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GAS CHROMATOGRAPHY WITH *IN SITU* PHOTOLYSIS*

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SUMMARY

A recently developed, very simple instrument that combines two-dimensional gas chromatography with photolysis in a single unit, has been tested in different operational modes and with various substrates. Photolysis can be carried out with the sample either flowing through or being trapped in the reactor, and with or without sensitizer (mercury-doped carrier gas). Irradiation time and temperature can be varied at will, and surprisingly precise first-order degradation plots are obtainable within a short time. Many compounds of different structure yield characteristic product patterns, and structural similarity leads to similar-appearing patterns. The chromatographic configuration around a reactor capable of trapping peaks can be used not only for photolytic but also for thermolytic or conventional chemical reactions.

INTRODUCTION

Recently we reported on the construction of a simple, two-column gas chromatograph with photolytic intersect[1]. The instrument was designed to combine some of the salient features of photochemistry and gas chromatography (GC) into an integrated unit. Its photolytic reactor was interposed between two GC columns; the first of which fed a valve-selected peak to the reactor for degradation, whereupon the second one separated photoproducts and residual analyte.

More than one compound could be trapped in the reactor and held there for a chosen irradiation time. The reactor could be heated or cooled, although the very simple arrangement did not permit precise temperature control.

Several photolysis experiments were performed in this study —primarily not for the sake of establishing product patterns (which were known in most cases from the literature (*e.g.*, ref. 2) anyway), but for appraising the instrument's capabilities and for demonstrating the kind of chromatogram one might expect to obtain from it.

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EXPERIMENTAL

The instrument has been described in the earlier paper[1]. Columns were, for most experiments, 9% OV-101 on Chromosorb W AW, 45–60 mesh; packed into 80 cm × 4 mm I.D. coiled borosilicate tubing. A 3% OV-101 packing, and a special phase based on Carbowax 20M (ref. 3), were also used where expedient.

Irradiation times generally varied between 5 and 10 min; except in "flow-through" experiments where the residence time in the reactor was approximately 6 sec. The light sources were low-pressure Hg discharge tubes (Pencil lamp; Spectronics, Westbury, N.Y., U.S.A.) with or without a 360–380 nm output tubular fluorescence conversion filter. The lamps emitted predominantly at 245 nm; but other Hg lines were present as well and their relative intensities changed, of course, with age and temperature of the lamps.

All compounds were injected onto the first column at temperatures suited to separate them from the solvent and/or impurities. A heart-cut of the compound was then trapped in the reactor. In most cases, the column bath (and with it the reactor) was allowed to cool down close to ambient temperature for irradiation. Then the product and the residual compound were released to the second column and the temperature program started.

RESULTS AND DISCUSSION

Most of the following figures are self-explanatory and comments will therefore be held to a minimum. It may be noted that dashed-line peaks appear in most chromatograms. These were rendered this way by depositing globs of "Liquid Paper" on the original chromatogram prior to photographing it; to indicate that they are of no concern to the discussion. (Such peaks arise from the flow configuration peculiar to the extremely simple GC instrument[1] and are included here merely for the sake of authenticity.)

Fig. 1 shows chromatograms of two *n*-hydrocarbons photolyzed in Hg-doped carrier gas in flow-through configuration, *i.e.* for about 6 sec. Relatively small but characteristic products are formed even within this short time span. Sensitization was obviously necessary since alkanes do not absorb at 254 nm, and mercury vapor proved a convenient sensitizer as it has for a long time in photochemistry[2-4]. [Of the two safety alternatives, *viz.* venting only the detector effluents or surrounding the whole gas chromatograph with a hood, the second one was chosen. Taking account of the carrier gas flow-rates and the fact that the vapor pressure of mercury at room temperature represents only some 200 times the permissible maximum atmospheric concentration (0.1 mg/m^3 time-weighted average, no hazard to a cautious operator should arise.]

The peak ratio of compound (residual analyte) to photoproduct depends on irradiation time. In our system, trapping peaks in the reactor and irradiating them for a few minutes proved preferable to "flow-through" photolysis for most purposes. Fig. 2 as well as all figures to follow were obtained by such peak trapping.

Fig. 2 shows the characteristic picture of photolyzed alkanes (For literature on photolysis of these and other compounds see available books on photochemistry, *e.g.* ref. 2.) Typical for homologues, the two chromatograms are appropriately shifted along the retention (temperature) axis, but are otherwise much alike. Here as

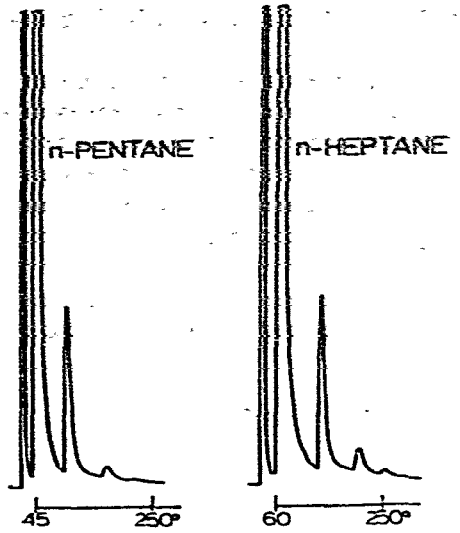

Fig. 1. "Flow-through" photolysis of pentane and heptane. Carrier gas saturated with Hg (at room temperature). Residence time in reactor *ca.* 6 sec. Biggest peak represents the residual analyte.

with other substrates used in this study, one expects compounds of higher molecular weight than the analyte (products of dimerization, etc.) to show strong dependence on sample concentration. To enhance such products, injections of neat material are advantageous.

Photolysis of heptane and octane was carried out conveniently at *ca.* 50°; *i.e* the GC column bath was close to ambient temperature during irradiation and the only heat source for the reactor was the discharge lamp itself. When the temperature of the reactor was changed, the extent of reaction and the distribution of products —

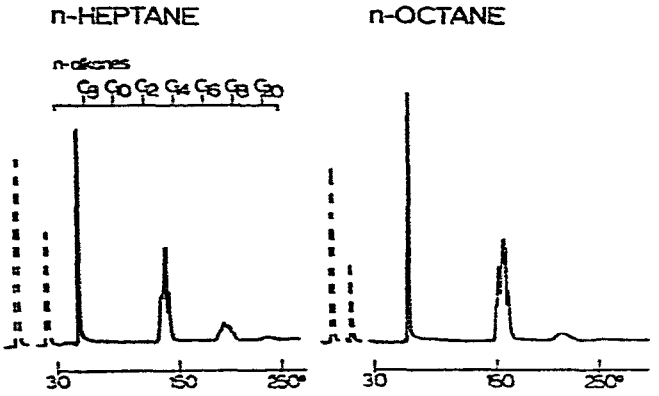

Fig. 2. Mercury-sensitized photolysis of trapped heptane and octane, injected neat. Irradiation: 10 min at ca. 50 °C. The inserted scale lists the retention of straight-chain hydrocarbons for comparison.

named "C-14 products" and "C-21 products" for the two humps shown in Fig. 2—changes considerably.

Now, temperature dependences of photochemical reactions are an interesting and sometimes controversial subject. The data contained in Fig. 3 can be easily obtained in an afternoon; however, they cannot yet be taken to reflect a true temperature dependence. This is due to the simplicity of the set-up: The discharge lamp is surrounded by the reactor; hence its spectral output will change with reactor temperature. Most important, however, is that, depending on temperature and concentration, some of the analyte, some of its products, or some of the sensitizer, can be adsorbed, liquified or solidified on the reactor walls. Using appropriate modifications and precautions, however, temperature effects in photochemistry could well be investigated in such a GC system.

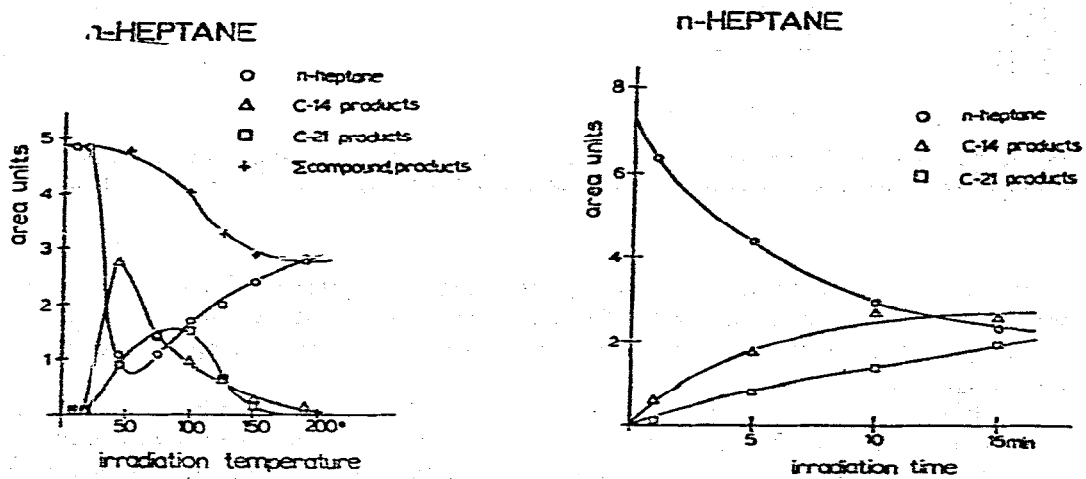

Fig. 3. Temperature dependence of heptane photoproduct pattern under Hg-doped conditions. Injection: 1 μl neat heptane. Heating via column bath, cooling via nitrogen stream (from LN_2). Irradiation time: 10 min. Temperature measurement by inserted thermocouple. See text for precautions in interpretation.

Fig. 4. Mercury-sensitized photolysis of heptane (injected neat) at 60°.

Given the limitations of the present instrument, a plot involving temperature, as is shown in Fig. 3, is primarily of utility in scouting experiments and in establishing suitable conditions for later analytical usage. It is also interesting to note that the sum of peak areas of compounds and products (a number roughly equivalent to the amount remaining in volatile form, if a flame ionization detector is used and all products are included) deviates, at the maximum of heptane conversion around 60°, very little from the ideal 100%. This ideal, of course, means the absence of any non-volatile materials remaining in the reactor.

Perhaps more solid kinetic information can be gleaned from plots involving irradiation time; similar to the one shown in Fig. 4. Consecutive reactions with many compounds involved (in the C-14 and C-21 products category) are, of course, difficult to follow. Considerable improvement could likely be obtained by using capillary column separations in such a case.

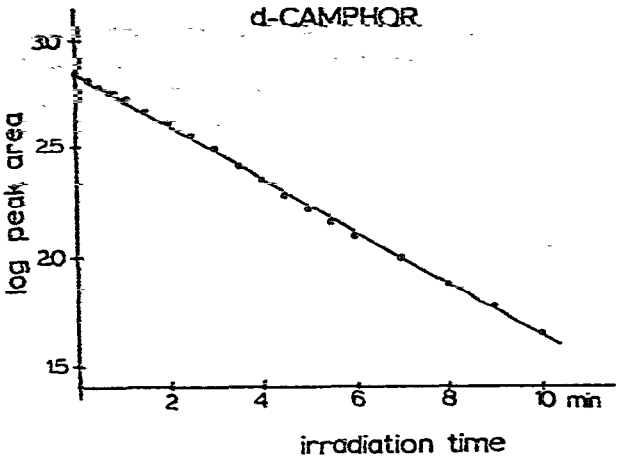

Fig. 5. First-order plot for *d*-camphor photolysis. Irradiation at 90°. Corrected for the contribution of non-irradiated camphor trapped in valve and connections to reactor.

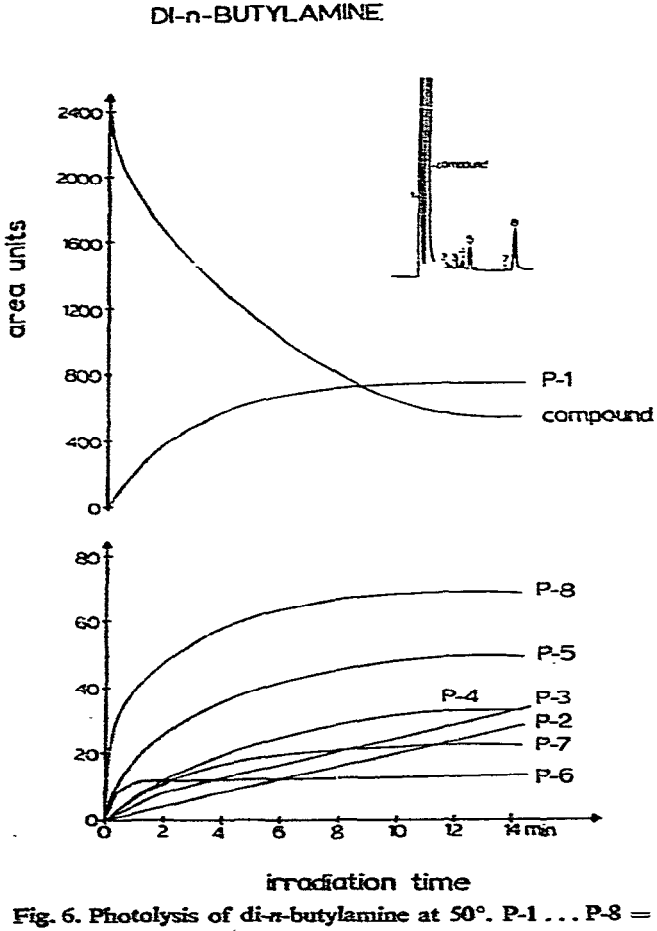

Fig. 6. Photolysis of di-*n*-butylamine at 50°. P-1 . . . P-8 = Products 1 . . . 8 as shown on inserted chromatogram.

Considering the simplicity of our apparatus, it is fair to question the precision of the data obtained from it. Fig. 5 shows the disappearance of *d*-camphor as a first-order plot. Each of the data points represents one injection, ergo one photolytic experiment. The whole series was run in less than a day. Its precision is comparable to that of simple GC itself.

Figs. 6 and 7 are again plots involving a variation of irration time; on a case of many products in Fig. 6, a case of a few distinct ones in Fig. 7. We do not intend to discuss the possible kinetic conclusions due these plots, but simply want them to demonstrate the ease and speed with which they can be obtained: Taking the data off a recorder chart and preparing the graph took time comparable to running the photolysis plus associated GC.

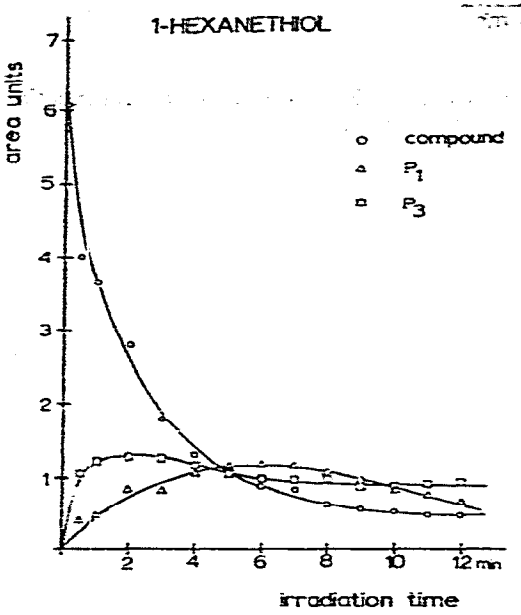

Fig. 7. Photolysis of 1-hexanethiol at 60°. P_1, P_3: see Fig. 9 for corresponding chromatogram.

It should perhaps be emphasized that the starting substance is purified very efficiently in the experiment itself: Only a "heart-cut" of only the peak of interest is transferred to the reactor. This, and the short time of manipulation in a high-purity gas system, adds to the reliability of results, especially when fairly labile compounds are involved.

This lability can be easily assessed by running "blanks", *i.e.* the compound is not subjected to irradiation but is otherwise treated exactly as its irradiated counterpart. Such blanks, though generally not shown here, were routinely included in each experiment.

In Fig. 8, we do show such a blank for the case of a labile substrate, 1-hexanethiol —the same compound as used for Figs. 7 and 9. The blank on the left reveals that minor conversion to the dimerization product P_3 occurs even without radiation (compare ref. 5). Chromatographic retention suggests that the product is the same as

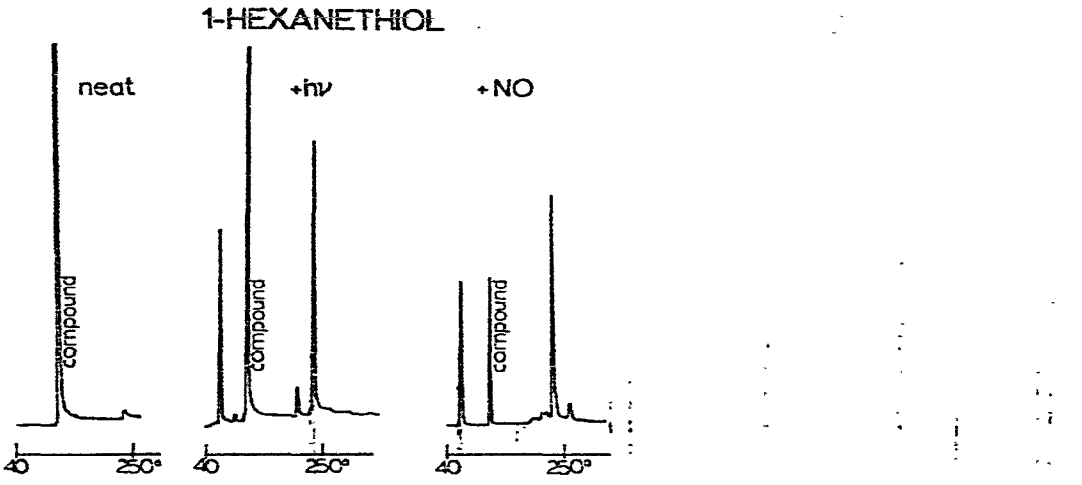

Fig. 8. Pyrolysis, photolysis, and reaction with nitric oxide, of 1-hexanethiol. Compound was exposed to the effects of a 100° → 250° temperature program during separation on the first column.

the one obtained by photolysis (middle) or a non-photolytic reaction with a reagent radical (right). It is obvious that a reactor as described can be deliberately used for other than photochemical reactions and that one has to guard against such reactions occurring when a purely photochemical study is intended.

The UV-induced pattern for hexanethiol is very much like that of octanethiol — only two methylene groups lower on the retention scale (Fig. 9). Obviously, such a pattern carries structural information. As early as 1965, Juvet and Turner[6] used photolytic degradation prior to GC as a means of organic structural determination in an effort to provide a technique similar to, but better reproducible than, pyrolysis–GC. Juvet *et al.*[7] worked with neat liquid samples in the mg range, deoxygenated and enclosed in capillaries for Hg-sensitized irradiation, and documented GC retention parameters for products from aldehydes, ketones, alcohols, esters and ethers. Leathard and Shurlock[8] provide a concise assessment of photolysis used in this form.

Fig. 10 shows two oxygen-containing compounds photolyzed in Hg-doped carrier gas in our system. Noteworthy are the strong product peaks eluting at high temperature. One would expect, of course, that some of the late peaks (*i.e.* any di- or polymerization products) would diminish as substrate concentration decreases.

The present GC system, simple as it is, is nevertheless capable of two-dimensional operation, *i.e.* it can isolate a single peak from an injected mixture and degrade it; chemically or photochemically. In instrumental terms, as well as in terms of the pyrolysis/photolysis analogy, experience from single peak processing in pyrolysis–GC is applicable here. (For an exceilent review, see ref. 8).

The obvious reason for degrading single peaks is confirmation of a suspected or, less often, determination of an unknown, solute structure. The first approach, so-called fingerprinting, is limited by how many, if any, fingerprints are identical. The second, structure determination, depends on how typical and accurate degradation patterns portray the particular functional and isomeric configuration.

In any case, clarity and "Gestalt" of the patterns are their important attributes. We thought it reasonable, therefore, to provide a few patterns of model substances.

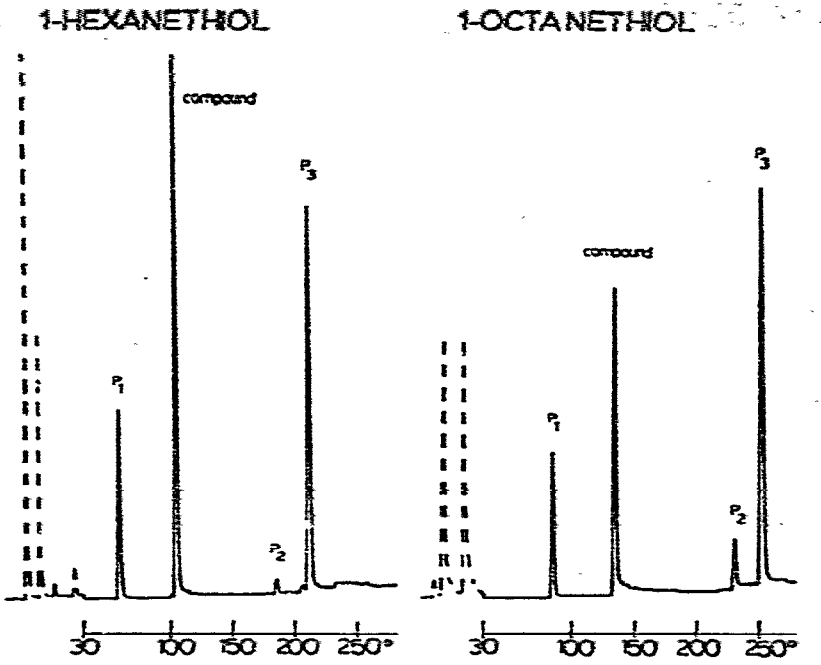

Fig. 9. Photolysis of two mercaptan homologues. Irradiation: 5 min at 50°.

Fig. 11 shows mercury-sensitized degradation of three C-6 hydrocarbons. Their patterns are distinctly different.

In Fig. 12, similar patterns arise from successive elimination of chlorine and substitution by hydrogen. The fairly constant retention difference between adjacent peaks is, of course, characteristic of this exchange.

One of the initial reasons for constructing a gas chromatograph with photolytic intersect was the potential capability of such an instrument for pesticide residue confirmation. Photolysis has been successfully used before to obtain characteristic

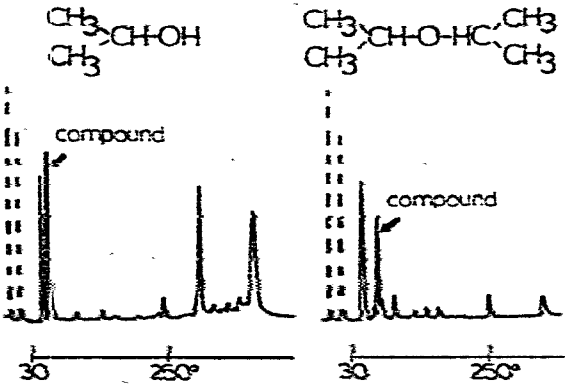

Fig. 10. Mercury-sensitized 5-min photolysis of isopropanol and diisopropylether, injected neat.

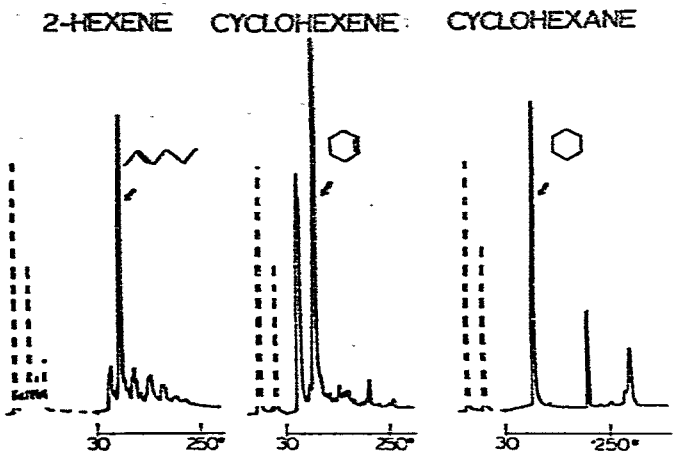

Fig. 11. Mercury-sensitized 10-min photolysis of three neat-inected C-6 hydrocarbons at 50°.

products for electron capture GC [9–13]. Aldrin and dieldrin, in particular, have been frequent targets of photolysis (*e.g.*, ref. 14).

In our case, however, the spectral output of the low-pressure lamp was ill-matched to the task, and it was difficult even to obtain the chromatograms shown in Fig. 13. More work would need to be done before this *in situ* approach had any chance of becoming of value to practical residue confirmation.

One type of compound that yields clear patterns easily, is the nitroalkane. Fig. 14 shows four examples, the two on the right being clearly distinguishable isomers.

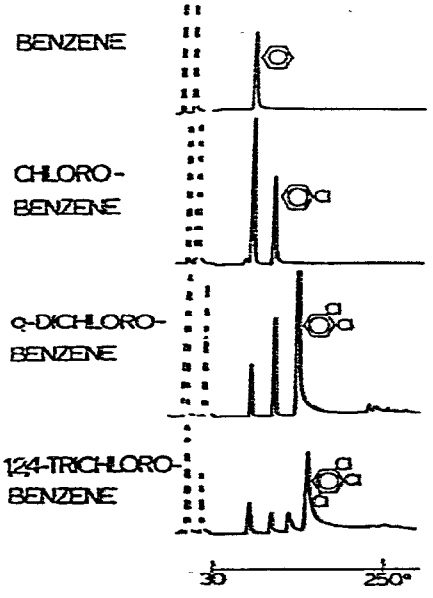

Fig. 12. Photolysis of benzene and various chlorobenzenes. Irradiation: 3 min at 50°.

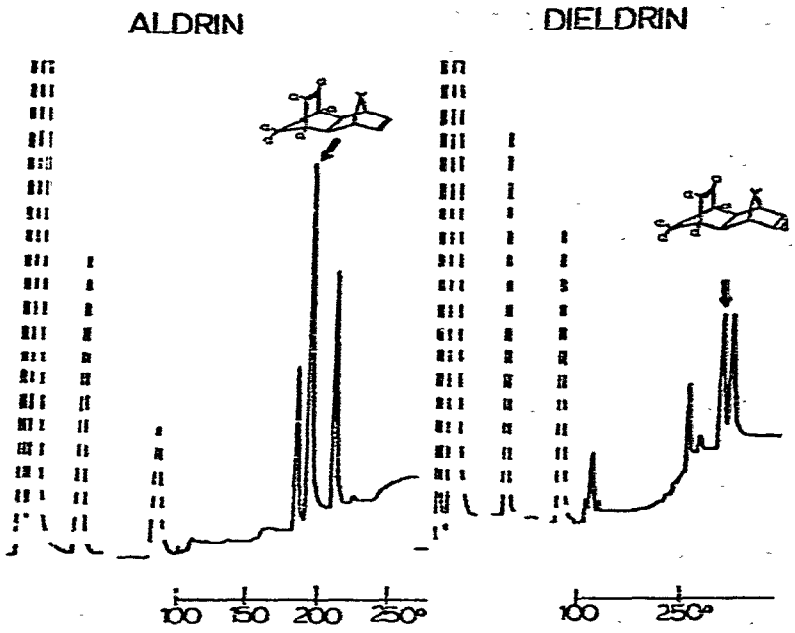

Fig. 13. Photolysis of aldrin and dieldrin. Aldrin: 4 μg injected. Irradiation: 10 min at 40°, switching lamp off for 20 sec once every minute. Dieldrin: 2.5 μg injected. Irradiated 10 min at 360–380 nm.

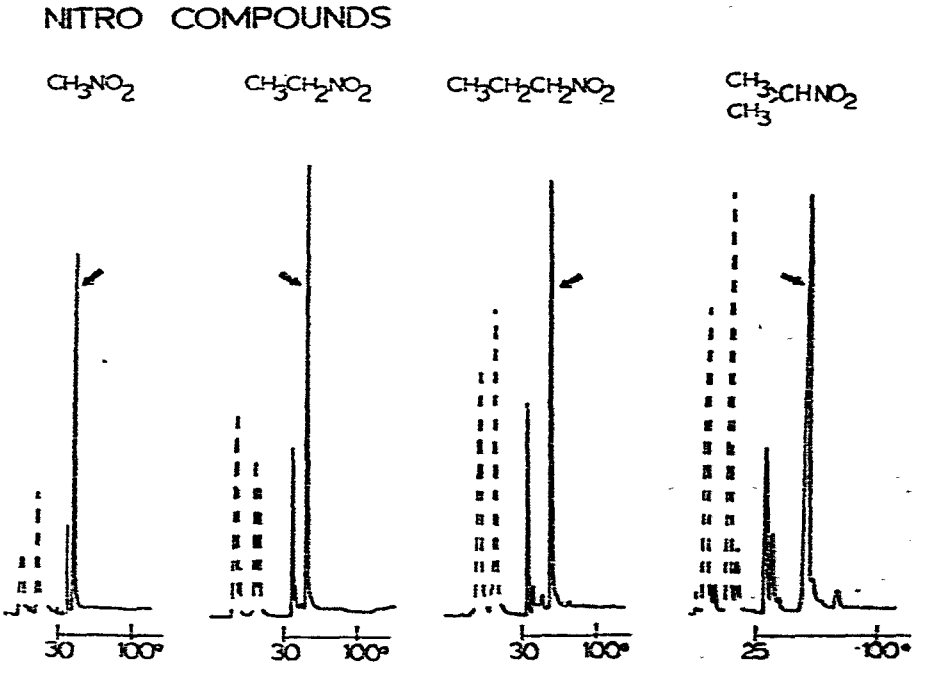

Fig. 14. Photolysis of various nitro compounds for 8 min at ca. 50°.

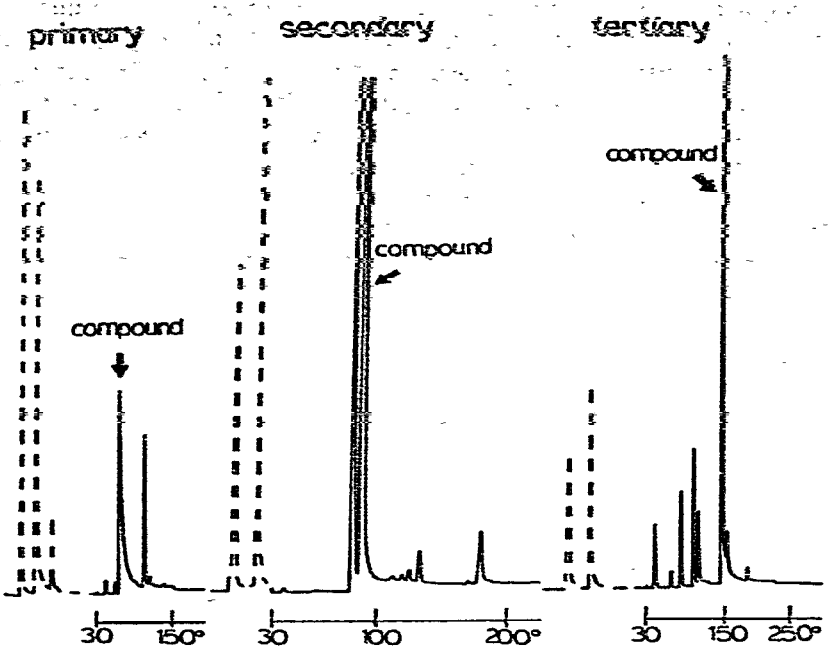

Fig. 15. Photolysis of the three *n*-butylamines. Irradiation times: primary amine 5 min, tertiary 10 min, secondary 6 min (different lamp); all at *ca.* 50°.

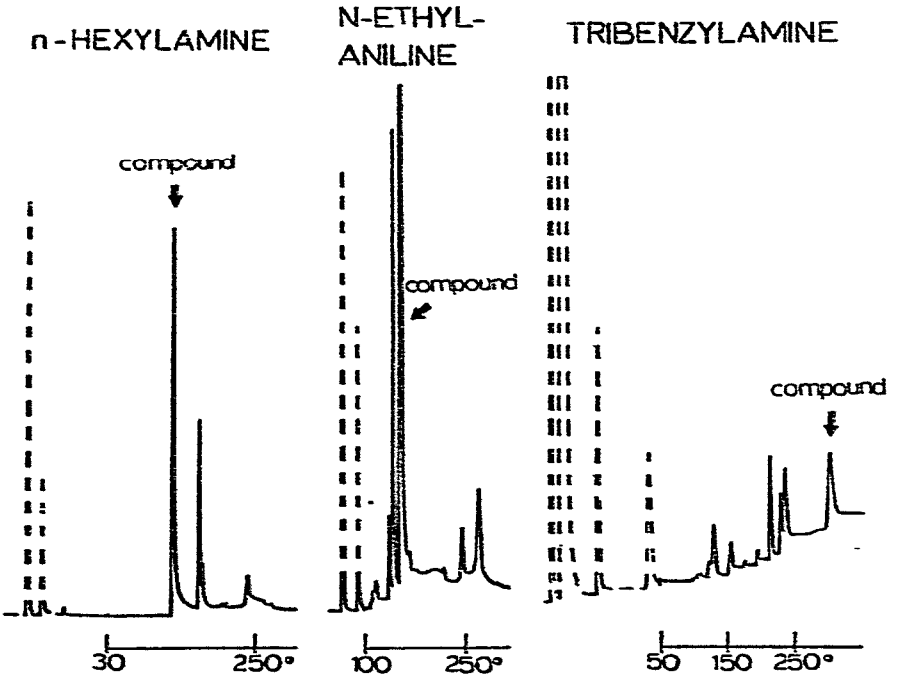

Fig. 16. Product patterns from selected primary, secondary and tertiary amines. Irradiation times and temperatures, respectively: 5 min, 60°; 7 min, 100°, 5 min, 150°.

A similar case can be made for amines. Fig. 15 shows the three *n*-butylamines, whose patterns look very different from each other. These can be compared, according to overall appearance (a human form of pattern recognition), to the chromatograms shown in Fig. 16. The first, second and third pattern of either figure —portraying, respectively, primary, secondary, and tertiary amines— correspond to each other, even though the various substituent structures are quite different.

From these few examples it appears that an integrated, two-dimensional *hv*–GC system —either in the extremely simple form described in this paper or in forms designed for greater flexibility or better reaction control— could be used with advantage toward physicochemical and/or analytical ends.

ACKNOWLEDGEMENTS

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