_9^+$-, 26% $C_6H_{11}^+$- and 11% $C_6H_9^+$-ions. Similar effects are present in earlier data [5]. This CI. reactivity increase has to be interpreted as a degree of freedom (DOF.) activation effect, which is discussed elsewhere on a more general basis [26]. In short, the percentage of thermally preactivated parent ions considering any of the *reactions II* to *VI*, at a given temperature, is higher for large size molecules than for smaller homologs because of the higher molar heat capacity. Therefore, large molecules are also more efficient sources for supply of reaction energy, or give the appearance of an increased effective temperature [26]. In summary, the low energy fraction of substrate species (within a near *Boltzmann* distribution) shows DOF. stabilization of the $MC_4H_9^+$ complex ions, whereas the corresponding high energy fraction gives DOF.-assisted progressive fragmentations.

Unbranched secondary alcohols. – The unbranched alkanols **4**, **4a**, **7** and **8** and the unsubstituted cycloalkanols **5** and **6** (*Fig. 2* and *Table 2*) share the absence of any potential centers of reactivity or configurational isomerism. The CI. behavior of the secondary *versus* the primary alcohol function can thus be compared with less interferences. As typical of the spectra of the secondary alcohols [5] [7], again the $(M-OH)^+$ alkyl ions generally give the base peak. However, the protonated substrate MH^+ is now a key ion ($\leqslant 50\%\ \Sigma 60$) and the adduct dehydration product $(MC_4H_9-H_2O)^+$ forms characteristic peaks of 1–2% abundance ($\%\ \Sigma 60$), whereas $MC_4H_9^+$ and $(M-H)^+$ become less important ions. The distinct $(MC_4H_9-H_2O)^+$ formation and the more rapid $MC_4H_9^+$ decomposition are due to the thermochemical preference (*Table 1, Fig. 1*) of the secondary alkyl intermediate and product ions. Long-lived gaseous ion-dipole intermediates are discussed in [11] [36–38]. The reversed abundances of the MH^+ and $(M-H)^+$ ions, compared to primary alcohol spectra, contradict thermochemical values and therefore must be mainly controlled by entropy effects. Secondary alcohols with only a single abstractable H(α)-atom, but one additional α-alkyl group, shielding the H(α)-atom against the t-$C_4H_9^+$ attack, accordingly yield few $(M-H)^+$ ions.

The above very diagnostic ion pattern is limited to the temperatures below 150° and to the alcohols with less than seven C-atoms, as in general agreement with previous data [5] [7]. An increase of the temperature and/or of the molecular size lead to increased fragmentation of the MH^+ and $(M-OH)^+$ ions. However, due to the higher stability of the alkyl ions derived from secondary alcohols, the

H_2 and alkene elimination from $(M-OH)^+$ is less sensitive to thermal and DOF. activation here than in the primary alcohol spectra, which parallels chemical activation effects [12].

Non-vicinal alkylcycloalkanols. The monocyclic secondary alcohols **6a**, **6b** and **6c** with remote alkyl substituents and the related bicyclic decalin-2-ols **9a** and **9b** *(Table 3)* are candidates for specific studies on the OH-group stereochemistry

Table 3. *Temperature dependence of isobutane CI. mass spectra of non-vicinal alkylcyclohexanols and the* cis- *and* trans-*decal-2-ols*

Ion source nominal temperature (°)	60	100	150	200	250	60	100	150	200	250
Ion	Relative abundances (% Σ60)[a]					Relative abundances (% Σ60)[a]				
	cis-3-Methylcyclohexanol (*c*-**6a**)[b]					*trans*-3-Methylcyclohexanol (*t*-**6a**)[b]				
$MC_4H_9^+$	2	0.7	0.3	0.1	0.01	0.8	0.03	0.07	0.04	0.01
$(MC_4H_9-H_2O)^+$	0.8	0.7	1	1	0.7	1	0.6	0.8	0.7	0.4
MH^+	3	2	1	0.9	0.5	1	0.5	0.4	0.3	0.2
$(M-H)^+$	5	4	4	4	3	6	4	4	2	4
$(M-OH)^+$	80	86	82	81	82	81	83	81	80	82
	cis-4-Methylcyclohexanol (*c*-**6b**)[b]					*trans*-4-Methylcyclohexanol (*t*-**6b**)[b]				
$MC_4H_9^+$	2	1	0.8	0.3	0.1	3	3	2	0.7	0.3
$(MC_4H_9-H_2O)^+$	1	2	2	1	1	1	1	1	1	0.8
MH^+	2	1	0.7	0.5	0.4	6	4	3	2	1
$(M-H)^+$	5	6	6	5	4	5	7	7	6	5
$(M-OH)^+$	74	78	81	80	82	65	72	76	79	80
	cis-4-Methylcyclohexanol-*1*-*d*[b])[c] (*c*-**6b**-*1*-*d*)					*trans*-4-Methylcyclohexanol-*1*-*d*[b])[c] (*t*-**6b**-*1*-*d*)				
$MC_4H_9^+$	1	0.5	–	–	–	3	2	0.1	–	–
$(MC_4H_9-H_2O)^+$	2	1	0.1	–	–	2	1	0.2	0.1	–
MH^+	4	1	–	–	–	11	5	0.9	0.4	0.3
$(M-D)^+$	5	4	2	1	2	6	5	3	2	2
$(M-OH)^+$	68	75	83	86	76	63	73	81	82	76
	cis-4-*t*-Butylcyclohexanol (*c*-**6c**)[d]					*trans*-4-*t*-Butylcyclohexanol (*t*-**6c**)[d]				
$MC_4H_9^+$		–	0.3	0.1	–		2	2	0.6	0.2
$(MC_4H_9-H_2O)^+$		0.4	1	0.4	0.2		0.5	0.9	0.6	0.3
MH^+		0.2	0.04	0.04	0.04		–	0.1	0.08	0.08
$(M-H)^+$		3	4	4	3		5	6	5	5
$(M-OH)^+$		75	73	74	73		74	74	74	72
m/z 99		3	2	1	2		1	0.4	0.4	0.4
m/z 83		2	3	4	6		3	3	4	5
	cis-"Decal-2-ol" (**9a**)					*trans*-"Decal-2-ol" (**9b**)				
$MC_4H_9^+$	0.7	0.2	–	–	–	0.7	0.4	–	–	–
$(MC_4H_9-H_2O)^+$	3	3	0.6	0.4	0.2	1	2	0.4	0.2	–
MH^+	0.4	0.2	–	–	–	0.7	0.2	–	–	–
$(M-H)^+$	3	3	2	1	1	2	3	1	0.8	0.6
$(M-OH)^+$	70	71	70	65	62	80	76	75	70	68
$(M-H_2O)^+$	3	5	6	6	7	3	4	5	6	7
$(M-H-H_2O)^+$	4	4	5	6	6	1	2	2	3	4
m/z 95	1	1	2	2	3	0.4	1	1	2	2
m/z 81	1	1	3	5	6	0.3	1	3	4	5

[a]) See *Table 2.* [b]) For **6b** and **6b-1-d** see *footnote b* in *Table 5.* [c]) $(M-H_2O)^+$ =3%; *d*) *m/z* 81 = 2%.

without OH/alkyl *gauche* interactions. Thus, the dehydration *(reaction Vb)* of MH^+ from the epimeric 3- and 4-methylcyclohexanols **6a** and **6b**, and/or the corresponding hydroxide abstraction *(Reaction Va)* depend on the predominant OH-conformation [27]. The $(M-OH)^+/MH^+$ intensity ratio is 3 to 4 times higher for the configurational isomers with mainly *axial* OH-conformation (*trans*-**6a** and *cis*-**6b**) compared to the other mainly *equatorial* isomers. This effect reflects the release of steric strain at the site of the *axial* OH-group during fragmentation. The stereospecificity of these reactions, though not their intensity, is largely independent of the ion source temperature.

The *Arrhenius* equation was used to calculate approximated values for the difference of the relevant activation energies for the *cis*- and *trans*-isomers. The

Table 4. *Temperature dependence of isobutane CI. mass spectra of vicinal alkylcycloalkanols*

Ion source nominal temperature (°)	60	100	150	200	250	60	100	150	200	250
Ion	Relatives abundances (% Σ 60)a)					Relative abundances (% Σ 60)a)				
	cis-2-Methylcyclopentanol (*c*-**5b**)b)					*trans*-2-Methylcyclopentanol (*t*-**5b**)				
$(MC_4H_9-H_2O)^+$	3	2	0.1	–	–	5c)	4c)	0.4	0.1	–
MH^+	0.2	0.1	–	–	–	0.4	0.2	0.02	–	0.05
$(M-H)^+$	15	12	5	4	5	5	5	3	2	2
$(M-OH)^+$	66	73	85	88	81	61	73	82	86	80
$(M-H_2O)^+$	2	2	2	1	3	4	3	3	2	4
$(M-H-H_2O)^+$	3	2	1	1	2	5	4	2	2	2
	cis-2-Methylcyclohexanol (*c*-**6e**)					*trans*-2-Methylcyclohexanol (*t*-**6e**)				
$(MC_4H_9-H_2O)^+$	–	0.1	0.4	0.3	0.2	0.5c)	1c)	2c)	2	1
MH^+	–	–	0.1	0.1	0.06	2	1	1	0.8	0.4
$(M-H)^+$	2	2	3	2	3	2	2	2	2	2
$(M-OH)^+$	86	88	83	84	83	87	87	82	83	83
$(M-H_2O)^+$	3	2	4	3	4	2	2	4	4	4
	cis-2-Ethylcyclohexanol (*c*-**6f**)					*cis*-2-Butylcyclohexanol (*c*-**6g**)e)				
M^+	0.4d)	0.4d)	0.2	0.2	0.2	0.4	0.2	0.03	–	–
$(M-H)^+$	1	2	2	2	2	0.5	0.8	0.5	0.3	0.3
$(M-OH)^+$	81	82	81	78	78	82	64	50	39	36
$(M-H_2O)^+$	2	3	4	4	5	1	1	1	1	1
$(M-H-H_2O)^+$	1	2	2	3	3	0.2	1	2	2	3
	cis-2-*t*-Butylcyclohexanol (*c*-**6h**)e)					*trans*-2-*t*-Butylcyclohexanol (*t*-**6h**)				
M^+	0.6	0.4	0.06	–	–	0.2	0.1	–	–	–
$(M-H)^+$	0.9	1	0.4	0.2	0.2	0.4	0.5	0.1	–	–
$(M-OH)^+$	80	74	51	49	29	79	68	47	48	28
m/z 83	2	5	18	19	23	4	10	27	27	31
	Menthol (**6i**)f)					"Neomenthol" (*neo*-**6i**)				
$(M-H)^+$	0.2	0.3	0.6	0.8	0.7	2	0.9	1	0.8	0.6
$(M-OH)^+$	84	82	76	70	62	77	76	69	50	22
$(M-H_2O)^+$	2	2	2	3	3	3	4	5	6	4
$(M-H-H_2O)^+$	4	4	6	6	5	1	1	2	3	3
m/z 83	1	1	3	6	12	1	3	5	13	31
m/z 81	1	1	2	2	4	1	1	2	5	8

a) See footnote *Table 2*. b) $M^+ = 1–2\%$. c) $MC_4H_9^+ = 0.1\%$. d) $(MC_4H_9-H_2O)^+ = 0.1\%$ and $MH^+ = 0.05\%$. e) *m/z* 80, 81 and 82 = 1–6%, *m/z* 99 = 1–4%. f) $(MC_4H_9-H_2O)^+ = 0.5–0.1\%$ for 60–250°.

obtained $\Delta(\Delta H^+)$ values ranging from 3 to 5 kJ/mol are in the order of the steric strain of an *axial* OH-group (2.9 kJ/mol) [39] and thus support the concept of conformational effects in cycloalkanol CI. fragmentation. This conformational approach based on bond cleavage energetics is the antitype to the conformational control of eliminations [40] [41] and internal proton transfer [42] with strict geometric requirements observed in the mass spectra of related cyclohexane systems.

In the C_{10}-alcohols **6c**, **9a** and **9b**, the conformational control is cancelled, as the MH^+ ion practically disappears because of the substrate-size assisted increase of the fragmentation reactions [26]. However, for small size ($\leqslant C_{10}$) cycloalkanols

Table 5. *Temperature dependence of isobutane CI. mass spectra of bicyclo[2.2.1]heptanols and tertiary alcohols*

Ion source nominal temperature (°)	60	100	150	200	250	60	100	150	200	250
Ion	Relative abundances (% $\Sigma 60$)[a]					Relative abundances (% $\Sigma 60$)[a]				
	endo-Norbornanol (*endo*-**11**)					*exo*-Norbornanol (*exo*-**11**)				
$(MC_4H_9-H_2O)^+$	2[c]	2[c]	0.3	0.08	0.02	1	1	0.4	0.2	0.08
MH^+	2	0.6	0.1	0.06	0.07	2	0.03	-	-	-
$(M-H)^+$	11	10	6	5	4	0.7	1	0.8	1	1
$(M-OH)^+$	72	74	76	77	71	87	86	87	84	82
$(M-H_2O)^+$	3	4	6	7	10	1	3	3	4	5
	Bornanol (*endo*-**11a**)[b]					Isobornanol (*exo*-**11a**)				
MH^+	-	-	0.04	0.03	0.02	-	-	0.03	0.03	0.01
M^+	1	1	0.7	0.5	0.3	0.2	0.6	0.6	0.3	0.2
$(M-H)^+$	0.3	0.4	0.9	1	1	-	0.2	0.7	1	1
$(M-OH)^+$	86	85	82	77	72	90	88	82	79	74
$(M-H_2O)^+$	0.4	1	2	3	3	0.3	1	3	4	4
m/z 81	2	2	3	6	10	1	1	2	3	7
	Bornanol (*endo*-**11a**)[b]					Fenchyl alcohol (**11b**)[c]				
MH^+	-	-	-	-	-	0.5	0.3	0.2	0.05	-
M^+	3	2	1	0.8	0.5	3	2	2	0.7	0.4
$(M-H)^+$	1	1	1	1	1	1	1	0.8	0.9	0.9
$(M-OH)^+$	81	70	61	56	52	63	70	69	53	42
$(M-H_2O)^+$	0.7	2	2	2	2	-	0.1	-	0.6	0.6
m/z 81	2	8	16	18	18	5	6	7	16	24
	2-Methylbutan-2-ol (**12**)					3-Methylpentan-3-ol (**12a**)[d]				
$(MC_4H_9-H_2O)^+$	6	3	2	0.8	0.3	1	0.5	0.2	-	-
MH^+	4	1	1	0.8	0.6	0.7	0.4	0.2	0.03	-
$(M-H)^+$	0.1	0.06	0.08	0.3	0.2	0.1	0.04	0.2	0.2	0.08
$(M-OH)^+$	77	85	88	86	86	81	83	84	83	81
$(M-H_2O)^+$	5	4	4	3	2	4	4	3	4	4
	1-Methylcyclopentanol (**13**)					1-Methylcyclohexanol (**14**)				
$(MC_4H_9-H_2O)^+$	1	2	-	-	-	1	0.3	0.3	0.1	0.1
MH^+	3	0.5	-	-	-	0.2	0.07	0.2	0.1	0.1
M^+	0.5	0.9	0.04	0.3	0.2	0.8	0.3	0.5	0.5	0.5
$(M-H)^+$	0.2	0.2	-	-	-	0.2	0.03	0.3	0.1	0.4
$(M-OH)^+$	85	86	90	88	85	88	90	87	88	88

[a] See *Table 2.* [b] Examples of reproducibility over a long period; for **11a** the spectra were taken at an interval of 6 months. See also *Table 3* for compounds *c*-**6b** and *c*-**6b-1-d**, the spectra of which were registered with an interval of about 6 months. [c] *m/z* 80 = 7–12%; [d] *m/z* 73 = 3–8%.

the steric compression energy method apparently enables configurational assignments in isobutane CI. spectra [27].

Strained alkylcycloalkanols. The vicinal alkylcycloalkanols **5b** and **6e** to **6i**, the tetramethylcycloalkanol **6d**, the 1-decalol **9c**, the adamant-2-ol (**10**) and the bicyclo[2.2.1] heptanols **11**, **11a** and **11b** (*Tables 4* and *5*, *Fig. 2*) are secondary alcohols with various C,C-bonds which are activated by steric and polar substituent effects. Thus, this section especially emphasizes constitutional effects. Beforehand, the conformational effect on the $(M-\mathrm{OH})^+/M\mathrm{H}^+$ ratio is in this series restricted (**6e**, **6f**) or lost (**5b**, **6g**, **6h**, **6i**, **11**, **11a**) due to steric strain and the absence of the $M\mathrm{H}^+$ ions. However, in the spectra of the cyclopentane systems **5b** and **11**, the more accessible *quasi* equatorial and *exo* H(*a*)-atoms give rise to increased hydride abstraction *(reaction IV)*, similar to the entropically favored H(*a*)-abstraction in the primary alcohols discussed before. At 60°, the ratios 15/5 and 11/1 (% Σ 60) for the $(M-\mathrm{H})^+$ ions are found for the **5b** *cis/trans* and the **11** *endo/exo* pairs, respectively. The steric shielding control in **5b** and **11**, which is cancelled in **11a** and **11b** by additional methyl shielding of the *exo* H(*a*)-atoms, is in agreement with previous observations on **11** [43] and epimeric protoadamantols [44]. Thus, steric shielding next to steric compression, is a second useful stereochemical concept in CI. spectra of cycloalkanols, which now are no longer outmatched by stereospecific H-bridge analysis in cycloalkanediols CI. spectra [24] [25] [44–46]. As to constitutional effects in the isobutane CI. spectra of primary and secondary alcohols, the fragmentation of the $(M-\mathrm{OH})^+$ alkyl ions at higher temperatures is suppressed by unstrained cyclization and branching of the C-chain, through favorable isomerizations to more stable tertiary alkyl ions either in a direct manner or already at a precursor ion stage. The primary C_7-alkyl ions decompose at 250° only in the spectrum of the unbranched alcohol **2**, but not in that of the cyclic compound **2a**. The more stable secondary alkyl ions are reactive only in the C_{10}-size series of this investigation, except for **7**, and give four groups of decreasing reactivity with respect to the general structure-reactivity criteria *(Table 6)*. As to the gaseous 2-norbornyl and 2-adamantyl cations (*cf.* **11** and **10**) [32], higher energies would be needed to attempt specific CI. data.

Table 6. *Reactivity of the* $(\mathrm{M}-OH)^+$ *alkyl ions from secondary* C_{10}*-alcohols*

Alcohol	Structural criteria	$(M-\mathrm{OH})^+$ % Σ60 at 250°	Upper temp. (°) for $(M-\mathrm{OH})^+ \geqslant 60\%$
8	Linear	10	150
6d, **6g**, **6h**	Cyclic (crowded, vicinal)	≈ 30	100–150
6i, **7**, **9c**, **11a**, **11b**	Bicyclic, minor strain	≈ 50	150–200
6c, **9a**, **9b**, **10**	Polycyclic, unstrained	$\geqslant 60$	250

The above high-energy $(M-\mathrm{OH})^+$ fragmentation characteristics are complemented by low-energy data on specific stabilities of the $M\mathrm{H}^+$ ions from small size secondary alcohols at lower temperatures *(Table 7)*. Facilitated isomerizations *(reactions VIIa* and *VIIb)* in the branched alcohols apparently almost erase the $M\mathrm{H}^+$ peaks compared to the spectra of the simple cycloalkanols **5** and especially

Table 7. *Reactivity of* MH^+ *ions from secondary* C_5- *to* C_7-*alcohols*

Alcohol	Structural criteria	MH^+ %Σ60 at 60°	100°	Lower temp. (°) for $(M-OH)^+ \geqslant 80\%$
5a, **5b**, **6a**, **6b**, **11**	Branched, cyclic	0-5	0-2	60-100
16, **17**	Olefinic, unbranched	20	10	150
4, **4a**, **5**	Unbranched	30-40	20	150
6	Cyclic, unstrained	40	40	250

6 which need additional energy for ring contraction [47] [48] to the corresponding tertiary alkyl ions as is observed in solution phase [49] [50]. However, any initial rearrangements *(reactions VIIa* or *VIIb)* under high-energy conditions cannot be specified *versus* $(M-OH)^+$ isomerizations here, and are not indicated in the exothermicity studies by *Herman & Harrison* [12] in line with radiolytic results on the cyclohexyl cation existence [47].

Tertiary alcohols. The ease of formation and the stability of tertiary alkyl ions $(M-OH)^+$ lead to a near constant single peak spectrum for the corresponding alcohols **12**, **12a**, **13**, **14**, **15** (*Table 5* and *Fig. 2*) over the whole range of temperature, with additional small diagnostic $(MC_4H_9-H_2O)^+$ signals. Some further fragmentation of the $(M-OH)^+$ ions is found for **15** at high temperatures, confirming again the 1-adamantyl cation as a tertiary carbocation [32]. The high $(M-OH)^+$ stability for the tertiary alcohols **12**, **13** and **14** is in line with known protonation exothermicity effects [12].

Unsaturated alcohols. A comparison of the allylic alcohols **16a** and **17a** and the benzylic compound **18** with the corresponding simple olefinic alcohols **16** and **17** and the saturated alcohols **4**, **6** and **2a** shows two findings. Firstly, the allyl-type alcohols establish a fourth distinct group of isobutane CI. spectra in addition to the spectra of the primary, secondary and tertiary alcohols we have studied. At the higher temperatures, the equally stable allyl-type and *t*-alkyl ions *(Table 5)* lead to similar $(M-OH)^+$ dominated spectra of the respective alcohols. However, at lower temperatures, the $(MC_4H_9-H_2O)^+$ substitution ion, which has been thoroughly investigated for benzyl alcohol by *Liehr et al.* [11], becomes a key ion in the allyl and benzyl alcohol spectra. This means that allylic and benzylic π-electron systems are directly involved in the dehydration process of $MC_4H_9^+$. The second important finding is that the alcohols with isolated olefinic bonds show only negligible isomerization in the isobutane CI. spectra, at least at low temperatures, and thus resemble their saturated analogs. However, specific implications apparently cause increased fragmentation in cyclohexen-4-ol (**17**) and furthermore, as reported by *Jalonen et al.* [16], stereochemical effects in the spectra of the 5- and 7-norbornenol epimers.

Conclusion. – The total of our results can be grossly arranged in a scheme of three reactivity regions:

- At the lower temperatures of 60 and 100°, the fragmentation is characteristic of the OH-group environment (C(α)-substitution and steric environment). For analytical studies of alcohols, the low-reactivity spectra are the most adequate ones. High sample concentrations are also favorable, but increasing the substrate size has an opposite effect.

- At 150° the spectra show almost exclusively the formal $(M-OH)^+$ ion.
- At the higher temperatures of 200 and 250°, the spectra carry information about the C-skeleton structure, mainly through the decomposition of the $(M-OH)^+$ ions.

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Experimental Part

The samples were commercial products except for **17** and **17a** which were synthesized in our laboratory according to [51]. The mass spectra were recorded with a *Finnigan 4023 GC/MS* equipment. The ion source was operated at 100 eV, with a nominal isobutane pressure of 0.35 Torr. The spectrum of each compound was recorded at the five nominal temperatures of 60, 100, 150, 200 and 250°. The measurements were performed in four series containing the compounds **6**, **6b** and **6c** in series No 1, **6a**, **6e**, **6i**, **11a** and **14** in series No 2, **1a**, **1c**, **2a**, **4a**, **5**, **5a**, **5b**, **6b-1-d**, **6f**, **6g**, **6h**, **9a**, **9b**, **9c**, **11**, *endo*-**11a**, **13**, **16** and **16a** in series No 3 and all the other ones in the last series. The compound mixtures in pentane solution were introduced into the ion source *via* the GC. system, using a 25 m × 0.32 mm i.d., *SP-1000* glass capillary column *(Jaeggi, Switzerland)*. Various GC. temperature programs were used in order to get the best possible separation in the shortest time.

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