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GAS CHROMATOGRAPHIC ANALYSIS OF RADIOLYSIS AND PLASMOLYSIS PRODUCTS

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SUMMARY

Gas chromatographic (GC) methods for the analysis of the products formed by action of γ radiation and radiofrequency discharges on saturated and unsaturated hydrocarbons and amines, alone or with addition of iodine and sulphur dioxide, are described. The preparation and purification of the samples, the control of their purity, separation of the products and their identification were accomplished in different ways depending on the composition and physical state of the parent compounds. The sensitivities of various GC detectors were evaluated and the smallest values of the radiochemical yields (G) that can be measured were calculated.

INTRODUCTION

For many years the radiolysis products of organic compounds have been studied by using gas chromatographic (GC) techniques[1–4], which permit both satisfactory sensitivity and a good separation of the complex mixtures formed by action of ionizing radiation. Recently, with the great interest in studies of radiofrequency plasmas and their effects on the chemical reactions of organic substances, several new problems have arisen for the analyst, who may have to identify and measure very small amounts of products in an environment characterized by very low pressures and high energy inputs, in order to elucidate the mechanisms of plasma decomposition (plasmolysis) or plasma polymerization reactions.

Mass spectrometry was found to be a powerful method for the simultaneous analysis of ions formed during discharges[5–7] but gave less satisfactory results from the point of view of the analysis of the final neutral products[8], mainly with very complex mixtures resulting from plasmolysis, which must be resolved into their components before quantitative analysis. A series of procedures were therefore studied in order to establish a rapid and reproducible GC analysis of the products of radiolysis and plasmolysis reactions, and to determine the sensitivity that can be achieved in practice under various experimental conditions.

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SAMPLE PURIFICATION AND PREPARATION

C_1–C_9 linear and branched-chain alkanes, ethylene, propylene, acetylene and ethylamine, alone or with various additives (iodine, sulphur dioxide), were used as parent compounds in order to study their behaviour under the effect of γ rays of radiofrequency (RF) plasma discharges. Substances of the highest purity commercially available were used, and were analysed for impurities that could influence the decomposition or polymerization kinetics, by using the same techniques as were used for the analysis of the products.

An impurity that was often found to be present, water, was removed by using activated molecular sieve traps or, for most alkanes, liquid sodium–potassium alloy. The latter dehydration reagent could not be used with olefins and amines, because of to possible chemical reactions, and an unexpected reaction, with evolution of hydrogen, was also observed between 2,3-dimethylbutane and sodium–potassium alloy. This was attributed to the reactivity of the two hydrogen atoms on the two adjacent tertiary carbon atoms causing hydrogen abstraction, which leads to the formation of 2,3-dimethyl-2-butene. Dehydration of 2,3-dimethylbutane and of higher homologues having adjacent tertiary carbon atoms was therefore not possible by using sodium–potassium alloy.

Simple contact or shaking of the liquid compounds with the desiccants did not ensure the complete removal of dissolved water. Therefore, satisfactory drying was achieved by passing the vapours of the parent compounds through silica gel, molecular sieves and, when possible, sodium–potassium alloy traps during the bulb-to-bulb distillation under vacuum used to transfer a suitable volume of sample from the reservoir to the irradiation vial or to the plasma discharge manifold (Fig. 1). The final determination of the residual water content was made by using an electron-capture detector[9] (see Table I).

Oxygen was removed from the liquid samples used for vacuum irradiation by repeated freezing–thawing cycles. When the evolution of air bubbles had ceased, the liquid was frozen again with liquid nitrogen, a vacuum of 10^{-4} Torr was reached and a pressure of 500–700 Torr of pure helium was restored in the vial. The samples were liquified with a flow of warm air, heating was continued for 10–30 min in order to permit diffusion of the inert gas into the liquid, and the samples were frozen again.

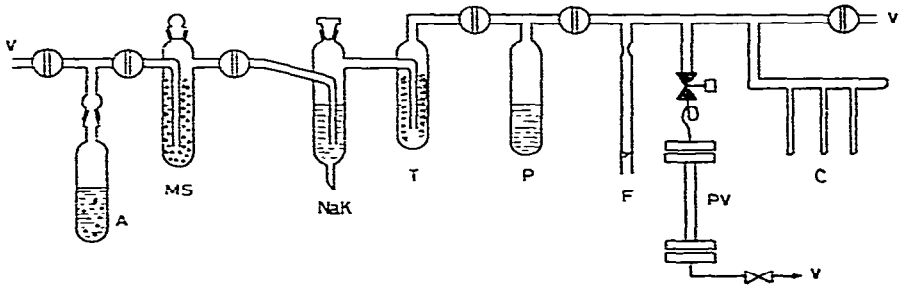

Fig. 1. Manifold for purification and preparation of liquid samples. A = Non-purified sample; MS = molecular sieve trap; NaK = liquid sodium–potassium alloy trap; T = glass-wool mist remover; P = purified sample reservoir; V = to vacuum. Various types of sample holder are shown: F = break seal glass vial; PV = steel pressure vessel; C = capillary vials.

TABLE I

ORDERS OF MAGNITUDE OF THE DETECTION LIMITS FOR GC ANALYSIS OF IMPURITIES IN THE COMPOUNDS USED FOR RADIOLYSIS OR PLASMOLYSIS STUDIES

Sample state	*Impurity*	*Analytical method**	*Detection limit (molar concentration)*
Liquid	Water	GGC + TCD	$3 \cdot 10^{-6}$
		GGC + ECD	$5 \cdot 10^{-7}$
	Oxygen	GSC + TCD*****,§	$5 \cdot 10^{-7}$
		GSC + HeD**,§§	$5 \cdot 10^{-9}$
		Measurement of inhibition period of main products (see text)	10^{-7}
	Organic compounds	GLC + FID	10^{-7}
	Organo-halogen compounds	GLC + ECD§§§	From 10^{-10} (CCl) to 10^{-5} (iodides)
	Sulphur compounds	GGC + FPD†	10^{-6} (mercaptans)
Gas	Inorganic gases	GSC + TCD***	10^{-7}
		GSC + HeD	10^{-9}
		GGC + HeD	$5 \cdot 10^{-9}$ (CO_2)
	Organic compounds	GLC + HeD	10^{-9} (light hydrocarbons)
	Organo-halogen compounds	GLC + ECD§§§	From 10^{-11} (CCl) to 10^{-5} (iodides)
	Organic compounds	GLC + FID	10^{-7}
		GGC + HeD	10^{-9} (light hydrocarbons)
	Organo-halogen compounds	GLC + ECD§§§	From 10^{-11} (CCl_4) to 10^{-5} (iodides)
	Sulphur compounds	GGC + FPD†	10^{-7} (SO_2, H_2S, COS)

* GGC = gas gel chromatography, using porous polymer bead columns; GSC = gas–solid chromatography; GLC, gas–liquid chromatography; TCD = thermal conductivity detector; ECD, electron-capture detector; HeD = metastable helium detector; FID = flame-ionization detector; FPD = flame photometric detector.

** Very sensitive to contamination of sample.

*** Amplified-type mean constant temperature TCD.

§ With pre-column and back-flushing to prevent contamination of molecular sieve column with liquid sample.

§§ With refrigerated trap or pre-column to prevent contamination of column and detector.

§§§ Glass columns.

† PTFE columns.

This cycle was repeated several times and effective removal of oxygen was achieved. The residual oxygen could not be satisfactorily monitored by any direct analytical method, mainly owing to the practical non-feasibility of a totally contamination-free liquid sampling system, but the results of the radiolysis permitted *a posteriori* control of the cleanliness of the sample. The yield of the products in the presence of oxygen in fact shows an induction period whose length depends on the concentration of the inhibitor, and changes linearly in the investigated range of 10^{-7}–10^{-4} mole l^{-1} of oxygen. The absence of any measurable induction period showed that the oxygen content was not so great as to influence the kinetics of the investigated process. Of course, the sensitivity of the method can be increased by using as a contamination index the yield of the main decomposition product or, in some instances, those of the

compound that can be detected with the highest sensitivity, *i.e.*, by means of specific detectors.

The amount of oxygen and other light impurities in the parent compounds that are gaseous at room temperature could be measured by using either a flame ionization (FID) or a metastable helium (HeD) detector (Table I). The column and analytical conditions were similar to those used for the analysis of the reaction products (see below), but as a rule the sampling problems were smaller, involving compounds generally available under pressure and thus permitting the use of standard sampling valves. For sensitive determination of traces of oxygen, nitrogen and carbon dioxide with an HeD, purged valves, enclosed in a box continuously purged with a flow of pure helium, were used to reduce the effects of small but unavoidable air diffusion through the valve cores, pressure seals, etc. Contamination due to noble gases was normally neglected as their effects on the reactions studied here are very small.

Other impurities were measured with specific detectors, as summarized in Table I. The detection limits reported refer to the compounds that were found as contaminants in the parent compounds used and therefore differ in some instances from the generally accepted sensitivity values of the various detectors[10,11]. The values are reported as molar concentrations because, as will be shown later, the yields in radiolysis and plasmolysis reactions are normally given as G values (molecules formed or decomposed per 100 eV absorbed) and therefore the molar concentration of the products had to be known.

IRRADIATION AND RF PLASMA TREATMENT

The irradiation of the liquid and gaseous samples was accomplished by using a Co^{60} γ-ray source[12] with dose rates between $5 \cdot 10^{16}$ and $4 \cdot 10^{17}$ eV g^{-1} min^{-1}, and total doses ranging between 10^{19} and 10^{21} eV g^{-1}. Doses were measured by Fricke dosimetry[13].

The plasma decomposition was studied with the RF plasma generation manifold described previously[14,15] both in closed systems and under flow conditions. Pressures in the reactor ranged between 0.25 and 1 Torr, the power input was of the order of 25–100 W and the total delivered energy was between 0.05 and 5 MJ g^{-1}.

For comparison between the energy units traditionally used in radiolysis and plasma studies, it must be taken into account that 1 eV g^{-1} roughly corresponds to $1.6 \cdot 10^{-19}$ J g^{-1}. The energy per gram involved in plasmolysis experiments is therefore 10^4 times greater than in radiolysis. On the other hand, while Fricke dosimetry permits the measurement of the absorbed dose, only the RF power delivered from the generator can be known correctly, while the energy distribution between optical, thermal, excitation and chemical effects is still unknown. Therefore, taking into account both the different energy ranges and sampling techniques, the sensitivity of the GC methods used was calculated separately for radiolysis and plasmolysis experiments.

SAMPLING AND ANALYSIS

The sampling of liquid irradiated samples was accomplished in two different ways, depending on the range of products that had to be analysed simultaneously and

on the volume of the sample. For the analysis of organic products at relatively large concentrations, owing to the high irradiation doses, small-volume samples (1–20 μl) were introduced directly into the GC apparatus, as the *G* values of the reaction products were high enough to permit their direct analysis by GC with an FID and temperature programming on packed non-polar or moderately polar columns.

When dynamic or pressurized irradiation systems were used (Fig. 2) small samples were periodically diverted from the main irradiated parent flow by means of a Valco internal volume sampling valve, manually or pneumatically operated, with core volumes of 1 or 5 μl. The valve can also be replaced by a manual sample pick-up point (septum).

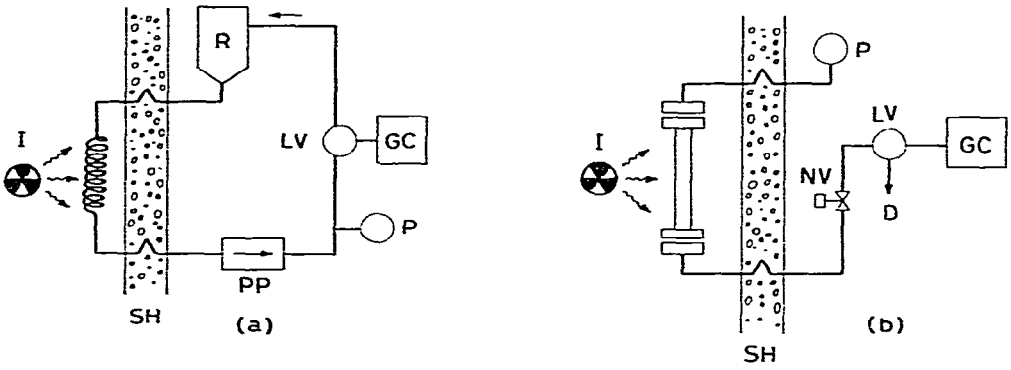

Fig. 2. System for repeated sampling of irradiated liquids. (a) Recirculating flow; (b) pressurized static system. I = Irradiation cell; SH = concrete shielding; R = sample reservoir; PP = peristaltic pump; P = pressure gauge; LV = liquid sampling valve; NV = needle valve; D = drain and sample recovery; GC = gas chromatograph.

When small capillary tubes of thin glass (10–20 μl) were used for irradiation with different doses, the irradiated samples were introduced into the column through a bulb crusher obtained by modifying the standard Varian injector of the 1520, 1800 and 1400 GC series (horizontal injection) (see Fig. 3). The asymmetric rod R was removed in order to permit the introduction of the capillary glass tube, and then inserted with the semi-cylindrical tongue protruding over the vial. When the pressure drop due to injector opening had ended, the GC baseline had returned to the proper value and the heated injector body had increased the temperature of the sample to the desired level, the rod R was rotated and the glass vial crushed between the protruding semicircular rod and the corresponding fixed part F. In order to remove the glass fragments, whose entry into the column was prevented by the metal gauze M, a short period of carrier gas back-flushing was actuated with the valve V when the rod was removed, through the heated Swagelock tee-piece, T, connecting the column C to the injector body. Vertical installation (with the rod inserted from the lower end) would permit the removal of crushed glass simply by gravity. This sampling technique gave satisfactory results mainly with the FID, while the thermal conductivity detector and HeD were too influenced by the air contamination when the microvial was introduced in the bulb crusher.

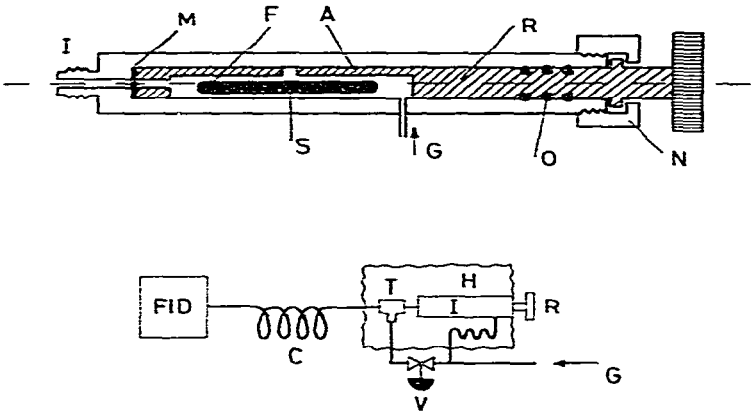

Fig. 3. Bulb crusher for introduction of the whole liquid sample. I = Enlarged bore Varian horizontal injector body; R = cylindrical rod with semi-cylindrical tongue A; O = PTFE O-ring seals; N = threaded retaining nut; F = fixed semi-cylindrical rod with metal gauze M; S = sample vial; G = carrier gas inlet; T = Swagelock tee-piece for back-flushing through valve V; H = heated injector zone; C = column.

As the excess of parent compound caused a very large and sometime tailing peak, long columns (up to 12 m) with large amounts of liquid stationary phase (up to 20% of SF-96 methylsilicone on Chromosorb W or P) were used, in order to permit an acceptable resolution of the products eluting close to the parent peak. Capillary columns were used only with the continuous sample flow system (Fig. 2) because the amount of sample coming from the bulb crusher seemed too large to ensure a long life of the expensive column, whereas if a high splitting ratio was used the resulting sensitivity was not satisfactory.

The injection of small volumes of irradiated liquid did not permit a satisfactory sensitivity for dissolved gases to be achieved. Gas extraction and concentration techniques were therefore applied. By using a modified Toepler gauge as described previously[14,16] a gas fraction was extracted from the refrigerated liquid, measured, pressurized with pure carrier gas and injected by means of a standard Valco gas sampling valve, with the calibrated sample loop connected directly to the top of the Toepler

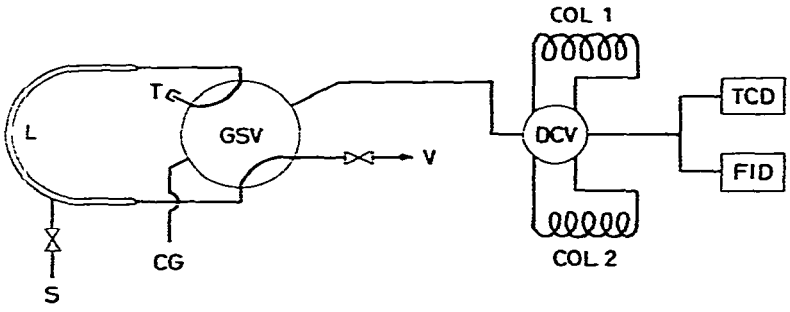

Fig. 4. Sampling system for the gas fraction from radiolysis of liquids and for analysis of plasmolysis products. GSV = Gas sampling valve; S = from sampling system; L = calibrated loop; CG = carrier gas input; T = closed valve port; V = to vacuum line; DCV = dual column switching valve; Col 1, Col 2 = columns in parallel arrangement; TCD, FID = detectors.

gauge, in order to be evacuated, filled with the sample and washed with the carrier gas flow (Fig. 4). A dual column switching valve permitted the sample to be analysed alternatively by polymer beads (Porapak or Chromosorb) and gas–liquid chromatographic columns.

A similar sampling system and column arrangement was used for the analysis of gaseous plasmolysis products formed by RF discharge on the gases in a closed system. The total amount of parent gas was very small (about $3 \cdot 10^{-5}$ moles) and therefore the whole content of the plasma reactor, or a large fraction of it, had to be sampled to ensure a satisfactory sensitivity[8,17,18].

When continuous flow plasma reactors were used[15] the samples could be slowly transferred from the reaction zone to previously evacuated vials and analysed later with the same technique used for closed plasma systems, in order to obtain an average composition in the various reactor points during the entire RF discharge time (Fig. 5a), or continuously extracted by means of an auxiliary pump (Fig. 5b) to permit instantaneous sampling in a given region of the reactor. Owing to the small amount of gas that can be sampled with this technique from a reactor having a pressure between 0.25 and 2 Torr without disturbing the RF discharge equilibrium, only sensitive detectors could be used [FID, HeD, electron-capture detector (ECD), flame photometric detector (FPD)] and the determination of the yields of the minor products was subject to great uncertainity. A similar sampling procedure was previously used[5–7] for analysis by mass spectrometry of the ionic species formed in the discharge. GC permits the analysis of neutral molecules resulting from reaction and recombination of the ions and, by addition of reactive iodine, the identification of iodoalkanes formed by scavenging of the primary radicals.

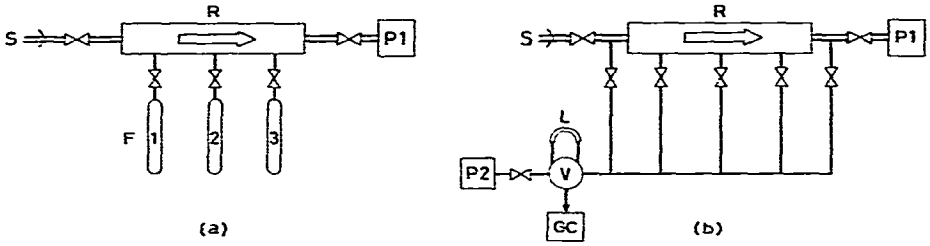

Fig. 5. Sample pick-up from flow RF plasma reactor; (a) average samples at various reactor points for delayed analysis; (b) instantaneous samples with simultaneous analysis. S = Plasma gas supply; R = reactor; P_1 = main pump; F = sampling vials; V = sampling valve with evacuated loop L; P_2 = auxiliary pump of the sampling system; GC = gas chromatograph.

The analysis of the products dissolved in the liquid irradiated samples or condensed from plasmolysis gases by refrigerated traps was carried out by separately injecting the liquid fractions into the appropriate column–detector system to detect the hydrocarbons and amine fraction (FID) or other components by means of specific detectors. Table II lists the columns used for the analysis of the various fractions of the products.

IDENTIFICATION

The final identification of the products was achieved by addition of known

TABLE II

COLUMNS USED FOR SEPARATION OF THE VARIOUS RADIOLYSIS AND PLASMOLYSIS PRODUCTS

Unless otherwise specified, all columns had a diameter of 1/8 in. and were made of stainless steel.

Product	*Column*	*Temperature (°C)*
H_2, air, CO,CO_2, light hydrocarbons	Porapak P (1.5 m) + S(3 m) Porapak Q (2 m) + S(1 m) Porapak R (3 m) Chromosorb 102 (3 m)	30–70
C_3–C_6	Dimethylsulpholane (20%) (4 m) + tetraisobutylene (20%) (2 m)	30
	Alumina, 100–120 mesh	30–120 at 20°C min^{-1}
Hydrocarbons up to C_{20}	SF-96 (20%) (12 m)	30–240 at 7°C min^{-1}
	Squalane capillary	80
Iodoalkanes	Tricresyl phosphate (15%) (3 m, glass)	60–80
H_2S,SO_2,COS, mercaptans, sulphides	Chromosorb 105 (80 cm, PTFE)	60–180 at 20°C min^{-1}
Alcohols, amines	Porapak R, S, T (3 m)	30–220
	Chromosorb 102, 104 (3 m)	Various with programming
	Carbowax 20M (10%) (3 m)	Various with programming
	Free fatty acid phase (FFAP) (10%) (3 m)	Various with programming

reference substances to the sample. Simple comparison of the retention times obtained in different runs could not ensure reliable identification when complex mixtures were analysed, mainly when the large excess of parent compound influenced the evaporation rate of the sample and the pressure surge due to the expansion could modify the column flow at the beginning of the analysis.

When complex product mixtures were analysed, a tentative identification was initially made by structure–retention correlations[19–21] and by the simultaneous use of universal (FID and HeD) and specific (ECD and FPD) detectors. In addition, in the radiolysis of liquid hydrocarbons, the identification of primary radicals by means of the iodoalkanes formed in the presence of scavenging iodine[22] permitted the most probable recombination products to be predicted, thus considerably reducing the choice among the various isomers. Peaks belonging to unsaturated products were identified, in temperature-programmed runs, by installing, between the injector and the column, a small heated pre-column filled with palladium catalyst (1% on Chromosorb W)[23]. By using hydrogen as the carrier gas, when the pre-column was held at the initial temperature of the column (60°C), the sample composition was not modified and the regular chromatogram of the products was obtained. When the pre-column was heated at 280°C by means of an auxiliary temperature control, catalytic hydrogenation of unsaturated compounds took place and the corresponding peaks were removed from the chromatogram of considerably reduced. The simultaneous increase of some of the peak belonging to identified alkanes gave useful indications of the structures of the hydrogenated alkenes.

SENSITIVITY

The overall sensitivity of the various methods was determined by taking into account the amount of parent compound subjected to irradiations or to plasma decomposition, the dose delivered, the amount of sample injected (with or without previous separation between the liquid and gas phases), the peak shape, depending on column length, flow and temperature, and the detector specificity and sensitivity.

Table III shows the minimum values of the radiochemical yield, G (molecules formed per 100 eV absorbed), that could be measured with an accuracy of better than $\pm 10\%$. This means that the reported values are about five times the minimum detectable quantity (MDQ), *i.e.*, the amount of a substance that gives a peak height twice the baseline noise. The choice of restrictive sensitivity values is justified by the fact that, whereas the MDQ often permits a tentative identification, hypotheses on the reaction mechanisms require a more accurate quantitative analysis.

TABLE III

VALUES OF THE RADIOCHEMICAL YIELD, G (MOLECULES/100 eV ADSORBED), THAT CAN BE MEASURED WITH THE DETECTORS AND SAMPLING SYSTEMS DESCRIBED IN THE TEXT WITH AN ACCURACY BETTER THAN $\pm$ 10%

Reported values refer to products having a molecular weight between 10 and 100, obtained with the lower irradiation dose. For molecular weight >100 the values must be multiplied by 10. For the highest irradiation dose reported the values must be multiplied by 10^{-2}.

Detector	*Products analysed*	*Detector sensitivity (g sec^{-1})*	*G values*	
			Radiolysis	*Plasmolysis*
ECD	Iodides	10^{-13}	10^{-4}	10^{-8}
FID	Hydrocarbons	10^{-12}	10^{-3}	10^{-7}
FPD	S compounds	10^{-10}	10^{-1}	10^{-6}
TCD	All	10^{-9}	10^{-1}	10^{-5}
HeD	Light gases	10^{-14}	10^{-5}	10^{-9}

The reported values were calculated by taking into account an average peak width between 10 and 100 sec, values that were often observed during analyses on long packed columns of products of intermediate molecular weight. Of course, narrow peaks permit a lower detection limit and a higher sensitivity to be achieved. The values shown in Table III are therefore representative of the order of magnitude of the G values that can be measured with sufficient accuracy to permit a study of the reaction mechanisms.

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