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Measurement of Negative Ions Formed by Electron Impact. VI. Negative Ion Mass Spectra and Ionization Efficiency Curves of Negative Ion of *m/e* 35 from Alkyl Chlorides

Satoru TSUDA, Akira YOKOHATA and Michihiro KAWAI

Department of Chemistry, Faculty of Engineering, University of Hiroshima, Senda-machi, Hiroshima

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The negative ion mass spectra of alkyl (methyl, ethyl, *n*- and *iso*-propyl) chlorides, with emphasis on their relative abundance to the positive ions under 80, 40, 20 and 15 eV electron energies, and the ionization efficiency (IE) curves of Cl^- ions to the extent of 30 eV electron energies were measured. In every sample, the electron impacts of 80 eV and 40 eV gave almost the same distribution of *m/e* for negative ion mass spectra, in which, besides the intense peaks of *m/e* 35 and 37 (Cl^-), a relatively strong peak of *m/e* 25 (C_2H^-) in ethyl chloride and *n*- and iso-propyl chlorides was characteristic. For 20 eV and 15 eV, Cl^- ions predominated other negative ions. The ratio of the abundance of negative ions to positive ions was the order 10^2—10^3 for CH_3Cl^+/Cl^-, $C_2H_5Cl^+/Cl^-$, $C_3H_6^+/Cl^-$ and $C_3H_7^+/Cl^-$ throughout the range of electron energies. Each onset value observed in IE curves was interpreted to correspond to the appearance of the following reactions, the reaction scheme for second process being tentative. For the first process $RCl+e^-\rightarrow R+Cl^-$, for the second process $CH_3Cl+e^-\rightarrow H+CH_2+Cl^-$, $C_2H_5Cl+e^-\rightarrow H_2+H+C_2H_2+Cl^-$, C_3H_7Cl(*n*- or iso-)$+e^-\rightarrow H+C_2H_4+CH_2+Cl^-$. For the third process the possibility of ion pair formation was pointed out. For the fourth process in ethyl chloride a brief discussion was made in view of the overlapping phenomena of a complicated dissociative electron capture process with an ion pair formation.

When molecules are bombarded with electrons in the ion source of a mass spectrometer, both positive and negative ions may be formed, the latter often several orders of magnitude less abundantly. If the energy of the ionizing electrons is greater than about 30 eV the relative abundance of the positive ions produced is generally independent of electron energy, and positive-ion mass spectral data for many molecules are available.[1-3] However, only a few data have been reported[4-8] regarding the identity and distribution of the negative-ion species produced when molecules of chemical interest undergo electron bombardment. Data on the ionization efficiency (IE) curves of negative ions are very limited.[9-12]

There are mainly three mechanisms by which ion formation for negative ions may occur; at low electron energies by electron capture, at intermediate energies by a dissociative resonance process and at higher electron energies by ion-pair formation. Hence the ions observed and their abundance are markedly energy-dependent.

In the present stage when information on negative ion mass spectra is lacking, further work is needed. This work was extended to alkyl chlorides, emphasis being placed on the relative abundance of negative ions to the positive ions in relation to the electron energies and on the measurement of IE curves of Cl^- ions.[*1]

Experimental

Experiments were performed on a Hitachi RMU-6D mass spectrometer equipped with a T-2M ion source having a rhenium filament. The ion detection circuit consisted of a ten stage electron multiplier having Ag-Mg dynode and of a Faraday collector. All the spectra were measured with a total emission current of 20 μA, accelerating voltage of 3.6 kV and electron multiplier voltage 2.5 kV, under the ionizing energies of 80, 40, 20 and 15 eV and pressure $\sim 10^{-6}$ mmHg in the source. Ionizing current varied from 10.5 to 6.4 μA in the range from 10 to 3 eV, while it was constant in the range higher than 10 eV (Fig. 1).

The electron energy was always calibrated in every measurement by the vanishing current method as compared to the ionization potential of argon for the positive ions and to the appearance potential of *m/e* 16 (O^-) from carbon monoxide, carbon dioxide and oxygen[13] for the negative ions.[8] Repeller voltage was adjusted to the best condition to collect the ions for positive and negative ions. The chemicals used were of research grade.

Results and Discussion

Negative Ion Mass Spectra. *Methyl Chloride.* In 80 eV electron impact experiment, negative ions of *m/e* 35(Cl^-) and *m/e* 37(Cl^-) besides a small peak of *m/e* 12(C^-) ion have mainly been observed (Fig. 2a), the most intense peak *m/e* being 35 (Cl^-) ion. The relative abundance of *m/e* 37 ion shows an isotope ratio of chlorine atom. Comparison of the yield of Cl^- ion (*m/e* 35) with that of CH_3Cl^+ ion (*m/e* 50, the most intense peak among the positive ions) gave $\sim 2.7 \times 10^2$ for CH_3Cl^+/Cl^-.

For 40 eV electron energies (Fig. 2b) the pattern of the negative ions was the same as that for 80 eV except for a small change in the yield of minor ions, and the ratio of CH_3Cl^+ to Cl^- was $\sim 4.5 \times 10^2$.

For 20 and 15 eV electron energies (Fig. 2c and 2d) Cl^- ions predominated other negative ions. The values $CH_3Cl^+/Cl^- \simeq 5.1 \times 10^2$ and 4.1×10^3 were obtained.

Table 1 shows the yield of minor negative ions for 80, 40, 20 and 15 eV. For 80 and 40 eV, *m/e* 12 (C^-), *m/e* 13 (CH^-), *m/e* 14 (CH_2^-), *m/e* 47 (CCl^-), *m/e* 48 ($CHCl^-$), *m/e* 49 (CH_2Cl^- or CCl^-), *m/e* 50($CHCl^-$) and *m/e* 51 (CH_2Cl^-) ions were found. The result for 40 eV was almost consistent with

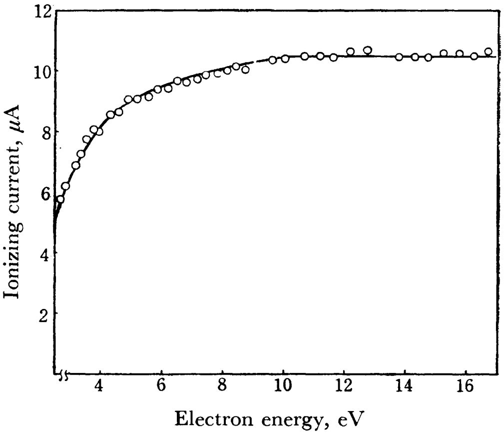

Fig. 1. The relation between ionizing current and electron energy (total emission current, 20 μA).

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1) Amer. Petrol. Inst. Research Project 44, Mass Spectral Tables.

2) ASTM Committee E-14, Unclassified Mass Spectral Data.

3) Uncertified Mass Spectral Data, (The Dow Chemical Company, Midland Michigan, U. S. A.).

4) C. E. Melton, "Mass Spectrometry of Organic Ions," ed. F. W. McLafferty, Academic Press, New York, N. Y. (1963), p. 163.

5) R. T. Aplin, H. Budzikieweiz and C. Djerassi, *J. Amer. Chem. Soc.*, **87**, 3180 (1965).

6) D. F. Munro, J. E. Ahnell and W. S. Koski, *J. Phys, Chem.*, **72**, 2682 (1968).

7) K. A. G. MacNeil and J. C. J. Thynne, *Trans. Faraday Soc.*, **64**, 2112 (1968).

8) S. Tsuda, A. Yokohata and M. Kawai, This Bulletin, **42**, 607 (1969).

9) E. W. MacDaniel, "Collision Phenomena in Ionized Gases," John Wiley & Sons, Inc., New York (1964), p. 368.

10) L. G. Christophorou, R. N. Compton, G. S. Hurst and P. W. Reinhardt, *J. Chem. Phys.*, **45**, 536 (1966).

11) L. G. Christophorou and R. N. Compton, *Health Physics*, **13**, 1277 (1967).

12) S. Tsuda, A. Yokohata and M. Kawai, This Bulletin, **42**, 614 (1969).

[*1] Recently, the measurement of ethyl chloride was reported. However, the method is different, and no detailed discussions were given (refer 10).

13) G. J. Schulz, *Phys. Rev.*, **128**, 178 (1962).

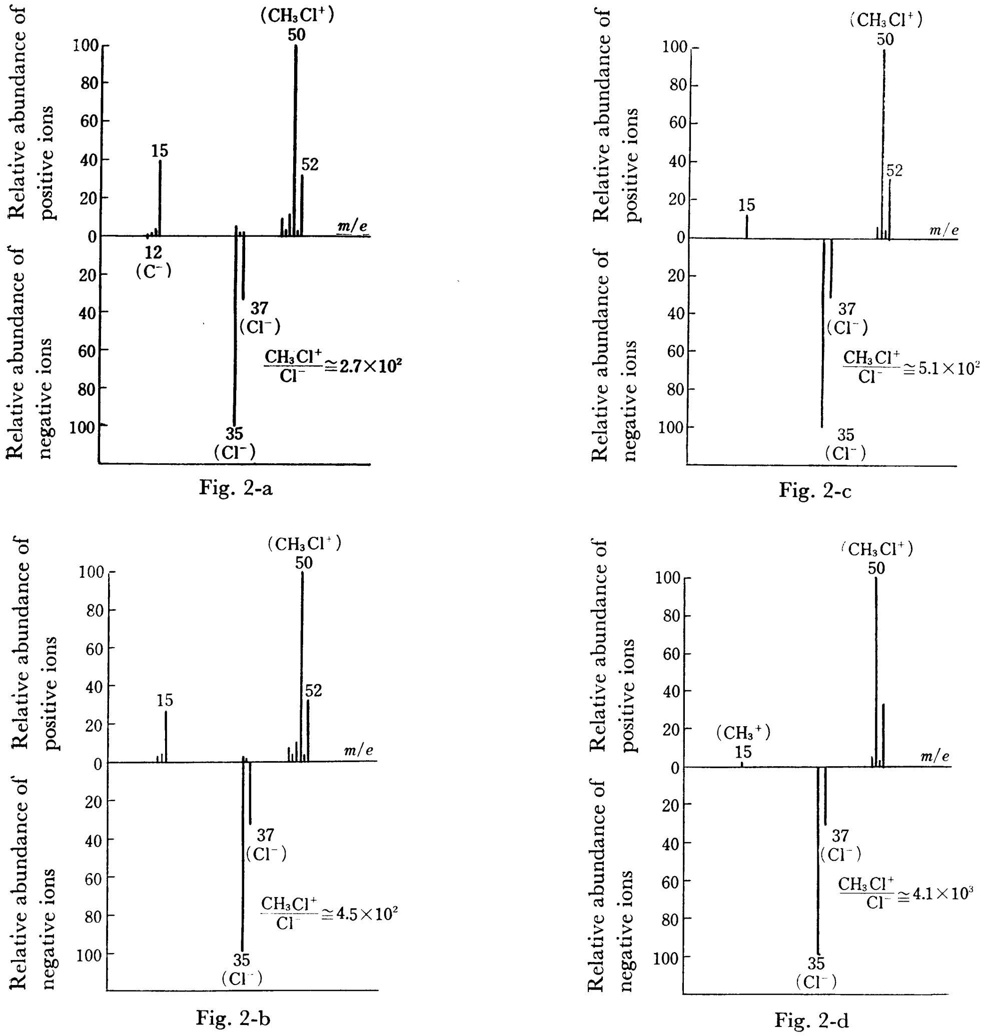

Fig. 2-a

Fig. 2-c

Fig. 2-b

Fig. 2-d

Fig. 2. Positive and negative ion mass spectra of methyl chloride (source pressure: ~10^{-6}mmHg).
a 80 eV b 40 eV c 20 eV d 15 eV

TABLE 1. MINOR NEGATIVE IONS FROM CH_3Cl
(Normalized to [m/e 35 (Cl^-)]=100)

m/e (ions)	Relative abundances for electron energies of			
	80 eV	40 eV	20 eV	15 eV
12 (C^-)	1.86	0.42		
13 (CH^-)	0.93	0.20		
14 (CH_2^-)	0.07	0.28		
35 (Cl^-)	100	100	100	100
47 (CCl^-)	1.1	0.2		
48 ($CHCl^-$)	0.19	0.36		
49 (CH_2Cl^-, CCl^-)	0.43	0.38	0.46	
50 ($CHCl^-$)	0.06	0.12		
51 (CH_2Cl^-)	0.14	0.12	0.14	

that of MacNeil *et al.*[7] except that the relative intensity of *m/e* 12 (C^-) ion to *m/e* 14 (CH_2^-) ion was reversed. It is probable that differences in the source pressure and in the geometry of the ion source are responsible for the discrepancy, which emphasizes the much greater sensitivity of negative ion mass spectrometry toward the change in experimental conditions as compared with positive ion mass spectrometry.

Molecular ion (CH_3Cl^-) was not observed, contrary to the formation of $CH_3NO_2^-$ ion from nitromethane at 80 eV and 40 eV electron impacts.

Ethyl Chloride. For the electron impact of 80 eV (Fig. 3a) negative ions of *m/e* 13 (CH^-), *m/e* 24 (C_2^-), 25 (C_2H^-), 35 (Cl^-) and 37 (Cl^-) have been mainly observed. The peak of molecular ion ($C_2H_5Cl^-$) was not found. When the yield of Cl^- ion (*m/e* 35) is compared with that of $C_2H_5Cl^+$ ion (*m/e* 64, the most intense peak among the positive ions),

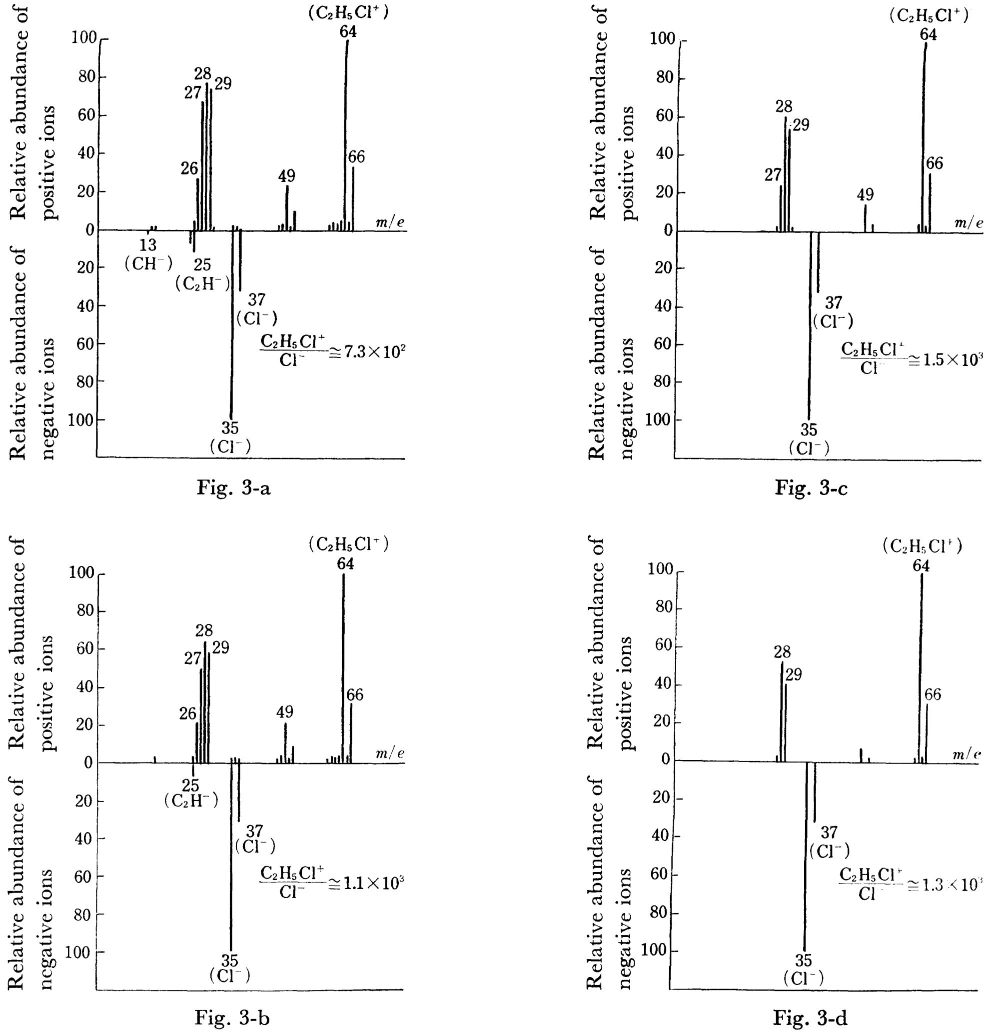

Fig. 3-a

Fig. 3-c

Fig. 3-b

Fig. 3-d

Fig. 3. Positive and negative ion mass spectra of ethyl chloride (source pressure: ~10^{-6} mmHg).
a 80 eV b 40 eV c 20 eV d 15 eV

$C_2H_5Cl^+/Cl^-$ gave ~7.3×10^2. A relatively large peak of *m/e* 25 (C_2H^-) ion among the negative ions arising from the ethyl group is quite similar to the situations in ethane,[4] ethyl alcohol[4] and nitroethane.[8]

TABLE 2. MINOR NEGATIVE IONS FROM C_2H_5Cl
(Normalized to [*m/e* 35 (Cl^-)]=100)

m/e (ions)	Relative abundances for electron energies of			
	80 eV	40 eV	20 eV	15 eV
12 (C^-)	0.71	trace		
13 (CH^-)	1.29	0.7		
14 (CH_2^-)		trace		
24 (C_2^-)	7.15	0.7		
25 (C_2H^-)	10.62	6.3		
35 (Cl^-)	100	100	100	100

Mass spectra for 40 eV (Fig. 3b) did not differ so much from those for 80 eV except for the decrement of peaks of *m/e* 13 (CH^-), 24 (C_2^-) and 25 (C_2H^-) ions. The ratio of $C_2H_5Cl^+/Cl^-$ gave ~1.1×10^3.

For 20 and 15 eV (Fig. 3c and 3d), *m/e* 35 (Cl^-) and 37 (Cl^-) ions predominated other negative ions. The values ~1.5×10^3 and ~1.3×10^3 for $C_2H_5Cl^+/Cl^-$ were obtained respectively.

Table 2 shows the yield of the minor negative ions in relation to electron energies. It should be noted that no ion is formed containing carbon, hydrogen and chlorine atoms, or carbon and chlorine atoms.

n- and Iso-propyl Chlorides. For the electron impacts of 80 eV and 40 eV, both samples gave almost the same negative ions except for a small change of minor ions (Figs. 4a, 5a and 4b, 5b). It is of great interest that a relatively strong peak of *m/e* 25 (C_2H^-) ion has been observed as one

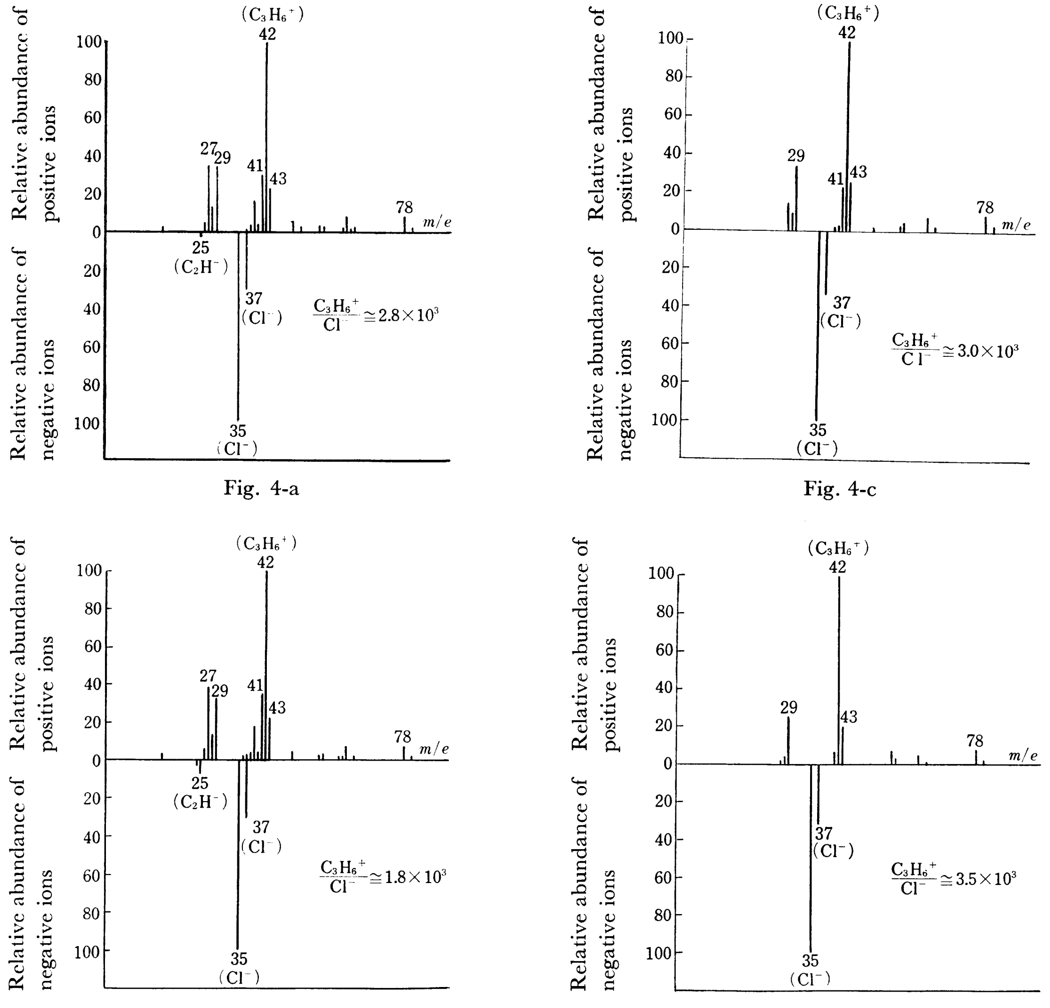

Fig. 4-a

Fig. 4-c

Fig. 4-b

Fig. 4-d

Fig. 4. Positive and negative ion mass spectra of *n*-propyl chloride (source pressure: ~10^{-6}mmHg). a 80 eV b 40 eV c 20 eV d 15 eV

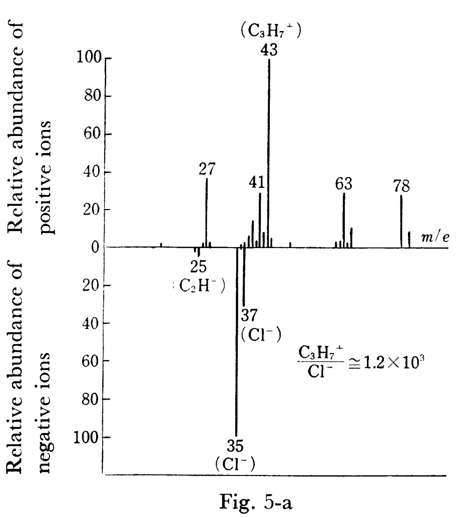

Fig. 5-a

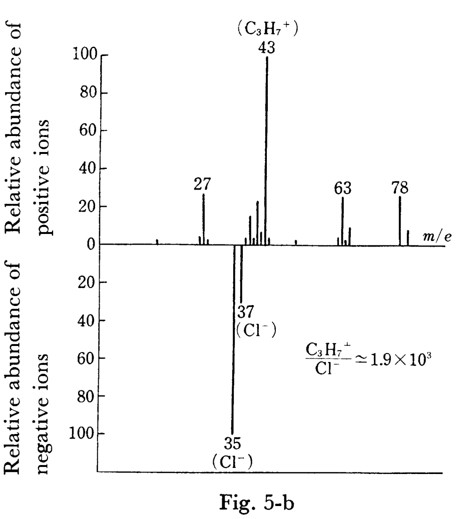

Fig. 5-b

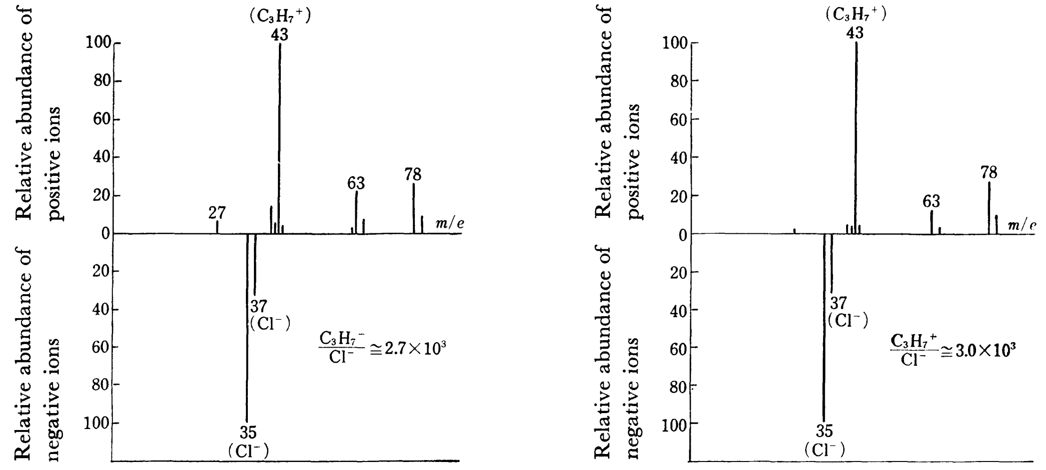

Fig. 5-c

Fig. 5-d

Fig. 5. Positive and negative ion mass spectra of isopropyl chloride (source pressure: ~10^{-6}mmHg).
a 80 eV b 40 eV c 20 eV d 15 eV

TABLE 3. MINOR NEGATIVE IONS FROM n-C_3H_7Cl (Normalized to [m/e 35 (Cl^-)] = 100)

m/e (ions)	Relative abundances for electron energies of			
	80 eV	40 eV	20 eV	15 eV
13(CH^-)	trace	0.91		
14(CH_2^-)	trace	0.23		
24(C_2^-)	3.01	0.23		
25(C_2H^-)	6.60	1.71		
26($C_2H_2^-$)	0.19			
35(Cl^-)	100	100	100	100
36(HCl^-)	0.68			

TABLE 4. MINOR NEGATIVE IONS FROM iso-C_3H_7Cl (Normalized to [m/e 35 (Cl^-)] = 100)

m/e (ions)	Relative abundances for electron energies of			
	80 eV	40 eV	20 eV	15 eV
13(CH^-)	0.94	0.4		
14(CH_2^-)		0.06		
24(C_2^-)	2.34			
25(C_2H^-)	4.53			
35(Cl^-)	100	100	100	100
36(HCl^-)	1.04			

of negative ions arising from the propyl group. This was consistent with the results in propyl alcohol[4] and nitropropane.[8]

Patterns obtained for 20 eV and 15 eV were quite similar in both samples (Figs. 4c, 5c and 4d, 5d). The most intense peak was always of Cl^- ions.

The values of $C_3H_6^+/Cl^-$ were ~1.8×10^3 at 80 eV, ~2.8×10^3 at 40 eV, ~3.0×10^3 at 20 eV and ~3.5×10^3 at 15 eV for n-propyl chloride and those of $C_3H_7^+/Cl^-$ were ~1.2×10^3, ~1.9×10^3, ~2.7×10^3 and ~3.0×10^3 for isopropyl chloride, respectively.

Tables 3 and 4 show the yield of minor negative ions for n- and iso-propyl chlorides in relation to the electron energies. It should be noted that neither ions containing carbon, hydrogen and chlorine, nor ions containing carbon and chlorine are observed. This is in sharp contrast with the observations for methyl chloride. This may be explained on the basis of the size, symmetry and bonding of the molecule or of the electron affinity of the radical,[7] but a quantitative explanation is not so easy in the present stage. Ferguson *et al.*[14] gave geometrical considerations for negative ion processes, but their discussions are limited to a few simple molecules.

IE Curves of Cl^- Ions. Figs. 6A-a, 6B-a, 6C-a and 6D-a show the ionization efficiency curves of Cl^- ions from methyl chloride, ethyl chloride, n- and iso-propyl chlorides, respectively. Figs. 6A-b, 6B-b, 6C-b and 6D-b show the same curves to the extent of electron energies of 30 eV on an enlarged scale. The result for ethyl chloride was consistent with that obtained by using the combined swarm-beam method by Christophorou *et al.*[10] In the three compounds except for ethyl chlrodie, the contributions of at least three processes can be observed. The first process appears at a considerably lower energy*[2] for all compounds, the second process at ~3.2 eV for methyl chloride, at ~3.5 eV for ethyl chloride, at ~4.1 eV for

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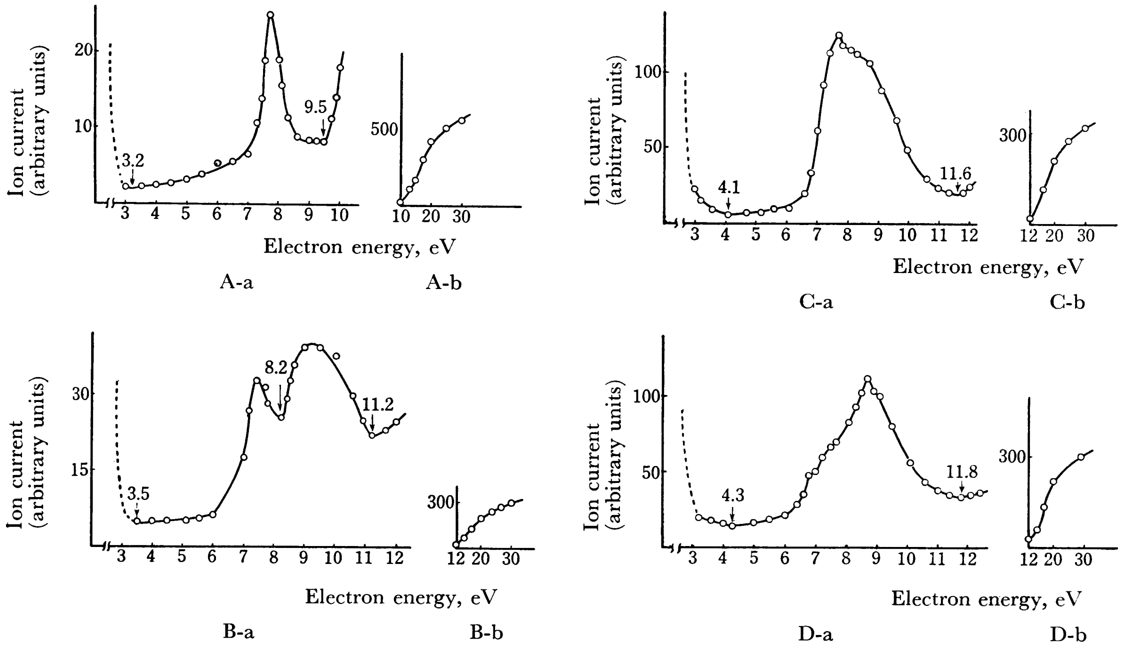
[14] E. E. Ferguson, F. C. Fehsenfeld and A. L. Schmeltekopf, *J. Chem. Phys.*, **47**, 3085 (1967).

*[2] Reliability of this work is restricted to electron energies above ~3 eV because of instrumental difficulty.



A-a A-b C-a C-b

B-a B-b D-a D-b

Fig. 6. Ionization efficiency curves of Cl^- from alkyl chlorides.
A CH_3Cl B C_2H_5Cl C n-C_3H_7Cl D *iso*-C_3H_7Cl

n-propyl chloride and at ~4.3 eV for isopropyl chloride, and the third process at ~9.5, ~8.2, ~11.6 and ~11.8 respectively.*3

In ethyl chloride, the fourth process was observed at ~11.2 eV.*4 As discussed later, this may not correspond to a simple reaction but an overlapping of two different reactions.

The plausible reaction schemes expected to occur at each onset value observed were sought on the basis of appearance potentials calculated by using $\Delta H_f(CH_3Cl) = -0.90$ eV, $\Delta H_f(C_2H_5Cl) = -1.16$ eV, $\Delta H_f(n\text{-}C_3H_7Cl) = -1.38$ eV, $\Delta H_f(iso\text{-}C_3H_7Cl) = -1.50$ eV,[15] $\Delta H_f(Cl^-) = -2.35$ eV,*5 $\Delta H_f(CH_3) = 1.39$ eV, $\Delta H_f(CH_2) = 2.5$ eV, $\Delta H_f(CH) = 6.16$ eV, $\Delta H_f(C_2H_2) = 2.35$ eV, $\Delta H_f(H) = 2.26$ eV, $\Delta H_f(C_2H_5) = 1.1$ eV, $\Delta H_f(C_2H_4) = 0.54$ eV, $\Delta H_f(C_2H_3) = 2.8$ eV, $\Delta H_f(n\text{-}C_3H_7) = 0.96$ eV, $\Delta H_f(iso\text{-}C_3H_7) = 0.73$ eV, $\Delta H_f(CH_3^+) = 11.23$ eV, $\Delta H_f(C_2H_5^+) = 9.88$ eV, $\Delta H_f(n\text{-}C_3H_7^+) = 9.65$ eV and $\Delta H_f(iso\text{-}C_3H_7^+) = 8.65$ eV.[16]

For the first process

		AP_{calc} (eV)*6
$CH_3Cl + e^- \longrightarrow CH_3 + Cl^-$	(1)	(−0.06)
$C_2H_5Cl + e^- \longrightarrow C_2H_5 + Cl^-$	(2)	(−0.09)
$n\text{-}C_3H_7Cl + e^- \longrightarrow n\text{-}C_3H_7 + Cl^-$	(3)	(0.01)
$\text{iso-}C_3H_7Cl + e^- \longrightarrow iso\text{-}C_3H_7 + Cl^-$	(4)	(−0.12)

For the second process

		AP_{calc} (eV)
$CH_3Cl + e^- \longrightarrow H + CH_2 + Cl^-$	(5)	(3.31)
$\longrightarrow H_2 + CH + Cl^-$	(6)	(4.71)
$C_2H_5Cl + e^-$		
$\longrightarrow H_2 + C_2H_2 + H + Cl^-$	(7)	(3.42)
$\longrightarrow 2H + C_2H_3 + Cl^-$	(8)	(6.13)
$n\text{-}C_3H_7Cl + e^-$		
$\longrightarrow H + C_2H_4 + CH_2 + Cl^-$	(9)	(4.33)
$\longrightarrow CH_3 + 2CH_2 + Cl^-$	(10)	(5.42)
$iso\text{-}C_3H_7Cl + e^-$		
$\longrightarrow H + C_2H_4 + CH_2 + Cl^-$	(11)	(4.45)
$\longrightarrow H + C_2H_3 + CH_3 + Cl^-$	(12)	(5.6)

For the third process

		AP_{calc} (eV)
$CH_3Cl + e^- \longrightarrow CH_3^+ + Cl^- + e^-$	(13)	(9.78)
$C_2H_5Cl + e^- \longrightarrow C_2H_5^+ + Cl^- + e^-$	(14)	(8.69)

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*3 Since the tailing due to the 1st or 2nd process might be overlapped with the appearance of the 2nd or 3rd process, the exact determination of appearance potential of the 2nd or 3rd process is difficult. In this work, the minimum values in IE curves were taken as the subject of discussion. (G. J. Schulz, *Phys. Rev.*, **113**, 816 (1959)).

*4 The situation is the same as *3.

15) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

*5 To be estimated from $\Delta H_f(Cl) = 1.25$ eV (Refer 9) and $EA(Cl) = 3.6$ eV (J. M. Williams and W. H. Hamill, *J. Chem. Phys.*, **49**, 4467 (1968)).

16) R. R. Bernecker and F. A. Long, *J. Phys. Chem.*, **65**, 1565 (1961).

*6 For the estimation of AP_{calc}, the kinetic energies of fragment ions are ignored, and the ions are assumed to be formed in ground state.

$n\text{-}C_3H_7Cl + e^-$

$\longrightarrow n\text{-}C_3H_7^+ + Cl^- + e^-$ (15) (8.68)

$\longrightarrow C_2H_5^+ + CH_2 + Cl^- + e^-$ (16)(11.41)

$iso\text{-}C_3H_7Cl + e^-$

$\longrightarrow iso\text{-}C_3H_7^+ + Cl^- + e^-$ (17) (7.8)

$\longrightarrow C_2H_5^+ + CH_2 + Cl^- + e^-$ (18)(11.53)

The first process observed in a lower energy than ~3 eV appears to correspond to the reactions (1)—(4) (the dissociative electron capture). The situation is similar to the reaction, $RNO_2 + e^- \rightarrow R + NO_2^-$ in nitroalkanes.[12]

As evident from Figs. 6A-a—6D-a, the second processes extend over the relatively broad range of electron energies and their dependence on electron energies is very small, especially near the onset. Although this makes it difficult to determine exactly each onset value, reactions (5), (7), (9) or (11) are likely to be assigned for each onset.

The third process seems to be more complicated. Although the simple ion pair formations such as (13), (14), (15) and (17) are expected, consistency of AP_{calc} with AP_{obs} is not so good. This is probably due to overlapping. In *n*- and *iso*-propyl chlorides, the possibility of reaction (16) or (18) is stronger than that of (15) or (17).

The fourth process in ethyl chloride might be also interpreted in terms of the overlapping of a complicated dissociative electron capture (for example, reaction (19)) and an ion pair formation (reaction (14)).

$C_2H_5Cl + e^- \rightarrow 3H + C_2H_2 + Cl^-$ (19) $AP_{calc} = 8.39$ eV

If each IE curve of reaction (19) and reaction (14) is expressed by curves (A) and (B) in Fig. 7, they would result in curve (C) which consists qualitatively of the last part (the part higher than 8.8 eV of IE curves in Fig. 6B-a). This is a tentative interpretation.

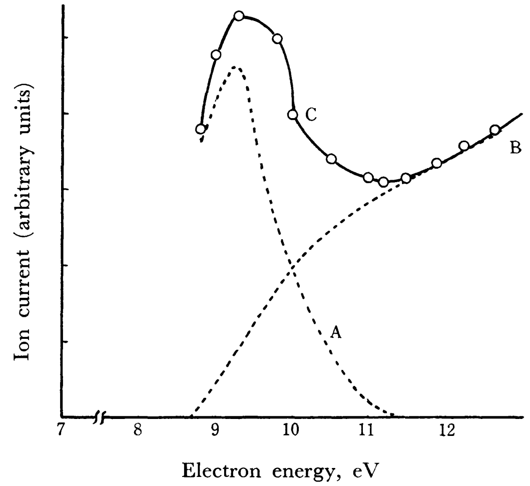

Fig. 7. An interpretation diagram for the fourth process in ethyl chloride.

It should be emphasized that (1) for ethyl chloride and *n*- or *iso*-propyl chlorides, neither ions containing carbon, hydrogen and chloride, nor ions containing carbon and chlorine are observed, (2) for all compounds the negative ions observed at electron energies lower than 20 eV are only Cl^- ion, and (3) for the Cl^- ion formation in the range of electron energies lower than about 12 eV the contribution of at least three different mechanisms are considered. The Cl^- ion yield increases monotonically with increasing electron energies in the range higher than about 12 eV.