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Short communication

Negative chromatographic peaks with oxygen doped electron capture detection of polychlorinated biphenyls

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Abstract

Electron capture detector make-up gas was doped with O_2 during polychlorinated biphenyl (PCB) analysis. At 6% O_2, PCB congeners 1, 3 and 4 produce negative peaks, with magnitude enhancement of 11 to 30-fold. For the other 14 PCB congeners studied, normal (positive) response enhancements of 3 to 30-fold are observed. Electron affinities may explain these results. © 1997 Elsevier Science B.V.

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1. Introduction

The electron capture detector (ECD) is commonly used in gas chromatography (GC) to detect chlorinated compounds. ECD response to various chlorinated hydrocarbons can be greatly enhanced (e.g., 228-fold for C_2H_5Cl) by the addition of small amounts (0.2–0.6%) of O_2 to the detector make-up gas ('O_2 doping') [1,2]. In this communication we extend O_2 doping to polychlorinated biphenyls (PCBs), an important class of environmental contaminants. We report the novel finding that some PCB congeners produce negative peaks under O_2 doping conditions. Weak electron affinities may explain the negative peaks. We also report modest response enhancements for the other PCB congeners studied.

2. Experimental

2.1. Reagents

Pure PCB congeners were obtained from Ultra Scientific (North Kingston, RI, USA). Individual congener solutions were made in hexane (EM Science, Gibbstown, NJ, USA). Dilutions of the original congener solutions were combined to make an isooctane (EM Science) solution containing 17 PCB congeners (listed with concentrations in Table 1).

2.2. Oxygen doping and gas chromatography

Analysis runs of the 17 PCB congener mixture were performed on a Hewlett–Packard 5890A GC with an ECD. Carrier gas (H_2, 99.999% purity, inlet pressure 1.84 bar) velocity was 50 cm s^{-1}. The injection port temperature was 300°C and injections (2 μl, Hewlett–Packard 7673A Autosampler) were performed in the splitless mode (0.7 min purge delay). The column was a J&W (Folsom, CA, USA)

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DB-5 capillary column (22 m×0.25 mm I.D., 0.25-μm film thickness). The oven temperature program was 90°C initial temperature, 5°C min^{-1} to 110°C, 2°C min^{-1} to 240°C and 10°C min^{-1} to 300°C.

For doping runs at 0.6% O_2, a pre-mixed cylinder of O_2 (99.998% purity) and N_2 (99.999% purity) was used. At the 6% doping level, O_2 (99.993% purity) was directly mixed into the N_2 make-up gas flow: the O_2 flow was adjusted to give an ECD baseline level ten times greater than the baseline of the pre-mixed cylinder at 0.6% O_2. For non-doping runs, N_2 make-up gas was used. Make-up gas flow-rate was 30 ml min^{-1} for all runs. The detector was held at 250°C, rather than the usual 330°C, to maximize O_2^- formation (the active species in O_2 doping) [2]. All gases (including the H_2 carrier gas) were passed through molecular sieve traps (J&W) installed upstream of the GC. The N_2 and H_2 were also passed through oxygen traps (J and W).

Detector signal was integrated by a Hewlett–Packard model 3392A integrator. Average peak areas ($n=3$) were used for responses. All peak areas for congeners 1, 3 and 4 were determined after transferring the chromatograms to a Macintosh computer.

3. Results and discussion

3.1. Negative peaks

Negative-going peaks of enhanced magnitude were observed for PCB congeners 1, 3 and 4 when O_2 comprised 6% of the ECD make-up gas (Fig. 1). We believe this is the first report of negative peak enhancement with the ECD. For a given compound, the response enhancement is defined as: response(doped)/response(normal) [2]. Congeners 1, 3 and 4 have enhancements of −17, −30 and −13, respectively (Table 1). For comparison, Fig. 2 shows a chromatogram obtained under normal, non-doping conditions. The retention times of the two chromatograms are identical within the experimental reproducibility, ±0.02 min.

With O_2 doping, inside the ECD a very small fraction of the O_2 molecules attach an electron to form O_2^- (Eq. (1)).

$$O_2 + e^- \leftrightarrow O_2^- \quad (1)$$

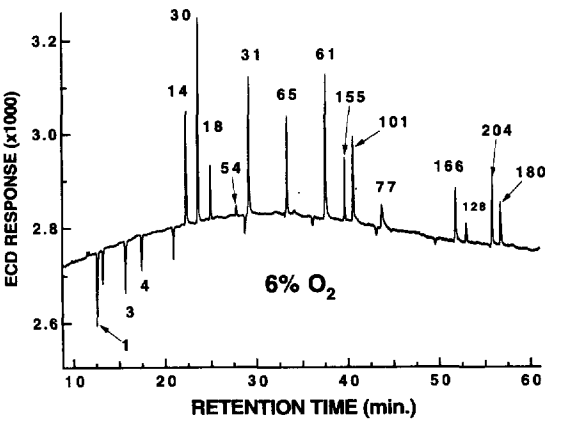

Fig. 1. ECD chromatogram of 17 PCB congener mixture with O_2 comprising 6% of the ECD make-up gas (balance N_2). ECD temperature = 250°C. Peaks are labeled with their PCB congener number. Note negative peaks for congeners 1, 3 and 4. Background detector response is approximately 170 times the normal background response. Note that vertical scale is 16 times smaller than in Fig. 2.

Table 1
ECD response enhancements with O_2 doping

PCB IUPAC[a]	Conc. (ng ml^{-1})	R.E.[b] (mean)	E.A.[c] (eV)
1	91.2	−17[d]	0.20
3	108.1	−30[d]	0.24
4	45.3	−13[d]	0.17
14	27.0	30	0.40
30	18.1	12	0.33
18	22.7	9	[e]
54	18.0	3	0.18
31	17.8	22	[e]
65	10.9	13	0.51
61	17.2	11	0.62
155	7.2	11	0.39
101	10.9	12	0.53
77	9.0	15	0.54
166	7.2	6	[e]
128	2.7	9	[e]
204	8.1	6	0.90
180	5.5	6	[e]

Conditions: 6% O_2 (balance N_2) in ECD make-up gas; detector temperature = 250°C.

[a] Structures corresponding to IUPAC number system may be found in Ref. [6].

[b] RE = response enhancement = peak area(doped)/peak area(undoped). Based on three measurements, except where noted.

[c] EA = electron affinity, in electron volts. Values from Ref. [5], accurate to ±0.2 eV.

[d] Peak with doping is negative. Based on 2 measurements.

[e] Not available; not reported in Ref. [5].

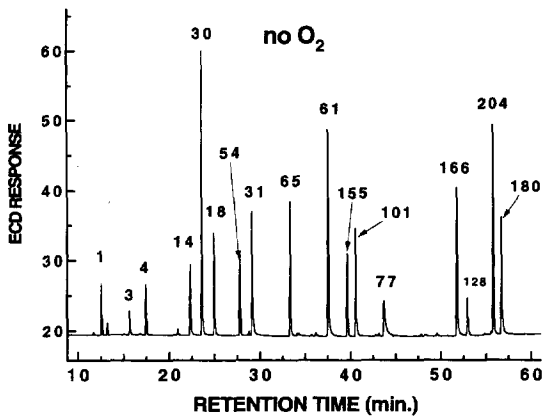

Fig. 2. ECD chromatogram of 17 PCB congener mixture with pure N_2 as ECD make-up gas. ECD temperature = 250°C. Peaks are labeled with their PCB congener number. All PCB peaks are positive. Background detector response is normal. Vertical scale is 16 times greater than in Fig. 1.

The reverse of Eq. (1) is also important in determining the O_2^- concentration, although strictly speaking, it is unclear whether equilibrium or steady state is established during the short period (40–400 μs) between detector pulses.

For analytes with poor normal ECD responses, electron capture is usually slow, although electron-transfer from O_2^- is very rapid (Eq. (2)) [3].

$$O_2^- + A \rightarrow A^- + O_2 \quad (2)$$

Analytes with large positive response enhancements either tightly bind the electron or undergo dissociative ionization ($X-Y \rightarrow X^{\cdot} + Y^-$) [3], permanently sequestering the electron. As Eq. (2) proceeds, O_2^- is depleted, slowing the reverse rate of Eq. (1) and thus allowing for a net uptake of free electrons by O_2. This couples the free electron population to the presence of the analyte [2].

PCB congeners 1, 3 and 4 form negative peaks because they have weak electron affinities (EAs); their molecular anions readily undergo thermal electron detachment (TED), Eq. (3), after receiving the electron in Eq. (2).

$$A^- \rightarrow A + e^- \quad (3)$$

For azulene, $k_{TED} = 1.0 \times 10^6\ T^{3/2}\ \exp(-EA/RT)$ [4], where EA is the electron affinity, R the gas constant and T the absolute temperature. Using this expression and the EAs [5] listed in Table 1, we estimate TED rate constants between 5×10^7 and $2 \times 10^8\ s^{-1}$ for congeners 1, 3 and 4. Under our conditions, these rates are even faster than the rate of Eq. (2) [3]. Furthermore, dissociative ionization, which normally would compete with Eq. (3), is probably unimportant here; the analogous compounds, chlorobenzene and the dichlorobenzenes, show only modest O_2^- doping enhancements [2].

Together, Eqs. (2) and (3) can quickly produce electrons, which would result in a negative peak. Furthermore, since the electron population in the ECD is markedly reduced at 6% O_2 doping (170-fold from non-doping conditions and 10-fold from 0.6% O_2); the relative increase in the electron population is very large. At the low doping level, the electron population is much larger. Therefore, Eqs. (2) and (3) would have much less relative effect, and no negative peaks would be observed. Finally, the more chlorinated congeners have much larger EAs [5]. This diminishes TED rates (e.g., for EA = 0.5 eV, we estimate $k_{TED} = 10^5\ s^{-1}$) and explains why the higher congeners exhibit positive peaks at both doping levels.

Interestingly, congener 54 does not produce a negative peak, even though its EA is comparable to congener 4. However, its enhancement is the smallest of the positive peaks. The rate of Eq. (2) depends directly on the analyte concentration; the relatively low concentration of congener 54 may explain the lack of negative peaks under these conditions. This implies that enhancement may not be constant with analyte concentration, nor linear with O_2 doping level, at least for PCB congeners with weak EAs. For instance, at 0.6% O_2 doping, congeners 1 and 3 had enhancements of +0.1 and +0.3, respectively. Thus, an analyte's molecular properties may determine the response enhancement as a function of O_2 doping level.

3.2. Response enhancements for the higher congeners

For the other 14 PCB congeners, response enhancements ranged between 1 and 2.6 at 0.6% O_2, and between 3 and 30 at 6% O_2 (Table 1). To compare our results, we also measured the enhancements for dichloromethane (13.5), chlorobenzene

(3.9) and 1,3-dichlorobenzene (5.7) at 0.6% O_2. Miller and Grimsrud report 324, 44 and 31, respectively [2]. Analyte residence times, about 10 times longer than in [2], may explain our much lower enhancements. Although doping still hastens analyte electron capture, the ultimate number of analyte molecules undergoing electron capture will not be strongly affected by doping if detector residence times are long. Since residence times are based on ECD volume and make-up gas flow-rate, O_2 doping might produce better results with smaller volume (~0.3 ml) detectors.

3.3. Detection limits

O_2 doping also increases detector noise. The detection limit will decrease only when the response enhancement outweighs the increased noise [1]. At the low doping level, response enhancements were very small (1–2.6). At 6% O_2, the largest enhancement was 30, but the baseline noise increased 400-fold. Therefore, we do not expect substantially lower detection limits with doping, even at intermediate O_2 concentrations.

4. Conclusions

(1) Doping at high O_2 levels produces negative peaks for analytes with weak electron affinities, like PCB congeners 1, 3 and 4, when dissociative ionization does not compete with thermal electron detachment.

(2) The presence and magnitude of negative peaks may depend strongly upon O_2 doping levels, analyte concentration and detector temperature. The ability to produce negative peaks under various conditions could be used to confirm analyte identity.

(3) O_2 doping moderately increases ECD sensitivity towards PCBs.

(4) Response enhancements do not outweigh increased noise. Thus, O_2 doping will not decrease detection limits for PCBs.

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