Journal of Chromatography, 148 (1978) 343–351

CHROM. 10,363

PRODUCTS FORMED IN AN ELECTRON CAPTURE DETECTOR FROM VARIOUS GAS CHROMATOGRAPHIC SOLUTES

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(Received June 29th, 1977)

SUMMARY

A variety of neutral, volatile, electron-capturing products was found to originate in the electron capture detector from certain pesticides and similarly structured analytes, such as the hexachlorocyclohexanes, penta- and tetrachloronitrobenzene, and various polychlorobenzenes. Some of these unexpected products have been tentatively identified by gas chromatographic retention data. According to these, product patterns arise from the loss of halide and/or nitro groups. These patterns are indicative of the analyte and can potentially be used to confirm peak identity in the lower picogram range, and determine the configuration of isomers.

INTRODUCTION

The nature of the products formed in an electron capture detector (ECD) from pesticides of the chlorinated variety was regarded worthy of closer investigation. That such products can be detected had been reported earlier[1,2]—a fact which is of potential importance for electron capture coulometry, for studies of relationships between ECD response and solute structure, and for analytical methodology.

In regard to electron capture coulometry, Lovelock and collaborators have pointed out in their pioneering paper[3] that this approach is feasible only if no strongly electron-capturing products are formed. First, such products would permit the capture of more than one electron by the actions of a single analyte molecule. Second, the arrangement of two detector cells in series (which is typical of coulometric electron capture) could not be used for the necessary calculation of ionization efficiencies, since the response from the first as well as from the second cell would be derived from *both* the analyte *and* its products; the ratio of analyte to products being different in the two cells. Presumably this ratio would depend on the initial concentration of the analyte, the electron capture cross-section of all species involved, the supply of thermal electrons, the flow and purity of the carrier gas (especially its oxygen content), the availability of a hydrogen donor, etc., and would thus be rather difficult to evaluate.

Even a very low response observed in the second ECD cell cannot be considered

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positive proof that no product is formed from this particular analyte: most or all of the product could have been consumed in the first cell. On the other hand, a higher response from the second cell than from the first could be taken to indicate the presence of electron capture products (the daughter being a better capturer than the parent). However, this conclusion presumes, first, that reaction rates, in conjunction with the available concentration of free electrons, allow a disproportionately larger amount of the parent substance to react in the first cell as compared with the daughter— even though the latter is the better capturer— and, second, that all reactions occurring are electron capture induced as opposed to, say, thermal or catalytic processes.

Even a separation and detection of products as achieved in this study by a column interposed between two detectors can give only limited information on whether or not electron capture coulometry is possible. Failure of the second detector to register products is no proof that they do not exist in the first: either they may have been totally consumed or they may not have been able to pass through the interposed gas chromatographic (GC) column. (Products with weak electron capturing properties are not seen, either, but these are of minor interest in this context.)

The above considerations do not preclude the use of coulometry in ECDs, but they do call for an awareness of possible error and a careful choice of analytes and analytical conditions. This conclusion seems to be borne out by the experiences of two groups using electron capture coulometry for air pollution studies[4,5].

Besides the coulometry aspect, the possible presence of products may also be important in correlations of analyte structure to ECD response, or conclusions on electron capture mechanism (associative *vs.* dissociative, etc.) based on the temperature dependence of response. If electron capturing products are (allowed to be) present in larger amounts, the measured capture coefficient could reflect the behaviour of analyte-*cum*-product rather than that of the analyte alone.

Making up for the limitations imposed by product effects, there may be some analytical advantage to their presence: their pattern can potentially be used for the confirmation of analyte identity at low concentration levels, and their genesis may prove interesting from the viewpoint of ion chemistry in the gas phase.

To gain more information on products, then, we decided to modify the earlier described instrument[1] in order to obtain better resolved product peaks, to evaluate the influence of different doping gases in the ECD cell, and to investigate a variety of solutes of interest.

EXPERIMENTAL

An insulated, heatable aluminum box designed to house the first GC column was affixed to a gas chromatograph. The effluents from the first column flowed to the detector bath and to the first ECD, then to the second column in the regular column bath, and on to the second ECD. The two columns could thus be held at different temperatures; the second one generally being kept some 40 to 50° lower than the first.

The first ECD's contribution to peak broadening was within tolerable limits owing to its small dimensions and smooth flow path. This ECD, which served the dual function of signaling the passage of the analyte and yielding its products, contained a ^{63}Ni foil and was operated in the d.c. mode.

Nitrogen, argon and helium were used as carrier gases. All three were purified

by passage through a cartridge containing charcoal, silica gel, and molecular sieve (Guild Corp., Bethel Park, Pa., U.S.A.) and through a heated oxygen scavenger cartridge (Supelco, Bellefonte, Pa., U.S.A.). Doping gases (hydrogen, carbon dioxide, ammonia, etc.) were added in small amounts through a fine metering valve with numerical counter, without further purification. Doping vapors (benzene, hexane, 2-pentene, isooctane, water, methanol, etc.) were added by sweeping controlled fractions of the carrier gas stream over the respective liquids. Hexachlorobenzene (HCB), pentachloronitrobenzene (PCNB,)2, 3,5,6-tetrachloronitrobenzene (TCNB), pentachlorobenzene, and γ-hexachlorocyclohexane (lindane) were used as standard solutes.

All experiments designed to yield product patterns were accompanied by "blank" runs in which the same compound was injected, but the first ECD was "turned off" by applying 1000 V. Only solvent and compound —but little or no products— should be observed under these conditions in the second ECD. Such blank runs serve as a precaution against erroneously including compounds arising from thermal decomposition among the (electron capture-induced) "products".

RESULTS AND DISCUSSION

Effects of doping gases

It is well known that the analytical performance of ECDs is affected, quite severely at times, by the nature and purity of the carrier gas. It was uncertain, however, whether and how product patterns would change with the deliberate introduction of various dopants into the carrier gas stream.

This part of the study was limited in several ways, the most important of which concerned the incompatibility of the GLC–ECD system with the chemical nature of certain interesting solutes and carrier gases. Furthermore, only the five standard test substances mentioned above were used in the doping experiments.

It should also be stressed that the instrument relies on a second regular GC column and ECD as separation and detection devices for electron capture-induced products formed earlier on. This means that these "products" need to be neutral, strongly electron-capturing compounds which elute within a reasonable time from the second GC column. Otherwise they would not be observed. Furthermore, retention time is the only available characteristic of a product in this system, subject to the well-known limitations of GC in terms of compound identification.

Within these severe limitations, then, the experiments gave a fairly clear answer: the nature of the carrier or doping gas did not significantly alter the product pattern as defined by retention times, but it did influence the amounts of products observed.

Small changes in the amount of products often occurred without any obvious change in conditions. The introduction of doping gases increased this effect. Roughly speaking, the amount of products increased with the molecular complexity of the dopant. The chemical nature of the latter, however, did not seem to play a significant role.

Thus, methanol, water, carbon dioxide, and methane all increased the amount of products as compared to that obtained with pure carrier gas, but did not differ much otherwise in their respective effects. Significantly larger amounts of products were obtained, however, with the more complex dopants: *n*-pentane, *n*-hexane, benzene,

cyclohexane, cyclohexene, heptane, and isooctane. This behavior is illustrated in Fig. 1 and 2. It may be of some significance in the choice of a carrier gas for electron capture coulometry, where the amount of products needs to be minimized.

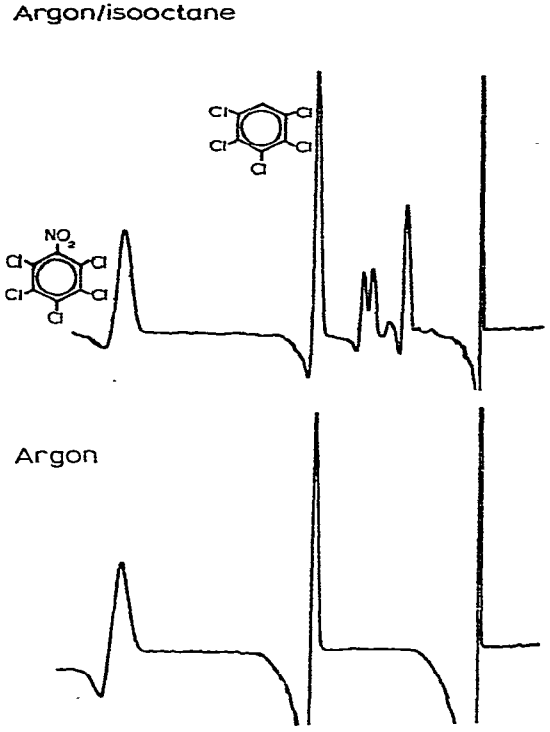

Fig. 1. Carrier effects in product formation: pure argon *vs.* argon doped with isooctane. Injected 200 pg of PCNB. Carrier flow at atmospheric pressure 30 ml/min. First column: Chromosorb W AW, 45–60 mesh, modified by a thin layer of Carbowax 20M with additional 3% OV-101 liquid phase load; 1 m × 0.2 cm I.D. borosilicate tube; 170°. Second column: same packing as in column 1, 1.75 m × 0.2 cm I.D. coiled borosilicate tube; 115°. First ECD/reactor: pressure 2.4 atm total, temperature 260°, d.c. mode, 50 V. Second ECD: pressure *ca.* 1 atm total, temperature 280°, pulsed mode, 60 V, 10-μsec width, 300-μsec interval. Chromatograms as seen by second ECD.

It is obvious that the choice of the doping gas may determine the nature of the positive species in the ECD. No significant qualitative changes were found to relate to the use of dopants in these experiments and it would be tempting to speculate that the only effect of the dopants, besides their possible function as hydrogen donors, would lie in their role as moderating third bodies picking up excess energy. The important steps would then involve the (quasi) unimolecular decomposition of negative solute ions (and subsequent radicals), followed by hydrogen abstraction from any suitable substrate. However, the experimental data from such a system are far too scarce to allow firm conclusions in regard to mechanism. A variety of processes, including surface reactions, could generate, or contribute to the products observed.

The results obtained by changing the gases flowing through the electron capture cell are parallelled by the results of a (very limited) study in which its temperature was

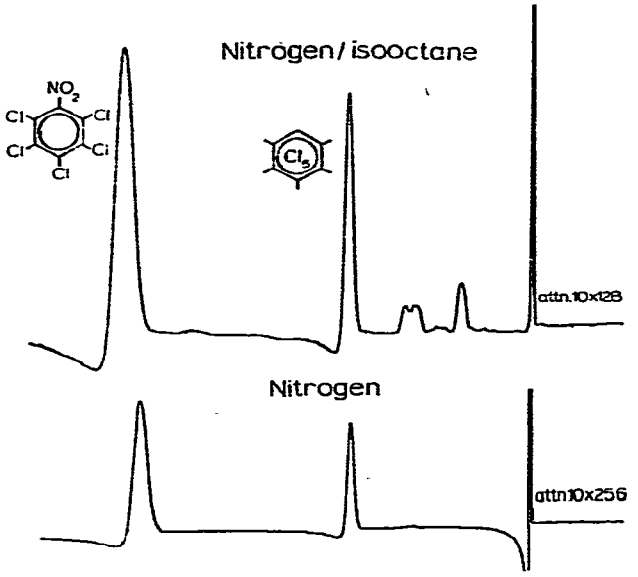

Fig. 2. Carrier effects in product formation: pure nitrogen *vs.* nitrogen doped with isooctane. Other conditions as in Fig. 1.

changed. The product patterns of PCNB and TCNB proved to be similar (within general fluctuation limits) between 190 and 310°.

Selected product patterns

Fig. 3 shows dual channel chromatographies (with the response of the first ECD overlaid in dashed line) of PCNB and pentachlorobenzene. The arrows mark the time at which the analyte passed through the first ECD, *i.e.* time zero for chromatography on the second column. The similarity in retention time between the pentachlorobenzene and the major product of PCNB, as well as the similarity of the other products, suggest (within the limitations outlined above) the loss of the nitro group of PCNB in preference to the loss of chloride. A similar behavior is shown by TCNB whose major product is 1,2,4,5-tetrachlorobenzene. There is no obvious evidence for initial loss of chlorine, *i.e.* the formation of tetrachloronitrobenzenes from PCNB or trichloronitrobenzenes from TCNB is not observed.

The apparent preferential loss of the nitro group was unexpected from the viewpoint of conventional organic chemistry. Some information exists on gas phase reactions of nitro compounds as seen by various ion-monitoring instruments, but these data also suggest that chlorine should have been eliminated in preference to the nitro group.

Nitrobenzene shows *associative* capture with thermal electrons, but *dissociative* capture only with electrons of *ca.* 1 and 3.5 eV; while various aromatic halides capture low energy (including thermal) electrons in a dissociative process which peaks at *ca.* 1 eV, as shown in swarm-beam experiments[6]. It was suggested that dissociative electron attachment in multiply-substituted halogenated compounds with a nitro group

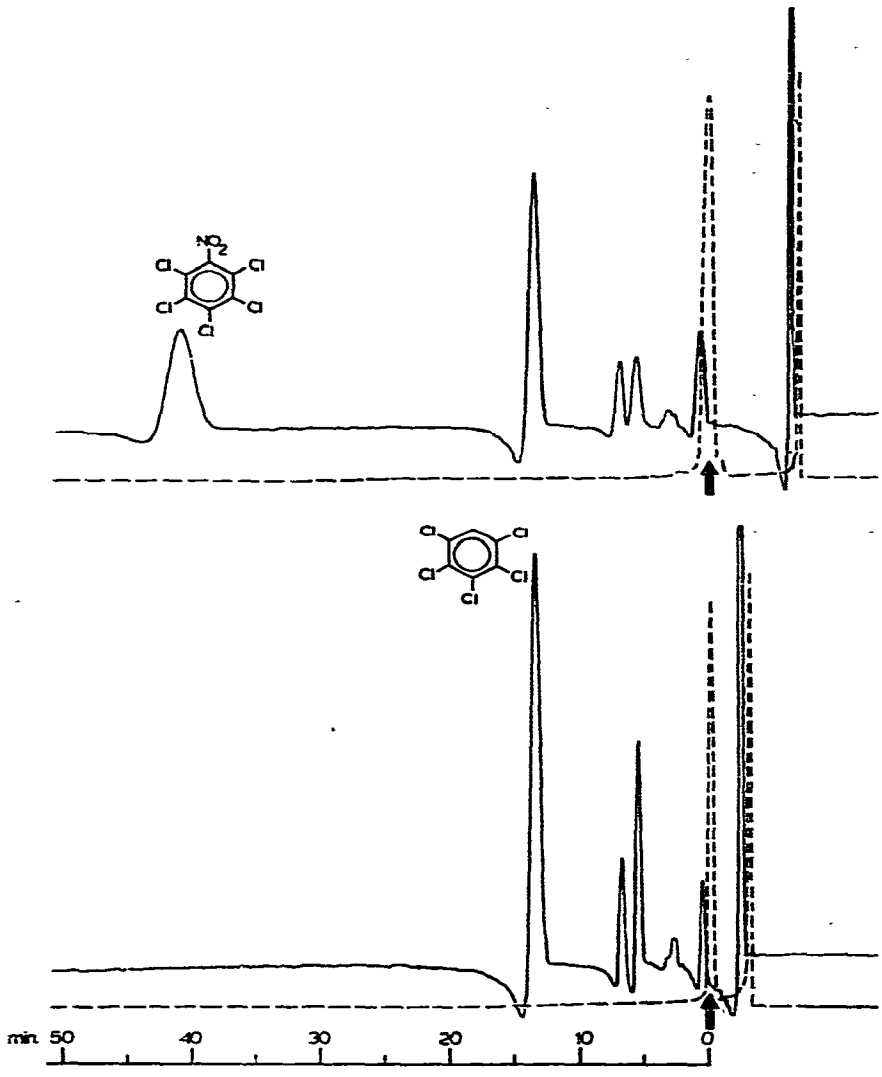

Fig. 3. Product patterns of PCNB and pentachlorobenzene. Injected 150 pg each. First ECD: dashed lines; second ECD: solid lines. Carrier: argon–isooctane. Other conditions as in Fig. 1.

would prevent the formation of long-lived parent-negative-ions[7] as are otherwise observed with NO_2-containing benzene derivatives.

In gas phase reactions of electrons in a *ca.* 200 V/cm field at atmospheric pressure (in "plasma chromatography"), loss of $-NO_2$ apparently occurs to some degree from trinitrotoluene[8], but only loss of halogen is observed from the *ortho*- and *para*-chloronitrobenzenes and various dihalonitrobenzenes[9]. Although plasma chromatography operates at conditions much closer to those typical of the ECD than, say, do electron swarm experiments, the two approaches are still not to be equated.

Rather, the instrument described in this paper is, in some respects, comple-

mentary to other systems since it detects neutral, volatile, electron-capturing compounds rather than ions. The NO_2^- ion, for instance, would be seen by mass spectrometry or plasma chromatography but not by our system. On the other hand, these techniques would not pick up (for a possible exception see ref. 10) a neutral, chloro-substituted phenyl radical—whereas, after hydrogen abstraction from a suitable donor, this derivative would chromatograph and show up in the ECD. It is also obvious that the products seen by the second ECD may be the end products of a complex sequence of reactions; although the product patterns' simplicity, and relative immutability in varying chemical environments, suggest that they reflect straightforward processes.

Fig. 4 shows the product patterns from positional isomers of tetrachlorobenzene. The number, retention times, and relative magnitude of the product peaks do indeed relate to those expected for the trichlorobenzenes formed by random removal of one chloride (singlet *vs.* 1:1 doublet *vs.* 1:2:1 triplet). Thus it would have been possible to deduce the structure of a particular tetrachlorobenzene from its trichlorobenzene product pattern.

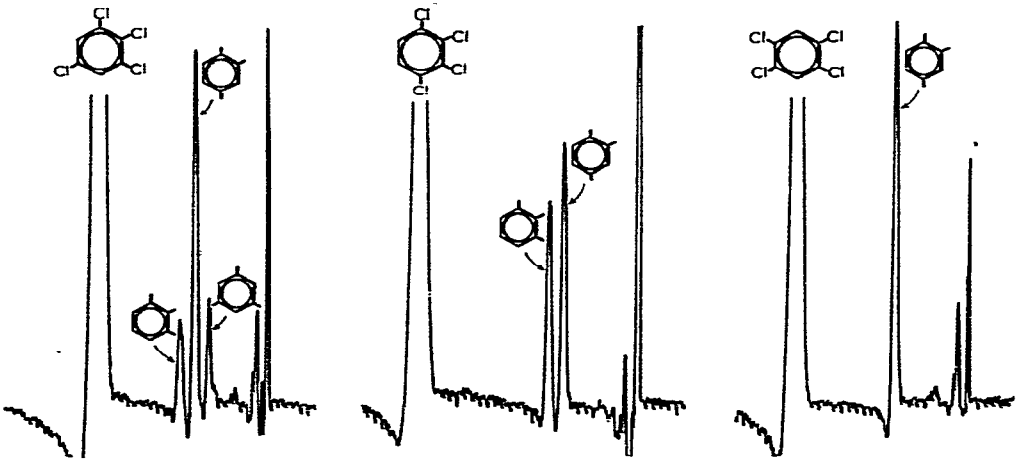

Fig. 4. Product patterns of the three tetrachlorobenzene isomers. Injected: 350 pg each. Conditions similar to those given in Fig. 1, but second column temperature 105°. Carrier: argon–isooctane.

Fig. 5 shows the product patterns of three isomers of hexachlorocyclohexane. The product structures are not known, but their patterns are clearly different. This indicates that structural features are largely preserved and suggests a relatively mild (low-energy) degradation. It has been suggested that complex organic structures are unlikely to remain intact on neutralization under regular electron capture conditions[3]. However, the high cell pressure and the presence of doping gases may help to accommodate the excess energy. Furthermore (in the case of dissociative electron capture) the neutralization would involve the chloride ion rather than the analyte (molecular) ion.

The approach of monitoring electron capture-induced, neutral products by GC means focuses on a group of analytes which is a very important, yet very restricted

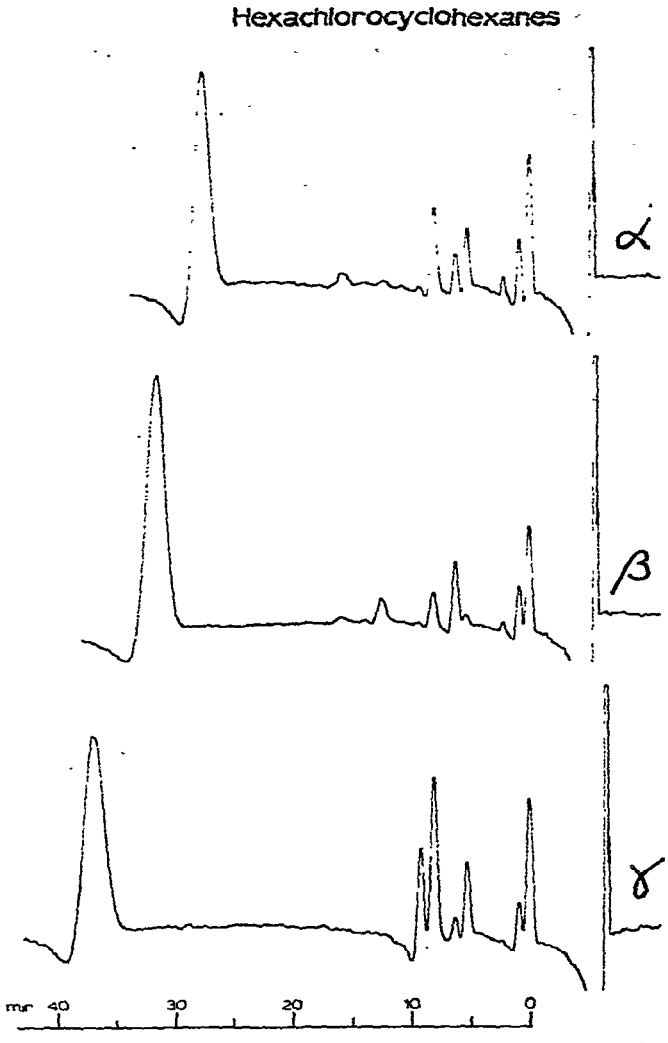

Fig. 5. Product patterns of three hexachlorocyclohexane isomers. Injected: 200 pg each. Second column temperature 115°. Carrier: argon–isooctane. Other conditions as in Fig. 1.

one in regard to compound structure and concentration in an analytical sample, *i.e.* pesticides containing halogen and nitro groups, explosives, etc. It is complementary to ion-monitoring methods based on the drift tube (plasma chromatography) and the various types of mass spectrometers in several ways. First, the process in the *chromatographic* system occurs under true electron capture conditions (potential, purity of carrier gas, etc.) and permits therefore an evaluation of electron capture mechanisms at a higher confidence level. Second, it allows a look at the isomer configuration of the products and, by induction, at that of the analyte. Third, it can establish whether or not certain electron-capturing products are likely to be formed from a particular compound whose use in electron capture coulometry or measurements of electron capture coefficients is planned. Perhaps most important of all, it is an approach which can be

carried out in the lower picogram range with a comparatively inexpensive and relatively easily-handled instrument.

ACKNOWLEDGEMENT

This study was supported by NRC grant A-9604 and AC grant EM7401/0-9606.

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