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GAS CHROMATOGRAPHIC IDENTIFICATION OF ALKYL RADICALS FORMED IN PLASMA RADIOFREQUENCY DISCHARGES BY USING IODINE AS A SCAVENGER

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SUMMARY

Alkyl radicals formed in low-pressure radiofrequency plasmas were identified by gas chromatography using iodine as a scavenger compound. Iodine vapours, injected into the glowing plasma discharge, reacted with active radicals in the gas phase, yielding various saturated alkyl iodides, that were trapped by freezing in an organic solvent and analyzed on Apiezon L and Carbowax 20M columns. Analyses carried out at different temperatures permitted the retention times and indices to be measured and the relative molar heats of solution to be calculated.

INTRODUCTION

The identification of intermediate species formed during reactions in low-pressure radiofrequency (RF) plasma discharges is essential for the study of chemical processes in environments characterized by low pressure and high energy input. Mass spectrometric¹⁻³ and spectrophotometric⁴⁻⁶ techniques have been applied for the detection and quantitation of ions and excited species in plasma. The gas chromatographic (GC) techniques suitable for the analysis of the products of radiolysis and plasmolysis reactions have been reviewed⁷.

The importance of radical mechanisms in the formation of the products in the radiolysis of hydrocarbons can be investigated by using iodine as a radical scavenger and by measuring both the decay of the final products and the amount of iodoalkanes formed⁸⁻¹⁰. Many different alkyl iodides are produced and their identification is complicated by the small amounts of some of them and by the simultaneous presence in the reaction mixture of a large excess of the parent compounds and of saturated and unsaturated products.

A previous approach to the identification of radiolytically formed alkyl iodides was made by irradiating with gamma-rays samples of liquid straight- or branched-chain alkanes containing different amounts of dissolved iodine and by analysing on a tricresyl phosphate column and by identifying all the halogenated compounds formed¹¹. The mixtures obtained can be used as qualitative standards, because the distribution of iodine compounds formed from the various hydrocarbons is typical.

This method requires a perfect reproducibility of the retention times or index values and can give quantitative results only if the simultaneous irradiation of the compound to be studied and of the reference alkane-iodine mixture can be accomplished, in order to permit the analysis of both samples on the same column and with the same electron-capture detector. Otherwise, the comparison of the chromatogram of the unknown iodide mixture with literature data or with previously irradiated alkane-iodine solution gives a qualitative indication of the elution order of the various electron-capture sensitive compounds.

The increasing development of studies on RF plasmas suggested the possibility of using a similar technique for the identification of radicals formed during plasma decomposition, polymerization of conventional or unconventional monomers (light hydrocarbons) or during the surface etching or grafting of polymers. A technique used for GC analysis of the formed alkyl iodides will be described here, while other results on plasma chemistry and reaction kinetics will be discussed elsewhere.

EXPERIMENTAL AND RESULTS

The alkyl iodides were formed in a low pressure plasma RF system (0.5 Torr, 50–100 W, 13.5 MHz) in two different ways, each of which can reveal different aspects of the reaction:

(a) iodine vapour was added to the plasma gas before discharge and halogen atoms were present in the system throughout the entire discharge time, therefore modifying the normal behaviour of the reaction, with a competition between iodine and other reactive species;

(b) iodine vapour was suddenly injected in the reactor during discharge, with a pressure surge which switched the plasma discharge off within few seconds. In this instance iodine should only react with the species active at the moment of its introduction, thus "freezing" the instantaneous distribution of radicals.

Iodine vapours were obtained by placing twice sublimed and degassed iodine crystals in a vial held at 85°C (corresponding to an iodine vapour pressure of 25 Torr) and connected to the plasma reactor by means of a needle valve. The alkyl iodides produced in the reaction were collected, along with all other condensable compounds, in another vial containing a suitable solvent previously degassed and frozen with liquid nitrogen.

GC analysis was performed by using two different electron-capture detectors: a Varian ^3H (250 mCi) concentric type detector, operated at -90 V, d.c., and a Varian ^{63}Ni (7.5 mCi) asymmetric cylinder detector, operated in the pulse-modulated mode. Nitrogen was used as carrier gas in both cases (flow-rate $30\text{ cm}^3/\text{min}$). Glass columns ($3\text{ m} \times 1/8\text{ in.}$), containing respectively Apiezon L (APL) and Carbowax 20M (CW 20M) liquid phases, both 15% on Chromosorb W DMCS (80–100 mesh), were used. The separation, identification and quantitative analysis of light iodides (methyl, ethyl, propyl, isopropyl) were easily achieved, because the corresponding standard samples are readily available. The identification of other compounds was more complicated in that many substances had to be synthesized in order to obtain the standards necessary for the identification of the various radiolytically formed iodides. Therefore, a systematic evaluation of the GC behaviour of these compounds on the polar and non-polar phases was carried out to permit further identification based only on GC methods.

Adjusted retention times, t'_R , and retention index values relative to *n*-alkanes, I , were measured at 75, 100 and 125°C. In order to permit the calculation of the retention values at any column temperature, the molar heats of solution relative to 1-iodobutane (1-IB) were also calculated with the following equation

$$\Delta H_s^0 (1-IB) = \frac{1.98 (\ln r_1 - \ln r_2)}{1/T_1 - 1/T_2} \quad (1)$$

where r are the retention values relative to 1-iodobutane and 1 and 2 refer to the different column temperatures T_1 and T_2 (°K)^{12,13}. 1-Iodobutane, used as the reference compound, is one of the probes suggested by McReynolds¹⁴ for the classification of the polarity of liquid stationary phases. Tables I and II show the values of t'_R , I and r at 75°C and ΔH_s^0 (1-IB) on APL and CW 20M. The alkyl radicals that are the most probable precursors of the various alkyl iodides are also listed in Table I.

The knowledge of the relative molar heats of solution permits one to calculate the retention time of each alkyl iodide at any temperature, by measuring the t'_R of

TABLE I

ADJUSTED RETENTION TIMES, t'_R , RETENTION INDICES, I , RETENTION RELATIVE TO 1-IODOBUTANE, r , AT 75°C AND ΔH_s^0 RELATIVE TO 1-IODOBUTANE FOR VARIOUS IODOALKANES ON APIEZON L AND RADICAL PRECURSORS

Iodoalkane	Radical	t'_R (min)	$I^{75^\circ C}$	r	ΔH_s^0 (kcal/mol)
1-Iodobutane	Butyl	19.3	898	1	—
2-Iodobutane	sec.-Butyl	14.5	862	0.75	0.138
1-Iodopentane	Pentyl	42.0	990	2.17	0.878
2-Iodopentane	1-Methylbutyl	28.1	942	1.45	0.337
3-Iodopentane	1-Ethylpropyl	28.6	945	1.48	0.449
1-Iodoheptane	Hexyl	92.8	1092	4.75	1.86
2-Iodoheptane	1-Methylpentyl	60.6	1037	3.13	1.41
3-Iodoheptane	1-Ethylbutyl	60.3	1036	3.12	1.29
1-Iodoheptane	Heptyl	205.1	1192	10.61	2.84
2-Iodoheptane	1-Methylhexyl	131.5	1136	4.80	2.52
3-Iodoheptane	1-Ethylbutyl	126.8	1131	6.56	2.18
4-Iodoheptane	1-Propylbutyl	117.1	1121	6.05	2.12
1-Iodo-2-methylbutane	2-Methylbutyl	33.7	964	1.74	0.552
1-Iodo-3-methylbutane	3-Methylbutyl	30.8	953	1.59	1.92
2-Iodo-2-methylbutane	1,1-Dimethylpropyl	21.4	910	1.10	1.13
2-Iodo-3-methylbutane	1-Methylisopropyl	27.7	941	1.43	0.308
1-Iodo-4-methylpentane	4-Methylpentyl	68.8	1053	3.56	1.45
2-Iodo-3-methylpentane	1-Methyl-sec.-butyl	60.2	1036	3.12	1.15
3-Iodo-2-methylpentane	1-Ethylisopropyl	56.8	1029	2.94	1.17
1-Iodo-2-methylpentane	2-Methylpentyl	67.9	1052	3.51	1.35
1-Iodo-3-methylpentane	3-Methylpentyl	71.2	1058	3.69	1.50
2-Iodo-4-methylpentane	1-Methylisopentyl	55.7	1026	2.88	0.806
3-Iodo-3-methylpentane	(1,1-Methylethyl)propyl	54.4	1023	2.82	0.653
2-Iodo-2-methylpentane	1,1-Dimethylbutyl	39.9	1025	2.07	2.65
1-Iodo-3,3-dimethylbutane	3,3-Dimethylbutyl	69.2	1054	3.58	2.95

TABLE II

ADJUSTED RETENTION TIMES, t'_R , RETENTION INDICES, I , RETENTION RELATIVE TO 1-IODOBUTANE, r , AT 75°C AND ΔH_s^0 RELATIVE TO 1-IODOBUTANE FOR VARIOUS IODOALKANES ON CARBOWAX 20M

Values of I at 100°C on tricresyl phosphate (TCP) columns are also shown for comparison.

Iodoalkane	t'_R (min)	Carbowax 20M		ΔH_s^0 (kcal/mol)	TCP: $I^{100^\circ\text{C}}$
		I	r		
1-Iodobutane	10.6	1065	1	—	986
2-Iodobutane	7.8	1019	0.73	0.295	945
1-Iodopentane	20.1	1160	1.89	0.772	1088
2-Iodopentane	12.8	1092	1.20	0.098	1031
3-Iodopentane	12.9	1093	1.21	0.125	1045
1-Iodoheptane	38.4	1257	3.61	1.55	1190
2-Iodoheptane	24.0	1186	2.26	1.00	1129
3-Iodoheptane	23.4	1182	2.19	0.907	1129
1-Iodoheptane	73.4	1353	6.89	2.33	1292
2-Iodoheptane	44.9	1280	4.22	2.56	1227
3-Iodoheptane	42.0	1270	3.94	1.55	1224
4-Iodoheptane	40.7	1265	3.82	1.39	1210
1-Iodo-2-methylbutane	15.4	1120	1.41	0.819	1054
1-Iodo-3-methylbutane	14.3	1108	1.34	0.534	1038
2-Iodo-2-methylbutane	12.8	1092	1.20	0.084	1032
2-Iodo-3-methylbutane	13.1	1095	1.22	0.043	1031
1-Iodo-4-methylpentane	28.8	1213	2.71	1.20	1148
2-Iodo-3-methylpentane	22.6	1177	2.12	2.61	1131
3-Iodo-2-methylpentane	21.6	1170	2.03	0.604	1125
1-Iodo-2-methylpentane	27.0	1204	2.53	1.61	1145
1-Iodo-3-methylpentane	29.0	1214	2.72	1.31	1150
2-Iodo-4-methylpentane	21.6	1171	2.03	0.40	1126
3-Iodo-3-methylpentane	22.9	1179	2.15	0.611	1131
2-Iodo-2-methylpentane	21.6	1171	2.03	0.605	1127
1-Iodo-3,3-dimethylbutane	18.4	1146	1.72	0.724	1084

1-iodobutane on the available column and by using the tabulated values of ΔH_s^0 and r_1 and eqn. 2 to obtain the r_2 and the $t'_R(x)_2$ of a given compound:

$$\ln \frac{t'_R(x)_2}{t'_R(1-IB)_2} = \ln r_1 - \frac{\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \Delta H_s^0}{1.98} \quad (2)$$

The usefulness of eqn. 1 for the calculation of relative molar heats of solution and of eqn. 2 for the determination of retention times at various temperatures depends on the linearity of the Arrhenius plot of $\ln t'_R$ as a function of the reciprocal of the absolute column temperature. In the range 50–150°C this linearity was tested experimentally and found to be satisfactory, with a correlation coefficient greater than 0.99 for linear iodoalkanes and 0.98 for the majority of branched chain compounds. Correlation coefficients smaller than 0.97 were generally a symptom of errors in the ex-

perimental measurements of the retention times (broad, tailing or poorly resolved peaks) and were corrected by further analyses.

For many compounds, the elution order was the same on both stationary phases, which therefore offer about the same separation possibilities. The polar phase Carbowax 20M yields higher retention index values, thus permitting the separation of traces of alkyl iodides from greater amounts of paraffinic or olefinic products that are eluted at the beginning of the chromatogram. The retention index values on a 15% tricresyl phosphate (TCP) column, calculated from previously published data at 100°C¹¹, and having values intermediate between those on Apiezon L and Carbowax 20M, are shown for comparison purposes in the last column of Table II. Some isomeric compounds exhibit different behaviours on the stationary phases tested; the choice of stationary phase is therefore dictated by the presence of given iodides among the products to be detected. The separation of 2-iodohexane from 3-iodohexane and of 2-iodo-3-methylpentane from 3-iodo-3-methylpentane was not previously achieved with TCP columns¹¹. APL gives a slightly better separation, while a complete separation was obtained on CW 20M. Generally, iodomethylpentanes have similar retention indices and their complete separation is difficult. The following compounds had very similar retention times and a long column is necessary to resolve them, when simultaneously present in the sample: 2-iodohexane; 3-iodohexane; 2-iodo-2-methylpentane, 2-iodo-3-methylpentane; 2-iodo-4-methylpentane; 3-iodo-2-methylpentane and 3-iodo-3-methylpentane. The use of CW 20M at low temperature (75°C) offers the best means of resolving them, except for the pair 2-iodo-2-methyl- and 2-iodo-4-methylpentane which are better resolved on APL. If one of more of these iodohexanes is available as a pure standard, its addition to the sample can give a reference time with which to correlate the tabulated value, allowing a better approximation than that obtained by comparison with 1-iodobutane which sometimes was eluted much faster than these compounds. The knowledge of the chemical structure of the parent molecules permits the prediction of the more probable radicals and the corresponding iodides, and therefore a very long and efficient column has only to be used for separation of the most complex mixtures.

The ΔH_s^0 values permit the calculation of the effect of changing column temperature on the retention times and elution orders of the interfering isomeric compounds. Appreciable differences between the ΔH_s^0 values of compounds with similar *I* values at a given temperature are a good indication of the possibility of increasing resolution by changing the analysis temperature.

Quantitative analysis requires the use of appropriate correction factors. For their determination, pure standards are necessary, sometimes available from producers of standard samples, but generally these have to be synthesized from the corresponding alcohol by treatment with hydriodic acid or by reaction with red phosphorus and iodine¹⁵. Relative sensitivities can also be deduced approximately from structures¹⁶, giving an idea of the abundance of the different radicals formed in plasma processes. Further studies are necessary to determine the reactivity of these radicals in this environment, the importance of competitive radical-radical and radical-iodine reactions and the stability of the iodides formed, whose decomposition can modify the distribution of the detected products.

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