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Note

Preparation of standard mixtures of iodoalkanes by irradiation of iodine solutions in alkanes

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The use of products of the radiolysis of organic compounds as standard mixtures has been suggested and discussed by Berezkin and co-workers¹⁻³, Armenante *et al.*⁴, and Rappoport and Gäumann⁵, studied the radiolytic spectra of *n*-alkanes and reported yields and retention values that permitted the hydrocarbon products to be identified. In the course of research involving the radiolysis of branched hydrocarbons, the importance of radical mechanisms in the formation of the products was evaluated by using iodine as a radical scavenger⁶ and by measuring both the decrease in yield of the saturated and unsaturated products and the yield of the iodoalkanes formed^{7,8}.

As many different radicals may be produced by irradiation, their qualitative identification is somewhat complicated, and much work has been necessary in order to study the gas chromatographic behaviour of the haloalkanes, to identify them and to measure the radical concentration⁹⁻¹³. In consequence, many data are available on the formation of iodoalkanes by irradiation of alkane-iodine solutions, and this method can be used to prepare qualitative standards of unusual iodoalkanes, the synthesis of which, if possible, is difficult and time-consuming.

By irradiating (in an accelerator or with gamma-rays) a solution of iodine in a suitable hydrocarbon, a known mixture of various iodoalkanes can be prepared; such a mixture may be used for the identification of iodides formed in radiolytic reactions or similar processes. From the radiochemical yield of the iodoalkanes (obtained by previous measurements or from the literature), one can, with some care, use this technique for preparing quantitative standards.

By using an electron-capture detector (ECD), the iodoalkanes can easily be determined in the presence of a large excess of the unreacted parent hydrocarbon or of other non-halogenated radiolysis products, as the sensitivity of the ECD to these compounds differs by several orders of magnitude from that to the iodoalkanes.

Both the hydrocarbons and the iodine to be dissolved in them must be completely free from other halogenated compounds in order to avoid interference. Although the requirement of this "capture purity" is stringent, the presence of hydrocarbons in small amounts does not influence the gas chromatographic results, as the hydrocarbons are practically undetected.

SAMPLE PREPARATION AND IRRADIATION

When iodine is added to the hydrocarbons in order to study the radiolytic mechanism, *i.e.*, to measure the variation in yield and the concentration of iodoalkanes, certain conditions must be fulfilled; the iodine concentration should not be higher than 1 mM¹⁴, and the solution should be thoroughly de-gassed and sealed under vacuum. A similar procedure is necessary when irradiation is used to produce a quantitative standard, but, for qualitative purposes, the sample preparation is much simpler.

The iodine solution (concentration about 0.2%) is poured into glass phials having glass or PTFE stoppers and irradiated at room temperature, at a dose of about 10⁵ rads.

The presence of air in the phial reduces the radiochemical yield, as the oxygen competes with the iodine and causes an induction period, but this is irrelevant from the qualitative point of view.

Irradiation is accomplished by using a cobalt-60 source of gamma-rays; the dose-rate is about 1000 rads/min.

GAS CHROMATOGRAPHIC ANALYSIS

The irradiation products were analysed on a Varian Aerograph A600 gas chromatograph, equipped with an ECD, a glass column (3 m × 0.125 in. O.D.) packed with 15% of tricresyl phosphate on DMCS-treated Chromosorb W (80–100 mesh), and an isothermal temperature controller. The carrier gas was nitrogen (20 ml per min), and both column and detector were operated at 100°, the detector polarising voltage being 90 V (d.c.). The samples (5 μl) were injected directly into the column in order to avoid decomposition.

All the hydrocarbons were analysed before the addition of iodine, in order to check their "capture purity" and to avoid interference from unknown electron-absorbing compounds; only the pure compounds were mixed with iodine and irradiated.

No special care was necessary for injection of the qualitative samples: the narrow range of linear response of the ECD may alter the shapes of the tops of the largest peaks, making them unsuitable for quantitation, but the retention times are unaffected, as the absolute amount of iodoalkanes is very small. When the samples

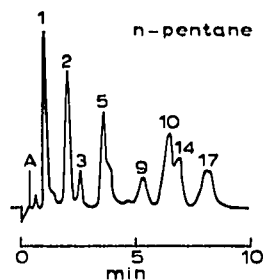


Fig. 1. Iodoalkanes from irradiated *n*-pentane (for peak numbers see Table I).

are used for quantitative purposes (for example, to measure correction factors), the ECD must be operated within the limits of linear response.

As both the sensitivity of the ECD and the yield of radiolysis products differ for various iodoalkanes, the same chromatogram may include "linear" and "saturated" peaks. This condition can be verified by injecting different amounts of irradiated solution or (in order to avoid syringe errors) by diluting the solution

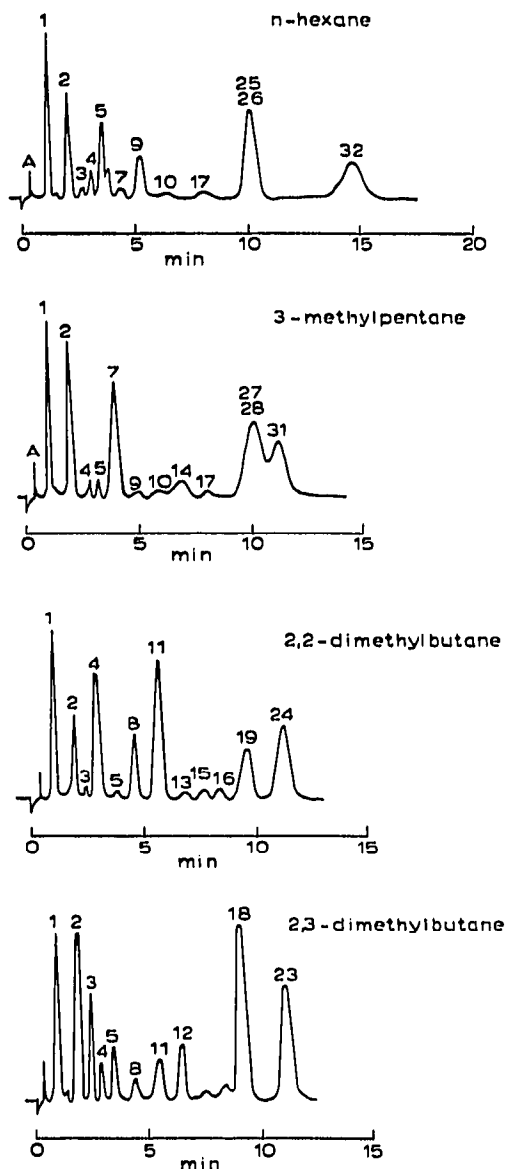


Fig. 2. Iodoalkanes from irradiated hexanes (for peak numbers see Table I).

several times. When the ratios of the peak areas are unaltered by changing the dilution factor, the linearity range has been found for all the peaks and the use of peak areas will permit correct calculations of amounts.

RESULTS

The following hydrocarbons were irradiated, together with iodine, and the

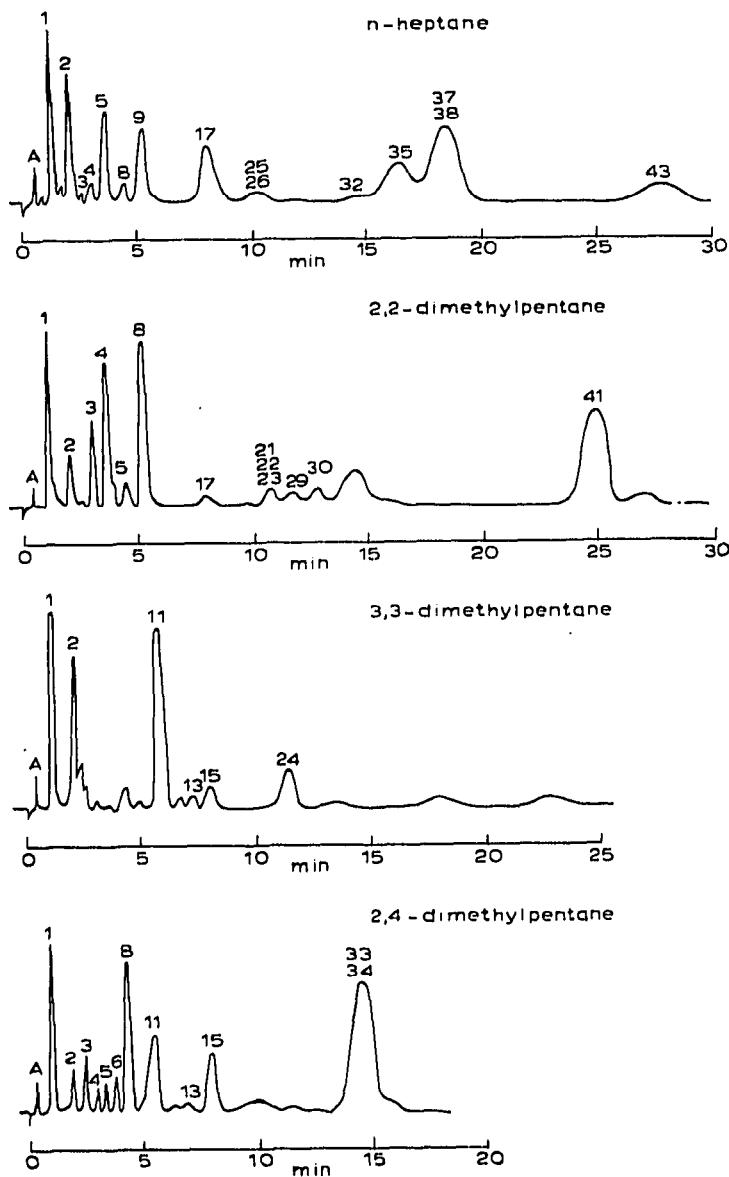


Fig. 3. Iodoalkanes from irradiated heptanes (for peak numbers see Table I).

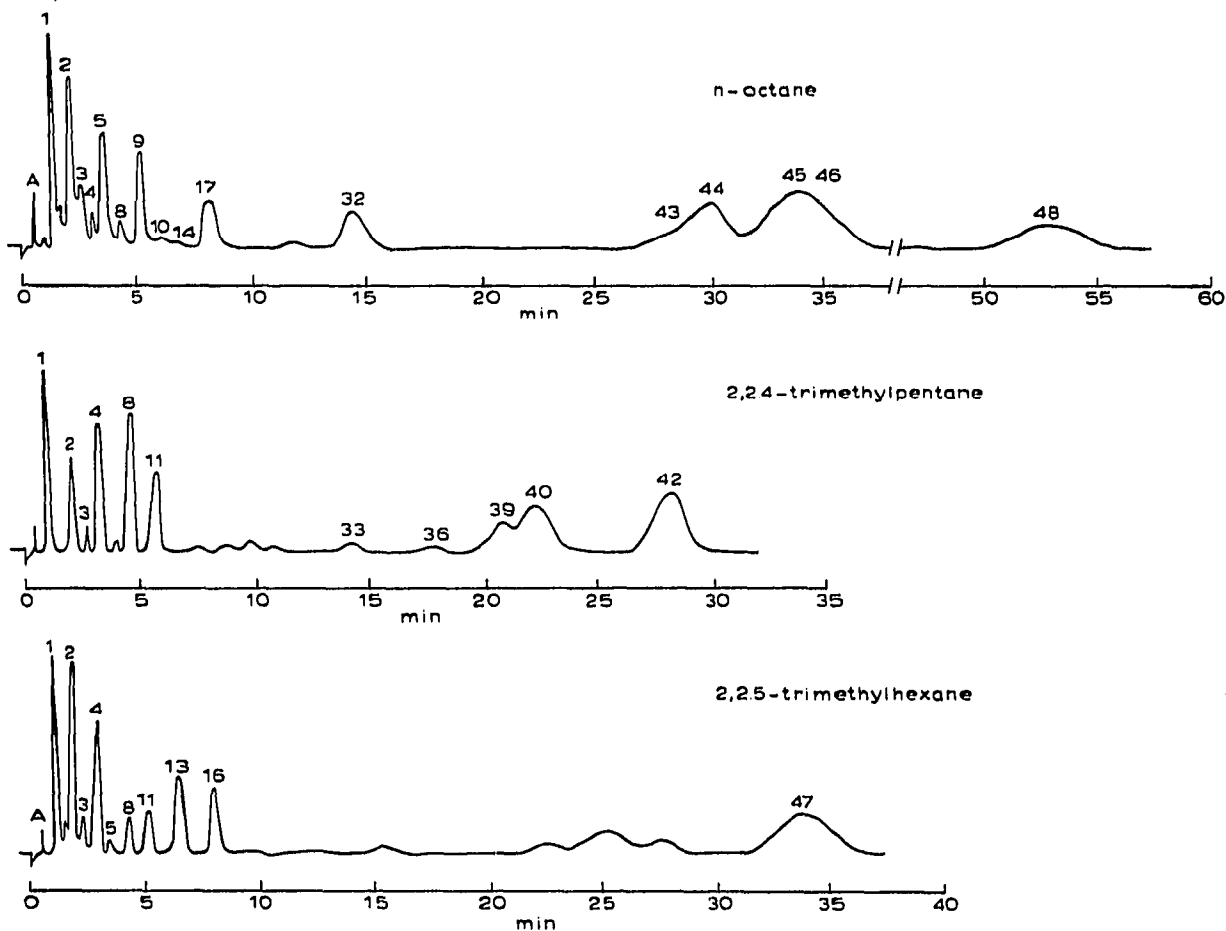


Fig. 4. Iodoalkanes from irradiated octanes and nonanes (for peak numbers see Table I).

products were analysed: *n*-pentane; *n*-hexane; 3-methylpentane; 2,2-dimethylbutane; 2,3-dimethylbutane; *n*-heptane; 2,2-dimethylpentane; 2,4-dimethylpentane; 3,3-dimethylpentane; *n*-octane; 2,2,4-trimethylpentane; and 2,2,5-trimethylhexane.

In Figs. 1-4 the resulting chromatograms are shown, and Table I shows the retention indices, relative to the linear iodoalkanes, I_{ni} (see ref. 9), calculated from the analytical results. The numbers shown on the chromatograms are those given to the compounds in the Table. The I_{ni} values are reported because they are more reproducible under different analytical conditions (length and temperature of the column, concentration of liquid phase, carrier-gas flow-rate) than are retention time, specific retention volume or other retention parameters.

The chromatograms differ widely and some groups of peaks are characteristic of each hydrocarbon, irrespective of gas flow-rate or temperature. This is very useful for identification purposes, because comparison with the reported chromatograms permits identification of the iodoalkanes under different analytical conditions.

The irradiation of linear alkanes in the presence of iodine mainly produces

TABLE I

RETENTION INDICES OF IDENTIFIED IODOALKANES RELATIVE TO LINEAR IODOALKANES ON THE TRICRESYL PHOSPHATE COLUMN

No.*	Compound	I_{rel}	No.*	Compound	I_{rel}
A	Air	—	25	2-Iodohexane	540
1	Iodomethane	100	26	3-Iodohexane	540.5
2	Iodoethane	200	27	2-Iodo-3-methylpentane	541
3	2-Iodopropane	245	28	3-Iodo-3-methylpentane	542
4	2-Iodo-2-methylpropane	270	29	1-Iodo-2-methylpentane	556
5	1-Iodopropane	300	30	1-Iodo-4-methylpentane	559
6	3-Iodopropene	317	31	1-Iodo-3-methylpentane	561
7	2-Iodobutane	359	32	1-Iodoheptane	600
8	1-Iodo-2-methylpropane	360	33	2-Iodo-2,4-dimethylpentane	604
9	1-Iodobutane	400	34	1-Iodo-2,4-dimethylpentane	605
10	2-Iodopentane	444	35	4-Iodoheptane	620
11	2-Iodo-2-methylbutane	445	36	Di-iodomethane	628
12	2-Iodo-3-methylbutane	448	37	3-Iodoheptane	633
13	1-Iodo-3-methylbutane	451	38	2-Iodoheptane	636
14	3-Iodopentane	458	39	3-Iodo-2,2,4-trimethylpentane	652
15	1-Iodo-2-methylbutane	467	40	1-Iodo-2,2,4-trimethylpentane	665
16	1-Iodo-3,3-dimethylbutane	496	41	Iodo-2,2-dimethylpentanes	680
17	1-Iodopentane	500	42	1-Iodo-2,4,4-trimethylpentane	695
18	2-Iodo-2,3-dimethylbutane	501	43	1-Iodoheptane	700
19	2-Iodo-3,3-dimethylbutane	504	44	4-Iodo-octane	705
20	3-Iodo-2-methylpentane	536	45	3-Iodo-octane	716
21	2-Iodo-4-methylpentane	537	46	2-Iodo-octane	719
22	2-Iodo-2-methylpentane	538	47	2,2,5-Iodohexanes	732
23	1-Iodo-2,3-dimethylbutane	538	48	1-Iodo-octane	800
24	1-Iodo-2,2-dimethylbutane	540			

* Entries in this column refer to the peaks on the chromatograms in Figs. 1-4.

linear iodoalkanes with less carbon atoms than has the parent hydrocarbon (coming from C-C bond cleavage) and iodoalkanes with the same number of carbon atoms coming from hydrogen abstraction. Such a mixture is therefore useful as a reference standard for the calculation of I_{rel} because the linear iodoalkanes (which produce the highest peaks) can easily be recognised when the irradiated reference standard is mixed with the sample to be identified. In addition, hydrogen abstraction and the subsequent reaction of the radicals formed with iodine produces a large amount of linear iodoalkanes with the iodine bonded to carbon atoms within the chain. The 2-iodo- and 3-iodo-alkanes normally have very close values of I_{rel} and cannot be separated with the column length used.

The irradiated branched alkanes form several branched iodoalkanes, which, owing to their lability, are very difficult to synthesise and rapidly decompose even at low temperature; their preparation by irradiation is therefore very convenient.

In general, the main halogenated products formed by irradiation of branched alkanes are the parent iodoalkanes substituted on primary or tertiary carbon atoms and those formed by cleavage of the molecule near to the quaternary or tertiary carbon atoms. Thus, careful choice of the hydrocarbon will permit the preparation of a mixture with a large amount of any desired iodoalkane. Some rearrangement

products are also present, as shown by the small peaks in the chromatograms of the products from irradiation of 3,3-dimethyl-, 2,4-dimethyl- and 2,2,4-trimethyl-pentane, but their concentration is very low, and their identification can be better accomplished by using mixtures containing larger amounts of them.

In the chromatogram of the products from irradiation of 2,2,5-trimethyl-pentane, the group of peaks having a retention time between 20 and 30 min is attributed to branched iodo-octanes (mainly 1- and 2-iodo-2,5-dimethylhexanes and 2-iodo-5,5-dimethylhexane) that were not unequivocally identified and are therefore not listed in Table I.

REFERENCES

- 1 V. G. Berezkin and L. S. Polak, *Gazovaya Khromatografiya*, Nauka, Moscow, 1964, p. 116.
- 2 N. A. Belikova, V. G. Berezkin and L. S. Polak, *Neftekhimiya*, 1 (1961) 827.
- 3 V. G. Berezkin, L. Sojak and J. Uhdcova, *J. Chromatogr.*, 98 (1974) 157.
- 4 M. Armenante, V. Santoro and G. Spadaccini, *J. Chromatogr.*, 52 (1970) 227.
- 5 S. Rappoport and T. Gäumann, *Helv. Chim. Acta*, 56 (1973) 531.
- 6 R. H. Schuler, *J. Phys. Chem.*, 62 (1958) 37.
- 7 G. Castello, F. Grandi and S. Munari, *Rad. Res.*, 45 (1971) 399.
- 8 G. Castello, F. Grandi and S. Munari, *Rad. Res.*, 58 (1974) 176.
- 9 G. Castello, G. D'Amato and E. Biagini, *J. Chromatogr.*, 40 (1969) 313.
- 10 G. Castello and G. D'Amato, *J. Chromatogr.*, 54 (1971) 157.
- 11 G. Castello and G. D'Amato, *J. Chromatogr.*, 58 (1971) 127.
- 12 G. Castello and G. D'Amato, *J. Chromatogr.*, 76 (1973) 31.
- 13 G. Castello and G. D'Amato, *J. Chromatogr.*, 79 (1973) 33.
- 14 R. H. Schuler, *J. Phys. Chem.*, 62 (1958) 37.