Journal of Chromatography, 189 (1980) 119–125

CHROM. 12,494

CONSTRUCTION OF A SIMPLE GAS CHROMATOGRAPH WITH PHOTOLYTIC INTERSECT*

WALTER A. AUE and ROSEMARIE AIGNER-HELD
5637 Life Sciences Center, Dalhousie University, Halifax, N.S. (Canada)
(Received September 24th, 1979)

SUMMARY

A simple, integrated system has been constructed for on-line photochemical conversion of gas chromatographic (GC) solutes. The unit is based on the essential flow sequence: First GC column–photolytic reactor–second GC column. Its photolytic intersect is capable of variations in time, temperature, and chemical environment. The expected advantages of such an integrated system —in an analytical and/or mechanistic context— are improved purity, speed and convenience of reaction.

INTRODUCTION

Gas chromatography (GC) and photochemistry have been of considerable benefit to each other. GC has been used extensively to separate photochemical reaction products obtained in mechanistic and environmental studies. On the other hand, photolysis has served as a convenient method of preparing samples for subsequent identification by GC; be it by recognition of the characteristic degradation pattern of a polymer[1], or by the appearance of a known derivative of a suspected pesticide residue (*e.g.*, ref. 2).

In spite of these mutual benefits, GC and photolysis have, to our knowledge, never been combined in a simple, integrated instrument. This is due to a variety of reasons, both historical and instrumental. An example of the latter may be that irradiation times are usually much longer than retention times.

Yet there seem to exist cogent reasons why such an instrument would be desirable; the two most important ones being speed and purity of reaction. An integrated GC system (of the type described in this paper) should also facilitate processing of small and/or complex samples. The use of GC makes *gas-phase* photolysis the most obvious mode of operation in a combined system; however, it is fairly easy to include also the capability for irradiating a *condensed* phase. Other capabilities include the variation of irradiation time and intensity. The ease with which sensitizers or reagents can be added on a continuous or intermittent basis is, of course, inherent to GC.

* Presented at the *172nd ACS National Meeting, San Francisco, Calif., Aug. 1976.*

The basic GC lay-out duplicates that of a chromatograph designed to separate products from electron capture reactions[3]; the flow sequence of both instruments is: Injection port–first GC column–reactor–second GC column–detector. The photolysis unit, however, makes use of an additional valve for peak isolation and control of reaction time. Otherwise it is simple: The valve and the reactor with its light source are the only parts necessary in addition to a standard gas chromatograph. It should be noted that the basic flow sequence is formally similar to one used for flow-through pyrolysis in a commercial instrument[4]. An excellent description of various flow patterns and their respective advantages for processing of gas chromatographic peaks can be found in the book by Leathard and Shurlock[5]. This monograph contains also a short review of photolysis GC. In our case, an outdated GC model with single detector channel was used. It was judged adequate for demonstrating feasibility of approach with a minimum of investment; but it was obvious in a chromatographic context that the use of a dual detector model and, a step further, the use of two independent temperature controls for columns I and II would have provided a much more elegant and convenient solution.

EXPERIMENTAL

A Varian Aerograph 1200 was modified according to the flow schematic shown in Fig. 1. Both columns were coiled borosilicate glass tubes, 1/4 in. O.D. × 4 mm I.D., about 70 to 80 cm in length. These were packed with 3% or 9% OV-101 on Chromosorb W, 45–60 mesh; or with the latter support coated with a non-extractable, thin film of Carbowax 20 M (ref. 6). The 4-port high-temperature valve (Valco Instruments, Houston, Texas, U.S.A.) was bolted to the inside (back) wall of the column bath such that its stem protruded through the left side of the instrument and the lever could be operated conveniently.

The quartz reactor, shown in detail in Fig. 2, was inserted through the column bath wall via an existing opening (ostensibly designed to accommodate a second injection port). Aluminum foil was wrapped over reactor parts situated inside the col-

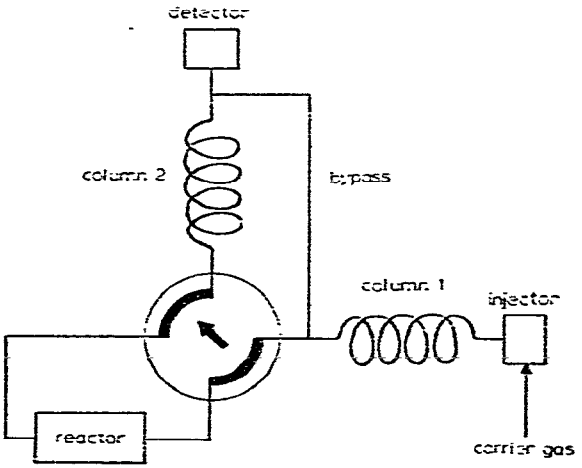


Fig. 1. Flow schematic of GC system.

umn bath. The various connections between columns, valve, reactor and detector were made by 1/16 in. stainless-steel tubing with Swagelock and Cajon fittings. The tubing used for the bypass between first column and detector contained a piece of Nichrome wire dimensioned to allow approximately one quarter of the first column's effluent to be diverted from the main flow path and routed directly to the flame ionization detector.

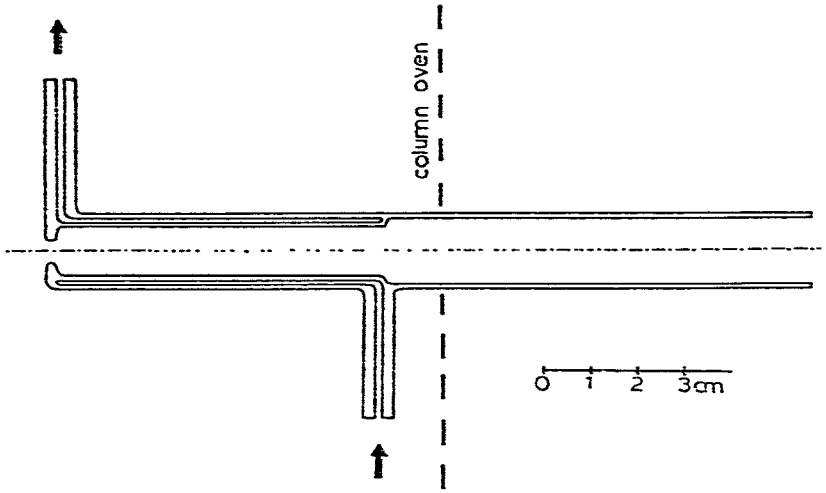


Fig. 2. Photochemical quartz reactor. The two capillary connecting tubes are angularly displaced for easier representation. The left part of the reactor is positioned inside the column oven and encloses the Hg discharge tube during irradiation; the right part protrudes through the oven wall to the outside.

The light source was a low-pressure Hg discharge tube (Quartz Pencil Lamp, Spectronics, Westbury, N.Y., U.S.A.) with most of its output at 254 nm. On occasion, a similar lamp with a fluorescence conversion filter for *ca.* 360–380 nm output, or appropriate tubular filters for the 254 nm lamp, were also used. In normal operation, the lamp was switched on (in a shielded place outside the gas chromatograph) about half an hour before use. For photolysis, the lamp was inserted into the reactor from the outside and kept there for the desired time of irradiation. Heating the reactor was essentially effected by heat transfer from the column bath (the discharge adding less than 30°); cooling by a stream of dry nitrogen, passing through 1/4 in. copper tubing coiled in a LN_2 dewar, and on into the reactor through 1/16 in. stainless-steel tubing inserted from the outside. The carrier gas was nitrogen at conventional flow-rates, about 45 ml/min. On occasion it was "doped", either by bubbling it through various liquids (for instance mercury) or merely by passing it over their surface in a long, horizontally coiled spiral tube.

Since mercury and other potentially harmful materials were used in these experiments, the whole gas chromatograph and accessories was surrounded by a hood, made in the laboratory from aluminium rod and heavy transparent plastic sheets, and connected to a high-flow exhaust duct.

Modes of Operation

"Flow-through" photolysis. In the first experiments, the valve was not used, *i.e.* solutes simply flowed through the reactor with carrier gas velocity, rather than being held there for a predetermined length of time. A variety of compounds were so tested, amoung them alkanes with, and ketones without, mercury sensitization. In "flow-through" as in all other configurations, "blank" runs (without UV) were used to confirm that any observed products were indeed due to photolysis.

"Trapped solute" photolysis. In this configuration, part of the solute peak was trapped in the reactor by turning the valve (the volume of the reactor, about 3 ml, was quite a bit smaller than the volume occupied by a peak). The moment when the valve needed to be switched for the peak of the peak to enter the reactor, was signaled by the detector response to the bypass stream. The amount trapped could be estimated, for instance, from the amount injected minus the amounts reaching the detector through both bypass and second column routes.

When the peak had been trapped, the Hg lamp was inserted for a suitable time (usually between 1 and 10 min), withdrawn, and unreacted compound and products released to the second column for separation. If desired, the reactor and/or the column bath temperature could be changed during various stages of this process.

Multiple compound trapping. To trap more than one compound, *e.g.* a reactant and its sensitizer, the reactor was cooled as described and the desired peaks from one or more injections condensed on the reactor wall. Then the temperature was raised (depending on whether gas-phase or condensed-phase photolysis was desired) and irradiation started.

This type of freeze-out was also used for trapping a certain amount of continuously added sensitizer from the carrier gas stream (like Hg); trapping reactants for a chemical (as opposed to photochemical) reaction; and adding an authentic standard to the reaction mixture after irradiation for product identification by co-chromatography.

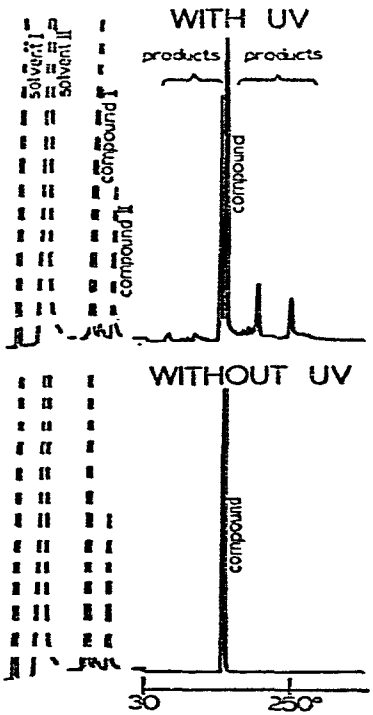
RESULTS AND DISCUSSION

One of the major concerns at the onset of this study was the question whether appreciable amounts of photoproducts could be obtained with the simple UV source within typical GC time spans. The "flow-through" experiments showed that this was indeed the case. In these, irradiation time can not be longer than solute residence time in the reactor. Considering a flow-rate of *ca.* 45 ml/min, a reactor volume of *ca.* 3 ml, and elevated pressure in the reactor, the residence time was in the order of 6 sec.

The second concern was whether the reactor wall would be coated after a few runs with non-volatile reaction products and would start to absorb significant amounts of UV; especially since many compounds were injected neat or in high concentration. Fortunately, such polymers did not pose a serious problem, although the reactor had to be cleaned on occasion with nitric acid to remove a yellow film; especially when heavy loads of aromatic compounds were injected repeatedly. On the average, the instrument was used 40 h/week and the reactor cleaned once every month. At the time of cleaning, the second column packing was also replaced. This column suffered particularly when heavy loads of sulfur or chlorine containing compounds were injected.

Two chromatograms typical of many runs are shown in Fig. 3. The upper trace shows residual compound together with products, the lower trace is the routinely-run blank. The early peaks in the chromatogram —dotted with globs of "Liquid Paper" to give them a dashed-line appearance— originate from the flow configuration peculiar to this extremely simple GC arrangement. The first two peaks are solvent peaks from the bypass line (I) and the second column (II), respectively; then follow the two compound peaks in the same order. The first of these provides on-line information for a "heart-cut" to be trapped in the reactor. The remaining front and rear sections of this zone then form the second compound peak. By that time, only the compound trapped in the reactor still remains in the GC. It is irradiated and, after appropriate temperature changes, the photochemical reaction mixture is released from the reactor and separated by the second column. This essential part of the chromatogram is shown in direct reproduction from the recorder chart, *i.e.* in full-line.

A different type of chromatogram is shown in Fig. 4. Here, two injections were made and two thiols trapped in the cooled reactor, then photolyzed together and released to the separating column. By comparing the product patterns of the pure thiols, it is easy to assign origin to the products. The interesting, though expected, feature of this run is, of course, the presence of a "mixed" product originating from *both* reactants, together with similar "pure" products, in an approximate 1:2:1 ratio.



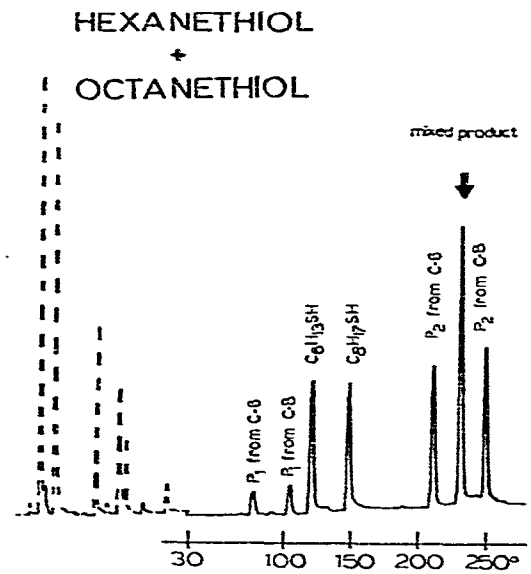


Fig. 3. Typical runs with and without irradiation. Solvent: Diethyl ether, Compound: Di-*n*-butylamine. Irradiation: 5 min at ca. 50°. Both columns 9% OV-101.

Fig. 4. Photolysis of a mixture of hexanethiol and octanethiol. Compounds injected separately and trapped in reactor at −30°. UV irradiation: 5 min at *ca.* 50°, followed by release of compounds and temperature program. Abbreviations: P_1 from C-6 = Product 1 originating from $C_6H_{13}SH$, etc.

It is obvious from these and other chromatograms obtained in the course of this study that the apparatus works well enough for the purpose at hand. It is equally obvious that it operates within certain limits and that some of these could be removed, though at a cost.

To have both columns, the valve, and the reactor in the same column bath presents a constructional as well as a procedural inconvenience. Independent thermal controls would be definitely helpful, especially in flow-through experiments resulting in early eluting products. Thermal control of the reactor should include two temperature zones: the photolysis cell itself, and (if light is not brought in some other way) the region of the discharge lamp.

The simple lamp used did perform satisfactorily within a fairly wide range of temperatures (about −40 to +200°), although extremes extinguished it and spectral output in the useable range must have been influenced by temperature to some degree.

While the various Hg lines from the low-pressure discharge lamp permitted a wide range of reactions to be run even without Hg sensitization, it may be advantageous or even mandatory for certain experiments to have the radiation source correlate better to the absorption spectrum of the compound under study.

For certain experiments, the use of two detectors (as opposed to one detector and a bypass line) may be of value. It should also be noted that mercury in the carrier gas depressed flame ionization detector response to a certain degree, and that, in general, the choice of detectors for such a system depends on whether sensitizers are to be used and which ones, whether temperature programming is necessary, etc.

Within the recognized limitations, then, the system has worked to our satisfaction. Various simulation experiments of analytical and photochemical approaches have been completed and will be contained in a reparate account. It would appear to us that the main potential advantages of this system (as compared to conventional combinations of photochemistry and gas chromatography) are its speed, convenience, flexibility and, though not explored in this study, sensitivity. There may also be other, less obvious benefits like freedom from contamination. The only possible contamination could come from column bleed — and bleed is easily evaluated and can usually be kept at a low level by an appropriate choice of column packing. The reactor and other parts are in a flowing, high-purity gas stream; with oxygen content, for instance, below 1 ppm. By trapping one peak in "heart-cut" fashion and letting solvent and contaminants pass on, one performs in most cases an extremely efficient reagent purification *in situ*. By cooling the reactor and trapping different compounds one can put together reagent mixtures of various composition, and photolyze them in solid, liquid or gas phase. It may even be possible to produce layered films of, say, reagent and sensitizer in solid state, etc.

In this study, however, experiments involving gas-phase photolysis predominated, owing to its obvious compatability with gas chromatographic instrumentation. Furthermore, the majority of photochemical studies involving heavier organic molecules are done in solution —sometimes to explore solvent effects but mostly for mere convenience— and we wanted to have a look at an equally convenient gas-phase system. The gas phase, literally, represents the "cleanest" system, and the very short time which the compound has to spend at elevated temperature (comparable to the time span of chromatographic separation itself) adds to the attraction by minimizing possible thermal degradation. Furthermore, the time between photolysis and detec-

tion is short and spent in a (relatively) inert environment, a fact which may be of crucial importance when the true pattern of somewhat reactive or labile products is in question.

Another possible consideration concerns the validity of photolytic degradation patterns obtained by irradiation of a complex matrix containing small amounts of analyte (*e.g.* pesticide residues in an extract of environmental or biological origin). Photolysis of *in situ* purified material (*i.e.* trapping of the pesticide peak) may offer a reassuring alternative. While gas-phase photolysis may be closer in kind to certain areas of atmospheric chemistry, and "cleaner" in general than the same type of reaction performed in solution, it is by no means an "ideal" system, at least not when carried out in the described, extremely simple set-up. One could, for instance, conceive of effects relating to photolysis of molecules adsorbed on the reactor wall, etc.

In the preceeding paragraphs, the potential "purity of reaction" in the described system has been discussed. It should be stressed, however, that this particular aspect is highly speculative (though quite plausible) at the moment; and that no experimental comparison between our approach and more conventional photochemical techniques has been carried out.

ACKNOWLEDGEMENTS

Thanks are due to M. Daniewski for preparing the bonded Carbowax 20M phase, to S. Kapila for instrumental assistance, and to J. Müller for making the glass columns and the quartz reactor. This study was supported by NRC grant A-9604, DRB grant 9502-04 and AC grant EM 7401.

REFERENCES

1 R. S. Juvet, Jr., J. L. S. Smith and K.-P. Li, *Anal. Chem.*, 44 (1972) 49.
2 K. A. Banks and D. D. Bills, *J. Chromatogr.*, 33 (1968) 450.
3 S. Kapila and W. A. Aue, *J. Chromatogr.*, 108 (1975) 13.
4 *Promotional Literature*, Chemical Data System, Oxford, Pa.
5 D. A. Leathard and B. C. Shurlock: *Identification Techniques in Gas Chromatography*, Wiley-Interscience, New York, 1970.
6 W. A. Aue, C. R. Hastings and S. Kapila, *J. Chromatogr.*, 77 (1973) 299.