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## EFFECT OF OXYGEN ON THE RESPONSE OF A CONSTANT-CURRENT $^{63}\text{Ni}$ ELECTRON-CAPTURE DETECTOR

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### SUMMARY

A constant-current electron-capture detector (ECD) with a  $^{63}\text{Ni}$  ionization cell has been used in a study of the effect of oxygen in nitrogen carrier gas on its response to several compounds. Because of the greatly increased linear dynamic range and the high temperature capabilities of this instrument, oxygen contamination of the carrier gas was found to be much less harmful to the chromatogram baseline than had been previously reported for earlier ECD models. Measurements of the changes in the molar responses of several compounds caused by the addition of up to 2000 ppm of oxygen to the nitrogen carrier gas have been made. For the chlorinated hydrocarbons studied, an effect of oxygen on their molar responses was observed only with the highest oxygen dopings. Anthracene behaved differently, showing an increased molar response at very low levels of oxygen doping. These results suggest that constant-current ECD analyses of polynuclear aromatics may be very sensitive to uncontrolled oxygen contamination of carrier gas, while those of halocarbons will not. For 1-chlorobutane a greatly enhanced response factor is caused by doping of the carrier gas with large amounts of oxygen. As this effect is observed at high detector temperatures where the baseline frequency is only moderately impaired by oxygen, oxygen doping is suggested as a means of improving the ECD sensitivity to molecules that have only one or a few halogen atoms. Two reaction mechanisms are proposed to account for the oxygen effects observed.

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### INTRODUCTION

The exceptional sensitivity and specificity of the electron-capture detector (ECD) in gas chromatography (GC), particularly to polyhalogenated organic molecules, has made it a valuable tool for the analysis of many compounds of environmental interest. As might be expected of analyses obtained with a device possessing extreme sensitivity of response, however, the reproducibility of measurements ob-

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tained with GC-ECD systems has frequently fallen short of desired limits<sup>1</sup>. It has been generally suspected that one of the most serious problems in ECD analyses has been the presence of uncontrolled amounts of impurities, such as water and oxygen, in the carrier gas.

The effects of oxygen on ECD performance have been studied or discussed several times by other workers. Very early in the development of the ECD, Lovelock<sup>2</sup> showed that the presence of oxygen in the carrier gas is undesirable owing to a resulting reduction of the standing current. Similarly, Guilbault and Herrin<sup>3</sup> found, in their attempts to use air as the carrier gas, the nearly complete loss of standing current and a corresponding loss in sensitivity to their sample. In a more recent study by Van de Wiel and Tommassen<sup>4</sup>, using a fixed frequency, pulsed ECD with a higher temperature range, small amounts of oxygen were again found to reduce the standing current to the point where drastic removal of oxygen from the carrier gas was deemed essential for satisfactory performance. They also noted, however, that at high detector temperatures (300° C), the harmful effect of oxygen on the standing current is much smaller. An additional influence of oxygen was noted in this study; the sensitivity of their ECD to some compounds such as butyl bromide appeared to increase when oxygen was intentionally added to the carrier gas. This observation suggests that in addition to affecting the ECD standing current, the molar response of a sample compound may be altered by the presence of oxygen. Because of the above studies, users of the ECD have been urged to take great care to eliminate oxygen and also water from their carrier gas. When the complete elimination of these is difficult or impossible (for example, when water or oxygen are major components of samples to be repeatedly analysed), one may justifiably be concerned about analytical errors caused by the presence of uncontrolled amounts of these compounds in the detector as the sought-for substance eludes from the GC column.

New insights into the causes of carrier gas impurity effects on the ECD have been made possible by the development of similar, but more sophisticated, analytical techniques such as the plasma chromatography and the atmospheric pressure ionization mass spectrometry (APIMS). In each, the conditions within their ionization source can be made identical with those of the ECD, but instead of measuring electron density as the ECD is thought to do, these devices are capable of monitoring the ions produced by electron-molecule interactions. Karasek and Kane<sup>5</sup> have shown by plasma chromatography that negative ions, presumed to be O<sub>2</sub><sup>-</sup> and its water clusters, are formed by the addition of oxygen to nitrogen carrier gas. They also noted a synergistic effect of water with oxygen: that is, added water caused increased negative ion formation only if oxygen was already present. Dzidic *et al.*<sup>6</sup> identified these ions more precisely by APIMS in air carrier gas, and raised further possibilities of oxygen dependence by the discovery that chlorinated aromatic compounds can form negative ions of mass [M - Cl + O] even under ideal ECD conditions where very pure nitrogen carrier gas (containing less than 0.5 ppm of oxygen) is used. More recently, Siegel and Fite<sup>7</sup> have shown that in addition to O<sub>2</sub><sup>-</sup> and its hydrates, O<sub>4</sub><sup>-</sup> is a favored terminal anion in the ionization of air at 1 atm pressure. Clearly, the formation of these ions and their subsequent ion-molecule reactions, constitutes a likely basis for ECD effects caused by oxygen and water.

In the last few years, significant changes and improvements in ECD instrumentation have been made. While a few years ago the typical ECD utilized a tritium

foil for ionization and a continuous d.c. voltage or a fixed-frequency pulsed voltage for measuring its electron density, more recent instruments offer ionization by  $^{63}\text{Ni}$  (ref. 8) and electron sampling by the frequency-modulated pulsed mode<sup>9</sup> (also known as the constant-current ECD). Two consequences of these improvements are that the maximal allowable temperature of the ECD has been increased from 200° to 400°C and the range of linear response to electron-absorbing compounds has been increased from about 2 to greater than 4 orders of magnitude. Because of these improvements, a more detailed study of the effects of oxygen in the carrier gas has been made possible and is reported here. In order to demonstrate the importance or unimportance of oxygen and water as carrier gas impurities on the quantitative response of a modern ECD, we have measured the baseline frequencies and the molar responses of several selected compounds as a function of the concentrations of oxygen and water that were intentionally added to nitrogen carrier gas. The sample compounds were chosen to reflect different electron-capture mechanisms and different types of terminal negative ion products that have been previously reported. The results are interpreted in terms of kinetic and thermodynamica data available in the literature for the reactions thought to be of importance.

## EXPERIMENTAL

1,4-Dichloro-2-nitrobenzene (Baker grade), 1-chlorobutane, 1,4-dichlorobenzene and 1-bromo-4-chlorobenzene (Eastman grade) and the remaining substrates (all Aldrich, Milwaukee, Wisc., U.S.A.) were weighed without further purification into 10-cm<sup>3</sup> volumetric flasks, dissolved in thiophene-free benzene (Baker analysed reagent) and diluted to concentrations that yielded small, but readily measurable peaks on the GC-ECD.

The gas chromatograph was a Varian Aerograph 3700 with constant-current, pulse-modulated operation and an 8-mCi  $^{63}\text{Ni}$  detector. The detector cell has displaced coaxial cylinder geometry and is polarized with negative voltage pulses of 50 V amplitude and 0.64  $\mu\text{sec}$  width. Integration of peak areas was accomplished with an Autolab Minigrator (Model 2300-010).

A stainless-steel column (20 in.  $\times$   $\frac{1}{8}$  in. O.D.) was packed with 5% OV-101 on Chromosorb G (100–120 mesh) and pre-conditioned at 325°C for 36 h. Each substrate was run separately and its retention time determined. Three different standards were then prepared in which a good separation of the substrates in each was achieved. One standard contained anthracene and anthraquinone and was run at a column temperature of 130°C; another contained 1-chlorobutane, pentachloroacetone, pentachloroethane, 1,1,1,2-tetrachloroethane and 1,1,2,2-tetrachloroethane, and was run with the column at 36°C. The remaining compounds comprised the third standard, which was run at 90°C. Flow-rates were measured directly at the detector outlet with a bubble flow meter and were adjusted to 50 cm<sup>3</sup> min<sup>-1</sup>.

The carrier gas was ultra-high-purity nitrogen (Matheson, East Rutherford, N.J., U.S.A.). It was passed first through a Varian inlet filter containing activated charcoal and molecular sieves to remove residual moisture and hydrocarbons, then through an Oxy-Trap (Alltech, Arlington Heights, Ill., U.S.A.) designed to remove oxygen down to 0.1 ppm, and finally through a 5-l exponential diluter before entering the column. Before each set of runs the carrier system was purged by flushing the

diluter several times and then allowing purified nitrogen to flow through the entire system overnight. Contamination in the diluter was checked by shunting carrier gas directly to the column, cutting out the diluter. A decrease in standing current indicated diluter contamination. Under clean conditions, peak areas of standard samples matched those of the same standard run on the previous day prior to oxygen doping and clean-up. Upon achieving satisfactory conditions, 1- $\mu$ l samples in benzene were injected and the resulting peak areas read. Each sample was run at least three times under conditions of pure nitrogen carrier gas to check precision.

Variation of oxygen concentration was accomplished by passing zero-grade air (Matheson) through a copper tube filled with 13X molecular sieve (Alltech) and injecting into the carrier gas line with a 10-ml gas-tight syringe just upstream of the diluter. After a diluter mixing time of about 5 min, a stable baseline was established and samples were quickly analysed. The lowest oxygen concentration was run first, followed by successively higher oxygen concentrations achieved by additional injections. The oxygen concentrations of Table I are those calculated at the beginning of a series of determinations, which included measurements at all three detector temperatures. During this time the oxygen concentration typically decreased by about 10%.

In some experiments a small amount of water was also added to the carrier gas. This was accomplished by injection of humidified nitrogen into the dilution volume. High-purity nitrogen was humidified by passing it through a bubbler containing triply distilled water. After purging for 30 min to allow any volatile substances in the water to be removed, an aliquot of the saturated nitrogen stream was transferred to the diluter with a 10-ml gas-tight syringe. The concentrations of water and oxygen added to the carrier gas were calculated in units of parts per million (v/v), and include a correction for the pressure difference between the diluter (20 lb in<sup>-2</sup> above atmospheric) and the transfer syringe (1 atm).

## RESULTS AND DISCUSSION

If errors are caused by the presence of impurities in the carrier gas of a GC-ECD, it is reasonable to assume that the source of the error is from one of two possibilities: either the baseline has been altered beyond the range in which a linear response of the detector to the substrate can be expected, or a basic change in the response mechanism is caused by the impurity and an uncontrolled alteration of the response factor results.

### *Baseline frequency measurements*

The effect on the baseline frequency of adding various amounts of oxygen to the carrier gas is shown in Table I for 0.4–2000 ppm of oxygen added to purified nitrogen at different detector temperatures. For a constant-current ECD, the baseline frequency is analogous to the standing current of the d.c. or the fixed-frequency pulsed ECD and provides a measure of the cleanliness of the ECD system. In our application an average  $3 \cdot 10^{-10}$  A of cell current is sampled at all times by an automatic variation in the rate at which a 50-V, 0.6- $\mu$ sec pulse is applied to the cell. When an electron-capturing compound is passed through the detector, the frequency of

TABLE I

BASELINE FREQUENCIES (kHz) OBSERVED USING CARRIER GAS DOPED WITH VARIOUS AMOUNTS OF OXYGEN AND WATER

Water content of carrier gas (ppm)	Temperature (°C)	Oxygen concentration added to carrier gas (ppm)							
		0.0	0.4	4.0	16	150	400	800	2000
0	350	3.8	3.8	3.8	3.8	5.3	6.1	8.4	13
	250	3.1	3.1	3.1	3.3	6.1	11	14	22
	150	4.3	4.3	4.5	5.8	16	40	100	
10	350	4.2	4.3	4.3	4.4	5.0	7.3	11	26
	250	3.9	3.9	3.9	4.7	6.0	15	24	150

pulsing increases to maintain the pre-selected cell current. The magnitude of frequency increase is taken as the measure of response to that sample.

Table I shows that at 350°C, oxygen increases the baseline frequency from 3.8 kHz to a high of 13 kHz with 2000 ppm of oxygen added, with no significant effect up to about 16 ppm of oxygen. Obviously, when small amounts of oxygen were added to the carrier gas and the baseline frequency was essentially unaffected, the range of linear response of the instrument to samples will be unimpaired. Using an instrument identical with ours, Patterson<sup>10</sup> has shown that linear response can be expected up to peak heights of about 100 kHz, after which saturation effects will begin to cause a diminished response. Therefore, even with 2000 ppm of oxygen in the carrier nitrogen at 350°C, the baseline frequency of 13 kHz is well below the point at which non-linear response, due to inherent limitations of the instrument itself, is to be expected.

At a detector temperature of 250°C, the effect of oxygen on the baseline frequency is noticeably greater. The baseline is now slightly changed upon the addition of 16 ppm of oxygen and reaches a baseline frequency of 22 kHz at 2000 ppm of oxygen added. Nevertheless, the baseline frequencies at 250°C are not yet high enough to predict the loss of linear response.

At 150°C the baseline frequency is slightly affected at 4 ppm of oxygen and increases much more rapidly than at the higher temperatures with further addition of oxygen. With 800 ppm of oxygen in the carrier gas, the baseline frequency is 100 kHz. At this point, the 0.6- $\mu$ sec sampling pulse is "on" 6% of the time, and is approximately where non-linearity of response begins to occur due to instrumental saturation<sup>10</sup>.

Also shown in Table I is the effect of oxygen on baseline frequency where the carrier gas also contained 10 ppm of added water. Very little or no effect of the added water itself is observed when the oxygen concentration is low. Only at high oxygen levels do the baseline frequencies begin to be significantly affected by water. Thus, at 2000 ppm of oxygen the addition of 10 ppm of water doubles the baseline frequency at 350°C and increases it several times at 250°C. This experiment suggests that our dried carrier gas is at least relatively dry, perhaps containing about 1 ppm or less of water. As suggested by Karasec and Kane<sup>5</sup>, the ECD response to oxygen appears to be significantly greater in carrier gas that is not ultra-dry.

*Sample response measurements*

The molar responses of our ECD to selected compounds under various levels of carrier gas doping with oxygen are shown in Table II. The subject compounds are listed roughly in order of the magnitude of their response in clean carrier gas. The first column, for zero oxygen added, lists molar responses all relative to the lowest response observed, *viz.*, that of 1-chlorobutane at 250°C. Thus, the first column of Table II provides a comparison of different compounds with each other under "ideal" ECD conditions. All other values in Table II, in the columns for various amounts of oxygen added to the nitrogen carrier gas, are also relative molar responses, but now with reference to the first value given in each row. In this manner, the effect

TABLE II

EFFECT OF OXYGEN ADDED TO CARRIER GAS ON THE ECD RESPONSE OF SELECTED COMPOUNDS

Compound	Temperature (°C)	Oxygen concentration added to carrier gas (ppm)*							
		No O <sub>2</sub> added	0.4	4	16	150	400	800	2000
Pentachloroethane	350	5.0 · 10 <sup>6</sup>	1.06	1.05	1.04	1.11	—	1.03	1.03
	250	4.2 · 10 <sup>6</sup>	0.86	0.86	0.82	0.90	—	1.03	1.91
1,1,1,2-Tetrachloroethane	350	1.7 · 10 <sup>6</sup>	1.04	0.98	0.91	1.10	—	1.11	1.00
	250	1.6 · 10 <sup>6</sup>	0.90	0.90	0.85	0.89	—	1.01	12.8
1,1,2,2-Tetrachloroethane	350	5.5 · 10 <sup>5</sup>	1.04	0.93	1.01	1.00	—	1.02	1.24
	250	3.8 · 10 <sup>5</sup>	0.90	0.90	0.87	0.96	—	1.42	9.23
Tetrachloroethylene	350	4.8 · 10 <sup>5</sup>	1.00	1.01	1.07	0.97	0.99	1.00	1.00
	250	3.8 · 10 <sup>5</sup>	1.10	0.93	1.00	1.06	1.02	1.39	1.29
Pentachloroacetone	150	3.5 · 10 <sup>5</sup>	0.57	0.74	0.73	0.64	—	1.57	—
	350	3.2 · 10 <sup>5</sup>	1.02	1.11	1.07	1.19	—	1.09	1.06
1,4-Dichloro-2-nitrobenzene	250	3.0 · 10 <sup>5</sup>	0.96	0.98	0.92	0.96	—	1.11	2.16
	350	8.1 · 10 <sup>4</sup>	0.98	1.04	1.05	0.95	1.00	1.01	1.03
1,2,3,4-Tetrachlorobenzene	250	7.7 · 10 <sup>4</sup>	1.07	0.98	1.00	0.95	0.92	1.05	1.14
	150	7.0 · 10 <sup>4</sup>	0.95	1.03	1.02	0.98	—	2.17	—
1-Bromo-4-chlorobenzene	350	5.6 · 10 <sup>4</sup>	0.99	0.99	1.07	0.96	0.99	1.02	1.05
	250	2.1 · 10 <sup>4</sup>	1.25	1.02	1.13	1.14	1.30	1.67	2.11
1-Bromo-4-chlorobenzene	150	1.5 · 10 <sup>4</sup>	0.85	1.04	1.15	1.35	—	20	—
	350	2.1 · 10 <sup>4</sup>	0.99	0.92	1.07	0.95	0.90	1.00	0.98
Anthraquinone	250	8.9 · 10 <sup>3</sup>	1.34	0.98	1.17	1.05	0.96	1.14	1.29
	150	2.7 · 10 <sup>3</sup>	0.87	0.98	1.00	0.94	—	2.46	—
3,5-Dichlorophenol	230	1.8 · 10 <sup>4</sup>	0.88	1.01	1.04	1.24	1.83	4.12	5.23
	180	1.6 · 10 <sup>4</sup>	0.96	1.03	1.14	1.27	1.78	5.18	—
1,4-Dichlorobenzene	350	7.0 · 10 <sup>3</sup>	0.99	0.97	1.03	0.99	1.05	1.16	1.22
	250	3.3 · 10 <sup>3</sup>	1.15	1.02	1.12	1.20	1.55	2.11	2.65
1,4-Dichlorobenzene	150	1.1 · 10 <sup>3</sup>	0.92	1.02	1.07	1.02	—	2.76	—
	350	1.5 · 10 <sup>3</sup>	1.01	0.80	1.15	0.94	0.81	1.05	0.97
Anthracene	250	2.2 · 10 <sup>2</sup>	1.68	1.48	1.42	1.30	1.28	1.86	2.14
	150	2.9 · 10 <sup>1</sup>	1.96	0.77	0.84	1.03	1.01	11.4	—
1-Chlorobutane	230	3.1 · 10 <sup>1</sup>	1.68	2.90	3.00	15.4	21.7	76	82
	180	2.3 · 10 <sup>2</sup>	1.05	1.68	1.98	5.5	8.3	27	—
1-Chlorobutane	350	1.1	1.03	1.12	1.40	4.70	—	13.6	55
	250	1.0	0.92	1.01	1.24	4.52	—	11.1	30

\* The responses listed under the first column are all relative to the lowest in that column, *i.e.*, that of 1-chlorobutane at 250°C; all other responses listed are relative to the first value in each row.

of oxygen contamination on the response of each compound at a given temperature is displayed.

The difference in sensitivities of our group of compounds extends over six orders of magnitude. The extent of halogenation together with structural considerations and changes in functional groups all influence the sensitivity in a manner roughly consistent with established trends<sup>11</sup>. The sensitivity of all of the halocarbons increases with increased temperature. This behavior has been generally associated with the dissociative electron-capture mechanism<sup>12</sup>, symbolised by the reaction



While the temperature dependence observed for these was generally not large, the halogenated benzenes 1,2,3,4-tetrachlorobenzene, 1-bromo-4-chlorobenzene, 3,5-dichlorophenol and 1,4-dichlorobenzene all showed about an order of magnitude increase in response upon increasing the detector temperature from 150° to 350°C. In spite of its similarity to the halobenzenes, 1,4-dichloro-2-nitrobenzene showed very little temperature dependence. The temperature dependence of anthracene is completely opposite that of the halocarbons. Its response is lowered very markedly with an increase in detector temperature. This behavior was expected for this compound and has been attributed to a resonance electron-capture mechanism<sup>13</sup>, symbolized by the reaction



One of the most striking features of the data in Table II is the general lack of significant effect on the molar responses of the halocarbons caused by the addition of small and moderate amounts of oxygen. At a detector temperature of 350°C, few compounds showed any effect of oxygen even up to 2000 ppm. Where large effects are observed, it is generally with the highest oxygen concentrations present in the carrier gas, and at the lower detection temperatures, and then the effect is generally to increase the molar response. For example, the sensitivity towards the two isomers of tetrachloroethane was increased by a factor of about 10 at 250°C by the addition of 2000 ppm of oxygen. At 250°C, however, the response of the halobenzenes were relatively unaffected. Of these at 150°C, only tetrachlorobenzene and dichlorobenzene showed large increases of response with high oxygen.

The general lack of oxygen dependence for the halobenzenes is particularly interesting, in view of the APIMS studies of Dzidic *et al.*<sup>6</sup>. They found that some halobenzenes form terminal negative ions which include an oxygen atom even in a carrier gas of ultra-high-purity nitrogen. Of the compounds examined here, tetrachlorobenzene and dichloronitrobenzene might have been expected to be of this type. Apparently, the reactions that lead to oxygen inclusion in the terminal phenoxide ions observed in the APIMS study occur after a rate-controlling electron-capture process and, therefore, the response factor is not sensitive to oxygen concentration.

A notable exception to the trends of the halocarbons again occurs with anthracene, for which a large oxygen dependence is observed throughout the addition of oxygen, even at the very lowest levels added. Also, in contrast to most other instances, the oxygen dependence is greatest at high temperatures. At 230°C the pres-

ence of 2000 ppm of oxygen in the carrier increased the molar response of anthracene to 82 times the response using pure nitrogen carrier gas; this was the largest response enhancement observed.

1-Chlorobutane is unique in that at a detector temperature of 350°C its response increased 55 times over that in pure nitrogen carrier gas. This is the only compound for which a response enhancement was observed at this temperature. As for the other halocarbons showing enhanced responses, the largest increase in the response factor of 1-chlorobutane occurs with the final addition of oxygen to the carrier gas. With the exception of anthracene, this form of oxygen dependence was the rule wherever large effects were observed. To emphasize this point, a plot of the response enhancements *versus* carrier gas oxygen concentration for four representative compounds is shown in Fig. 1.

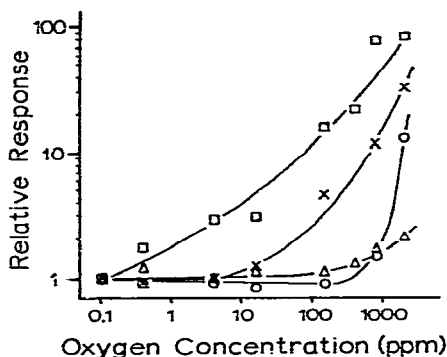


Fig. 1. Relative ECD response of several selected compounds as a function of the concentration of oxygen added to the carrier gas at 250 °C.  $\Delta$  = 1,2,3,4-tetrachlorobenzene;  $\circ$  = 1,1,1,2-tetrachloroethane;  $\times$  = 1-chlorobutane;  $\square$  = anthracene (at 230 °C).

The effect of oxygen on ECD responses in carrier gas intentionally doped with 10 ppm of water was also measured. The results of these measurements can be summarized by the statement that no significant effect of this amount of added water on the sample was observed where oxygen itself had caused no effect on response. In other words, for all cases in Table II where relative responses near unity were observed, the addition of 10 ppm of water together with oxygen produced no change in response. At the very highest oxygen concentrations for the cases where significant response enhancements were caused by oxygen, the addition of 10 ppm of water may have had an effect on response. We have not reported these data because of the extreme sensitivity of response to small variations in oxygen concentration under the condition of high oxygen doping. This rendered a reliable determination of the effect of water alone in this region difficult with the means of controlling oxygen and water concentration used here.

#### Proposed mechanisms

In interpreting data obtained with an ECD, one is immediately faced with a serious problem in that literature accounts of the events occurring within the ionization cell are conflicting. Perhaps the most commonly held view states that in the pulsed mode, all electrons within the cell are removed with each pulse<sup>8,13</sup> and the



relatively sluggish ions are left behind and, further, the negative ion products of electron-capture reactions are preferentially removed by fast recombination with positive ions<sup>14</sup>. Recently, however, Siegel and McKeown<sup>15</sup> have argued that at the charge densities present in the ECD, charge balance between positive and negative particles will be maintained and, also, that the recombination rates of positive ions with negative ions are not orders of magnitude larger than positive ion-electron recombination rates, but are very similar in magnitude and probably are even somewhat smaller. These latter ideas are incompatible with the major points of conventional ECD theory, and suggest that in the pulsed and d.c. modes of ECD operation, our understanding of the basis of ECD signals is at present incomplete. In addition to these uncertainties, there are other important chemical details of ECD reactions that have not yet been sufficiently determined, such as the electron-capture reactivity of the neutral products formed by dissociative electron capture or by recombination reactions. While these species and the events that produce them may be important factors in causing an ECD response, they are difficult to include in reaction models because little is known of them. With these fundamental uncertainties in mind, an attempt can be made to interpret cautiously our results in terms of likely reaction sequences, realizing that modification may be required as additional fundamental information becomes available.

Siegel and Fite<sup>7</sup> have recently shown by APIMS that the principle negative ions formed in dry air with a  $^{63}\text{Ni}$  ionizer similar to ours are  $\text{O}_2^-$  and  $\text{O}_4^-$ , and that in wetter air the water clusters of these will also be prevalent. Perhaps the most important reactions leading to these are the following:



Additional hydration reactions leading to larger water clusters of  $\text{O}_2^-$  and  $\text{O}_4^-$  could also be included but, as will be shown, these are probably not important under the conditions of our experiments. As the analytical method under consideration is thought to respond only to free electron concentration, reaction 3 is the only reaction that will affect directly the ECD response to oxygen. If a condition approaching the equilibrium of reaction 3 exists, however, reactions 4 and 5 can indirectly affect an ECD response to oxygen by consuming  $\text{O}_2^-$  and shifting reaction 3 to the right.

In assessing whether ion-molecule reactions 4 and 5 are important, we may first consider their thermodynamic feasibility. In Table III are listed the thermochemical values describing equilibria reactions 4 and 5. Using these, we have calculated (Table IV) the relative concentrations of the ions,  $\text{O}_2^-$ ,  $\text{O}_2^-(\text{H}_2\text{O})$  and  $\text{O}_4^-$ , that are predicted for equilibrium under the conditions listed. The clear results of this consideration is that in dry (1 ppm of water) carrier gas,  $\text{O}_2^-$  is to be considered the dominant negative ion species at the temperatures studied here. Even with 2000 ppm of oxygen added at the lowest temperature, 150°C,  $\text{O}_4^-$  will be only 0.002 as abundant as  $\text{O}_2^-$ . Thus, for the oxygen concentrations used here, it appears that reaction 4 and  $\text{O}_4^-$  are not important and can be ignored. Considering differences in temperature

TABLE III

THERMOCHEMICAL VALUES FOR THE CLUSTERING REACTIONS OF  $O_2^-$  WITH  $O_2$  AND  $H_2O$ 

Reaction	$-\Delta H^0$ (kcal mole <sup>-1</sup> )	$-\Delta S^0$ (cal mole <sup>-1</sup> °K)	Reference
$O_2^- + O_2 \rightleftharpoons O_4^-$	13.5	31.8	16
$O_2^- + H_2O \rightleftharpoons O_2^-(H_2O)$	18.4	20.1	17

and oxygen concentration, this prediction is not inconsistent with the data of Siegel and Fite<sup>7</sup>, who observed  $O_4^-$  in excess of  $O_2^-$  by a factor of 3 in air ( $2 \cdot 10^5$  ppm of oxygen) and at 125°C. For their experimental conditions, the thermochemical values in Table III predict about equal intensities of  $O_2^-$  and  $O_4^-$ . This must be considered excellent agreement and lends support to the validity of applying thermochemical data to the ECD and APIMS plasmas.

In relatively dry carrier gas, Table IV indicates that  $O_2^-(H_2O)$  also is expected to be much less abundant than  $O_2^-$ . Only at 150°C, where a relative abundance of 0.14 for  $O_2^-(H_2O)$  is predicted, would the hydrated ion concentration become significant. If the carrier gas is only moderately dry, thermochemistry allows the hydrated species to increase proportionately in abundance. Thus, at an assumed 10 ppm of water, the water cluster of  $O_2^-$  becomes predominant at 150°C, noticeable (0.02) at 250°C, but is still insignificant (0.001) at 350°C. As previously pointed out, the baseline data in Table I has suggested that our dried, ultra-high-purity carrier gas probably contains closer to 1 ppm than 10 ppm of water.

As thermodynamic considerations suggest that reaction 5 (and only under certain conditions) together with the electron-capture reaction 3 should be important in accounting for the oxygen ion chemistry within the ECD, consideration will be given to the time dependence of these reactions. The rate constant for the forward reaction 3 is  $k_3 = 1.1 \cdot 10^{-31} \text{ cm}^6 \text{ sec}^{-1}$  in nitrogen<sup>18</sup> at 25°C and seems to be relatively independent of temperature<sup>19</sup>. As oxygen and water will always be in large excess

TABLE IV

RELATIVE NEGATIVE ION ABUNDANCES PREDICTED\* FOR VARIOUS ECD CONDITIONS

Conditions			Relative abundance		
$O_2$ (ppm)	$H_2O$ (ppm)	$T$ (°C)	$O_2^-$	$O_4^-$	$O_2^-(H_2O)$
1	1	350	1.00	$4 \cdot 10^{-9}$	$1.2 \cdot 10^{-4}$
1	1	250	1.00	$5 \cdot 10^{-8}$	0.002
1	1	150	1.00	$1.0 \cdot 10^{-6}$	0.14
2000	1	350	1.00	$1.2 \cdot 10^{-5}$	$1.2 \cdot 10^{-4}$
2000	1	250	1.00	$1.0 \cdot 10^{-4}$	0.002
2000	1	150	1.00	0.002	0.14
2000	10	350	1.00	$1.2 \cdot 10^{-5}$	0.001
2000	10	250	1.00	$1.0 \cdot 10^{-4}$	0.021
2000	10	150	0.71	0.0015	1.00

\* Calculated using the thermochemical values listed in Table III.

over ions and electrons in the ECD, pseudo-first-order decay times of ions and electrons can be calculated from the rate constants. In purified nitrogen, assumed to contain 1 ppm of oxygen, the half-life of the electron consumption via reaction 3,  $\tau_3$ , will be 7 msec. If oxygen is added, the rate of the forward reaction 3 increases to a maximal rate at 2000 ppm of oxygen when  $\tau_3$  is 4  $\mu\text{sec}$ . The rate constant of the reverse reaction 3 in pure oxygen is  $k_{-3} = 9 \cdot 10^{-17} \text{ cm}^3 \text{ sec}^{-1}$  at  $100^\circ\text{C}$  and increases very rapidly with temperature to  $1.4 \cdot 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$  at  $200^\circ\text{C}$ <sup>19</sup>. Assuming this rate constant will be about the same in nitrogen, we estimate that the half-life of  $\text{O}_2^-$  against electron detachment,  $\tau_{-3}$ , is about 50  $\mu\text{sec}$  at  $150^\circ\text{C}$  and much less than 1  $\mu\text{sec}$  at  $250^\circ$  and  $350^\circ\text{C}$ . The rate of forward reaction 5 is  $k_5 = 1.6 \cdot 10^{-28} \text{ cm}^6 \text{ sec}^{-1}$  at  $27^\circ\text{C}$ <sup>20</sup>. This reaction is probably somewhat slower at higher temperatures. Assuming it to have a negative activation energy of about 2 kcal mole<sup>-1</sup> (ref. 20), its rate will be about one-sixth as fast at  $350^\circ\text{C}$  as the indicated value. Thus, a  $\tau_5$  of about 10–30  $\mu\text{sec}$  is predicted in very dry (1 ppm of water) carrier gas and a correspondingly lower  $\tau_5$  in moister carrier gas. The rate of the reverse reaction 5 can be calculated from the forward rate and the thermodynamic data in Table III. The result is that  $\tau_{-5}$  is very fast ( $<1 \mu\text{sec}$ ) at the temperatures of interest.

The consequences of the above thermodynamic and kinetic considerations of reactions 3, 4 and 5 can now be summarized. As oxygen is added to the nitrogen carrier gas, only  $\text{O}_2^-$  and under certain conditions  $\text{O}_2^-(\text{H}_2\text{O})$  can be formed via reactions 3 and 5. The achievement of steady-state electron and ion concentrations that reflect true chemical equilibrium, however, may be kinetically hindered. The slowest reaction of importance in relatively clean nitrogen is the first one, electron-capture by oxygen (forward reaction 3). In pure nitrogen (1 ppm of oxygen) its rate is about  $10^3$  slower than the others and even with 16 ppm of oxygen added it will be much slower. Thus, if a kinetic bottleneck to equilibrium is present, it will be at the forward reaction 3. The observable result of this will be to lock the free electrons into a steady-state concentration greater than that favored by thermodynamics. At high levels of oxygen, however, forward reaction 3 becomes relatively fast and a steady-state condition closer to true equilibrium is probably achieved within the ECD. Thus, an important consequence of oxygen (in addition to the obvious one of moving the favored equilibrium position of reaction 3 to the right) is to reduce the kinetic bottleneck of reaction 3. If water is added to the dry carrier gas, the fast reaction 5 will tend to move the achievable equilibrium point further to the right, but in the absence of added oxygen, water may have little or no observable effect on the electron density because of the slowness of reaction 3. Arguments similar to these<sup>7</sup> have been used to explain the presence of  $\text{H}_2\text{O}^+$  in positive ion API mass spectra in spite of its thermodynamic instability.

The baseline frequencies in Table I have been described and are in reasonable agreement with the model just discussed. At low levels of added oxygen, the baseline frequencies are not changed much by variations in temperature, water or oxygen. Under these conditions the temperature-independent reaction 3 is slow, and holds electrons in their free state. Thus, the shifts in the equilibrium positions of reactions 3 and 5 which might be predicted for these changes do not occur, and the pulse frequencies observed are less sensitive to these variables. With 2000 ppm of added oxygen, however, the baseline frequency is very sensitive to changes in temperature, water and oxygen in a manner roughly consistent with the predicted affects of these

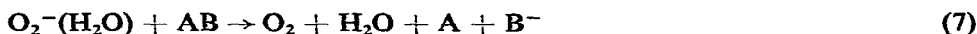
variables under the assumption that a condition nearer true equilibrium reactions 3 and 5 is attained.

An aspect of the data in Table I which we find difficult to explain, however, is the magnitude of the baseline frequency increase caused by the addition of 10 ppm of water to the oxygen-doped carrier gas. For example, at 250°C with 2000 ppm of added oxygen, this amount of water increased the baseline frequency from 22 to 150 kHz. On the basis of our predictions shown in Table III, only about 2% of the  $O_2^-$  ions would be converted into  $O_2^-(H_2O)$ , so a much smaller effect might have been expected.

In extending this model to account for the effect of oxygen on the ECD response to sample compounds, it is reasonable to add the following irreversible ion-molecule reactions as likely additions to the negative reaction sequences:



and, if the carrier gas is not dry,



Reactions 6 and 7 can be envisaged as affecting an ECD response in the same manner in which reaction 5 has been described as affecting the baseline frequency. Reaction 6 may consume  $O_2^-$  while AB passes through the ECD and, thereby, shift the position of equilibrium reaction 3 to the right. Again, this perturbation of equilibrium 3 may not occur in a carrier gas containing little oxygen because of the slowness of forward reaction 3. With relatively large amounts of added oxygen, however, reaction 3 is fast in both directions, and an additional route for electron consumption by the sample is created. The sum of reactions 3 and 6 is identical with direct electron capture by AB (reaction 1). The difference is that reaction sequence 3 and 6 utilizes  $O_2^-$  as a catalyst. If the rate of this additional  $O_2^-$ -catalyzed route of electron attainment by AB is sufficiently fast, an enhanced ECD response will be observed.

Fehsenfeld *et al.*<sup>21</sup> found the rate constants for the reactions of  $O_2^-$  and  $O_2^-(H_2O)$  with  $CFCl_3$  at 30°C to be  $7.6 \cdot 10^{-10}$  and  $< 1 \cdot 10^{-11}$   $cm^3 \text{ sec}^{-1}$ , respectively. For comparison with these, Christophorou<sup>22</sup> found the rate constant for electron attachment to  $CFCl_3$  at 30°C to be about  $10^{-8}$   $cm^3 \text{ sec}^{-1}$ . Thus, for reaction with highly chlorinated molecules, one might expect that  $O_2^-$  will be slower, but possibly competitive with the free electron. For substrate molecules that have very low rates of electron capture, their reactions with  $O_2^-$  may be faster than with the free electron. This prediction is supported by the general observation that rates of electron-capture processes are much more substrate dependent than are ion-molecule reaction rates. For example, at modest detector temperatures, the ECD response to  $CF_2Cl_2$  is at least two orders of magnitude less than that of  $CFCl_3$ , suggesting a corresponding difference in rates of electron capture. Fehsenfeld *et al.*<sup>21</sup> found, however, that at 30°C the reaction rates of  $O_2^-$  with  $CF_2Cl_2$  and  $CFCl_3$  differ only by a factor of three.

The molar response factors of the halocarbons shown in Tables II and Fig. 1 can be rationalized in terms of the model described. The highly chlorinated molecules experience little response enhancement from the alternative electron attachment route provided by  $O_2^-$  because their rate of direct electron capture is much

faster. However, at the very highest oxygen doping and at the lower detector temperatures, the ratio of  $\text{O}_2^-$  to free electron concentration becomes great enough so that response enhancements are observed for some of the polychlorinated compounds. At the other extreme of electron-capture reactivity, 1-chlorobutane experienced the greatest response enhancement of the halocarbons caused by oxygen. Its reaction with  $\text{O}_2^-$  is probably much faster than its slow rate of electron capture. As oxygen is added a new, faster mechanism becomes dominant, which, as the kinetic bottleneck of forward reaction 3 is reduced by the increased presence of molecular oxygen, results in an increased response.

Probably the rate of forward reaction 3, not the rate of reaction 6, limits the response enhancements observed for 1-chlorobutane. This conclusion follows if one assumes that the reduction in the electron concentration accompanying oxygen doping causes an equal increase in  $\text{O}_2^-$  concentration<sup>15</sup>. Electron concentration within a modulated frequency pulsed ECD is thought<sup>1,10</sup> to be proportional to  $1/F$ . Thus, the loss of electrons and the increase in  $\text{O}_2^-$  will be proportional to  $1/F_0 - 1/F$ , where  $F_0$  and  $F$  are the baseline frequencies before and after doping the carrier gas with oxygen, respectively. The baseline frequencies at 250°C caused by oxygen doping have been plotted as  $1/F_0 - 1/F$  versus oxygen added in Fig. 2. Assuming this function to be proportional to  $\text{O}_2^-$  concentration, it can be seen that the concentration of  $\text{O}_2^-$  rises quickly, approaching a maximal value at about 400 ppm, and then increases slowly. This is not the form of oxygen dependence observed for the response enhancement of the halocarbons and, therefore,  $\text{O}_2^-$  and reaction 6 are not the limiting factors in achieving increased responses. The rate of the slow reaction 3, however, will increase continuously with and in proportion to the addition of oxygen. Therefore, for the case cited at 250°C, the response of 1-chlorobutane continues to increase strongly beyond the addition of 400 ppm as the rate of reaction 3 is increased.

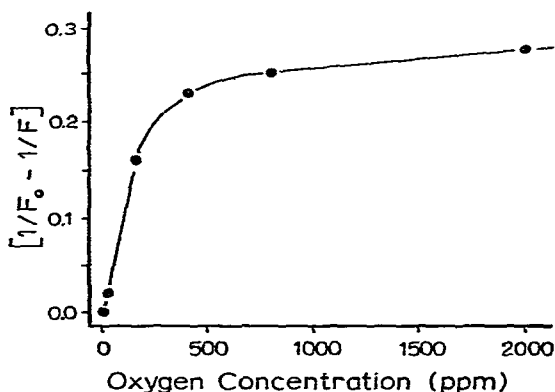


Fig. 2. Change in the reciprocal of the baseline frequency caused by oxygen doping of the carrier gas at a detector temperature of 250 °C.

As has been previously described and illustrated in Fig. 1, anthracene does not follow the pattern of oxygen dependence described for the halocarbons in that its response factor increases throughout the addition of oxygen, starting immediately

with only 0.4 ppm added. As anthracene is the only compound of those examined here thought to undergo electron capture via the resonance capture mechanism (reaction 2), a different type of oxygen dependence may also be a reasonable expectation. Another mechanism by which response enhancements may occur in the presence of oxygen seems especially appropriate for anthracene. Instead of oxygen serving as a catalyst to increase the rate of electron attachment of the substrate, the opposite situation could also be envisaged, that is, the substrate could be acting as a catalyst for the attainment of electron-capture equilibrium 3 by facilitating its slow forward rate. Following the resonance capture reaction 2, which forms the sample molecular ion,  $AB^-$ , the following charge-exchange reaction may occur:



The chemical sum of reactions 2 and 8 is equivalent to the slow reaction 3 and, if it is sufficiently faster than 3, will allow the steady-state condition of electrons and oxygen to approach a position closer to true equilibrium while AB passes through the ionization cell. This process would also cause a loss of free electrons and a normal ECD response. A requirement of this mechanism is that while the rate of electron attachment to AB must be faster than electron attachment to  $O_2$ , the electron affinity of AB must be lower than that of  $O_2$ , so that reaction 8 will occur. Anthracene is thought to form a radical anion by the resonance capture process<sup>13</sup>. If the anthracene radical anion is to charge-exchange to oxygen, however, its electron affinity will have to be less than that of oxygen, which is probably<sup>23</sup> about 0.44 eV. This condition is not satisfied if one accepts the value of 0.55 eV for the electron affinity of anthracene reported by Wentworth *et al.*<sup>13</sup>. However, as their method of determining this value was the pulsed ECD, it is possible that they mistakenly attributed the responses they observed to the resonance capture process alone, where, as is being suggested here, the origin of the anthracene response is more complex even in relatively oxygen-free (1 ppm) carrier gas. Also, the many assumptions made in the method of Wentworth *et al.* may have led to significant errors in the determination of electron affinities. Results obtained by APIMS provide further interesting insight into this problem. Carroll *et al.*<sup>24</sup> reported that in their search of API negative-ion spectra of polynuclear aromatic compounds they were unable to detect any ions characteristic of the sample. The ECD mechanism proposed here for anthracene predicts that no terminal ions of the sample are necessarily formed and is, therefore, consistent with this observation. In the solution phase an analogous catalytic role is played by the closely related compound naphthalene, in the electrochemical reduction of 1-chlorobutane in dimethylformamide<sup>25</sup>, that is, the rate of electrochemical reduction of 1-chlorobutane is greatly enhanced by the addition of naphthalene, which readily forms a radical anion and quickly reverts to molecular naphthalene by reaction with *n*-butyl chloride.

## CONCLUSION

Because of the greatly increased linear dynamic range of the modulated-pulse ECD and the high temperature capability of the <sup>63</sup>Ni ionization cell, the increase in the baseline accompanying the presence of oxygen in the carrier gas is not as serious

as has previously been described in studies using earlier ECD instruments. In fact, at detector temperatures of 250° and 350°C, relatively large amounts of oxygen can be tolerated with modest effects on the baseline. If the carrier gas is not ultra-dry, however, the effect of oxygen on baseline can be significantly greater. Another possible source of analytical error presented by the presence of uncontrolled amounts of oxygen is the variation in the ECD mechanism and the molar response factors of the sample compounds. The halocarbons studied, however, showed no significant response variations with the addition of modest amounts of oxygen to the carrier gas. Therefore, for these, the uncontrolled presence of a few parts per million of oxygen in a carrier gas is probably not, in itself, a source of analytical error. For anthracene, however, oxygen does cause a response increase at very low levels. Therefore, for the analysis of anthracene and perhaps other polynuclear aromatic compounds by the ECD, far greater control of oxygen contamination of the carrier gas is recommended.

By adding relatively large amounts of oxygen (2000 ppm), large ECD response increases can be caused for some compounds which, as for 1-chlorobutane, significantly improve the ECD response factors for otherwise poorly responding compounds. As this effect was observed at the high detection temperatures for 1-chlorobutane, a minimal sacrifice to baseline noise increase by oxygen is required. Therefore, the intentional doping of the carrier gas with a definite amount of oxygen may hold some promise for the improved analysis of monochlorinated organics.

The effect of adding small amounts of water to the carrier gas has been examined and found to be of importance to baseline frequencies and molar responses only under conditions when the presence of oxygen has first produced an effect. Thus, it appears that small amounts of water present in a carrier gas with a low oxygen content poses no great threat to the ECD analysis of at least the halocarbons examined here if analyses are performed with a constant-current  $^{63}\text{Ni}$  high-temperature instrument.

Considering the limitations of earlier ECD instruments which used a fixed frequency pulse or a d.c. voltage, and/or tritium ionization source of limited temperature range, the contradictory warnings of the past concerning the detrimental effects that trace amounts of oxygen and water in the carrier gas will have on ECD analyses are understandable and, in fact, consistent with our findings. The conclusion and intent of this study is not to recommend more relaxed standards of carrier gas purity, but to try to identify real sources of error in analyses by the ECD wherever they might occur.

Two mechanisms have been suggested by which enhanced responses may be caused by the addition of oxygen. In one of these,  $\text{O}_2^-$  serves as a catalyst for electron capture by the sample. This mechanism probably accounts for the response enhancements observed for the halocarbons studied here under the condition of high oxygen doping. In another mechanism, a radical anion formed from the sample serves as a catalyst for the achievement of electron-oxygen equilibria within the ECD. This possibility seems to provide a reasonable explanation for the oxygen dependence observed for anthracene. Studies are presently underway which will explore in more detail some of the specific suggestions of this survey of oxygen dependence.

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