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REACTION AND RESPONSE IN ELECTRON-CAPTURE DETECTORS*

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SUMMARY

Response and reaction —the latter as indicated by consumption of analyte— have been monitored simultaneously in an electron-capture detector. Its response could be varied in d.c. mode by a factor of thirty through a change in interelectrode distance; the extent of electron-capture reaction, however, remained constant throughout. Similarly, response was varied in a pulsed mode by a factor of 2.5 through a change in the pulse interval; again, the extent of electron-capture reaction remained constant. These findings are consistent with an alternative response mechanism[1], which we have recently suggested for the d.c. mode of electron-capture detectors.

INTRODUCTION

The alternative mechanism for d.c. electron-capture response that we have recently suggested[1] envisions larger numbers of negative ions migrating to the anode (rather than being immediately neutralized according to the classical view). The model predicted a correlation of electron-capture response with the voltage profile measured under reversed-field conditions. This prediction was found to hold true under a variety of experimental conditions[2].

The experiments of ref. 2 were carried out with both ^{3}H and ^{63}Ni foils and involved mainly variations in interelectrode distance and cell pressure. These parameters were similar in their effects on response. An increase in distance or pressure brought about an increase in response. We attributed this increase to the increased counter-field (space charge) of migrating negative ions.

One could have argued, however, that such increases in response may have simply been due to an increased reaction rate of the analyte with electrons in the larger or more dense reaction volume. This classical view of electron-capture detec-

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tion (for a review, see ref. 3) presents the rate of electron capture as essentially synonymous with response. Response is seen as the removal of electrons from the cell current via capture by the analyte; thus reaction and response are inexorably linked. (It was for this direct link that the unexpected finding of "hypercoulometric" response[4] prompted us to suggest an alternative electron-capture mechanism.) In this mechanism reaction and response have been conceptually separated though not completely divorced: Obviously, response will still be (approximately) proportional to reaction when analytes of different electron-capture cross-section are compared under otherwise similar conditions. ("Approximate" because of the different mobility of various negative ions as well as the generation of electron-capturing products in certain cases.) However, for a given analyte under changing conditions, response is seen mainly as a function of cell geometry and pressure, rather than as a direct measure of reaction rate as in the classical view.

It thus became interesting for us to investigate the correlation of response with the extent of reaction, using only one analyte but different geometric settings. Response is defined easily enough; but measuring the "extent of reaction" presents a problem. An obvious way would be to sample ions by mass spectrometry from an operational electron-capture detector (ECD) (*cf.* refs. 5,6). Lacking this type of instrumentation, a different and much simpler measurement was adopted: the analysis of the detector effluents for residual analyte.

Such an analysis is easily achieved in a two-column system[7]. Despite its ease, however, this approach may be subject to error. First, the analyte may be consumed by processes other than electron capture, *e.g.* by charge transfer from positive ions or by reactions with radicals generated by various degradations. Second, one can not exclude the possibility of an analyte molecule undergoing electron capture but surviving, or being re-formed in, the subsequent processes. Yet, while the precise relation of apparent analyte consumption and the "extent of reaction" (the sum of electron-capturing processes by the analyte and its products) may be undefined at present, the use of analyte consumption data in a simple response correlation experiment such as this appears reasonable.

EXPERIMENTAL

Fig. 1 shows a schematic and self-explanatory representation of the gas chromatographic arrangement; Fig. 2 presents a more detailed drawing of the experimental ECD (EC-1). Its interelectrode distance could be easily varied by moving the electrodes through Vespel (DuPont) ferrules. EC-2, the second ECD of Fig. 1, was a commercial model (Tracor). Throughout the experiments, 10 pg 2,3,5,6-tetrachloronitrobenzene (TCNB) was used as the analyte. Other conditions were similar to those described in our recent paper[2].

RESULTS AND DISCUSSION

Fig. 3 shows a typical series of experimental results. In this case, the interelectrode distance was kept at 8 mm. A ^{3}H-Sc foil was used as the radioactive source. The response of EC-1 and EC-2 to the analyte, in coulombs peak area, is shown in heavy line at the top of the graph. Finer lines represent the voltage profiles for

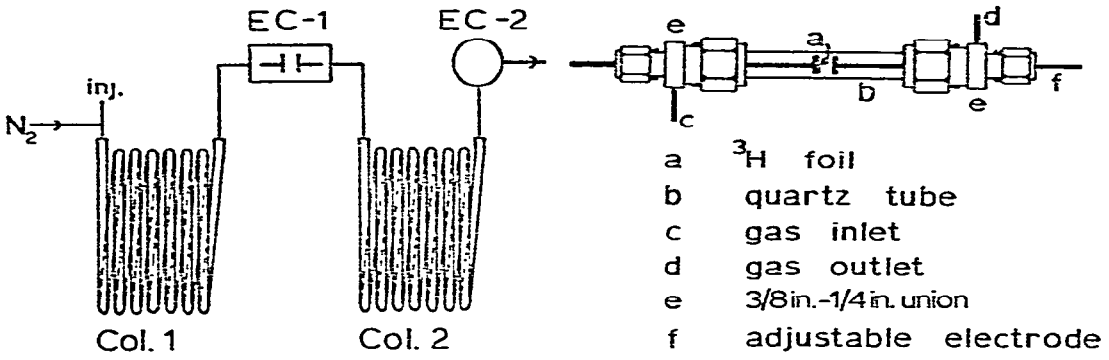

Fig. 1. Flow schematic of chromatographic set-up.

Fig. 2. Schematic of EC-1.

regular-field (V^-) and reversed-field (V^+) configurations ("voltage profiles" are current–voltage curves of the system in the absence of analytes).

The ECD under investigation, EC-1, was interposed between two columns, hence operated at elevated pressure. It was expected to perform similar to the ECD versions described in our earlier paper[2]. That it performed indeed according to expectation is shown in Fig. 4. Response —the maximum obtainable under each set of conditions— is an approximate linear function of the difference between the two voltage profiles, measured at 50% of maximum available current. For a comparison with out earlier results, a "percent of maximum current for maximum response" curve is included on top of the graph.

Running through a series of measurements that involve varying interelectrode distances and monitoring response in the first and second detector, it becomes immediately apparent that the response in the first ECD changes drastically, while the

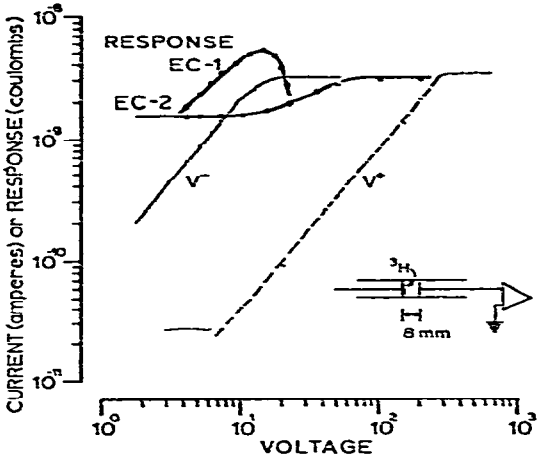

Fig. 3. Response of EC-1 to 10 pg TCNB, and of EC-2 to residual amount of TCNB. Baseline current (in amperes) for radioactive foil of EC-1 polarized with negative (V^-) or positive (V^+) potential. (The convergence of EC-2 response with the maximum current level is incidental.)

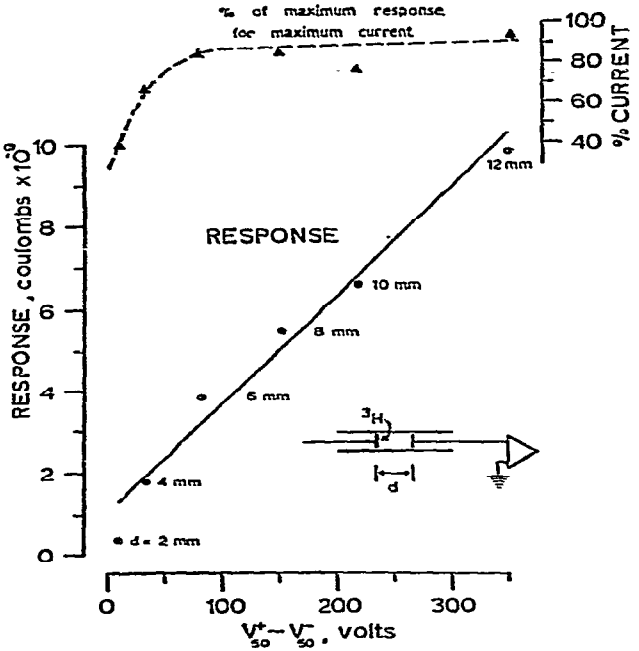

Fig. 4. Correlation of response at different electrode distances, with difference in voltage profiles at 50% of maximum current.

amount of residual analyte, hence the presumed extent of reaction, hardly charges at all. Chromatograms from two typical runs are shown in Fig. 5. The arrow points to the position of the TCNB peak under conditions where it is barely visible. Shown

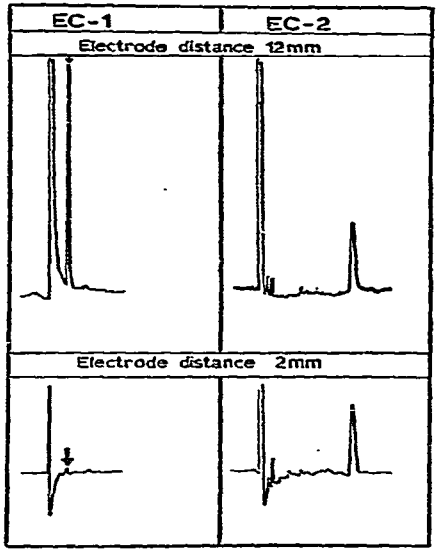

Fig. 5. Typical chromatograms from a series of measurements at various electrode distances. The arrow marks the elution time of TCNB in EC-1. The prominent peak on the right-hand chromatograms is from residual TCNB in EC-2.

above it is a much more pronounced peak obtained by widening the electrode gap. At the same time, the amount of residual TCNB as shown by EC-2 remains virtually the same (about 50% of the injected).

When such data are combined in a graph, a very clear picture emerges as demonstrated in Fig. 6. Response varies greatly with electrode distance, while the percentage of vanished analyte keeps at an even level. This percentage is measured at the same voltage at which EC-1 response is determined, *i.e.*, at the voltage necessary for maximum response. This means that the voltage increases in Fig. 6 from left to right with each set of data points. This may be one of the reasons why the fraction of analyte consumed is so surprisingly constant. As the interelectrode distance increases, the voltage necessary for maximum response increases even faster and with it the drift velocity of the electrons.

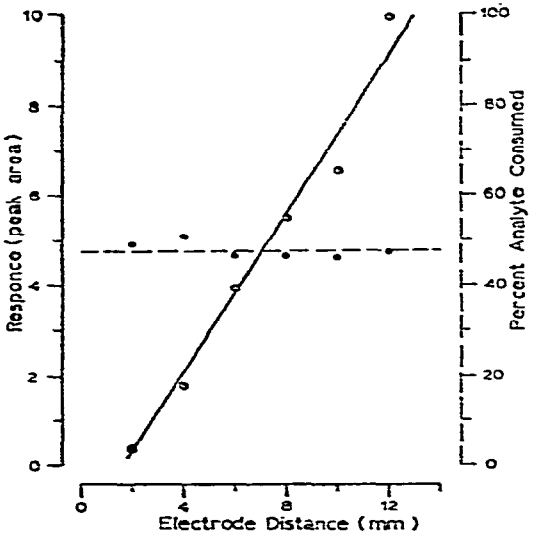

Fig. 6. Comparison of d.c.-ECD response to 10 pg TCNB (full line) and percent TCNB consumed (dashed line) at various electrode gaps.

It is also informative in this context to estimate the ratio of analyte molecules to available electrons. There are $3.8 \cdot 10^{-13}$ moles of analyte in a peak (assumed to be gaussian for this estimate, of which, according to EC-2, about 50% have reacted with electrons). The total electrons available during, say, a time slice equivalent to 2σ of the peak—*i.e.*, the distance across at half-height of the familiar quantitation triangle—is only $6.1 \cdot 10^{-13}$ Faradays. During that time, $2.8 \cdot 10^{-13}$ moles TCNB have passed through the detector. Thus, a relatively large fraction of available electrons were, in fact, captured by the analyte.

The main message of Fig. 6, however, is that response of this d.c.-ECD appears separated from (though, of course, dependent on) the initial electron-capture reaction; thus supporting the "alternative mechanism"[1].

A short experiment using the pulsed constant frequency mode of electron-capture detection, with 10 pg of TCNB as the analyte, was also conducted. As is well known, response of this mode often increases with pulse interval. This is usually and

easily explained by higher concentrations of electrons accumulated during longer, field-free periods between pulses. Consequently, the percentage of analyte consumed should increase with pulse interval. Fig. 7 shows that this is not the case: The response increases as expected, but the residual analyte remains the same. Thus, Fig. 7 may permit the speculation that even in the pulsed mode of electron capture, space charge effects similar to those discussed in an earlier paper[1] could perhaps play a not completely insignificant role.

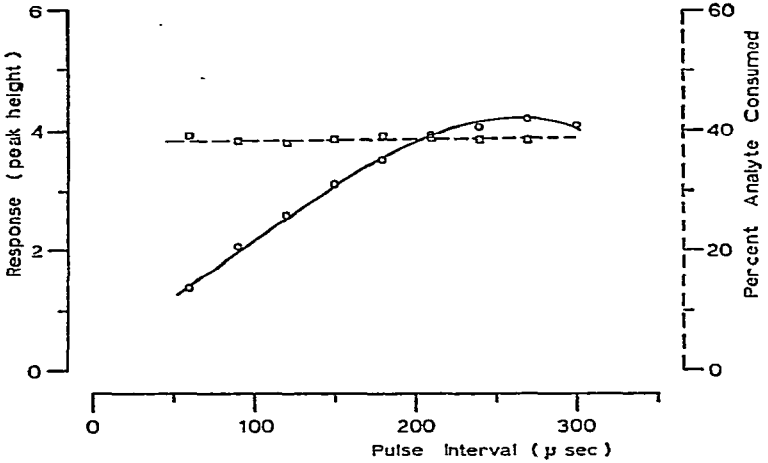

Fig. 7. Comparison of pulsed ECD response (full line) and percent analyte consumed (dashed line) at various pulse intervals. Pulse width 5 μsec, electrode distance 3 mm.

ACKNOWLEDGEMENTS

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