ELSEVIER

Destruction of halogenated methanes by non-electron capture processes within an electron capture detector

J.A. Culbertson, E.P. Grimsrud*

Department of Chemistry, Montana State University, Bozeman, MT 59717, USA

Abstract

The rates of destruction of 8 halogenated methanes by processes other than dissociative electron capture (EC) reactions have been measured within an ionization cell for which conditions are identical to those existing within an electron capture detector (ECD) for gas chromatography (GC). It is shown that additional destructive processes are distinctly operative for CCl_4 and $CBrCl_3$, but not for CH_2Br_2, CH_3I, $CHBr_3$, $CHFBr_2$, CF_2Br_2, and $CHCl_3$. In these measurements, $CFCl_3$ serves as a reference compound for which no extra-EC destruction with an ECD is assumed. This assumption is based on previous uses of $CFCl_3$ as a reference compound in related studies and on additional measurements provided in the present study. It is shown that the most likely mechanism for the extra-EC destruction of CCl_4 is a reaction of this compound on the walls of the ion source which have been chemically activated by the deposition of gas phase free radicals. The rate of this wall-assisted destruction of CCl_4 is increased with use of lower temperatures and approaches unit efficiency upon wall collisions at room temperature. The implications of these results for the quantitative analysis of halogenated compounds by the ECD are discussed.

Keywords: Detectors, GC; Electron capture detector; Methanes, halogenated

1. Introduction

Of the numerous detectors that have been applied to the analysis of gas chromatographic (GC) effluents [1], the electron capture detector (ECD) has proven to be one of the most powerful [2]. This is due, in part, to its unmatched sensitivity to a wide variety of halogenated compounds that have been shown to be of environmental importance. Throughout this period of use, an increased understanding of the ECD's quantitative response has been continuously sought in order to gain various advantages in analyses, such as increased sensitivity, selectivity, or quantitative reproducibility [2–4]. In some of these studies, the goal has been to understand the ECD's quantitative response so completely that the ECD could be used as a gas phase coulometer for which no calibration standards would be necessary [5,6]. In all of these endeavors, a common assumption has been that the primary means by which the compound of interest is destroyed in an ECD is by the EC reaction itself. This is not an unreasonable assumption in that the rate constants for electron capture by EC-active compounds are generally much greater than any other gas phase processes that might be envisaged to occur within an ECD [6]. However, in recent studies of the chemical dynamics operative within ion sources used for high-pressure electron-

*Corresponding author.

capture mass spectrometry (HPECMS), it has been shown that surface-assisted destruction processes are operative and competitive with EC reactions under the low-Torr pressure conditions of those ion sources [7,8]. In view of the similarities that exist between the ECD and the HPECMS ion sources, is reasonable to consider the possibility that wall-assisted, extra-EC processes might also be operative within the ECD. In order to address this question, experiments are described here from which the magnitude of extra-EC processes in the destruction of several EC-active, halogenated methanes in an ECD has been determined.

2. Experimental

The principal experimental apparatus used here is shown in Fig. 1. It includes a gas chromatograph (GC) equipped with an electron capture detector (ECD) (Hewlett-Packard Model 5890A). Housed within the GC oven are two GC columns that are separated by a stainless-steel reaction block containing the two cylindrical cells shown in Fig. 2. One of these cells is termed the "reactor cell" because it contains a 13 mCi ^{63}Ni-on-Ni foil (DuPont-Merck)
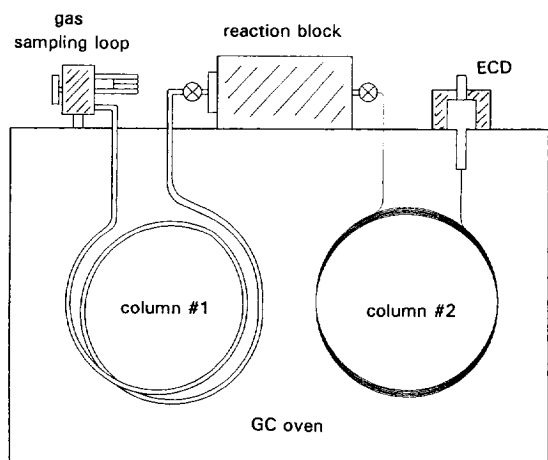

Fig. 1. Gas chromatographic apparatus used here for measurements of extra-EC destruction processes. Detection is by an electron capture detector (ECD). A more detailed view of the reaction block is provided in Fig. 2. The temperature of the reaction block was variable from 30° to 180°C. The temperature of the GC oven was maintained at 30°C for all experiments.
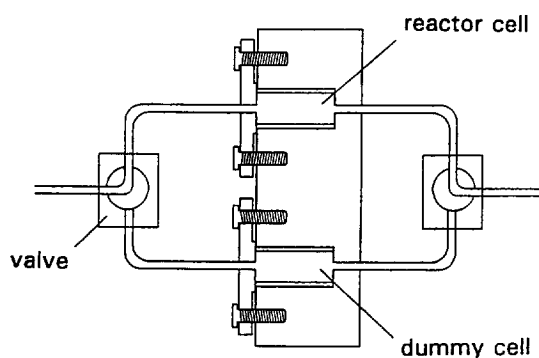

Fig. 2. The reaction block includes two 1.5 cm³ cells of cylindrical shape. The reactor cell has a radioactive ^{63}Ni-on-Ni foil that causes continuous ionization of the gas within it. The dummy cell has a non-radioactive Ni foil. The GC carrier flow can be passed through either one of these cells by control of the two valves shown.

that causes a low level of ionization in this cell by beta particle emission. For the present study, the effective activity of the ^{63}Ni foil was reduced by covering the foil with a stainless-steel mesh that has only 3% open area. This reduced the population of thermal electrons in the reactor cell to a level that caused no more than about 90% destruction of any compound studied. The other cell shown in Fig. 2 is termed the "dummy cell" because it does not contain a radioactive Ni foil. By control of the valves shown in Fig. 2, the GC carrier gas flow stream could be passed through either the reactor or dummy cell, as desired, with pure carrier gas then flowing through the unused cell. Since the volumes (1.5 cm³) and shapes (1.0 cm diameter, 1.9 cm length) of the reactor and dummy cells are identical, the chromatographic retention times and peak widths of all compounds as measured by the ECD in Fig. 1 were independent of which cell was chosen. The temperature of the reaction block was variable from 30°C to 180°C.

In preliminary experiments, the significance of having a stainless-steel cylindrical wall versus a Ni cylindrical wall within the dummy cell was tested by comparing the ECD responses observed for all compounds with and without placement of a non-radioactive Ni foil within the dummy cell. This change was found to cause no detectable alterations in the ECD responses observed for all compounds after passage through the dummy cell. In addition,

changes in the temperature of the dummy cell from 30° to 180°C also caused no changes in the ECD responses of all nine of the compounds investigated here. From these preliminary experiments, it was concluded that no destruction of the compounds occurs in the dummy cell under any of these conditions. Nevertheless, in all experiments reported here, the non-radioactive Ni foil was left in the dummy cell because Ni is generally thought to provide a less reactive surface than stainless-steel. This provided additional assurance to the general assumption made here that no destruction occurs within the dummy cell. Column #2 in Fig. 1 is an SE-54 fused-silica wide-bore (diameter=0.53 mm) capillary column of 12 m length (Alltech). Column #1 is a 0.3175 cm stainless-steel column of either 3.05 m or 7.62 m length packed with 10% SF-96 on chromosorb W (Alltech). The GC oven was maintained at 30°C. The carrier gas was nitrogen that was first passed through oxygen-removing (Alltech oxy-trap) and water-removing ($CaSO_4$ and 13X molecular sieve) traps. The carrier gas flow-rate was 32 cm^3 min^{-1}, as measured at the exit of the ECD. The absolute pressure within the reaction cell was 1.33 atm (372 Torr above the local ambient atmospheric pressure of 636 ± 10 Torr). Under these conditions, the volumetric flow-rate, F, of carrier gas through the reaction cell is 0.33 cm^3 s^{-1}.

Gaseous samples of all compounds were prepared by injection of known quantities of the pure substances into large glass carboys that contained above-ambient pressures of nitrogen. These samples were then introduced to the GC by use of a 0.25 cm^3 gas-sampling loop. Pairs of chromatograms were then obtained, first with the GC carrier gas flow passing through the dummy cell and then with the carrier gas flow passing through the reaction cell, as shown in Fig. 3. In these paired analyses, the ratio of peak area responses is of fundamental interest. However, since the peak heights, H_0 and H, were found to be proportional to their respective peak areas, the ratios of peak heights, H_0/H, were used as a measure of response ratios. Paired analyses of this type were repeated at least three times for each compound of interest at each temperature of interest. Care was taken to use only very small sample sizes (generally less than 2 ppb of the compound of interest in nitrogen), where changes in the amount of
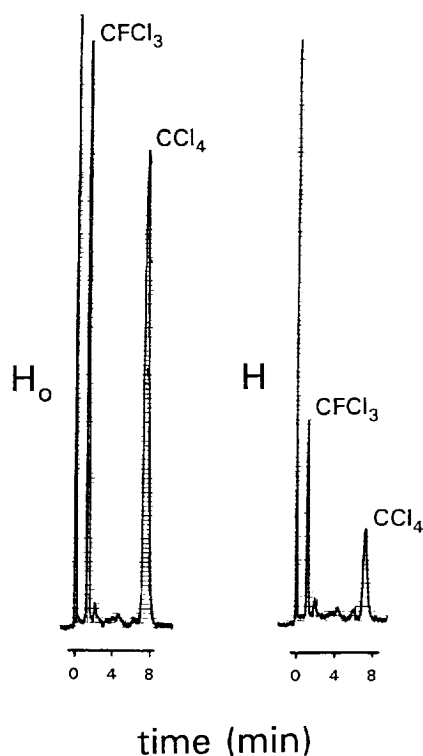

Fig. 3. Typical GC–ECD analyses of gas sample containing about 1.0 ppb $CFCl_3$ and 1.0 ppb CCl_4 in nitrogen obtained with the apparatus shown in Figs. 1,2. For the ECD responses labeled H_0, the carrier gas flow was passed through the dummy cell shown in Fig. 2. For the ECD responses labeled H, the carrier gas flow was passed through the reactor cell. The first peak in each chromatogram was due to trace oxygen present in the samples. The temperature of the reaction block was 180°C. The ratio of responses, H_0/H, for $CFCl_3$ was used to determine the electron population existing within the reactor cell. The ratio of responses, H_0/H, for CCl_4 was used to determine the extent of CCl_4 destruction by the sum of all processes occurring within the reactor cell.

sample injected did not change the measured response ratios, H_0/H. Under these small-sample conditions, only a small fraction of the electron population within the reactor cell is consumed as the EC-active compound passes through the cell, thereby ensuring that the total electron population within the reactor cell remains relatively constant at all times.

In order to change the nature of the positive ions present within the reactor cell, various amounts of trimethylamine (TMA) were added to the carrier gas flow [9,10]. This was accomplished by the injection

of gaseous TMA into a 1.0-l stainless-steel vessel that was inserted in the carrier gas flow stream immediately ahead of the GC. The concentrations of TMA in the nitrogen buffer gas varied from about 1 ppm up to about 1 part per thousand. As expected [9,10], the addition of TMA to the carrier gas had no observable effect on the standing current of the ECD or on the electron density existing within the reactor cell.

In the interpretation of the data to be presented here, it is necessary to know the EC rate constants for the compound under consideration. Since these were not known for three of the halogenated methanes, several EC rate constants have also been measured here at 120°C in atmospheric pressure nitrogen buffer gas using an independent ECD-based method [11]. By this method, the response of a specialized tandem ECD to the compound of interest is compared to that of $CFCl_3$, whose EC rate constant is well known. In these experiments, conditions within the ECD are carefully controlled so that the observed molar responses are assured to be directly proportional to the EC rate constants of each compound.

3. Treatment of data

In the ^{63}Ni reactor cell shown in Fig. 2 (reactor cell), a population of electrons and positive ions will be continuously maintained throughout its volume [12] as pure nitrogen buffer gas is passed through it at a pressure of 1.33 atm. As small amounts of a compound, RX, are passed through the reactor cell, dissociative electron capture (reaction 1) will occur with rate constant, k_{ec}, thereby destroying the original molecule, RX.

$$RX + e \rightarrow R + X^- \tag{1}$$

The molecule RX may or may not also be destroyed by unknown extra-EC processes. A first-order rate constant, k_d, will be used to represent the rate at which these destructive extra-EC processes occur. Because the dimensions of the reactor cell are large relative to the diameter of its entrance and exit ports, a compound entering the cell with the carrier gas flow will tend to be well-mixed throughout the

reaction volume so that a single expression [RX], can be used to describe its steady-state concentration. The following conservation equation can then be written for the production and loss of RX within the reactor:

$$[RX]_0 F/V = [RX] k_{ec}N_e/V + [RX] k_d + [RX] F/V \tag{2}$$

where $F = 0.33$ cm^3 s^{-1} is the volumetric gas flow through the reactor cell, $V = 1.50$ cm^3 is the volume of the cell, $[RX]_0$ is the concentration of RX in the gas stream that is flowing into the reactor cell, N_e is the number of electrons within the reactor, and k_{ec} and k_d have been defined above. While the left side of Eq. (2) describes the rate of RX production by flow into the reactor, the three terms on the right provide the rate of RX loss by reaction 1, by extra-EC processes, and by flow out of the reactor.

In the paired chromatograms shown in Fig. 3, it is reasonable to assume that the peak heights observed when the dummy cell is used will be proportional to the quantity, $[RX]_0$, since no destruction of RX is expected in this cell. Similarly, it is reasonable to assume that the peak heights observed when the reactor cell is used will be proportional to the quantity, [RX]. By combination of the resulting relationship, $H_0/H = [RX]_0/[RX]$, with Eq. (2), the expression for k_d shown by Eq. (3) is obtained:

$$k_d = (H_0/H - 1.0 - k_{ec}N_e/F) F/V \tag{3}$$

For those cases where k_d is determined to be zero, Eq. (3) can be rearranged into the form of Eq. (4),

$$k_{ec} = (H_0/H - 1.0) F/N_e = \alpha \tag{4}$$

where the combination of measured parameters shown (hereafter to be referred to as α) on the right side should be equal to k_{ec}.

The number of electrons in the reactor cell, N_e, was determined by use of the reference compound, $CFCl_3$, for which k_{ec} values have been previously determined over the temperature range of interest here [13] and for which k_d is assumed to be zero at all temperatures. The suggestion that $k_d = 0.0$ for $CFCl_3$ was indicated in a previous study of the EC chemistry of SF_6 in which $CFCl_3$ served as a reference compound [11]. In that study, accurate EC rate constants for SF_6 were obtained if $k_d = 0.0$ was

assumed for $CFCl_3$. Additional support for the validity of this assumption will also be provided in the present study, as discussed in Section 4. By application of Eq. (4) to measurements of H_0/H for $CFCl_3$, N_e was found to be about 8.4×10^6, 6.4×10^6, 4.0×10^6 and 2.4×10^6 electrons at 30, 75, 120 and 180°C, respectively. An exact determination of N_e was made at the moment of every measurement

reported here by inclusion of the reference compound, $CFCl_3$, in each gaseous sample analyzed.

4. Results and discussion

The magnitudes of k_d [from Eq. (3)] for all compounds studied here are listed in Table 1. For

Table 1
Summary of results

Compound	Temp. (°C)	$N_e \times 10^{-6}$ [a]	H_0/H [b]	$\alpha \times 10^{x}$ (cm^{-3} s^{-1})[c]	$k_{ec} \times 10^{x}$ (cm^{-3} s^{-1})[d]	k_d [e] (s^{-1})	k_{dif} [f] (s^{-1})	Φ [g]
CH_2Br_2	30	8.4	3.1	8.4	9.4[h]	−0.06		0
	75	6.4	2.6	8.6				
	120	4.0	2.6	13.0				
	180	2.4	2.1	16.0	16.0[h]	−0.01		0
CH_3I	30	8.4	4.6	14.0	12.0[h]	0.12		0
	75	7.2	3.9	14.0				
	120	5.6	3.4	14.0	14.0[i]	0.00		0
	180	3.2	2.7	18.0	18.0[h]	−0.01		0
CCl_4	30	10.0	22.7	74	39[j]	2.2	2.5	0.88
	75	7.3	18.5	82		2.0[k]	3.1	0.65
	120	5.8	13.7	74	38[j]	1.32	3.7	0.35
	180	3.2	7.4	68	37[j]	0.62	4.5	0.13
CCl_3Br	30	12.0	5.6	13.0				
	75	7.9	7.8	29				
	120	6.5	7.6	35	11.0[i]	0.97	4.4	0.23
	180	4.0	6.1	43				
$CHBr_3$	30	8.5	4.6	14.0				
	75	5.1	2.6	11.0				
	120	5.0	2.3	8.8	13.0[i]	−0.15		0
	180	3.4	1.6	6.1				
$CHFBr_2$	30	8.4	4.0	12.0				
	75	6.4	3.3	12.0				
	120	4.0	2.6	14.0	15.0[i]	−0.05		0
	180	2.4	2.4	19.0				
CF_2Br_2	30	8.4	9.1	33	31[j]	0.05		0
	75	6.4	8.7	41				
	120	4.0	6.4	46				
	180	2.4	3.9	41	40[j]	0.00		0
$CHCl_3$	180	3.4	1.15	1.5	1.7[j]	−0.01		0

[a] Population of electrons existing in the reactor cell determined by the observed responses to the reference compound, $CFCl_3$.
[b] Ratio of ECD responses observed with use of the dummy and reactor cells.
[c] A combination of experimentally determined parameters as indicated in Eq. (4) that is expected to equal k_{ec} for those cases where k_d is found to be zero.
[d] Independently determined values of k_{ec} obtained either from the literature or in the present study.
[e] Rate constant for the extra-EC destruction of the compound as determined from present measurements and Eq. (3).
[f] Calculated first-order rate constant for diffusion of the compound to the walls of the reactor cell.
[g] Efficiency for destruction of the compound upon contact with the walls of the reactor cell.
[h] From Ref. [14].
[i] From present EC rate constant measurement determined at one atmosphere pressure as described in Section 2 and in Ref. [13].
[j] From Ref. [15].
[k] This value is obtained by assuming that k_{ec} at 75°C will be the same as that observed at 30° and 120°C.

each compound, an entry for k_d is made only at those temperatures for which k_{ec} is known either from the literature [12,14,15] or from the independent k_{ec} determinations made in the present study at 120° Section 2. The compounds for which destruction by extra-EC processes is clearly indicated in Table 1 are those for which the determined magnitude of k_d is in excess of about 0.15 s^{-1}. Measurements of k_d that fell within the range 0.00 ± 0.15 s^{-1} were not considered to indicate a detectable level of extra-EC destruction of that compound, because this range of k_d values could be attributed to the estimated uncertainties of the k_{ec} values used here (about $\pm 20\%$).

For CHCl$_3$, measurements are reported in Table 1 only at the highest temperature, 180°, where the measured ratio, H_0/H, differed measurably from unity and, therefore, Eq. (3) could be meaningfully applied. At all lower temperatures, $H_0/H = 1.0$ was observed. This result was not unexpected since the k_{ec} values for CHCl$_3$ are known to be extremely low at these lower temperatures [15]. However, these measurements of CHCl$_3$ at the lower temperatures are noteworthy in that they clearly indicate that $k_d = 0.0$ for CHCl$_3$ at the lower temperatures.

It is seen in Table 1 that a detectable level of extra-EC destruction ($k_d > 0.15$ s^{-1}) was observed only for CCl$_4$ and CBrCl$_3$. Since k_{ec} for CBrCl$_3$ is known only at 120°C, the magnitude of its k_d could be determined only at this temperature. For the case of CCl$_4$, k_{ec} is known at three temperatures and can be reasonably estimated at the fourth, so that its k_d could be deduced at all temperatures indicated. Note that these measurements clearly indicate that k_d for CCl$_4$ decreases with increased temperature. It is also noted that no extra-EC destruction of CH$_3$I was detected at any temperature. This is somewhat surprising in view of the fact that the C–I bond in CH$_3$I is much weaker (by about 80 kJ/mol) than the C–Cl bonds in CCl$_4$ [16].

4.1. Mechanism of extra-EC destruction

In attempting to identify the extra-EC mechanism by which CCl$_4$ and CBrCl$_3$ are destroyed in an ECD, three possibilities have been envisaged. The first is that the positive ions, whose population is equal to that of electrons [11], destroy these compounds by

ion–molecule reactions. This possibility does not seem likely in that the rate constants for ion–molecule reactions could not be greater than about 0.01 times the EC rate constant for CCl$_4$ [17]. Nevertheless, to test this possibility, about 1 ppm trimethylamine was added to the carrier gas stream in order to convert the positive ions within the reactor cell to a more stable and unreactive set of positive ions [9,10]. As expected, this change had no significant effect on the extent of CCl$_4$ destruction within the reaction cell, thereby ruling out this possibility. A second possible explanation for the extra-EC destruction of CCl$_4$ and CBrCl$_3$ is the reaction of these compounds with gas phase free radicals that are also produced in the beta irradiation of the carrier gas. However, the rate constants for these reactions would be at least three or four orders of magnitude less than the EC rate constant of CCl$_4$ [7]. Therefore, this possibility also does not seem likely. A third possibility is that CCl$_4$ reacts with reactive free-radical species that have been deposited on the walls of the reactor cell. These reactive species originate from the continuous irradiation of the carrier gas and once formed, will have a significant propensity for adsorption onto the walls. This general process has been shown to be operative and competitive for fast EC reactions in closely-related ion sources used for chemical ionization mass spectrometry [7,8]. In order to further assess the feasibility of this potential explanation, the rate constants for the first-order diffusion of CCl$_4$ and CBrCl$_3$ to the surface of the reactor cell, k_{dif}, have been calculated here using a set of equations described elsewhere [7] and are also listed in Table 1. The fact that k_{dif} is greater than the measured value of k_d in all cases supports the suggestion that diffusion to the cell walls, followed by reaction at the walls, could be the means by which extra-EC destruction occurs. Within this wall-reaction model, the efficiency of reaction, Φ, upon contact of the parent molecule with the walls will be given by $\Phi = k_d/k_{dif}$ and these values are also listed in Table 1 for CCl$_4$ and CBrCl$_3$. It is interesting to note that Φ for CCl$_4$ is near unity at 30°C and decreases continuously with increased temperature so that only about one-tenth of the CCl$_4$ wall collisions result in destruction at 180°C. An inverse temperature dependence of this general type is consistent with the expectation that the adsorption of gas phase

reactive species to the walls of the ion source would be disfavored by increased temperatures.

4.2. Verification of reference compound behavior

The results reported in Table 1 also provide very strong support for the assumption described in Section 3 that $k_d = 0.0$ for the reference compound, $CFCl_3$. If $k_d > 0$ for $CFCl_3$, the real magnitudes of N_c would have been less than those indicated in Table 1 for all experiments. In that case, the values of k_d and Φ for CCl_4 determined by measurements of H_0/H and Eq. (3) would then have been even larger than those indicated in Table 1. This would have lead to $\Phi > 1.0$ for CCl_4 at 30°C, which, of course, is not possible. Also, it is noted in Table 1 that $k_d \approx 0.0$ is deduced for six different compounds and at more than one temperature for three of these six compounds. It will also be recalled that $H_0/H = 1.0$ was observed in all $CHCl_3$ measurements attempted here at the lower temperatures, clearly indicating that $k_d = 0.0$ for this compound at the lower temperatures. The most plausible explanation for this set of $k_d \approx 0$ measurements is that the k_d values for these six compounds and for $CFCl_3$ are, in fact, equal to zero. As will be shown in Section 4.3, the assumption of $k_d = 0.0$ for $CFCl_3$ also leads to k_{ec} determinations for five of these six compounds that are in excellent agreement with independent measurements of k_{ec}.

4.3. Electron capture rate constants

As mentioned above in the discussion of Eq. (4), for those cases where k_d is found to be zero, the measured parameter, α, is expected to be equal to k_{ec} for that compound. Inspection of Table 1 supports this expectation, where it is seen that α is, indeed, nearly equal to k_{ec} for the cases, CH_2Br_2, CH_3I, $CHFBr_2$, CF_2Br_2, and $CHCl_3$, at the temperatures where k_{ec} has been independently determined. Only for the case of $CHBr_3$ is the experimentally determined value of α significantly less (by only about 30%) than its independently determined k_{ec} value and the reason for this is unknown. The values of α for CCl_4 and CCl_3Br greatly exceed their respective k_{ec} values because k_d for these compounds is greater than zero and, therefore, α for these compounds is not expected to be equal to k_{ec}.

In view of the above discussion, it appears that the α values reported in Table 1 provide a valid set of EC rate constant measurements for all compounds listed, except CCl_4 and $CBrCl_3$. Many of the measurements therefore provide the first-ever reported at several of the temperatures indicated. An unusual feature of these measurements is that the α values for $CHBr_3$ suggest that k_{ec} for this compound has a negative temperature dependence.

5. Conclusion

It is concluded that some EC-active compounds, including CCl_4 and $CBrCl_3$, will decompose readily upon contact with the walls of an ECD due to their reaction with adsorbed reactive species. Since many of the compounds for which the ECD is commonly used are also highly chlorinated, this detrimental process is probably a common cause of reduced sensitivity and reduced quantitative reproducibility in analyses by the ECD. The efficiency, Φ, of destruction by this process can be very high, approaching unity (one reaction per wall collision) for the case of CCl_4, at room temperature. It is important to note, however, that Φ was found to be decreased by use of higher detector temperatures. This beneficial effect of increased temperature is thought to be due to a reduced amount of wall-absorbed reactive species at high temperatures and contrasts sharply with the common view that the use of increased ECD temperatures might be detrimental due to increased thermal degradation of the analyte on a hotter surface.

It is interesting to note that while free radicals on the walls of the ECD are thought to cause the efficient destruction of CCl_4 and $CBrCl_3$, they did not appear to cause significant destruction of seven other, sometimes closely-related halogenated methanes. This result is somewhat surprising in view of the common observation that gas phase free radicals are usually quite indiscriminate in their reactions with closely-related compounds. However, in prior studies of free radicals absorbed onto the walls of high pressure mass spectrometry in sources, large differences in the chemical reactivity of these with closely-relative halogenated compounds have also been noted [7,8,18,19]. Apparently, surface-

assisted free radical reactions of this type are much more sensitive to small structural and chemical changes in the substrate molecule than are their gas phase counterparts.

The results reported here reinforce the importance of those ECD designs in which physical contact of the analyte with the walls is minimized by use of laminar gas flow through an ECD of relatively small internal diameter [20], rather than by mixing the GC effluent into an ECD of relatively large internal diameter. These results also have direct implications for the use of the ECD as a gas-phase coulometer, in which all reactions of the analyte must be quantitatively understood and corrected for [6].

Acknowledgments

References

[1] M. Dressler, Selective Gas Chromatographic Detectors, Elsevier, New York, 1986.

[2] A. Zlatkis and C.F. Poole, Electron Capture, Theory and Practice in Chromatography, Elsevier, New York, 1981.

[3] E.P. Grimsrud, in H. Hill and D. McMinn (Editors), Detectors for Capillary Chromatography, Wiley, New York, 1992, p. 83.

[4] E.P. Grimsrud, Mass Spectrom. Rev., 10 (1992) 457.

[5] J.E. Lovelock, R.J. Maggs and E.R. Adlard, Anal. Chem., 43 (1971) 1962.

[6] S.W. Warden, R.J. Crawford, W.B. Knighton and E.P. Grimsrud, Anal. Chem., 57 (1985) 659.

[7] L.J. Sears, J.A. Campbell and E.P. Grimsrud, Biomed. Environ. Mass Spec., 14 (1987) 401.

[8] J.A. Culbertson, L.J. Sears, W.B. Knighton and E.P. Grimsrud, Org. Mass Spectrom., 27 (1992) 277.

[9] E.P. Grimsrud, Anal. Chem., 56 (1984) 1797.

[10] E.P. Grimsrud, J. Chromatogr., 312 (1984) 49.

[11] P.L. Gobby, E.P. Grimsrud and S.W. Warden, Anal. Chem., 52 (1980) 473.

[12] D. Smith, N.G. Adams and E. Alge, J. Phys. B: At. Mol. Phys., 17 (1984) 461.

[13] J.A. Culbertson and E.P. Grimsrud, Int. J. Mass Spec. Ion Proc., 149/150 (1995) 87.

[14] E. Alge, N.G. Adams and D. Smith, J. Phys. B, 17 (1984) 3827.

[15] D. Smith, C.R. Herd, N.G. Adams and J.F. Paulson, Int. J. Mass Spec. Ion Proc., 96 (1990) 341.

[16] R.C. Weast, M.J. Astle and W.H. Beyer, CRC Handbook of Chemistry and Physics, CRC, Boca Raton, FL, 1988.

[17] A.G. Harrison, Chemical Ionization Mass Spectrometry, CRC, Boca Raton, FL, 2nd ed., 1992.

[18] E.A. Stemmler and R.A. Hites, Anal. Chem., 57 (1985) 684.

[19] E.A. Stemmler and R.A. Hites, Electron Capture Negative Ion Mass Spectra of Environmental Contaminants and Related Compounds, VCH, New York, 1988.

[20] P.L. Patterson, J. Chromatogr., 134 (1977) 25.