Ionization and Dissociation by Electron Impact: Normal Propyl Chloride and Tertiary Butyl Chloride

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In an effort to gain further insight into the unimolecular dissociation reactions of hydrocarbons and related molecules which follow ionization by electron impact, we undertook a mass-spectroscopic investigation of some alkyl halides. Due to circumstances beyond our control, the research was terminated with the work on n-propyl and t-butyl chlorides only partially completed. Since the data which have been acquired seem of interest, we report them herewith.

The apparatus and technique have been briefly described in an earlier paper.[3] The n-propyl and t-butyl chlorides were Eastman Kodak Co. white label compounds, used without further purification. The electrons were obtained from the same oxide-coated platinum filament used in the preceding work.[3] This pair of halides very markedly decreased the activity of the filament. When the vapors were removed from the tube the filament regained its original activity. A similar, but less pronounced, effect had been noted with the unsaturated hydrocarbons, propylene and isobutylene. The latter, however, left the voltage scale calibration (correction for contact potentials) unchanged. The propyl chloride decreased the correction, as determined from the ionization efficiency curve of argon, by a little over one volt. This effect provides full justification for the extra effort involved in admitting the calibration gas, argon, simultaneously with the substance under investigation.

The relative intensities of the principal ions in the mass spectrum of t-butyl chloride are given in Table I for some round values of the bombarding electron energy. Due to the almost immeasurably small current of the parent ion, $C_4H_9Cl^+$, the principal ion in the spectrum, $C_4H_9^+$, has been used as the reference standard. The complete lack of stability of the t-butyl chloride ion was both surprising and irritating. It precluded the measurement of the appearance potential of this ion and thus the vertical ionization potential of the molecule.
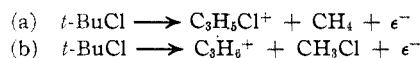
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(3) D. P. Stevenson and J. A. Hipple, THIS JOURNAL, 64, 1588 (1942).

It will be noted that even though the breaking of a carbon–carbon bond (loss of a methyl radical) is favored by the greater number of such bonds,[3] the molecular ion has a greater tendency to lose a chlorine atom. Similarly, the isobutane molecular ion loses a methyl radical more readily than a hydrogen atom,[3] despite the greater number of C–H than C–C bonds. These reaction probabilities of the molecular ions are apparently directly related to the strength of the bond that breaks since in the order of their decreasing strength the bonds are C–H, C–C, and C–Cl.

One of the more characteristic reactions of propane and the butanes is the one giving rise to a lower olefinic ion and methane, ethane or hydrogen. By analogy one would expect the reactions

$$\text{(a)} \quad t\text{-BuCl} \longrightarrow C_3H_5Cl^+ + CH_4 + \epsilon^-$$
$$\text{(b)} \quad t\text{-BuCl} \longrightarrow C_3H_6^+ + CH_3Cl + \epsilon^-$$

to contribute to the spectrum of t-butyl chloride to a much greater extent than is observed. As in the isobutane spectrum, the relative abundance of the allene (or methylacetylene) ion, $C_3H_4^+$ is much smaller than those of the ions $C_3H_5^+$ and $C_3H_3^+$, and the ethylene (or ethylidene) ion is less abundant than $C_2H_5^+$ and $C_2H_3^+$.

The mass spectrum of normal propyl chloride, given in Table II, presents a marked contrast to that of tertiary butyl chloride. In the first place, the parent ion, $C_3H_7Cl^+$, is present in quite large abundance. Because of the apparent similarity of the dissociation reactions involved, one would expect $C_3H_7^+$ to be much more abundant than $C_3H_6^+$, since the current of $C_4H_9^+$ from t-butyl chloride is about twelve times as great as that of $C_4H_8^+$. That our expectation is not fulfilled is the more surprising when it is noted that the relative abundances of $C_2H_5^+$, $C_2H_4^+$ and $C_2H_3^+$ have the same pattern in both chlorides.

Although their relative abundances are not very large, it is to be noted that both $C_2H_5Cl^+$ and CH_3Cl^+ are present in the spectrum of the propyl chloride. Although methane and ethane are formed in the dissociation of the butane ions, careful search failed to reveal any trace of the ions CH_4^+ or $C_2H_6^+$ in the spectra.[3] It is conceivable

TABLE I
MASS SPECTRUM OF t-BUTYL CHLORIDE (INCOMPLETE[a])

V⁻ (volts)	$C_4H_9Cl^+$	$C_3H_6Cl^+$	$C_3H_5Cl^+$	$C_3H_4Cl^+$	$C_2H_3Cl^+$	HCl^+	Cl^+
30	<0.1	39	...	...	...	<0.1	<0.1
50	<0.1	43	3.4	0.5	<1	<0.1	<0.1
100	<0.1	47	3.5	...	...	<0.1	<0.1

V⁻ (volts)	$C_4H_9^+$	$C_4H_8^+$	$C_3H_7^+$	$C_3H_6^+$	$C_3H_5^+$	$C_3H_4^+$	$C_3H_3^+$	$C_2H_5^+$	$C_2H_4^+$	$C_2H_3^+$
30	99	...	...	...	55	...	7.3	..	...	..
50	100	7.9	4.5	0.7	73	2.7	23	32	6.6	20
100	107	...	...	...	78	...	23	..	...	..

[a] Absence of an ion from table does not necessarily imply absence from spectrum. The relative abundances have been corrected for C^{13} in its natural abundance, 1.1%.

TABLE II
MASS SPECTRUM OF n-PROPYL CHLORIDE[a]

V⁻ (volts)	$C_3H_7Cl^+$	$C_2H_4Cl^+$	CH_2Cl^+	$C_3H_7^+$	$C_3H_6^+$	$C_3H_5^+$	$C_3H_4^+$	$C_3H_3^+$
30.0	100	51.3	14.8	108	368	102	..	26.7
40.0	107	57.0	25.6	114	382	116	..	60.1
60.0	111	59.0	28.3	118	392	124	14.5	63.2
100.0	113	60.0	27.2	121	412	129	..	60.5

V⁻ (volts)	$C_2H_5^+$	$C_2H_4^+$	$C_2H_3^+$	$C_2H_2^+$	C_2H^+	CH_3^+
30.0	184	60.5	163	..	..	7.6
40.0	204	87.5	216	..	..	24.7
60.0	219	96.5	250	32.0	3.5	31.1
100.0	224	100	255	..	..	29.5

V⁻ (volts)	$C_3H_6Cl^+$	$C_3H_5Cl^+$	$C_3H_4Cl^+$	$C_2H_5Cl^+$	$C_2H_3Cl^+$	$C_2H_2Cl^+$	C_2HCl^+	Cl^+
60.0	3.9	2.2	2.4	0.9	8.8	4.3	1.9	2.5

V⁻ (volts)	CH_3Cl^+	$CHCl^+$	CCl^+	$C_3H_2^-$	C_3H^+	C_3^+	HCl^+
60.0	3.0	2.8	3.1	4	2	2	2

[a] The relative abundances have been corrected for isotopic effects.

that the $C_2H_5Cl^+$ and CH_3Cl^+ are present in the spectrum of C_3H_7Cl because of ethyl and methyl chloride impurities. For this to be the case one would expect the relative abundances to be in the reverse order, i. e., $C_2H_5Cl^+ > CH_3Cl^+$, rather than the observed $C_2H_5Cl^+ < CH_3Cl^+$.

The appearance potentials, which were determined from the "initial breaks"[3] of the ionization efficiency curves are listed in Table III. When two values are noted, the second refers to the position of a marked inflection in the ionization efficiency curve. The ionization potential of argon was taken equal to 15.76 e. v.[4] for calibration purposes.

TABLE III
APPEARANCE POTENTIALS IN THE t-BuCl AND n-PrCl SPECTRA

Process	$A(X^+)$
t-$C_4H_9Cl \longrightarrow C_3H_6Cl^+ + CH_3 + e^-$	$10.7_7 \pm 0.1$ e.v.
$\longrightarrow C_4H_9^+ + e^- + Cl$	$10.2_7 \pm 0.2;\ 18.5 \pm 1$
$\longrightarrow C_3H_5^+ + \ldots + e^-$	$12.4_1 \pm 0.2;\ 16.0 \pm 1$
$\longrightarrow C_3H_3^+ + \ldots + e^-$	16.1 ± 1
n-$C_3H_7Cl \longrightarrow C_3H_7Cl^+ + e^-$	10.7 ± 0.2 e. v.
$\longrightarrow C_2H_4Cl^+ + CH_3 + e^-$	12.0 ± 0.3 e. v.
$\longrightarrow C_3H_7^+ + Cl + e^-$	11.1 ± 0.3 e. v.

The value $A(C_3H_7Cl^+) = 10.7$ e. v. in the n-C_3H_7Cl spectrum is to be associated with the vertical ionization potential of this molecule. The vertical ionization potential of t-butyl chloride must be less than the appearance potential of the ion $C_4H_9^+$ in its spectrum, that is, I_{vert} (t-BuCl) < 10.2 e. v. These values stand in contradiction to the suggestion made by Price[5] that there should be no further reduction in the ionization potentials of the alkyl chlorides beyond that found in going from methyl chloride to ethyl chloride. In the light of the large decrease in the vertical ionization potential in the sequence ethane, propane, butane (11.6, 11.0, 10.2, respectively[3]), the results on the propyl and butyl chlorides are not entirely surprising.

By use of the rules formulated by Kistiakowsky and co-workers[6] in combination with the data summarized by Rossini[7] one can estimate the heat of the reaction n-C_4H_{10} + HCl = n-C_3H_7Cl + CH_4, to be $\Delta H^0_{298.1} = 0.15 \pm 0.05$ e. v. From Table III we have n-$C_3H_7Cl \rightarrow$ n-$C_3H_7^+$ + Cl +

(4) R. F. Bacher and S. Goudsmit, "Atomic Energy States," McGraw-Hill Book Co., New York, N. Y., 1932. See footnote to Table I of the preceding paper on isobutylene, etc.
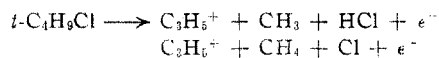
(5) W. C. Price, J. Chem. Phys., 4, 539, 547 (1936).
(6) J. B. Conn, G. B. Kistiakowsky and E. A. Smith, THIS JOURNAL, 60, 2764 (1938).
(7) F. D. Rossini, Chem. Rev., 27, 1 (1940).

ϵ^-, $A(C_3H_7^+) = 11.1$ and from earlier work,[3] $n\text{-}C_4H_{10} \rightarrow n\text{-}C_3H_7^+ + CH_3 + \epsilon^-$, $A(C_3H_7)^+ = 11.2_1$. Herzberg[8] gives 4.43 e. v. for the dissociation energy of HCl. Combining these data with the assumptions described elsewhere,[9] we find $4.4_2 \pm 0.2$ e. v. for the strength of the first carbon-hydrogen bond in methane. The excellence of the agreement of this estimate of $D(CH_3\text{-}H)$ with that made from other similar pairs of appearance potentials, $4.3_8 \pm 0.2$ e. v., provides further justification for an assumption there made, namely, that in the reaction $C_3H_8 \rightarrow C_3H_7^+ + H + \epsilon^-$, the $C_3H_7^+$ is the isopropyl rather than the normal propyl ion.

If the value of $A(C_4H_9^+)$ in the t-BuCl spectrum is combined with that of the same ion in the isobutane spectrum and the heats of formation of isobutane[7] and tertiary butyl chloride,[10] one finds 3.7 e. v. for the dissociation energy of HCl. This value is 0.7 e. v. lower than the accurate value quoted above.[8] In making this estimate, we have assumed that the $C_4H_9^+$ in the isobutane spectrum has the tertiary structure. If the appearance potential $A(C_4H_9^+) = 11.6 \pm 0.3$ e. v.[8] corresponds to the formation of the isobutyl ion from isobutane, the calculated value of the dissociation energy of HCl would be too low by an amount equal to the energy of the isomerization process, $i\text{-}C_4H_9^+ \rightarrow t\text{-}C_4H_9^+$. Since this latter quantity is probably of the order of 0.4 e. v., the assumption that isobutane yields the isobutyl ion would explain most of the discrepancy. The determination of the appearance potential of $C_4H_9^+$ in the isobutyl chloride spectrum would make possible a decision as to whether or not the explanation of the discrepancy is the correct one.

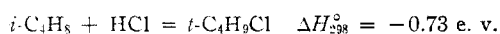The reaction giving rise to $C_3H_5^+$ in the spectrum of t-BuCl may be either of the following pair

$$t\text{-}C_4H_9Cl \longrightarrow C_3H_5^+ + CH_3 + HCl + \epsilon^-$$
$$C_3H_5^+ + CH_4 + Cl + \epsilon^-$$

since the two pairs of un-ionized fragments are of very nearly the same energy. The following simple calculation shows the observed value of $A(C_3H_5^+)$ to be consistent with either of the reactions. From reference 10 we have

$$i\text{-}C_4H_8 + HCl = t\text{-}C_4H_9Cl \quad \Delta H^o_{298} = -0.73 \text{ e. v.}$$

while

$$i\text{-}C_4H_8 = C_3H_5^+ + CH_3 + \epsilon^- \quad A(C_3H_5^+) = 11.5_1 \text{ e. v.}[11]$$

Adding, we find, $t\text{-}C_4H_9Cl \rightarrow C_3H_5^+ + CH_3 + HCl + \epsilon^-$, $A_{calcd.}(C_3H_5^+) = 12.2_5$ e. v. in excellent agreement with the observed value. Since $D(CH_3\text{—}H)$ and $D(H\text{—}Cl)$ are equal to within 0.1 e. v., the products could also be CH_4 and Cl. A possible reaction which can be eliminated is

$$t\text{-}C_4H_9Cl \longrightarrow C_3H_5^+ + CH_3Cl + H + \epsilon^-$$
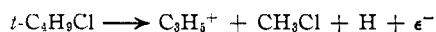
From the data given by Bichowsky and Rossini[12] one finds $CH_4 + HCl = CH_3Cl + H$, $\Delta H^o_{291} = 0.91$ e. v. Thus $A_{calcd.}(C_3H_5^+)$ for the latter un-ionized products is 0.8 e. v. greater than the observed value.

Until further data on related molecules are acquired, it is not profitable to discuss the reactions $t\text{-}C_4H_9Cl \rightarrow C_3H_6Cl^+ + CH_3 + \epsilon^-$ and $n\text{-}C_3H_7Cl \rightarrow C_2H_4Cl^+ + CH_3 + \epsilon^-$, further than to state that the appearance potentials observed seem to be consistent with the reactions as written.

In closing, we should remark that no search was made for negative ions, which undoubtedly are formed.

Summary

The mass spectra of tertiary butyl and normal propyl chloride are tabulated and briefly discussed. The appearance potentials of a few ions in these spectra were measured. The vertical ionization potential of normal propyl chloride is 10.7 ± 0.2 e. v. An estimate of $D(CH_3\text{—}H)$ from the present data leads to the value $4.4_2 \pm 0.2$ e. v. in agreement with the value deduced from other electron impact data.

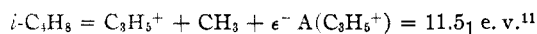(8) G. Herzberg. "Molecular Spectra," Prentice-Hall, Inc., New York, N. Y., 1939.

(9) D. P. Stevenson, J. Chem. Phys., 10, 291 (1942).

(10) G. B. Kistiakowsky and C. H. Stauffer, THIS JOURNAL, 59, 165 (1937).

(11) D. P. Stevenson and J. A. Hipple, ibid., 64, 2769 (1942).

(12) F. R. Bichowsky and F. D. Rossini, "Thermochemistry," Reinhold Publishing Co., New York, N. Y., 1936.