equal. On the other hand, the relative importance of the three fragment groups $C_kH^+_{2k+1}$, $C_kH^+_{2k}$ and $C_kH^+_{2k-1}$ varies with pressure. The reason for this is not clear, but the result illustrates that CI spectra from different sources cannot necessarily be directly compared.

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10. The Chemical Ionization of Organic Compounds

2nd Communication[1]

Linear Alkyl Halides

by **Raymond Houriet** and **Tino Gäumann**
Department of Physical Chemistry of the EPF, CH–1007 Lausanne, Switzerland

(21. VII. 75)

Summary. The chemical ionization spectra of linear alkyl halides with up to nine carbon atoms have been studied using water as protonating agent. An alkyl ion with the same number of carbon atoms as the halide is produced. With more than six carbon atoms in the chain, fragmentation becomes important. The results show that excited hydronium ions participate as intermediates and the fragments of the resulting alkyl ions have branched structures.

1. Introduction. – In previous publications, we studied the mass spectral fragmentation by electron impact (EI) of *n*-alkyl ions [2] [3] and showed that this pro-

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[1] 1st Communication see [1].

cess is complex. As an extension of this work, we have used chemical ionization (CI) in order to create alkyl ions with more or less well-defined internal energy; the protonation of olefins [1] was the first publication in this series. In the work here described we have measured the CI spectra of *n*-alkyl halides C_nH_{2n+1} X containing one to nine carbon atoms. We have concentrated on the use of water as ionizing gas since the resulting spectra are particularly simple. In a subsequent publication we shall deal with the CI of ^{13}C-labelled compounds.

In contrast to EI, where the fragmentation varies with the nature of the halide X, CI shows only minor differences. The use of D_2O as ionizing gas enables us to study the incorporation in the alkyl ion of the deuteron transferred, but the results show that CI(D_2O) can only be used for fragmentation of alkyl ions with more than six carbon atoms.

2. Experimental. – For experimental details see [1]. We use a single focusing mass spectrometer, a source pressure of 0.1 to 0.3 Torr, an ion repeller field normally of 8.7 V · cm^{-1} and an electron energy of 400 eV. The instrument allows measurement of temperature dependence in the range from 60° to 120°. The results are given for a pressure of 0.25 Torr and a temperature of 120°. The products used were of commercial grade, purified by gas chromatography whenever necessary.

3. Results and discussion. – 3.1. *Energetic considerations.* The reaction of an alkyl halide RX with an ionizing gas YH^+ can be described as follows:

$$RX + YH^+ \rightarrow R'^+ + Y + HX \qquad (1)$$

The reaction enthalpy ΔH_r depends on the nature of the ionizing gas and the structure of the resulting ion R'^+ (see Table 1). The values given are calculated for linear 1-alkyl halides with more than five carbon atoms. For compounds containing the halide atom in a secondary position, the values should be decreased by about 8 kJ/mol. The values of the enthalpy of formation are either taken from [4] or are estimated by the group-increment method described by *Franklin* [5a cf. 5b]. The ΔH_r values show that the only product which can be formed by an exothermic reaction with H_3O^+ in the ground state is a tertiary alkyl ion. However it should not be forgotten that the H_3O^+ ion is initially formed in a reaction that is exothermic by 79 kJ/mol[1].

Table 1. *Reaction enthalpies used* ($n > 5$)

Y	R'^+ prim.	sec.	tert.
H_2O	+ 138	+ 33	– 29 kJ/mol
CH_4	– 54	– 159	– 222 kJ/mol
C_2H_4	+ 115	+ 10	– 52 kJ/mol

3.2. *CI(D_2O) spectra of* n-*alkyl iodides.* The spectra of the 1-alkyl iodides with one to nine carbon atoms are given in Table 2 and those of 1-heptyl iodide for different ionizing conditions in the Figure. The iodides with up to six carbon atoms show features similar to the spectra of the corresponding alcohols studied by *Field* with isobutane as ionizing gas [6]. They are characterized by the absence of alkyl fragments of lower mass than the 'parent' fragment $P^+ = C_nH_{2n+1}{}^+$. A dimeric protonated ion can be observed for the two lowest members of the homologous series. With D_2O a deuter-

Table 2. *The CI(D_2O) spectra of linear alkyl iodides $C_nH_{2n+1}I$ at a source pressure of 0.25 Torr. Fragment ion-intensities are given as % of total measured ion-intensity for each compound*

Fragment	CH_3I	C_2H_5I	C_3H_7I	C_4H_9I	$C_5H_{11}I$	$C_6H_{13}I$	$C_7H_{15}I$	$C_8H_{17}I$	$C_9H_{19}I$
$(RI)_2D^+$	5	4							
RID^+	16	77	17	4					
RI^+	59	14	3						
I^+	20	5	3						
$C_nH_{2n}D^+$			20	15	1.5	1.4			
$C_nH_{2n+1}^+$			57	81	98	98	82	70	46
$C_6H_{13}^+$									12
$C_5H_{11}^+$								16	24
$C_4H_9^+$							17	14	18
$C_4H_7^+$							1		

onated molecular ion is observed for ions up to $C_4H_9ID^+$. Nevertheless the distributions of the C_nH_{2n+1} and $C_nH_{2n}D^+$ ions for the higher members of the series show that here also the deuteronated molecular ion – although not observable – must be present as an intermediate.

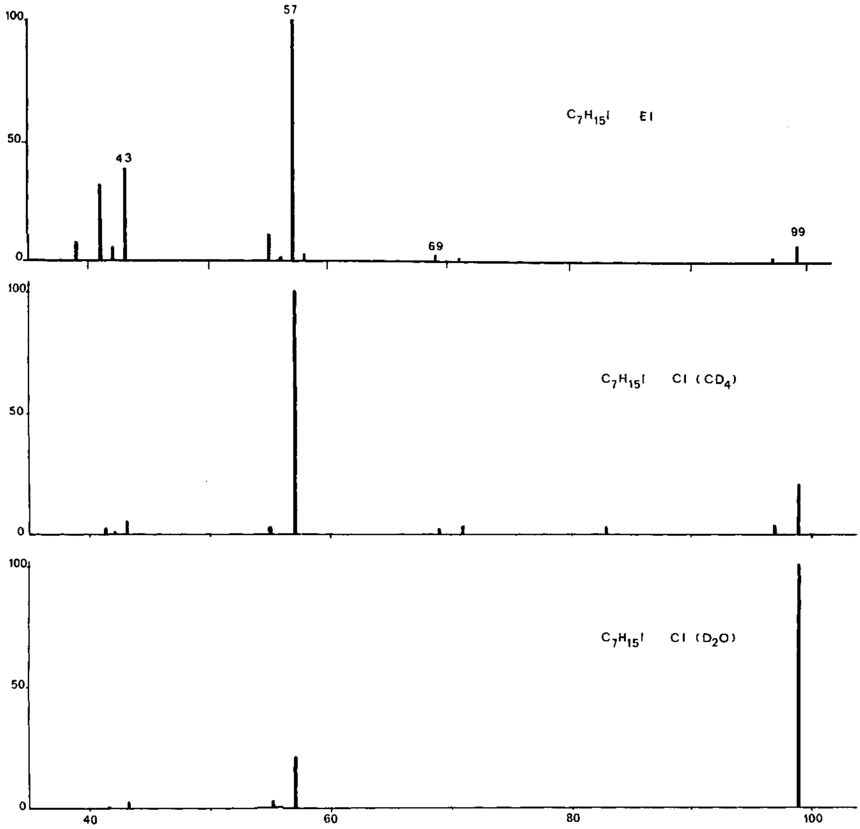

Fig. *Mass spectra of 1-heptyl iodide using different ionizing conditions*

The CI spectra of the homologous series from propyl iodide upwards show an important contribution from the parent alkyl ion. The hexyl ion shows little tendency to fragment in spite of the fact that the reaction energy is comparable to the higher homologs, where fragmentation can be observed. This behaviour is similar to the CI spectra of olefins [1]. The formation of a *t*-butyl ion from 1-heptyl iodide is endothermic by 54 kJ/mol. This value is outside the limits of error of our estimate of the enthalpy of formation, which is about 15 to 20 kJ/mol. We therefore must assume the participation of excited D_3O^{+*} ions.

3.3. *Pressure dependence.* In a previous publication we showed that the ratio $C_7H_{15}^+ / C_4H_9^+$ varies linearly as a function of H_2O pressure [1]. If we assume competition between deactivation of the excited D_3O^{+*} or $C_7H_{15}^{+*}$ ions and fragmentation of the heptyl ion, we can derive a simplified expression of the form:

$$C_7H_{15}^+ / C_4H_8^+ = (k_{\text{coll.}}/k_f)\ H_2O \tag{2}$$

where $k_{\text{coll.}}$ corresponds to a collision frequency and k_f to the fragmentation of the excited heptyl ion to butyl ion. Since we do not know the number of collisions required to deactivate the excited ion, we shall obtain only an approximate figure for k_f when using the collision frequency for $k_{\text{coll.}}$. Equation (2) is valid for zero repeller field strength. We measured the pressure dependence of the spectrum of 1-heptyl iodide for repeller field strengths up to 18 $V \cdot cm^{-1}$. From the slope of $C_7H_{15}^+ / C_4H_9^+$, extrapolated to zero field strength and an average collision frequency, we obtain a value for k_f of $8 \cdot 10^5 s^{-1}$ with an experimental error of about ±20%. This value can be compared with a similar value obtained for 1-heptene of $5 \cdot 10^6 s^{-1}$ [1]. Since the protonation of 1-heptene is 80 kJ/mol more exothermic than that for 1-heptyl iodide, the smaller value for the latter seems reasonable, although the accuracy of this result might be questionable in view of the assumptions made above.

The pressure dependence of the fragmentation of 1-nonyl bromide was measured and gave the ratio

$$C_9H_{19}^+/\Sigma(\text{fragment ions}) = a + b\ ([D_2O] - 0.25) = 0.98 \pm 0.01 + (0.38 \pm 0.05)\ ([D_2O] - 0.25)$$

with $[D_2O]$ in Torr and the repeller field at the standard value of 8.7 $V \cdot cm^{-1}$. These values should be compared with similar values obtained for 1-nonene, a = 0.32 and b = 1.7 resp. [1]. Here too for the halides as compared with the corresponding alkenes, the smaller degree of fragmentation by CI is evident.

3.4. *Temperature dependence.* As shown by *Field* [7] and in our previous publication [1], the plot of $C_7H_{15}^+ / (C_7H_{15}^+ + C_4H_9^+)$ as a function of temperature gives an activation energy, assuming equilibrium conditions. We find a value of $E_a = 21 \pm 2$ kJ/mol which should correspond to the excess energy needed for fragmentation.

3.5. *1-Butyl halides.* In contrast to EI, CI shows little difference in spectra for the different halides (Table 3). Together with the retention of the deuteron transferred (Table 2) this allows the assumption that from a $C_4H_9XD^+$ ion first formed a hydrogen or deuterium halide is subsequently split off. The distribution of the values for $m/e = 57$ and 58 shows that the probability of retention of the deuteron is about 25%, compared to the statistical expectation of 10% for a random elimination. There-

Table 3. *Comparison of the EI and CI (0.25 Torr D_2O) spectra of the different 1-butyl halides. Relative intensities are given*

Fragment	C_4H_9Cl		C_4H_9Br		C_4H_9I	
	EI	CI	EI	CI	EI	CI
$C_4H_9XD^+$				1		4
$C_4H_9X^+$	1		10		35	
$C_4H_8D^+$		22		21		19
$C_4H_9^+ + (C_4H_7D^+)$	7	76	76	78	64	77
$C_4H_8^+$	92	2	14		1	

fore we measured the CI(H_2O)-spectra of the isomeric deuteriated *n*-butyl halides given in Table 4. The results are not sufficient to enable us to draw any conclusions about the structure of the resulting butyl ion, but they do show clearly that on elimination the halide atom preferentially abstracts a hydrogen atom which is not situated on the same carbon atom. In the collision complex $C_4H_9XD^+$ the added deuteron apparently has a well defined position and exchanges only slowly with any one hydrogen atom. By comparison, we found previously that the hydrogen atoms in butyl ions produced by electron impact scramble rather rapidly ($k \sim 2 \cdot 10^9 s^{-1}$) [8].

Table 4. *CI(0.23 Torr H_2O) of deuterium labelled butyl iodides. The relative intensities given are corrected for naturally occurring ^{13}C and incomplete deuteriation*

m/e	$CH_3 \cdot CH_2 \cdot CH_2 \cdot CD_2I$	$CH_3 \cdot CH_2 \cdot CD(I) \cdot CH_3$
58		57
59	20	943
60	980	

We also measured the pressure dependence for the CI(D_2O) spectrum of *n*-C_4H_9I and found a linear relation for the ratio

$$C_4H_8D^+ / C_4H_9^+ = 0.24 \pm 0.2 + (2.0 \pm 0.3)\,([D_2O] - 0.25),$$

where $[D_2O]$ is expressed in Torr. This seems to indicate that the formation of butyl ion might proceed by two reaction paths, *i.e.* a direct abstraction of the iodine atom:

$$C_4H_9I + D_3O^+ \longrightarrow C_4H_8^+ + DI + D_2O \tag{3}$$

or the formation of an intermediate complex:

$$C_4H_9I + D_3O^+ \longrightarrow C_4H_9ID^+ + D_2O \tag{4}$$

$$C_4H_9ID^+ \begin{array}{l} \nearrow C_4H_9^+ + DI \quad (5a) \\ \searrow C_4H_8D^+ + HI \quad (5b) \end{array}$$

Such a formation of the molecular-ion complex would be favoured by high pressure.

3.6. *Halide-position effects.* Table 5 shows the dependence of the spectrum on the position of the bromine atoms in the linear heptyl chain. They indicate little or no difference between secondary bromides. The increased fragmentation of the 1-heptyl bromide can be explained by its higher enthalpy of formation (12 kJ/mol) as com-

Table 5. *Relative intensities of the peaks due to $C_7H_{15}^+$, $C_4H_9^+$ and $C_4H_7^+$ ions in the $CI(H_2O)$ spectra of isomeric* n-*heptyl bromides*

m/e	1—$C_7H_{15}Br$	2—$C_7H_{15}Br$	3—$C_7H_{15}Br$	4—$C_7H_{15}Br$
$C_7H_{15}^+$	77	86	84	88
$C_4H_9^+$	22	13	15	12
$C_4H_7^+$	1.4	1.2	0.7	0.5

pared to the secondary isomers. It seems that the heptyl ions formed have identical structures. It might be recalled that the intensity of the heptyl ion in the EI spectrum of 1-heptyl bromide amounts to only 5% of the intensity of this ion in the EI spectra of the secondary bromides. Furthermore the $C_4H_8Br^+$ ion is practically absent in CI($<$ 0.3%), whereas it is rather intense in the EI spectrum.

3.7. *Conclusions.* The CI(H_2O) spectra of the alkyl halides $C_nH_{2n+1}X$ are characterized by the preponderance of the parent alkyl ions $C_nH_{2n+1}^+$ for the lower members of the series, and by the high proportion of parent alkyl ions together with certain alkyl fragments for the higher members of the series; the position and the nature of the halide functional group exert very little effect.

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11. Asymmetric Alkenes Hydroesterification by Palladium Complexes Containing (—)-DIOP. Double Bond Migration and Formation of Isomeric Esters

by **Giambattista Consiglio**

Technisch-Chemisches Laboratorium der ETH, Universitätstr. 6,
8006–Zurich, Switzerland

(18. XI. 75)

Summary. The formation of isomeric esters in the title reaction takes place through different mechanisms; one of them does not imply formation of isomerized substrate.

The asymmetric synthesis of esters through palladium catalyzed hydrocarboxylation of alkenes using (—)-2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-