

## STUDIES BY THE ELECTRON CYCLOTRON RESONANCE (ECR) TECHNIQUE.

### VIII. Interactions of low-energy electrons with the chlorine-containing molecules $\text{CCl}_4$ , $\text{CHCl}_3$ , $\text{CH}_2\text{Cl}_2$ , $\text{C}_n\text{H}_{2n+1}\text{Cl}$ ( $n = 1$ to 4), $\text{C}_2\text{H}_3\text{Cl}$ , $\text{COCl}_2$ , $\text{NOCl}$ , $\text{CNCl}$ and $\text{Cl}_2$

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Rate constants, in some cases also activation energies and energy dependences, were measured for the capture of low-energy electrons by the molecules  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{C}_n\text{H}_{2n+1}\text{Cl}$  ( $n = 1$  to 4),  $\text{C}_2\text{H}_3\text{Cl}$ ,  $\text{COCl}_2$ ,  $\text{NOCl}$ ,  $\text{CNCl}$  and  $\text{Cl}_2$ . Potential energy curves were calculated for a number of negative ions.

For ineffective scavengers the possibility of contributing scattering effects on the observed changes in signal intensity upon electron energy variation is indicated. In  $\text{CCl}_4$  the observed energy dependence suggests the existence of intermediate negative ions. For  $\text{Cl}_2$  good agreement was obtained between the calculated curves based on experimental data for electron capture and a recent self-consistent field analysis.

### 1. Introduction

This study is a continuation of our effort to apply the cyclotron resonance technique to the investigation of interactions between thermal electrons and polyatomic molecules [1–5]. It has been shown earlier that quantitative information can be obtained with this method on the elementary step of electron capture in the gas phase [1–3]. Furthermore, total scattering cross sections can be calculated from an analysis of the experimental ECR signals in the thermal energy range [4,6].

This paper describes a study of the low-energy capture processes in some chlorine-containing molecules. Energy dependences and in some cases also temperature dependences are given. The halogenated methanes have previously been investigated by a number of authors [6–17]. For some compounds considerable disagreement exists between the results obtained with the different techniques in use. This contribution indicates possible sources for these differences. A discussion of the capture mechanism is

given using the kinetic model of Wentworth and co-workers [10,17,18].

### 2. Experimental

The experimental set-up for ECR studies using argon as carrier gas and NO as the electron donor was reported in previous publications [2,19–21]. A quartz flow tube of 22 mm diameter and a 9-inch magnet were used. The microwave system has been modified to allow for power-input variations to the cavity in the range  $\geq 0.01 \mu\text{W}$  to about  $300 \mu\text{W}$ . A double-walled flow tube with one mixing chamber permitted the study of temperature effects.

Rate constants for the electron capture process at thermal energies are determined by two ways: The intensity of the cyclotron resonance signal is followed either as a function of the scavenger concentration at constant reaction time or by variation of the reaction time at constant scavenger concentration. For the determination of the energy dependence of the attachment process, the relative intensity of the absorption signal was followed as a function of microwave power input at constant reaction time and constant electron scavenger leak rate.

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Table 1  
Rate constants  $k$  ( $\text{cm}^3 \text{s}^{-1}$ ) for the capture of thermal electrons by  $\text{CCl}_4$  ( $T = 300 \text{ K}$ )

$k_{\text{th}}$	Carrier gas	Method	Reference
$4.1 \times 10^{-7}$ a)	Ar + NO	ECR	Mothes (1971) [1]
$4.1 \times 10^{-7}$	<i>n</i> - $\text{C}_6\text{H}_{14}$	microwave	Warman (1971) [14]
$3.55 \times 10^{-7}$ b)	$\text{H}_2$ , He, CO, $\text{CH}_4$ , $\text{CO}_2$ , $\text{C}_2\text{H}_4$	drift-dwell-drift	Davis (1973) [16]
$3.3 \times 10^{-7}$ c)	90% Ar + 10% $\text{CH}_4$	pulse sampling	Wentworth (1967) [8]
$2.9 \times 10^{-7}$	$\text{N}_2$	electron swarm	Blaunstein (1968) [9]
$2.9 \times 10^{-7}$ b)	$\text{CO}_2$ , $\text{CH}_3\text{OH}$ , $\text{C}_2\text{H}_2$	electron swarm	Bouby (1965) [22]
$1.5 \times 10^{-7}$	$\text{N}_2$	electron swarm	Lee (1963) [7]

a) Concentration dependence at constant reaction time.

b) Average value from measurements with various carrier gases.

c) Determined from  $\ln(KT^{3/2})$  versus  $(1/T)$  plot (fig. 2 of ref. [8]) using  $k_{\text{D}} = 2.4 \times 10^3 \text{ s}^{-1}$  [see W.L. Wentworth, E. Chen and J.E. Lovelock, J. Phys. Chem. 70 (1966) 445].

The potential energy diagrams were programmed and plotted with the aid of a Hewlett/Packard system (Model 9830A calculator, Model 9866A printer, Model 9862A calculator plotter).

### 3. Results

#### 3.1. Chlorinated alkanes

**$\text{CCl}_4$**  The rate constant for the capture of thermal electrons by  $\text{CCl}_4$  has been investigated by several groups using different techniques [2,7-9,11,16,22]. A compilation of the results published is given in table 1. Except for the value reported by Lee [7], close agreement was obtained with the  $k$ -value\* of  $4.1 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  of the ECR study [2]. A small negative activation energy of  $-0.6 \text{ kcal mole}^{-1}$  was observed [10,11].

In general, the signal intensity  $\ln(h_0/h)$ , where  $h_0$  and  $h$  are the peak-to-peak heights of the ECR signals without and with the electron scavenger, is considered as the measure of the electron attachment [1-5]. In fig. 1 the energy dependence for the attachment rate, as measured by the ECR technique, is given. A pronounced structure is seen in this plot. No such structure was observed in electron-swarm studies [9]. The swarm results appear to represent the envelope of the

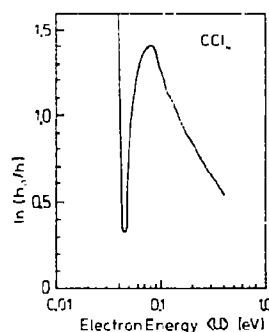


Fig. 1. Energy dependence of the attachment of low energy electrons to  $\text{CCl}_4$ .

low energy behaviour below 0.7 eV. The increase at energies  $> 0.7 \text{ eV}$  [9,13], which is well established from electron beam experiments [23-26], cannot be followed in ECR studies because of the limited energy range accessible to this technique [21].

**$\text{CHCl}_3$**  Good agreement exists also on the absolute rate constant for the attachment of thermal electrons to chloroform at room temperature. The value of  $2.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  calculated from the time dependence of the reaction at  $[\text{CHCl}_3] = 1.15 \times 10^{11} \text{ cm}^{-3}$  and the value of  $2.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  determined from concentration variations of the scavenger are given in table 2 together with rate constants determined by other techniques. An activation energy of 2.4 kcal/mole was obtained in the present ECR experiments in good agreement with the value of 2.2 kcal/mole of Warman

\* For convenience, the units for rate constants and concentrations are given as  $\text{cm}^3 \text{ s}^{-1}$  and  $\text{cm}^{-3}$  rather than  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $\text{molecule cm}^{-3}$ , respectively.

Table 2  
Rate constants  $k$  ( $\text{cm}^3 \text{s}^{-1}$ ) for the capture of thermal electrons by  $\text{CHCl}_3$  ( $T = 300 \text{ K}$ )

$k_{\text{th}}$	Carrier gas	Method	Reference
$2.6 \times 10^{-9}$ a)	Ar + NO	ECR	present work
$2.2 \times 10^{-9}$ b)	Ar + NO	ECR	present work
$2.2 \times 10^{-9}$ c)	<i>n</i> -C <sub>6</sub> H <sub>14</sub>	microwave	Warman (1971) [14]
$1.8 \times 10^{-9}$ d)	<i>n</i> -C <sub>6</sub> H <sub>14</sub>	microwave	Warman (1971) [14]
$4.9 \times 10^{-9}$	N <sub>2</sub>	electron swarm	Lee (1963) [7]
$3.8 \times 10^{-9}$	N <sub>2</sub>	electron swarm	Blaunstein (1968) [9]
$6.2 \times 10^{-9}$ e)	90% Ar + 10% CH <sub>4</sub>	pulse sampling	Wentworth (1967) [8]

a) Time-dependence measurements at  $[\text{CHCl}_3] = 1.15 \times 10^{11} \text{ cm}^{-3}$ .

b) Concentration-dependence measurements at constant reaction time.

c) Determined at a total pressure of 33 torr [14].

d) Determined from  $\ln k$  versus  $(1/T)$  plot (fig. 6 of ref. [14]) at 17 torr total pressure.

e) Determined from  $\ln(KT^{-3/2})$  versus  $(1/T)$  plot (fig. 2 of ref. [8]) using the thermal rate constant  $k_{\text{th}} = 2.41 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  for SF<sub>6</sub> of E. Chen, R.D. George and W.L. Wentworth, J. Chem. Phys. 49 (1968) 1973.

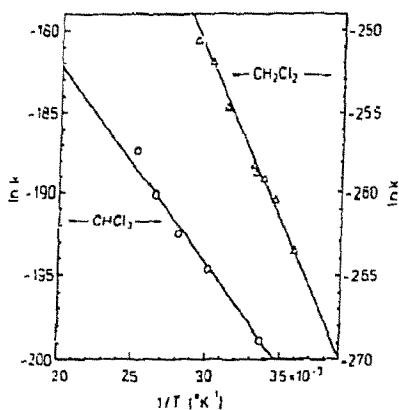


Fig. 2. Arrhenius plot for the electron capture by  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$ .

and Sauer [14]. The value is lower than the activation energy of 3.1 kcal/mole measured by Wentworth et al. [10]. The Arrhenius plot is reproduced in fig. 2.

The energy dependences of the capture process as measured by the ECR technique and in swarm experiments, respectively, are shown in fig. 3. The maximum attachment rate has been measured by Blaunstein and Christophorou [9] and reanalyzed by Christodoulides and Christophorou [13]. It occurs at 0.37 eV. The curve in the present experiments appears to be broader than that reported in swarm studies [9,13]. This fact may be attributed to different electron energy distributions in the two experimental set-ups.

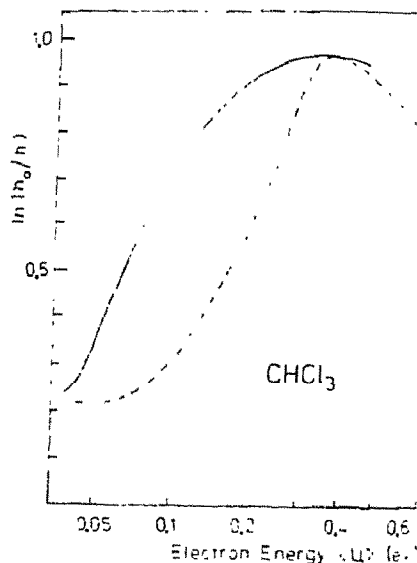


Fig. 3. Energy dependence of the attachment of low-energy electrons to  $\text{CHCl}_3$ . The curves from ECR (—) experiments and swarm (---) data were normalized at 0.37 eV.

**$\text{CH}_2\text{Cl}_2$**  The rate constants for the capture of thermal electrons by  $\text{CH}_2\text{Cl}_2$  at room temperature as determined by the microwave conductivity/pulse radiolysis and by the ECR techniques are in good agreement. The values are smaller than the data obtained in swarm experiments. Rate constants reported in the literature are summarized in table 3. It is noticed that the  $k$ -value determined in the study of

Table 3  
Rate constants  $k$  ( $\text{cm}^3 \text{s}^{-1}$ ) for the capture of thermal electrons by  $\text{CH}_2\text{Cl}_2$  ( $T = 300 \text{ K}$ )

$k_{\text{th}}$	Carrier gas	Method	Reference
$4.1 \times 10^{-12}$ a)	Ar + NO	ECR	present work
$5.4 \times 10^{-12}$ b)	Ar + NO	ECR	present work
$4.7 \times 10^{-12}$	$\text{C}_3\text{H}_8$	microwave	Fessenden (1970) [12]
$1.6 \times 10^{-10}$	$\text{N}_2$	electron swarm	Lee (1963) [7]
$1.5 \times 10^{-11}$	$\text{N}_2$	electron swarm	Blaunstein (1968) [9]
$1.7 \times 10^{-12}$ c)	90% Ar + 10% $\text{CH}_4$	pulse sampling	Wentworth (1967) [8]

a) Time-dependence measurements at  $[\text{CH}_2\text{Cl}_2] = 2.4 \times 10^{13} \text{ cm}^{-3}$

b) Concentration-dependence measurements at constant reaction time.

c) Determined from  $\ln(KT^{3/2})$  versus  $(1/T)$  plot (fig. 2 of ref. [8]) using the thermal rate constant  $k_{\text{th}} = 2.41 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  for  $\text{SiF}_6$  of E. Chen, R.D. George and W.E. Wentworth, J. Chem. Phys. 49 (1968) 1973.

the concentration dependence of the attachment process is larger than the constant obtained from the time dependence of the reaction. This difference as well as the discrepancies of the values obtained with the different techniques will be discussed in the following section.

From the temperature dependence of the rate constant an activation energy of 4.1 kcal/mole was determined. The Arrhenius plot is given in fig. 2. Wentworth et al. [8,10] reported a higher value of 7.5 kcal/mole, while a value of 6.1 kcal/mole was calculated [10] on the basis of thermodynamic considerations.

In earlier ECR studies of the energy dependence for the attachment of electrons to inefficient polar scavengers, an apparent maximum in signal intensity around 0.06 eV was observed [21]. An increase in the attachment rate at low energies was also indicated in swarm measurements [7,9,13]. Similar observations were obtained with the monochlorinated alkanes.

**$\text{CH}_3\text{Cl}$  and higher homologues** Considerable disagreement exists in the literature on the rate constants for electron capture by methyl chloride. A summary of data found in the literature is given in table 4.

From microwave conductivity and pulse sampling measurements, rate constants on the order of  $10^{-14}$ – $10^{-16} \text{ cm}^3 \text{ s}^{-1}$  were obtained. Only an upper limit  $< 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  was measured following the time dependence by the ECR technique with argon as carrier gas and NO as electron donor at a  $[\text{CH}_3\text{Cl}]$  of  $9.2 \times 10^{13} \text{ cm}^{-3}$  [27].

Measurements in nitrogen carrier with  $\text{CH}_3\text{NH}_2$  as electron donor indicated also a rate constant of

$10^{-13} \text{ cm}^3 \text{ s}^{-1}$  [28]. Preliminary recent ECR results obtained from time-dependence measurements at  $\text{CH}_3\text{Cl}$  concentrations up to  $\sim 5 \times 10^{15} \text{ cm}^{-3}$  yielded an upper limit of  $< 5 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ . Details will be given elsewhere [29]. A very high value of  $\sim 6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  was reported in a swarm experiment [7]. Generally, Lee's [7]  $k$ -values for poor electron scavengers are much higher than well accepted rate constants [29]. Apparent rate constants as high as  $10^{-12} \text{ cm}^3 \text{ s}^{-1}$  were obtained in ECR studies, when the rate was followed as a function of scavenger concentration [21,27] at constant reaction time. It is suggested that one possible source for the apparent large  $k$ -values at thermal electron energies might be related to the large total scattering cross section for collisions between slow electrons and unreactive polar molecules.

Similar discrepancies as noticed for methyl chloride also exist for  $\text{C}_2\text{H}_5\text{Cl}$ . By microwave conductivity measurements [15] a value of  $< 1.5 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$  was obtained. ECR studies in argon yielded an upper limit  $< 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  at low  $[\text{C}_2\text{H}_5\text{Cl}]$ . In swarm experiments values of  $6.4 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  [30] and  $3.2 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  [31] were obtained.

All other monochlorinated alkanes studied, i.e.,  $n$ - and  $i$ -propylchloride and the three isomer butylchlorides ( $n$ -,  $sec$ -, and  $isobutyl$  chloride) gave rate constants  $< 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  for electron capture in argon at low concentrations. No data were found in the literature for these compounds except  $k = 1.1 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$  for  $t$ - $\text{C}_4\text{H}_9\text{Cl}$  estimated from pulse sampling investigations by Wentworth et al. [10].

Changes in relative signal intensity as a function of electron energy for the molecules  $\text{CH}_3\text{Cl}$  and  $\text{C}_2\text{H}_5\text{Cl}$ .

Table 4  
Rate constants  $k$  ( $\text{cm}^3 \text{s}^{-1}$ ) for the capture of thermal electrons by  $\text{CH}_3\text{Cl}$  ( $T = 300 \text{ K}$ )

$k_{\text{th}}$	Carrier gas	Method	Reference
$< 10^{-12}$ a)	Ar + NO	ECR	present work
$< 10^{-13}$ b)	Ar + NO	ECR	present work
$< 5 \times 10^{-15}$ c)	Ar + $\text{CO}_2$	ECR	Christodoulides (1975) [29]
$< 1.9 \times 10^{-15}$	$\text{CH}_3\text{Cl}$	microwave	Bansal (1972) [15]
$6.1 \times 10^{-11}$	$\text{N}_2$	electron swarm	Lee (1963) [7]
$7.0 \times 10^{-16}$ d)	90% Ar + 10% $\text{CH}_4$	pulse sampling	Wentworth (1969) [10]
$8.5 \times 10^{-14}$ e)	90% Ar + 10% $\text{CH}_4$	pulse sampling	Wentworth (1969) [10]

- a) Concentration-dependence measurements at constant reaction time.  
 b) Time-dependence measurements at  $[\text{CH}_3\text{Cl}] = 9.2 \times 10^{13} \text{ cm}^{-3}$ .  
 c) As in b), at  $[\text{CH}_3\text{Cl}] = 5.3 \times 10^{15} \text{ cm}^{-3}$ .  
 d) Determined from extrapolation of  $\ln(KT^{3/2})$  versus  $(1/T)$  plot (fig. 1 of ref. [10]) using the thermal rate constant  $k_{\text{th}} = 2.41 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  for  $\text{SiF}_6$  of E. Chen, R.D. George and W.E. Wentworth, J. Chem. Phys. 49 (1968) 1973.  
 e) As in d), from the plateau of the  $\ln(KT^{3/2})$  versus  $(1/T)$  plot.

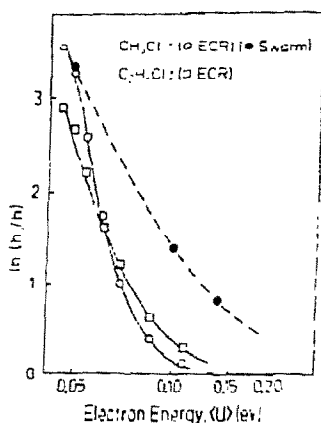


Fig. 4. Energy dependence of the apparent attachment rate of low-energy electrons to  $\text{CH}_3\text{Cl}$  (●) and  $\text{C}_2\text{H}_5\text{Cl}$  (□). Electron-swarm data [7] normalized to ECR results for  $\text{CH}_3\text{Cl}$  (●) were included.

as obtained by the ECR technique, are given in fig. 4. The measurements were taken at constant reaction time and must be regarded as a concentration-dependence study. The other monochlorinated alkanes, i.e., *n*- and *i*-propyl chloride and the isomer butyl chlorides, showed similar behaviour. For comparison, normalized data were included for  $\text{CH}_3\text{Cl}$  (fig. 4) obtained in electron swarm experiments [7] and recalculated [9] using the known electron energy distribution functions in  $\text{N}_2$ . This increase in relative signal intensity with decreasing electron energy should not be related to a separate capture process at thermal energies but

might be due to an energy-dependent scattering process.

### 3.2. Other chlorine-containing molecules

The rate constants obtained for the disappearance of electrons in the presence of  $\text{Cl}_2$  depended strongly on the experimental conditions, particularly on the concentration of the scavenger in the system. From the time-dependence study in the concentration range  $5 \times 10^{11}$  to  $2.1 \times 10^{12} \text{ cm}^{-3}$ , a limiting  $k$ -value of  $3.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  was obtained [29]. At an order of magnitude lower  $\text{Cl}_2$  concentration, a value of  $1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  was measured [21]. A full investigation of the concentration- and time-dependence measurements for the molecules  $\text{Cl}_2$ ,  $\text{HCl}$  and  $\text{CH}_3\text{Cl}$  is in progress [29].

From concentration-dependence measurements at constant reaction time in Ar carrier with NO as electron donor, the rate constants for the thermal electron capture by the molecules  $\text{NOCl}$ ,  $\text{CNCl}$ ,  $\text{COCl}_2$  and  $\text{C}_2\text{H}_5\text{Cl}$  were found to be  $6.9 \times 10^{-10}$ ,  $1.1 \times 10^{-10}$ ,  $5.0 \times 10^{-8}$  and  $4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , respectively (table 5). Except for the  $k$ -value of  $\text{COCl}_2$ , which is a very effective electron scavenger, the other three  $k$ -values must be accepted with reservation as at least upper limits [29].

The energy dependence of the electron capture by  $\text{Cl}_2$  is shown in fig. 5. The capture rate increased sharply from the thermal energy region and reached a very broad maximum around 0.25 eV. No change in

Table 5

Rate constants  $k$  ( $\text{cm}^3 \text{s}^{-1}$ ) for the capture of thermal electrons by chlorinated compounds ( $T = 300 \text{ K}$ )

Compound	$k_{\text{th}}^{\text{a)}$	Carrier gas	Reference
$\text{Cl}_2$	$1.1 \times 10^{-9} \text{ b)}$	Ar + NO	present work
$\text{Cl}_2$	$3.1 \times 10^{-10} \text{ c)}$	Ar	Christodoulides (1975) [29]
NOCl	$6.9 \times 10^{-10}$	Ar + NO	present work
CNCl	$1.1 \times 10^{-10}$	Ar + NO	Mothes (1971) [11]
$\text{COCl}_2$	$5.0 \times 10^{-8}$	Ar + NO	present work
$\text{C}_2\text{H}_3\text{Cl}$	$4.0 \times 10^{-10}$	Ar + NO	present work

a) All values are from ECR measurements.

b) Time-dependence measurements at  $[\text{Cl}_2] = 1.0 \times 10^{11} \text{ cm}^{-3}$ .

c) As in b), at  $[\text{Cl}_2]$  between  $5 \times 10^{11}$  and  $2.1 \times 10^{12} \text{ cm}^{-3}$  (see ref. [29]). The rest of the values in this table are from concentration-dependence measurements.

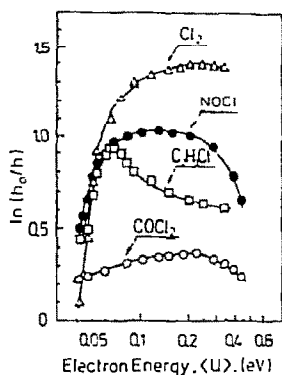


Fig. 5. Energy dependence of the attachment of low-energy electrons to  $\text{Cl}_2$  ( $\Delta$ ), NOCl ( $\bullet$ ),  $\text{C}_2\text{H}_3\text{Cl}$  ( $\square$ ) and  $\text{COCl}_2$  ( $\circ$ ).

the line width with or without  $\text{Cl}_2$  was observed. Similar findings were observed with He carrier gas. The energy dependence for the attachment of electrons to  $\text{COCl}_2$  and NOCl show a broad maximum at 0.22 eV and 0.13 eV respectively. For  $\text{C}_2\text{H}_3\text{Cl}$  a similar behaviour as for the other monochlorinated alkanes was found. In fig. 5, the signal intensity  $\ln(h_0/h)$  was plotted as a function of electron energy for the molecules  $\text{COCl}_2$ , NOCl and  $\text{C}_2\text{H}_3\text{Cl}$ .

#### 4. Discussion

*Comments on the determination of  $k$ -values in chlorinated alkanes at thermal energies* It has been suggested in the preceding paragraph that scattering processes might be responsible for the differences in

rate constants observed for these compounds when the  $k$ -values were obtained in studies of the scavenger concentration-dependence of the capture process at constant reaction time, called  $k_{\text{t}}$ , as compared to studies of the time-dependence of the reaction at constant scavenger concentration, called  $k_{\text{c}}$ .

In ECR experiments this scattering process influences the line shape of the resonance signal [6] and thus causes an apparent decrease in signal intensity resulting in too high rate constants. It has been shown recently [4] that this effect can be applied for the quantitative determination of collision cross sections for non- and weakly-attaching molecules.

A careful analysis of the resonance signal is needed to discriminate between scattering and attachment. Scattering will change the line shape but will not affect the area under the resonance absorption signal which is a measure for the electron concentration. Attachment processes, on the other hand, are related to changes of the area under the absorption signal. Therefore, the experimental signals should be integrated in order to eliminate effects due to changes in line shape. In experiments in which the influence of additives on the signal intensity is followed as a function of the reaction time at constant scavenger concentration, scattering processes will cancel out.

In all types of swarm experiments, in which measurements at constant reaction times are carried out, effective scattering processes will reduce the drift velocity  $w$  in the mixture when the concentration of the scavenger is increased. The calculation of rate data is usually based on the assumption of an unchanged value for  $w$  [32]. If, however, weakly attaching gases

having a high dipole moment are added at concentrations on the order of 0.1% of the total pressure, then the decrease in  $w$  should be taken into account. Decreases in  $w$  show up in broadening of the absorption signal in ECR experiments because the relation [4,21]

$$\langle \sigma \rangle_{\text{RX}} [\text{RX}] \ll \langle \sigma \rangle_{\text{Ar}} [\text{Ar}] \quad (1)$$

is not fulfilled. In eq. (1),  $\langle \sigma \rangle$  is the average total elastic scattering cross section of the chlorinated alkane RX or of Ar carrier gas.

If this was the main reason for some of the discrepancies pointed out, agreement between  $k_c$  and  $k_t$  should improve at electron energies  $> e_{\text{therm.}}$ , where scattering by polar molecules diminishes.

In ECR experiments it is possible to discriminate between scattering and capture processes by measuring concentration dependences or time dependences, separately. In the time dependence study, reactions in the field-free flow tube are monitored. Results obtained in this way are comparable to the microwave conductivity measurements in which the changes of resonance frequency are followed as a function of time. On the other hand, varying the concentration of a polar inefficient scavenger in the system, effects are observed, which predominantly occur within the cavity. In resonance, the electrons are exposed to an accelerating field comparable to conditions in a dc-drift tube. In such a system, addition of a polar gas will influence the energy distribution and the collision frequency. The latter will cause a change of the resonance line shape in ECR experiments. In swarm experiments changes in drift velocity are to be expected. Both effects will show up as an enhanced apparent attachment rate (see fig. 4). For swarm experiments, however, this effect alone cannot explain the large  $k$ -values observed in the thermal energy region for some poor electron scavengers, such as  $\text{CH}_3\text{Cl}$ .

It is suggested that the change in ECR-signal intensity, as shown in fig. 4, is not necessarily due to a genuine attachment process which peaks at low energies. It rather results, in part at least, from elastic scattering which becomes more predominant at low electron energies.

**The reaction path** Attempts were undertaken to elucidate the mechanism of the capture process by calculating the potential energy diagrams for the

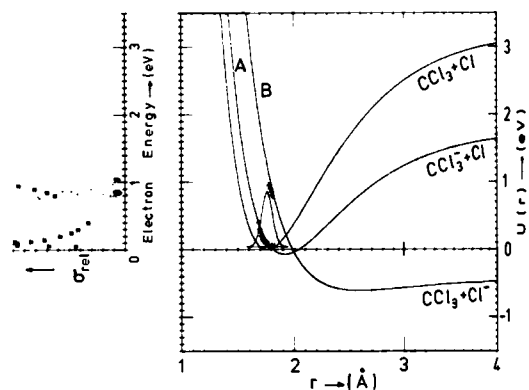


Fig. 6. Potential energy curves for  $\text{CCl}_4$  and  $\text{CCl}_3^-$ . The experimental energy dependence for electron capture is given along the ordinate (see text).

negative ions  $\text{RCl}^-$  together with the neutral molecule  $\text{RCl}$  and describing the reaction path in terms of these energy curves.

It was considered [10] that the excitation of the carbon-chlorine vibrational mode was principally responsible for the dissociative electron capture process, since dissociation leads to the halide ion  $\text{Cl}^-$  plus the organic radical. The Morse function was selected to approximate the potential energy of the neutral molecule as a function of C-Cl bond distance. The ionic states were approximated through an empirical approach suggested by Wentworth and coworkers [10,17,18] and through the reflection method described by Hagstrum and Tate [33]. Experimental results from the ECR investigation were used together with swarm and beam data, respectively, found in the literature.

**$\text{CCl}_4$**  The potential diagram for  $\text{CCl}_4$  shown in fig. 6 has been calculated with the aid of the experimental data compiled in table 6.

Using an electron affinity for the fragment  $\text{CCl}_3$  of 1.43 eV [34] and a value  $U_{\text{max}}$  of  $\sim 0.08$  eV for the electron energy of the peak of the attachment process, curve A is obtained. At  $U_{\text{max}} \approx 0$  eV, a slightly lower potential curve resulted. Curve B is obtained using  $\text{EA}(\text{Cl}) = 3.613$  eV [35] for the attachment process beginning at  $\sim 0.7$  eV [13] with a possible  $U_{\text{max}}$  around 1 eV. The higher energy process could not be observed in the present investigation

Table 6  
Parameters used for the calculation of the potential energy diagrams for the molecules  $\text{CCl}_3$  and  $\text{Cl}_2$

Parameter	Value a,b)	Parameter	Value a,b)
$D(\text{CCl}_3-\text{Cl})$	3.165 <sup>(1)</sup>	$D(\text{Cl}-\text{Cl})$	2.475 <sup>(12)</sup> , 2.4734 <sup>(13)</sup>
$EA(\text{CCl}_4)$	2.12 <sup>(2)</sup>	$EA(\text{Cl}_2)$	2.36 <sup>(14)</sup>
$EA(\text{CCl}_3)$	1.435 <sup>(2)</sup>	$U_{\text{max}}$	$\sim 0.25$ <sup>(4)</sup> , 2.4 <sup>(15)</sup>
$EA(\text{Cl})$	3.613 <sup>(3)</sup>	$E_{\text{act}}$	0.05 <sup>(16)</sup>
$U_{\text{max}}$	$\sim 0$ <sup>(4-7)</sup> , $\sim 0.08$ <sup>(4)</sup> , $> 0.7$ <sup>(6,7)</sup>	$\omega_0$	564.9 $\text{cm}^{-1}$ <sup>(12)</sup> , 559.7 $\text{cm}^{-1}$ <sup>(13)</sup>
$E_{\text{act}}$	$-0.025$ <sup>(8)</sup> , $-0.026$ <sup>(9)</sup>	$r_0$	1.988 $\text{\AA}$ <sup>(12)</sup> , 1.9878 $\text{\AA}$ <sup>(13)</sup>
$\omega_0$	778 $\text{cm}^{-1}$ <sup>(10)</sup>		
$r_0$	1.761 $\text{\AA}$ <sup>(11)</sup>		

a) All values are given in eV (1 eV = 23.063 kcal mole<sup>-1</sup>), except as noted.

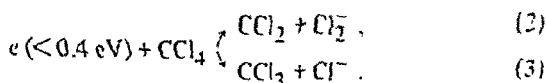
b) The numbers between parentheses refer to the following publications.

- (1) J.A. Kerr, Chem. Rev. 66 (1966) 465.
- (2) A.I. Gaines, J. Kay and I.M. Page, Trans. Faraday Soc. 62 (1966) 874.
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since it is beyond the energy range accessible to the ECR technique. The sections of curves A and B (shown as (+) in fig. 6) were determined directly through the reflection method [33] from the experimental relative cross sections,  $\sigma_{\text{rel}}$ , shown in the ordinate of fig. 6 (indicated by \*). The structure in the cross section curve, as shown in fig. 1, might indicate the following two possibilities:

- (a) Occurrence of different chemical processes in the low energy range  $< 0.4$  eV resulting from the formation of the negative ions in different states.
- (b) Observation of a vibrational structure in a negative ion state.

(a) The following net electron attachment processes can be visualized:



On thermodynamic grounds the occurrence of process (2) can be excluded since it is expected to have a high activation energy. With the heats of formation  $\Delta H_f^0$  for  $\text{CCl}_4$  and  $\text{CCl}_2$ , given in table 7, and an electron affinity for  $\text{Cl}_2$  of 54.4 kcal mole<sup>-1</sup> [36], the heat of reaction  $\Delta H_r^0$  of process (2) is calculated as  $\sim 23$  kcal mole<sup>-1</sup> through the relation

$$\Delta H_r^0 = \Delta H_f^0(\text{CCl}_2) + \Delta H_f^0(\text{Cl}_2^-) - \Delta H_f^0(\text{CCl}_4) \quad (4)$$

Although  $\text{Cl}_2^-$  was observed in electron impact studies ( $\sim 45$  times less abundant than  $\text{Cl}^-$ ) no such diatomic negative ion could be formed by simple dissociation from  $\text{CCl}_4$  [7].

The electron affinity for  $\text{CCl}_4$  was reported [34] as 2.12 eV and the C-Cl bond energy in the neutral molecule as  $\sim 3.16$  eV [38]. With these values and the electron affinity for Cl of 3.613 eV [35], the carbon-chlorine bond energy in the  $\text{CCl}_3^-$  ion in the ground



Table 7  
Heats of formation of neutrals and ions in kcal mole<sup>-1</sup> a)

Species	$\Delta H_f^\circ$	Species	$\Delta H_f^\circ$
Cl <sup>-</sup>	-55.9 <sup>(1)</sup> , -58.8 <sup>(2)</sup>	C <sub>2</sub> H <sub>5</sub> Cl	-25.1 <sup>(3,9)</sup>
Cl	28.9 <sup>(1)</sup> , 28.94 <sup>(3)</sup> , 29.1 <sup>(2)</sup>	C <sub>2</sub> H <sub>5</sub>	23.7 <sup>(3)</sup> , 25.7 <sup>(6)</sup> , 26 <sup>(7)</sup>
Cl <sub>2</sub> <sup>-</sup>	-58.8 <sup>(2)</sup>	NOCl	12.37 <sup>(1)</sup>
Cl <sub>2</sub>	0 <sup>(1,3,4)</sup>	NO	21.6 <sup>(10)</sup>
CCl <sub>2</sub>	56.5 <sup>(5)</sup>	CNCl	32.2 <sup>(11)</sup> , 32.80 <sup>(12)</sup> , 32.97 <sup>(1)</sup>
CCl <sub>3</sub>	18.6 <sup>(6)</sup> , 19 <sup>(2)</sup> , 19.2 <sup>(7)</sup>	CN	101 <sup>(7)</sup> , 103.3 <sup>(13)</sup> , 109 <sup>(6)</sup> , 111 <sup>(1)</sup>
CCl <sub>4</sub>	-24.6 <sup>(2)</sup> , -25.5 <sup>(3)</sup> , -26 <sup>(1)</sup>	COCl <sub>2</sub>	-53.3 <sup>(3)</sup>
CHCl <sub>3</sub>	-24 <sup>(3)</sup> , -24.4 <sup>(8)</sup> , -25.0 <sup>(1)</sup>	COCl	-3.7 <sup>(11)</sup> , -3.8 <sup>(3)</sup>
CH <sub>2</sub> Cl <sub>2</sub>	-21 <sup>(3)</sup> , -22.1 <sup>(2)</sup>	CO	-26.4 <sup>(3)</sup> , -26.42 <sup>(1)</sup>
CH <sub>3</sub> Cl	-19.6 <sup>(3,9)</sup>	C <sub>2</sub> H <sub>3</sub>	64 <sup>(6)</sup> , 65 <sup>(4)</sup>
CH <sub>3</sub>	32.1 <sup>(9)</sup> , 33.2 <sup>(2)</sup> , 34 <sup>(7)</sup>	C <sub>2</sub> H <sub>3</sub> Cl	7.5 <sup>(3)</sup>

a) The numbers between parentheses refer to the following publications

- (1) D.R. Stull, JANAF thermochemical tables, PB 168 370-1.2.3 (Dow Chemical Company, Michigan, USA, 1966/68).
- (2) J.J. De Corpo, D.A. Bafus and J.L. Franklin, *J. Chem. Phys.* 54 (1971) 1592.
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electronic state is estimated through the relation

$$D_0(\text{CCl}_4^-) = D_0(\text{CCl}_4) + \text{EA}(\text{CCl}_4) - \text{EA}(\text{Cl}) \quad (5)$$

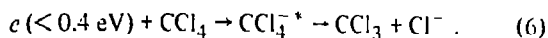
as 1.67 eV. Thus, the parent negative ion  $[\text{CCl}_4^-^*]$  formed in the capture process, will dissociate, according to process (3) if no stabilizing collision remove the excess vibrational energy.

Different electronic states, as evidenced for Cl<sub>2</sub> in the calculations by Gilbert and Wahl [39], are expected to have a larger energy spacing than the one observed in this work, where the peak at ~0.08 eV (see fig. 1) is attributed to an excited state. The high capture cross section, equivalent to  $k = 4.1 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ , requires the electron scavenging process to have another maximum at thermal or subthermal energies. No maximum was obtained for this process in the present study, although the cross section increased with decreasing microwave power input. No informa-

tion can be obtained in ECR experiments on the possibility that the reaction occurs for electrons with energy less than zero, such as suggested for iodine from the analysis of charge-transfer bands [40,41]. Electron transfer and formation of CCl<sub>4</sub><sup>-</sup> ions, however, has recently been observed [42] in crossed beam experiments with K atoms, indicating that a capture process is possible for electrons with less than zero energy.

(b) The second possibility is suggested by the coincidence between the curve A obtained using a modified Morse function [18] and the low-energy part of the cross section curve reflected on the density distribution function  $\psi_0^2$  of the neutral parent molecule CCl<sub>4</sub>. Good agreement also resulted from the reflection of the high energy part on the dissociative potential curve B. Although not too much significance is placed on this coincidence, the assumption of an inter-

mediate state A with a potential minimum would allow for the presence of a structure in the cross section curve of fig. 1 which can be related to a vibrational structure of the negative ion  $\text{CCl}_4^-$ . A vibrational spacing of the order of  $\sim 0.1$  eV is also to be expected for this molecule. The difficulty of detecting the ion  $\text{CCl}_4^-$  in mass-spectrometric investigations can also be understood on the basis of the calculated potential energy curves: The intermediate negative parent ion will cross-over from A to state B which is assumed to possess a shallow minimum and may then dissociate. Thus the capture of thermal electrons by  $\text{CCl}_4$  could be described by the process



The pressure invariance of the  $k$ -value for the capture process for  $\text{CCl}_4$ , as determined by Warman and Sauer [14], can also be understood with this model.

The involvement of two separate states in the dissociative capture process at low energies has been suggested in several earlier studies [9,13,23-26,43,44] although the pronounced structure at the energies seen in this ECR study was not observed. It is noted that electron-beam studies cannot resolve the existence of such a structure at thermal energies due to the limitations of the very poor energy resolution in this energy region and the observed [43] high reactivity of  $\text{CCl}_4$  on the heated filament.

$\text{Cl}_2$  The potential energy diagram for the neutral molecule and for a number of negative ion states has recently been calculated by Gilbert and Wahl [39] using the self-consistent field (SCF) approximation. Thus, the experimental data from the present ECR study can be directly compared with the results of this SCF calculation. In fig. 7 sections of the calculated [39] potential energy curves for the states  $\text{Cl}_2^- * (^2\Sigma_u^+)$ ,  $\text{Cl}_2^- * (^2\Pi_g)$  and the ground state of the  $\text{Cl}_2$  molecule were plotted. The values for the parameters used in this calculation are given in table 6. In the ordinate, indicated by \*, the experimental ECR and mass-spectrometric results [45] of the energy dependence for the electron capture at lower ( $\leq 0.4$  eV) and higher ( $> 1.6$  eV) energies were also plotted. From mass-spectrometric studies the  $\text{Cl}^-$  resonance capture peak was found [45] to have an onset energy at  $\sim 1.6$  eV and a peak maximum at 2.4 eV. This part of the capture curve is beyond the capabilities of the ECR technique.

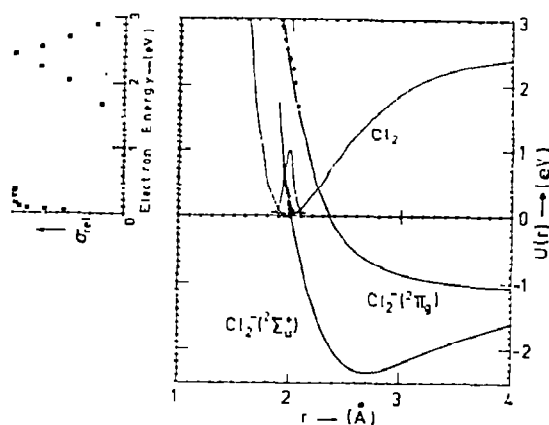


Fig. 7. Potential energy curves for  $\text{Cl}_2$  and  $\text{Cl}_2^-$ . The experimental energy dependence for electron capture is given along the ordinate (see text).

It is seen from fig. 7 that using the reflection method, very good agreement between calculated and experimental results was obtained.

From the high energy process in the mass-spectrometric study [45] it is most probable that the  $\text{Cl}^-$  ions were being produced by transitions to the highly repulsive excited  $\text{Cl}_2^- * (^2\Pi_g)$  state in a dissociative electron attachment process. The observed low energy process in this study can be assigned to an electron capture process via the excited  $\text{Cl}_2^- * (^2\Sigma_u^+)$  state. Dissociation, leading to  $\text{Cl} + \text{Cl}^-$ , is likely to follow the formation of the intermediate temporary negative ion  $\text{Cl}_2^- *$  with possible stabilization at high pressures. Additional support for the low energy assignment is the small activation energy of  $\sim 0.05$  eV for the thermal capture process observed in another ECR study [29].

$\text{NOCl}$  From the dissociation energy of the  $\text{NO}-\text{Cl}$  bond of 1.6 eV [46] and the electron affinity of 3.613 eV [38] for  $\text{Cl}$ , it can be deduced that capture of thermal electrons by  $\text{NOCl}$  will lead to dissociation into the fragments  $\text{NO}$  and  $\text{Cl}^-$ . On the other hand, the heat of reaction for this dissociative process is highly exothermic, as calculated from the heats of formation for  $\text{NOCl}$ ,  $\text{NO}$  and  $\text{Cl}^-$  (see table 7). The Wentworth approach [8,10,18] for ionic potential energy diagrams was not possible to be applied for  $\text{NOCl}$ .

**CNCl** The bond energy  $D(\text{CN}-\text{Cl})$  is reported [47] to be 4.33 eV, while the heat of formations for CNCl and CN are 32.97 kcal mole<sup>-1</sup> [48] and 103.3 kcal mole<sup>-1</sup> [49], respectively. Various values of the electron affinity for CN were reported [32] in the range 3.16–3.8 eV. On energetic grounds dissociation following thermal electron capture by CNCl may then be excluded.

**COCl<sub>2</sub>** The appearance of a Cl<sub>2</sub><sup>-</sup> peak was observed in an ICR mass-spectrometric study [50] at low electron energies. Thus, it is assumed that electron capture by this molecule, which is a very effective scavenger, can be described by



This process is highly exothermic with a heat of reaction of -32 kcal mole<sup>-1</sup>, as can be obtained from the values given in table 7.

**C<sub>2</sub>H<sub>3</sub>Cl** Electron capture by C<sub>2</sub>H<sub>3</sub>Cl might lead to dissociation into the fragments C<sub>2</sub>H<sub>3</sub> and Cl<sup>-</sup>, although the exothermicity of this process is only about -1 kcal mole<sup>-1</sup>.

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