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GAS–LIQUID CHROMATOGRAPHIC ANALYSIS OF ISOPHORONE BY-PRODUCTS

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SUMMARY

Of the intermediate mixtures obtained during the production of acetone-derived products such as diacetone alcohol, mesityloxide, methyl isobutyl ketone and isophorone, those in isophorone production, are the most complex. A gas–liquid chromatographic method for analysis and control during different stages of isophorone production is proposed. For the separation of multi-component mixtures of polar isophorone byproducts and also the main product, a stationary phase of the polyglycol type (PEG 20M) and a deep acid-washed support (Chromosorb P) are used.

A transmission electron microscopic investigation of the diatomite surface before and after deep acid washing was carried out. The electron micrographs showed the important effect of the removal of iron impurities on the surface homogeneity. For peak identification linear temperature programming was applied and retention indices were calculated from Van den Dool and Kratz's equation. *n*-Alkanols were selected instead of *n*-alkanes as fixed points on the retention index scale of isophorone byproducts. Experimental data on retention parameters and quantitation were evaluated for their reproducibility.

INTRODUCTION

The gas–liquid chromatographic (GLC) analysis of acetone-derived products belonging to various homologous series and with a wide boiling-point range is difficult. Undoubtedly capillary column GLC will continue to be the most reliable and useful separation technique for such complex mixtures, but it involves well known difficulties[1,2], the greatest of which concerns quantitation. In this connection, we have investigated the possibility of using a packed column for the analysis of acetone-derived products such as diacetone alcohol (DAA), mesityl oxide (MO), methyl isobutyl ketone (MIBK) and isophorone (IPH). The intermediate mixtures obtained during isophorone production are the most complex, as they contain unconverted acetone (A) together with higher boiling byproducts.

In this work we successfully used a pink support deactivated by deep acid washing[3,4] and coated with 15% (w/w) PEG 20M for the analysis of acetone-derived compounds and achieved the routine control of the products at different stages of production.

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The retention indices of isophorone byproducts were measured by using linear temperature programming (LTP) conditions[5]. It was demonstrated that with LTP the retention of *n*-alkanols increases linearly with increasing number of carbon atoms (C_N) as does that of *n*-alkanes. The identification of isophorone byproduct peaks carried out in this manner is reliable.

EXPERIMENTAL

Apparatus

The GLC measurements were carried out with a Model 304 Pye Unicam (Cambridge, U.K.) chromatograph, equipped with a dual flame ionization detector and a Model PU 4800 microcomputer, with a built in integrater. Glass columns (1.0 m × 4 mm I.D.) deactivated with dimethyldichlorosilane (DMDCS) were used; the packing and LTP conditions are given in Fig. 2. Argon (or nitrogen) was used as the carrier gas at a flow-rate of 35 ml min^{-1}. The injector and detector temperatures were maintained at 240 and 260°C, respectively. The samples were introduced with a Hamilton 1.0-μl microsyringe.

An SP 191 atomic-absorption spectrometer (Pye Unicam) and a Model B-ER-420 electron paramagnetic resonance (EPR) spectrometer (Bruker, Karlsruhe, F.R.G.) were used for determining the iron content after the second day of acid-washing procedure of the Chromosorb P.

A Model EM 400 transmission electron microscope (Philips, Eindhoven, The Netherlands) with an Edwards (Crawley, U.K.) Model 306 vacuum evaporator was used for examination of the support surface (Figs. 1–3). Samples were prepared using the C–Pt replica technique.

Chemicals

Chromosorb P was supplied by Johns-Manville (Denver, CO, U.S.A.), PEG 20M by E. Merck (Darmstadt, F.R.G.) and DMDCS by Fluka (Buchs, Switzerland). *n*-Alkanes and *n*-alkanols were supplied by Poly Science (Evanston, IL, U.S.A.). The isophorone byproducts were of analytical-reagent and GLC grades.

Preparation of column packing

Acid washing of Chromosorb P (60–80 mesh) with 6 *M* hydrochloric acid was carried out in a modified Soxhlet apparatus of our design[3,4] and the iron content was reduced to 0.015% after 24 h. The support was first washed with distilled water and then rinsed with acetone and dried under vacuum at 75°C for 2 h. This support was coated with 15% PEG 20M. The packed column was conditioned at 210°C for 8 h with an argon flow-rate of 20 ml min^{-1} and for 2 h at 40 ml min^{-1}.

GLC measurements

The retention behaviour of isophorone byproducts was expressed as the retention time (t_R), adjusted retention time (t'_R) and retention index (I_{LTP}) under LTP conditions[5]. For t'_R and I_{LTP} the following equations were used:

$$t'_R = \frac{T_{R(s)} - T_0}{R_T} \tag{1}$$

where $T_{R(s)}$ is the retention temperature of the solute (°C), T_0 the initial programming temperature (°C) and R_T the rate of temperature programming (°C min^{-1}), and

$$I_{LTP} = 100\left[\frac{T_{R(s)} - T_{R(n)}}{T_{R(n+1)} - T_{R(n)}} + n\right] \tag{2}$$

where $T_{R(n)}$ and $T_{R(n+1)}$ are the retention temperatures of the fixed points and n is the carbon number of the fixed points.

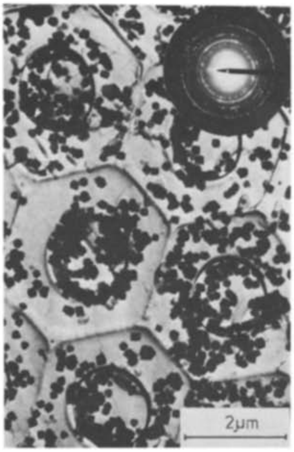
The retentions of homologous series of *n*-alkanes and *n*-alkanols *versus* carbon number were obtained (Figs. 5 and 6). The retention indices of the samples were determined by employing *n*-alkanols (Fig. 7), which were added to the sample as references to standardize the retention indices.

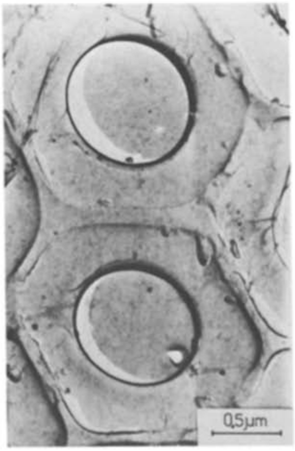
The reproducibility of retention (t_R, t'_R and U_{LTP}) and of quantitation were evaluated from the mean value ($\bar{x}$), standard deviation (S.D.) and relative standard deviation (R.S.D., %) using the PU 4800 microcomputer (Tables I–III).

The relative response factors for the flame ionization detector were determined as follows: A, 1.6; isopropanol (IP), 1.4; MIBK, 1.0; MO, 1.1; DAA, 1.6; and IPH, 0.87.

RESULT AND DISCUSSION

It is known[3,4] that the presence of metal impurities imparts catalytic and adsorptive activity to the support surface and causes no less deterioration in its homogeneity than silanols. Investigations have been carried out on the use of electron





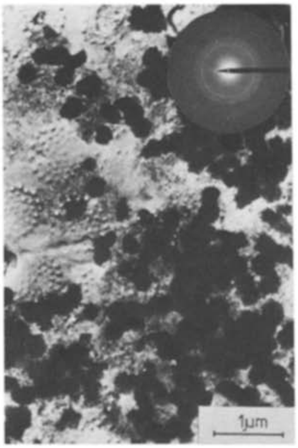
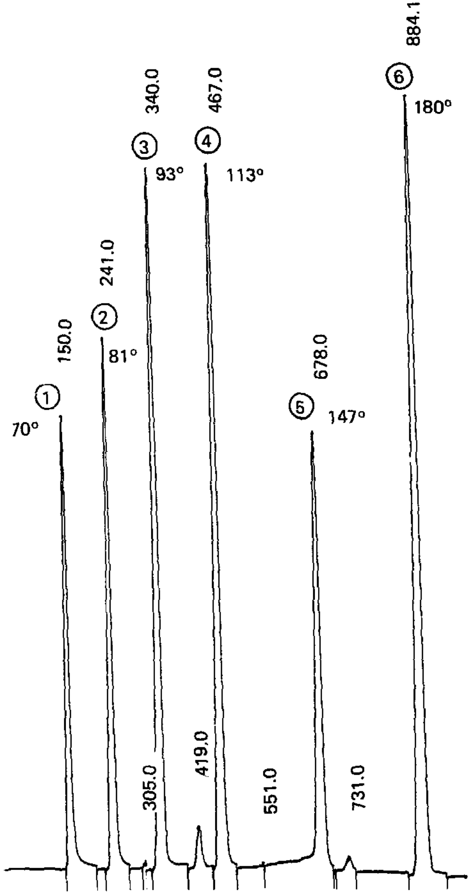


Fig. 1. Electron micrograph of non-acid washed Chromosorb P and electron diffraction pattern obtained from the crystalline area of Fe_2O_3.

Fig. 2. Electron micrograph of acid-washed Chromosorb P (0.015% Fe).

Fig. 3. Electron micrograph of Chromosorb P AW loaded with 15% PEG 20M and electron diffraction pattern from the crystalline area of PEG 20M.



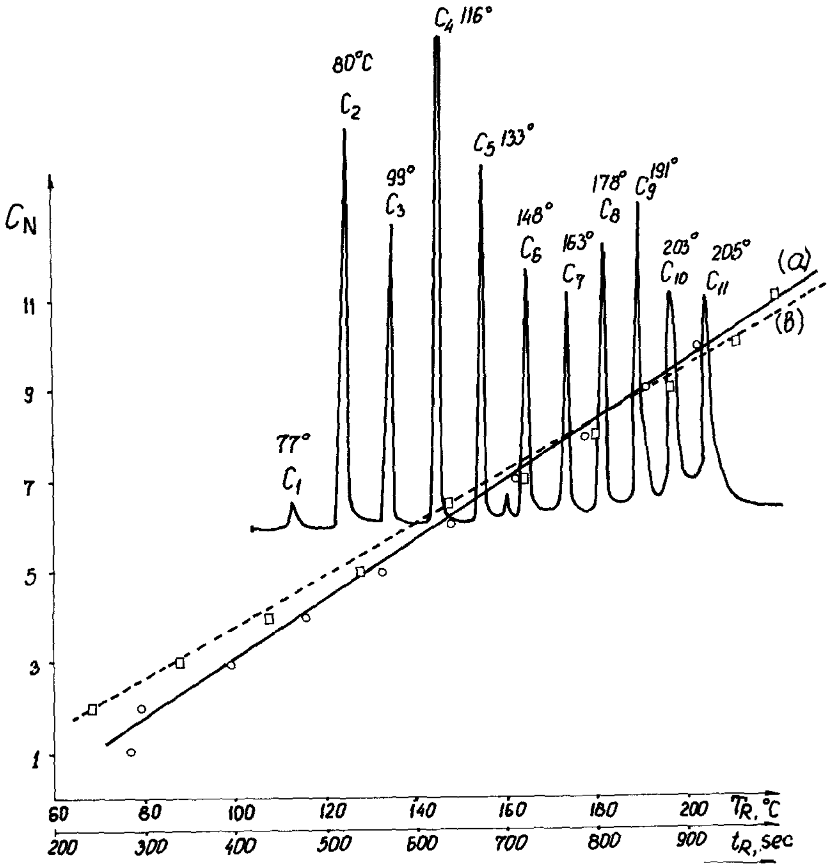
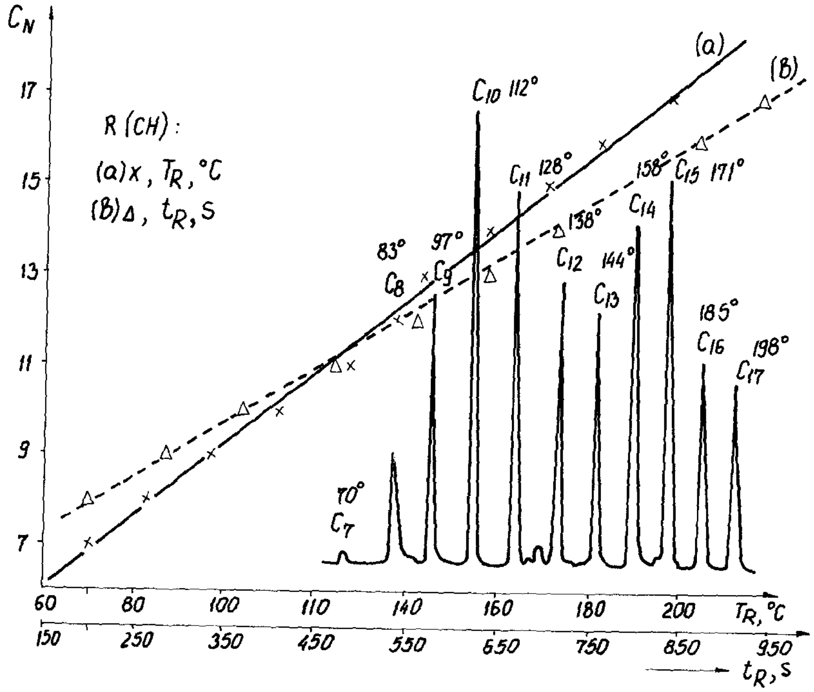


Fig. 4. Chromatogram of the isophorone byproducts obtained on the printer–plotter of the PU 4800 instrument. A glass column (1.0 m × 4 mm I.D.) packed with 15% (w/w) PEG 20M on Chromosorb P AW (0.015% Fe), was used with LTP from 60 to 190°C at 10°C min^{-1}. Peaks: 1 = A; 2 = IP; 3 = MIBK; 4 = MO; 5 = DAA; 6 = IPH.

Fig. 5. Plot of the number of carbon atoms (C_N) for a mixture of *n*-alkanols (C_1–C_{11}) against (a) retention temperature (T_R) and (b) retention time (t_R) obtained under LTP conditions as in Fig. 4. (C_N corresponds to *n* in eqn. 2).



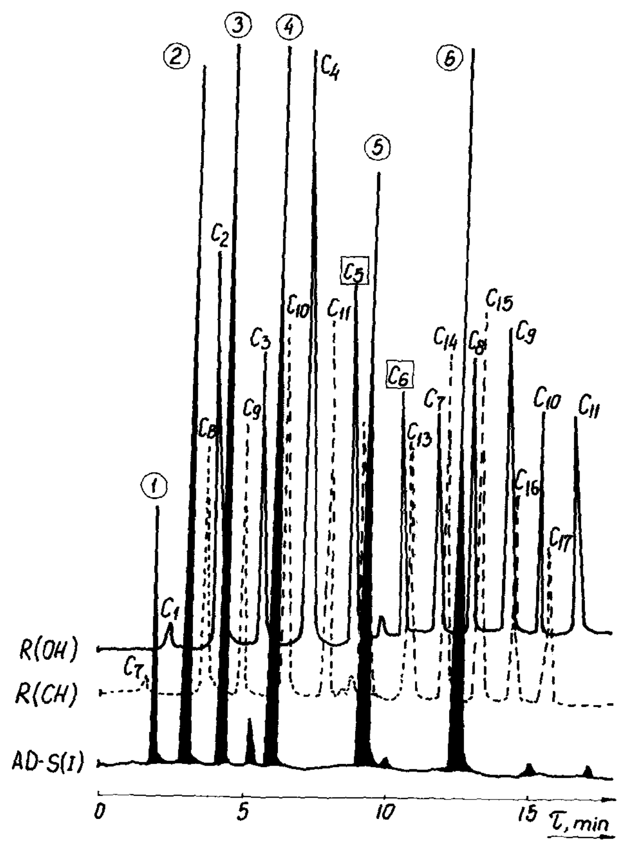


Fig. 6. Plot of C_N for a mixture of *n*-alkanes (C_6–C_{17}) against (a) R_R and (b) t_R obtained under LTP conditions as in Fig. 4.

Fig. 7. Chromatograms of the isophorone byproducts and the fixed points (*n*-alkanols, *n*-alkanes) under LTP conditions. Peaks as in Fig. 4.

TABLE I

REPRODUCIBILITY OF RETENTION TIMES (t_R) AND CONCENTRATIONS (C_i) OF ISOPHORONE AND ITS BYPRODUCTS (MEAN VALUES, n = 5)

Compound	t_R *(s)*			C_i *(%)*		
	$\bar{x}$	*S.D.*	*R.S.D. (%)*	$\bar{x}$	*S.D.*	*R.S.D. (%)*
A	150.1	0.57	0.38	11.27	0.27	2.42
IP	241.1	0.73	0.30	12.48	0.28	2.28
MIBK	339.9	1.24	0.36	18.31	0.26	1.43
MO	466.5	1.66	0.36	18.30	0.26	1.43
DAA	676.6	1.93	0.28	13.20	0.63	4.79
IPH	883.3	3.60	0.41	23.98	1.13	4.73

microscopy in surface studies of different sorbents[6,7]. It is known[6] that transmission electron microscopy is better than the scanning mode for studying diatomite supports, probably because the pores in Chromosorb P (2–3 μm) are larger, for instance, than those in Chromosorb 101 (0.3–0.4 μm).

A well deactivated Chromosorb P surface was achieved by deep acid washing[3,4] and a high phase loading (15%). It was found that after a 24-h washing procedure the iron content was constant at 0.015%, as demonstrated by atomic-absorption and EPR spectrometry. The electron micrographs showed the importance of the removal of iron impurity in obtaining surface homogeneity (Figs. 1 and 2). The spreading of PEG 20M on the diatomite surface, shown in Fig. 3, indicate that the zones were covered to a great extent.

The determination of retention indices[8] under LTP conditions is more attractive than that under isothermal conditions, as the dead time (t_d) need not be determined and complex mixtures can be more easily identified. Van den Dool and Kratz's method[5] as used here was simpler than those of Zhu[9] and separated isophorone byproduct mixtures with only a constant heating rate (Fig. 4). Retention indices were determined with n-alkanols instead of n-alkanes[5] as fixed points (Figs. 5 and 6) as it

TABLE II

REPRODUCIBILITY OF RETENTION WITH LINEAR TEMPERATURE PROGRAMMING (LTP) IN TERMS OF ADJUSTED RETENTION TIMES (t'_R) AND RETENTION INDICES (I) (MEAN VALUES, n = 5)

Compound	$t_{R(LTP)}$			I_{LTP}*		
	$\bar{x}$	*S.D.*	*R.S.D. (%)*	$\bar{x}$	*S.D.*	*R.S.D. (%)*
A	0.32	0.02	9.97	–	–	–
IP	2.10	0.07	3.37	205.17	0.15	0.07
MIBK	4.20	0.07	1.86	294.85	0.17	0.06
MO	6.22	0.04	0.77	411.81	0.17	0.04
DAA	9.26	0.05	0.59	633.12	0.26	0.04
IPH	13.28	0.13	1.01	884.64	0.24	0.03

* C_1–C_{11} n-alkanols used as fixed points.

TABLE III

RECOVERIES OF ISOPHORONE AND ITS BYPRODUCTS (MEAN VALUES, $n = 4$)

Compound	*C_i (g/ml)*		*R.S.D. (%)*
	Added	*Found ± S.D.*	
A	0.155	0.151 ± 0.006	4.09
IP	0.155	0.150 ± 0.005	3.51
MIBK	0.157	0.158 ± 0.006	3.58
MO	0.169	0.173 ± 0.010	5.93
DAA	0.184	0.189 ± 0.008	4.58
IPH	0.180	0.184 ± 0.004	2.29

was shown experimentally that under LTP conditions the retentions of *n*-alkanols increased linearly with increasing number of carbons atoms (C_N), as for *n*-alkanes. Comparison of the carbon numbers of the isophorone byproducts with those of the *n*-alkanols and *n*-alkanes showed that they corresponded better with those of *n*-alkanols. For example, the retention of DAA (with C_6) was between those of C_5 and C_6 *n*-alkanols whereas it was between those of C_{11} and C_{12} *n*-alkanes (Fig. 7).

The proposed temperature programmed conditions should be useful for routine quantitative analyses of complex isophorone byproduct mixtures. The retention induces could be reproduced with an S.D. of 0.15–0.26 index units (Table II). The good reproducibility of the experimental results for isophorone byproducts in terms of both retention and amounts (Tables I–III) showed that the proposed packed column and LTP conditions were suitable for the proposed analysis.

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