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VOLTAGE EFFECTS IN A d.c. ELECTRON CAPTURE DETECTOR

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SUMMARY

The effects of various constant potentials on reaction and response of typical model compounds were measured by a commercial electron capture detector (ECD). The effluents from this detector were separated by a second gas chromatographic column and detected by a second ECD. This arrangement allowed to distinguish between the parent substances and their products (where such could be detected), and to estimate how much of the parent substance had been consumed in the first ECD. Model substances included a variety of biologically active compounds that are usually determined by electron capture gas chromatography, such as chlorinated hydrocarbon insecticides. While all compounds shared a common voltage profile pattern, product formation depended on the individual structures. Potential mechanistic and analytical uses of the simple dual-channel system are indicated.

INTRODUCTION

When an electron capture detector (ECD) operates in d.c. mode, its response over a voltage range will show a maximum; and the particular voltage at which this maximum occurs is indicative of detector and carrier gas purity. This well-known fact, however, discloses little about the reaction between electrons and the analyte or, for that matter, about any subsequent reactions. The observed maximum of detector response does not coincide with the maximum reaction rate and, in most cases, it is unknown to what extent the analyte survives the reaction, and how much primary or secondary product, if any, is formed. The need to know, in this case, can arise from several premises.

First, the elegant technique of "coulometric" electron capture with two detectors in series[1] calls for compounds whose reaction products have little or no electron capture response by themselves. When "absolute" calculations are attempted[2], an ultimate ratio, most likely 1:1, between the captured (really: the decrease in collected) electrons and analyte molecules needs to be assumed; and electron-capturing products should again be absent.

Products from electron-initiated reactions have been found and sometimes identified by a variety of techniques, *e.g.* drift tubes, electron swarm experiments, negative mass spectrometry, plasma chromatography, glow discharges with gas

chromatography–mass spectrometry (GC–MS), etc. To our knowledge, however, a regular ECD has never been deliberately used for obtaining neutral products. This is due, at least in part, to the very small amounts of substance that can be reacted, considering the limited number of electrons available under conventional circumstances. On the other hand, it is these "conventional circumstances" that should be preferred for experiments designed to characterize ECD behavior. In this paper, the difficulties posed by sample size are circumvented by using a second column and a second ECD, for analysis of the "reaction mixture" obtained from the first ECD. It should be noted, though, that this approach will neglect products that are not strong electron absorbers.

Secondly, the calculation of molecular electron affinities from detector response data (*e.g.* ref. 3), or the estimation of ultimate detection limits (*e.g.* ref. 4), may be influenced by the presence of electron-capturing reaction products.

Thirdly, a better understanding of the reactions typical of an ECD might lead to improvements in analytical techniques, although we consider this matter a fairly unpredictable one at the moment.

We do realize that the pulsed electron capture mode is often preferred in several aspects to d.c. operation, not the least of which is the possibility to calculate electron concentrations in the cell. Most of the physical chemistry performed on ECDs did, in fact, rely on pulsed systems. That we chose to use the d.c. mode for this study may be explained partially by the specifications of equipment available to us, and partially by a certain neglect which the d.c. mode has encountered in all but straightforward analytical usage.

EXPERIMENTAL

A bench-type gas chromatograph with two ^{63}Ni ECDs (Tracor Model 550) was purchased and its two-channel output used to connect the two columns and two detectors in series as shown in Fig. 1. The carrier-gas, nitrogen, flowed through the usual molecular sieve filter, a rotameter, a commercial trap for oxygen and water (Supelco, Bellafonte, Pa., U.S.A.), the injection port, a 5-ft. GC column, ECD No. 1, a 3-ft. GC column, ECD No. 2, and through a restricting valve to exhaust. Both GC columns

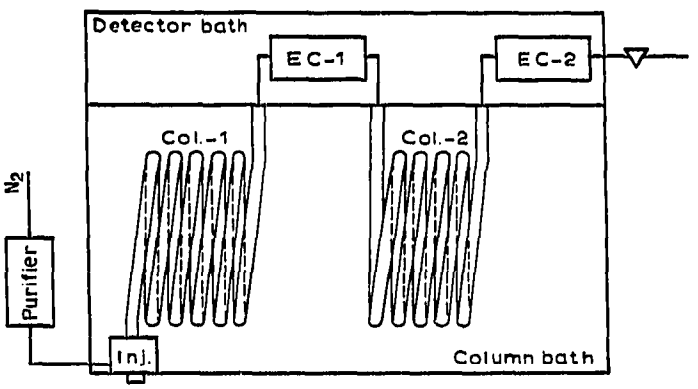

Fig. 1. Arrangement of chromatographic columns and detectors.

were 6 mm O.D., 4 mm I.D., coiled Pyrex tubes filled with 3% OV-101 on 40–60 mesh Chromosorb W AW. The detectors had been made leak-tight by carefully grinding the adjoining surfaces of the top, middle and base parts of the detector to a relatively smooth finish with garnet paper. They were tested every week or so, under operating conditions, by closing the valve at the end of the flow-path and watching the ball of the rotameter at its beginning drop to zero. (This was the only purpose for having a rotameter in the system, since flow measurements were done by a bubble flow meter connected to the exit line.)

Both ECDs were used in d.c. mode exclusively, detector 1 being polarized by a Keithley 1200 V Model 240A, detector 2 by the regular Tracor electron capture power supply. The latter was adjusted from time to time to the voltage that gave maximum response. Regular operating conditions were as follows: nitrogen flow-rate at ambient pressure, 60 ml/min; injection port temperature, 210°; transfer region temperature, 235°; temperatures of detectors 1 and 2, 290° and 320°; respectively; column temperature, as required by solute. Both detectors were monitored simultaneously.

Detector 1 was used in a variety of configurations, *i.e.* carrier entering from the top or the bottom; and positive or negative potential being applied either to the top or the bottom electrode, with the other electrode serving as sensor. Most experiments, though, used the conventional configuration (carrier enters from the top, top electrode negative, bottom electrode connected to electrometer).

The substances analyzed were obtained from various kits (PolyScience, Niles, Ill., U.S.A.; Chem-Service, West Chester, Pa., U.S.A.) and chemical supply houses (Aldrich, Milwaukee, Wisc., U.S.A.; K & K, Plainview, N.Y., U.S.A.). No effort was made to purify the compounds, but a few potentially interesting materials that showed up as confusing mixtures in the ECDs were excluded from further experimentation.

Exploratory testing was done on the following compounds: 1,1,2,2-tetrabromoethane, octachloropropane, 1,4-dibromobutane, 1,2,3,4-tetrabromobutane, 3-chloro-1,2-propanediol, diethyl fumarate, bromocyclohexane, hexachlorobenzene, hexabromobenzene, *o*-chlorophenol, *o*-dinitrobenzene, 2,5-dichloroaniline, *o*-nitroaniline, 4-chloro-2-nitroaniline, 2,6-dichloro-4-nitroaniline, cinnamaldehyde, hexachloroethane, chlorocyclohexane, nitrobenzene, *m*-chloronitrobenzene, *p,p'*-DDT, 1,1,2,2-tetrachloroethane, bromobenzene, benzyl chloride, *o*-chloronitrobenzene, *p*-chloronitrobenzene, lindane, heptachlor, aldrin, heptachlor epoxide, dieldrin, decachlorobiphenyl, and methyl parathion.

Only the last seventeen, however, were tested throughout the full voltage range with negative potential and only the last twelve were tested additionally with positive potential on the polarizing electrode.

RESULTS AND DISCUSSION

The experimental set-up as shown in Fig. 1, starting from a freshly bought and modified gas chromatograph, took about a week of operation to stabilize, *i.e.*, the voltage at which maximum response occurred in the two detectors kept decreasing during that time. The second detector then reached maximum at about 10–15 V, while the first one, presumedly owing to higher pressure, showed maxima between

30 and 60 V. The exact position of the maximum is a function of detector contamination, column bleed, and carrier gas pressure, and will therefore vary, among other parameters, with column flow and temperature. The response from the two detectors —which are otherwise exactly alike— differed by about a factor of four, detector No. 1, with its higher pressure, being the more sensitive one.

It should perhaps be stressed that commercial ECDs differ quite a bit from each other in construction, and that some of the following results may be valid only for the particular detector geometry used. Most significant, perhaps, the ECDs of this study are asymmetric as compared to most concentric or parallel plate designs: The upper chamber containing the ^{63}Ni foil plus first (polarizing) electrode is separated by a channel from the lower chamber containing the second (collecting) electrode. In conventional configuration, the column effluent enters into the upper and exits from the lower chamber.

The experiment perhaps most influenced by this geometry is the determination of the voltage necessary to "turn off" the electron-capture reaction, *i.e.* to let the solute pass through the detector unscathed. This technique is, of course, well known, having been used by Lovelock *et al.* in their pioneering study on coulometric response[1].

This turn-off occurs at much higher potential when the upper chamber (the ionizing region) represents the positive end of the electrical field. The plot of the baseline (or standing) current *vs.* voltage, as could be expected, also reflects the situation: the less mobile cations have a much longer distance to travel in this type of electron-capture cell, and saturation current is achieved only at high voltages. There is little difference between the two configurations in which a field of this direction can operate, *i.e.* between having the upper electrode provide the (positive) potential and using the lower electrode as collector (for cations), or having the upper electrode as collector (mainly for electrons) and using the lower electrode to provide the (negative) potential. Similarly, of course, either of two configurations can be used when the field is reversed to the commonly used direction. Obviously, the "resistance" of the ECD then drops and reaction shuts off at much lower voltages.

Figs. 2 and 3 illustrate this situation for chromatography of two levels of dieldrin: the characteristic S-shaped curve for the unchanged substance reaching the second detector is shifted to stronger fields when the polarizing potential is positive (in defining the field direction, the upper electrode is always taken as the polarizing one).

There was little difference among the substances thus examined: 1,1,2,2-tetrachloroethane, bromobenzene, benzyl chloride, *o*-chloronitrobenzene, *p*-chloronitrobenzene, lindane, heptachlor, aldrin, heptachlor epoxide, dieldrin, decachlorobiphenyl, and methyl parathion.

The differences between compounds were rather to be found in their tendency to form products which could be sensed by the second detector. The term "product" is applied in this context to any extraneous peak that shows up only in the second detector and tends to decrease at high voltages. (Thermal decomposition of solutes in the relatively hot first detector leading to extraneous peaks in the second detector cannot be excluded with certainty, but volatile decomposition products from such reactions should show the S-shaped profiles characteristic of the original substances.)

All the products which have been observed so far had shorter retention times than their parent substances. This was to be expected since most electron-capture

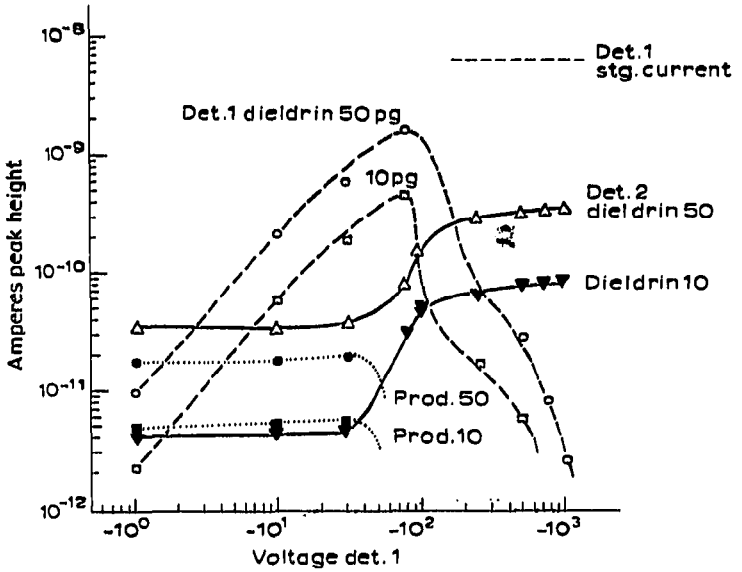

Fig. 2. Effects of voltage change in detector No. 1 on response of dieldrin in detector No. 1; and response of residual dieldrin and its product (formed in detector No. 1) as seen by detector No. 2; measured with 10 and 50 pg amounts per injection. Negative voltage applied to upper electrode in detector No. 1; gas chromatographic effluent enters from top. Column temperature, 200°. ○---○, Response det. 1–50 pg; □---□, response det. 1–10 pg; △—△, residual analyte from 50-pg injection as seen by det. 2; ▼—▼, residual analyte from 10-pg injection as seen by det. 2; ●···●, product from 50-pg injection as seen by det. 2; ■···■, product from 10-pg injection as seen by det. 2.

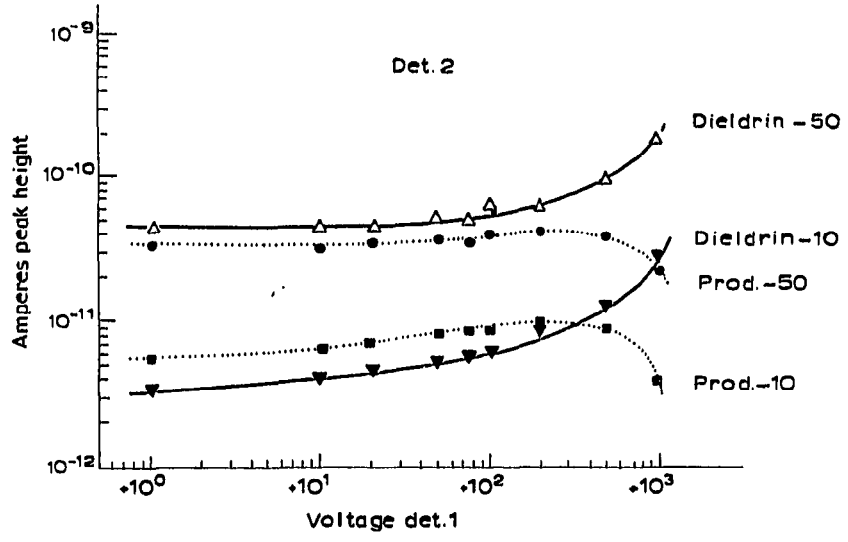

Fig. 3. Effects of voltage change in detector No. 1 on the response of residual dieldrin and its product (formed in det. 1) as seen by det. 2. Positive voltage applied to upper electrode. Other conditions as given in Fig. 2.

reactions of chlorinated hydrocarbons are assumed to involve loss of halide, and the relatively low concentration of the remaining organic radicals makes their combination, based on collision rates, seem unlikely. Besides, the isothermal condition of the gas chromatograph might not allow a compound resulting from combination of two heavy fragments to make it through the second column. However, the possible occurrence of products with longer retention times than their parent substance should not be completely ruled out.

Compared to dieldrin, which responds well in an ECD, other compounds show much less pronounced profiles, simply because only a small amount of the substance reacts in the first detector. This is illustrated in Fig. 4 with benzyl chloride.

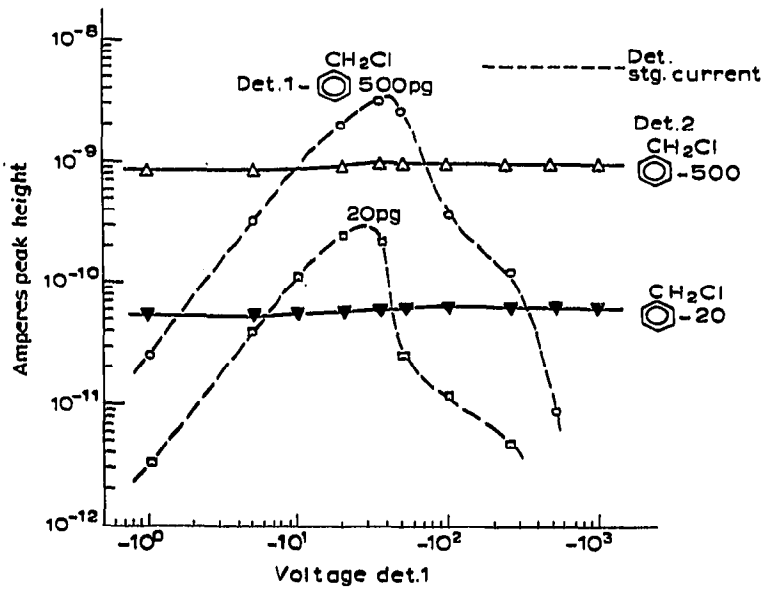

Fig. 4. Similar to the experiment shown in Fig. 2, but using 500 and 20 pg injections of benzyl chloride at a column temperature of 95°. No products seen.

On the other side, one of the best-responding substances was hexachloroethane and its voltage profiles were consequently interesting ones to trace. They are shown in Fig. 5. Fig. 6 shows some of the obtained chromatograms —arranged side by side instead of the experimental dual-channel output— for a clearer visual impression. It should be noted, perhaps, that 50 pg of hexachloroethane are way beyond the linear range of detector 1 at optimum voltage, but that this excessive amount had to be used in order to pick up both the compound and its product throughout the entire voltage range.

Fig. 5 shows some interesting details, for instance, the amount of product formed. The maximum displayed at medium voltages has also been seen with a few of the test compounds. Others, however, show only a steep decrease of product formation in the upper voltage regions. It is conceivable —though mere speculation at this time— that this peculiar maximum represents a kinetic effect: the "product" is formed but also consumed in the detector reactions and both reactions depend on cell

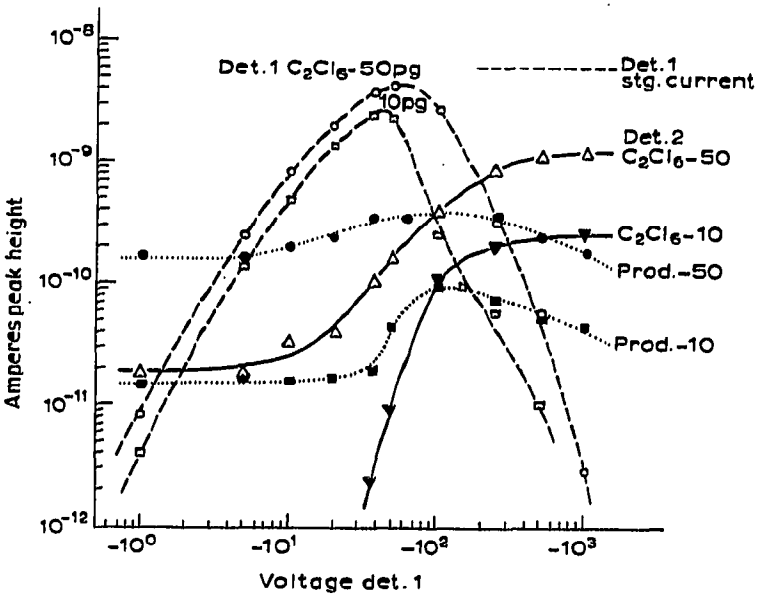

Fig. 5. Plot of voltage change *vs.* response of hexachloroethane similar to the one shown in Fig. 2. Column temperature, 90°. Column effluent enters from bottom.

voltage for the concentration of reactant species. However, energetic effects (cross sections, dispersal of excess energy, etc.), or different reaction mechanisms (positive ion formation) cannot be ruled out.

Another interesting aspect to consider is the characteristic S-shape of hexachloroethane as seen in the second detector. Firstly, the first detector is remarkably efficient in breaking down the compound at low voltages —more than 99% of it. (In computing this figure, the peak height data from Fig. 5 had to be corrected for non-linearity of the calibration curve of the second detector.)

Secondly, it is quite evident that the maximum of reaction and the maximum of response do not coincide. This effect is, of course, well known for d.c.-mode detectors. It may be interesting, though, to speculate on the extent of reaction at lower voltages. One of the possible approaches is to estimate these values by multiplying response by a correction factor f = (baseline current at high voltage)/(baseline current at the chosen voltage), assuming that the attenuation of both response and baseline current —due to incomplete collection of free electrons— are the same. Another, and obvious, approach is to use the S curve obtained from the second detector, and calculate from it the amount of "analyte consumed" in the first detector.

It is also interesting to go one step further and attempt a rough estimate of "response" in the first detector from the "analyte consumed" data obtained above —rough because of the severe linearity problems involved, because of the role of the product in adding to the response, and, last but not least, because very few hard data are available on the ion processes, the possible cross-section dependence on kinetic electron energy, and the chances for survival of particular negative ions upon neutralization. (The large neutralization energy is generally supposed to cause fragmentation, see ref. 1.) For the estimate, the S-curve from the second detector was corrected

for linearity and used to compute "analyte consumed" values, which were then corrected for efficiency of charge collection (the factor *f* mentioned above) and multiplied by an empirical constant (equating the highest responses from measured and calculated voltage profiles) to account for the sensitivity difference between the two detectors. The values thus derived bore some resemblance, particularly in the position of the maximum, to the response actually measured in detector 1; and Fig. 7 shows a typical example of such a correlation.

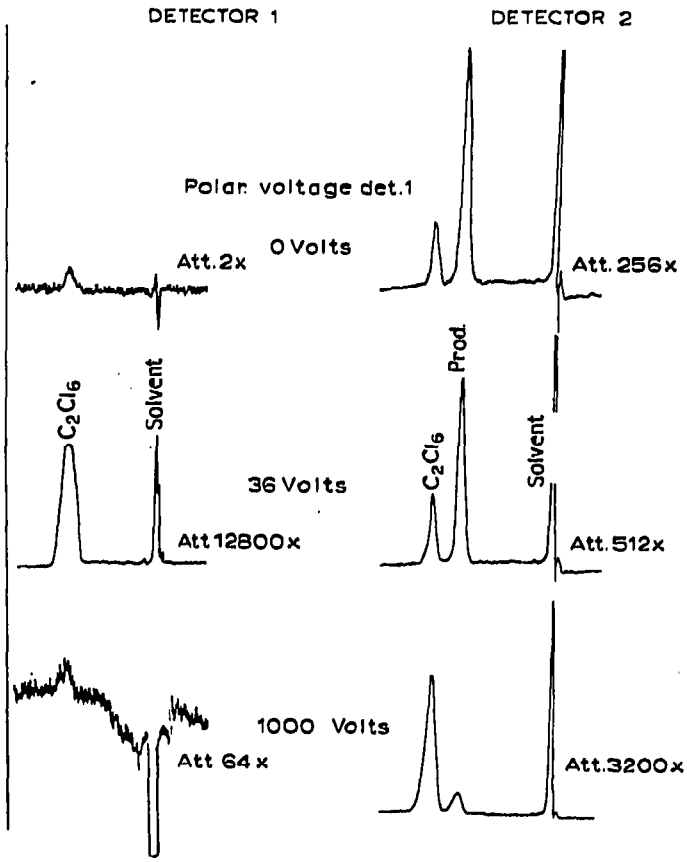

Fig. 6. Chromatograms obtained from 50 pg hexachloroethane as seen by two detectors. Simultaneously obtained chromatograms are placed side by side. Voltage in detector 1: 0, 36, or 1000 V; voltage in detector 2: constant (optimum).

In this example, involving aldrin, as well as in several other cases thus examined, an obvious discrepancy between measured and calculated values occurred at the high-voltage side of the response profile. It may be tempting, for instance, to speculate whether this discrepancy were related to the formation of positive ions from the analyte —leading to compound fragmentation without commensurate representation on the detector signal— or whether it were due to collection (as opposed to neutralization) of heavy negative ions (*e.g.*, M^-, Cl^-, etc.), or both. Both processes

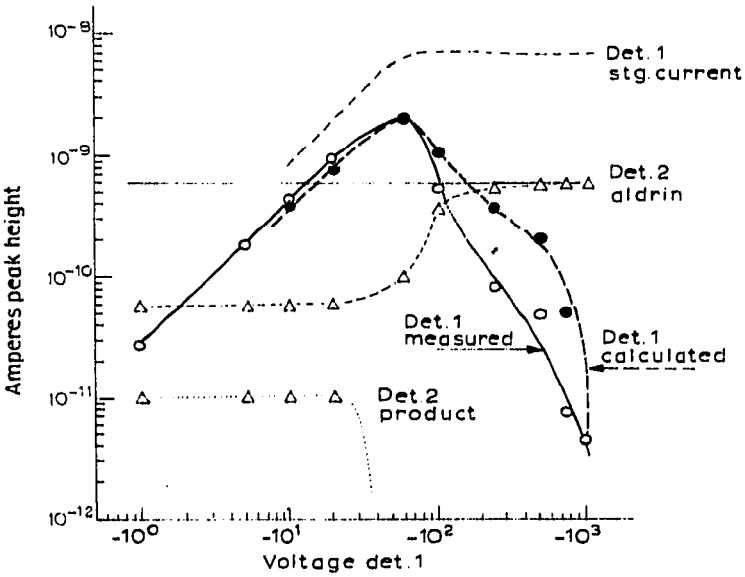

Fig. 7. Plot similar to the one shown in Fig. 2, but using 50 pg injections of aldrin. The response of detector No. 1 was calculated (●---●) from the amount of aldrin consumed in det. 1 (as shown by det. 2, ——— minus △--- △), and standing current in det. 1, as outlined in text. Column temperature, 200°.

would be expected to be more pronounced at higher voltages, but only detailed and much more extensive studies could provide conclusive evidence for these and/or other possible processes.

In this study we were satisfied to point out an obvious avenue for future inquiry. Other kinetic, mechanistic and analytical (*cf.* ref. 5) uses of the described, simple dual-channel system appear possible.

ACKNOWLEDGEMENTS

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