THE OXIDATION OF HYDROCARBONS

PART 2.—EXAMINATION OF THE PRODUCTS OF THE VAPOUR PHASE OXIDATION OF *n*-HEPTANE AND OF METHYLCYCLOHEXANE

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A study has been made of the products of oxidation of *n*-heptane and of methylcyclohexane at temperatures of approximately 310° C for the former hydrocarbon and of 330° C and 380° C for the latter. The aldehydes present were determined by oxidizing them with silver oxide to give a mixture of carboxylic acids the constituents of which were estimated by the chromatographic method described by Raine and Garner [1] in part 1.

It was found possible to identify some of the ketones in the products of oxidation of methylcyclohexane by preparing the 2 : 4-dinitrophenylhydrazones, after removal of the aldehydes, and separating these by chromatography on columns of alumina. The individual 2 : 4-dinitrophenylhydrazones obtained from the eluted solutions were identified either by mixed melting-point determinations or by comparison of their X-ray spectrograms with those of the derivatives of a number of pure ketones suspected to be likely constituents of the oxidation products.

In the vapour phase oxidation of hydrocarbons the products are known to contain a mixture of aldehydes, ketones and acids in addition to small quantities of peroxides. It is necessary to find methods for the analysis of these oxidation products in order to throw more light upon the complicated series of reactions which occurs during the oxidative degradation of hydrocarbons.

In the present work the products of oxidation of *n*-heptane and of methylcyclohexane have been examined. The acids were estimated individually by the partition chromatographic method described in part 1 by Raine and Garner.[1] The individual aldehydes were estimated by oxidizing them with silver oxide according to the method described by Mitchell and Smith.[2] (This method was first tested using propionaldehyde and butyraldehyde, and found to give over 99 % oxidation of these aldehydes, this being unaffected by the presence of ketones.) The constituents of the resulting mixture of carboxylic acids were then estimated by partition chromatography as described in part 1. This method of determining aldehydes in the products of combustion has also been developed independently by Bailey and Knox,[3] although the experimental details differ from those of the present authors.

In the present work, however, the analytical methods have been extended and it has been found possible, for methylcyclohexane, to identify some of the individual ketones present in the oxidation products. This was done by preparing the 2:4-dinitrophenylhydrazones by the method of Brady[4] and separating these by chromatography on columns of alumina. The individual 2:4-dinitrophenylhydrazones were obtained from the eluted solutions by distilling off the solvent. Several of these derivatives were identified by mixing melting-point determinations; others were submitted to X-ray analysis and the X-ray spectrograms were compared with those obtained for the 2:4-dinitrophenylhydrazones of a number of pure ketones considered to be likely constituents of the oxidation products. This method of identifying 2:4-dinitrophenylhydrazones has been described by Clarke, Kaye and Parks[5] and by Malkin and Tranter.[6] The complete analytical technique developed has been found to be of considerable value in the examination of the products of hydrocarbon oxidation.

EXPERIMENTAL

PROCEDURE.—Since substantial quantities of the liquid products of the oxidation were required for detailed analysis, a continuous flow system was used for carrying out the oxidation. Products of oxidation were cooled, first in a Liebig condenser where most of the water vapour condensed out and then in an ice-cooled spiral in which the remaining water vapour and some hydrocarbon vapour were condensed. The final coolers were immersed in a mixture of solid CO_2 and kerosine and in these the remaining condensable products were collected.

The products of oxidation consisted of two phases, aqueous and hydrocarbon, between which the intermediate products were divided. The mixed products were separated into aqueous and hydrocarbon layers and the total acid in each layer was determined by titration with standard alkali solution.

Fractional distillation of the dried oxidation products of methylcyclohexane was carried out using a column 32 in. long and ¾ in. diam., packed with Fenske glass helices. In the products of oxidation at 380° C no high boiling ketones were found, but in the distillation of the products of oxidation at 330° C, there was a small fraction about 140-160° C which corresponds roughly to the boiling points of methylcyclohexanones (allowing for impurities). This fraction gave a yellow precipitate when treated with a saturated alcoholic solution of 2:4-dinitrophenylhydrazine. The product was filtered and recrystallized twice from alcohol, but did not give a sharp melting point. It is suggested that this fraction probably contained more than one of the three isomers:

2-methylcyclohexanone	b.p. (°C)	166
3-methylcyclohexanone	,,	169
4-methylcyclohexanone	,,	170

DETERMINATION OF THE INDIVIDUAL CARBOXYLIC ACIDS.—The acids in the hydrocarbon phase of the oxidation products were extracted with sodium hydroxide solution and the aqueous layer was studied separately. The carboxylic acids were removed by steam distillation. Formic acid was determined by oxidation with mercuric oxide and by comparing the acid content of the distillate before and after the oxidation of the formic acid, the amount of this acid was obtained.

The remaining acids were submitted to a Duclaux distillation. The distillate fractions were combined with the residue from the distillation and dried. The acids were extracted with a mixture of chloroform and butanol and separated by partition chromatography using a column of prepared silica gel. The composition of the acid mixture was checked with the figures from the Duclaux distillation. The above methods are described in detail by Raine and Garner[1] in part 1.

SEPARATION OF ALDEHYDES FROM KETONES.—20-30 ml of the oxidation products were placed in a 100 ml flask together with 3 g silver oxide and 20-30 ml of diluent, with distilled water for the aqueous layer and dioxane and water for the hydrocarbon layer.

The flask was tightly corked and suspended in a water bath for 1 h at 60° C. The flask was shaken vigorously every 7 min. After cooling the contents were transferred to a distillation flask together with 25 ml of water and 25 ml of 0·5 N sodium hydroxide solution used for washing the original flask. The mixture was neutralized with 0·5 N sodium hydroxide solution and a few ml of the alkali solution were added in excess. The mixture was diluted to 150 ml and distilled almost to dryness. The residue was diluted with 30 ml of distilled water and redistilled. The distillate was used in the determination of the ketones. The residue containing the silver salts was diluted to 150 ml and acidified with a few drops of 10 N sulphuric acid. The mixture was agitated to ensure that all the salts had been dissolved and decomposed to give the free acids. The solution of acids was then steam distilled and the individual acids determined by the method described in part 1. The result gave the amounts of the individual acids and consequently the amounts of the lower aliphatic aldehydes could be obtained by difference since the amounts of the corresponding carboxylic acid present in the products of oxidation had been determined.

DIRECT DETERMINATION OF FORMALDEHYDE.—The amount of formaldehyde present was checked by direct determination using Schryver's method.[7] A sample of the products of oxidation containing less than 0·5 mg of formaldehyde was diluted to 30 ml in a 50 ml Nessler tube using distilled water for the aqueous layer and alcohol (free of aldehyde) for the hydrocarbon layer. To this solution were added the following in order: 1 ml of a 1 % aqueous solution of phenylhydrazine hydrochloride, 1 ml of a 2 % aqueous solution of potassium ferricyande, 3 ml of a 10 N solution of hydrochloric acid.

The resulting solution was diluted to 50 ml and compared colorimetrically with standards containing a known amount of formaldehyde (checked by hydroxylamine hydrochloride). The distillate obtained from the separation of the aldehydes from the ketones contained a mixture of ketones. The total amount present was estimated by the hydroxylamine hydrochloride method.

A sample of the distillate containing approximately 4×10^{-4} mole of ketone (usually about 50-100 ml) was mixed with 50 ml of a saturated solution of 2:4-dinitrophenylhydrazine in 2 N hydrochloric acid. The containing vessel was then immersed in an ice bath for 1 h. The precipitate of the mixed 2:4-dinitrophenylhydrazones was then filtered off, washed twice with 20 ml of dilute hydrochloric acid and dried *in vacuo* over concentrated sulphuric acid. The precipitate was weighed and redried until its weight was constant.

The precipitate of the mixed 2:4-dinitrophenylhydrazones of the ketones was then dissolved in benzene and a chromatographic procedure was employed for the separation of these derivatives. The adsorbent used was alumina (B.D.H.) employed in the form of a column 2 cm diam. and 70 cm in length confined in a long tube with ground-glass joints at the top and bottom to which reservoirs and receivers could be fitted. The adsorbent was supported in the tube by a sintered-glass disc and a stopcock was provided at the lower end of the tube to enable the flow to be regulated. In order to obtain a uniform column of adsorbent, the tube was filled with the developing solvent (petroleum ether 60-80° with 3 % benzene) and the alumina was then introduced and allowed to settle. The solvent was allowed to run slowly from the tube as the alumina was introduced. After sufficient alumina had been added, the solvent was allowed to drain from the column and when nearly dry a few ml of the sample were placed on the top of the column. The remaining portion of the sample was washed into the column with a few ml of developing solvent. A large volume of this solvent was then placed in the reservoir at the top of the column and development was allowed to take place. If no bands could be seen to form on the column, the developing solvent was changed, greater concentrations of benzene (3, 5, 10 and 15 % solutions in petroleum ether) being used successively. The yellow bands constituting the chromatogram were eluted in order and collected as separate fractions. In certain cases no bands could be separated and the yellow zone was eluted and collected as several fractions.

The 2:4-dinitrophenylhydrazones were obtained from these eluted fractions by distilling off the solvent, care being taken to avoid overheating which tended to cause decomposition of the derivatives giving resinous instead of crystalline products. Resinous products were formed from certain fractions even where special care was taken in their isolation. Several of the ketones were identified by melting-point determinations on the 2:4-dinitrophenylhydrazones, and their identity confirmed by mixed melting-point determinations with the pure 2:4-dinitrophenylhydrazone of the suspected ketone. In some cases vague melting points showed that the derivatives had not been obtained in a pure state by the chromatographic separation and such products were examined further by X-ray analysis.

X-ray powder diffraction spectra were obtained using a rotating anode X-ray tube producing copper K_α radiation. The powder to be examined was compressed into a small rectangular briquette and mounted in the camera so that it could be rotated in the beam of X-rays. A convenient exposure time was found by trial and error for each specimen—this varied for different specimens from 7 to 90 min. The resulting X-ray spectrograms of the 2:4-dinitrophenylhydrazones of the unknown ketones were compared with those obtained for the 2:4-dinitrophenylhydrazones of the following pure ketones: acetone, methylethyl ketone, methyl *n*-propyl ketone, methyl *n*-butyl ketone, methyl *n*-amyl ketone, diethyl ketone, ethyl butyl ketone, di-*n*-propyl ketone, methyl-*iso*propyl-ketone, ethyl *iso*amyl ketone, methyl *iso*butyl ketone, cyclohexanone, 3-methyl-cyclohexanone. This procedure enabled several of the unknown ketones in the products of oxidation to be identified.

RESULTS

The results of the analytical work on the products of oxidation of *n*-heptane with stoichiometric hydrocarbon/oxygen ratio at 310° C are shown in table 1. Two sets of results denoted " experiment A " and " experiment B " are presented and give an indication of the reproducibility attained. In table 2, the analytical results are presented for the products of the oxidation of methylcyclohexane with stoichiometric hydrocarbon/oxygen ratio at two temperatures, viz. 330° and 380° C.

TABLE 1.—OXIDATION OF *n*-HEPTANE WITH STOICHIOMETRIC HYDROCARBON/OXYGEN RATIO

	temp. of oxidation			
products	310° C mole/mole of hydrocarbon introduced	% of total carbonyl	310° C mole/mole of hydrocarbon introduced	% of total carbonyl
	experiment A		experiment B	
aldehydes				
HCHO	0·081	10·2	0·076	9·1
CH_3CHO	0·378	45·5	0·344	41·0
C_2H_5CHO	0·043	5·2	0·047	5·6
C_3H_7CHO	0·007	0·8	0·006	0·7
C_4H_9CHO	0·004	0·5	0·005	0·6
total aldehydes	0·513	62·2	0·478	57·0
ketones	0·317	37·8	0·361	43·0
	mole/mole of hydrocarbon introduced	% of total acids	mole/mole of hydrocarbon introduced	% of total acids
acids				
HCOOH	0·014	27·4	0·016	27·6
CH_3COOH	0·030	58·8	0·035	60·4
C_2H_5COOH	0·005	9·8	0·005	8·7
C_3H_7COOH	0·001	2·0	0·001	1·7
C_4H_9COOH	0·001	2·0	0·001	1·7
total acids	0·051	100·0	0·058	100·0

Table 3 indicates the proportions of the individual aldehydes expressed as a percentage of the total aldehyde, for each experiment. An interesting feature of these results is that the proportions of formaldehyde, acetaldehyde and propionaldehyde, remain practically the same irrespective of the nature of the hydrocarbon oxidized or the temperature of oxidation (within the relatively narrow range studied). This suggests that the composition of the mixture of aldehydes in the products of oxidation may depend upon the relative stability of the aldehydes to further oxidation or to thermal decomposition in the presence of oxygen. Letort and Niclaus [8] have pointed out that the pyrolysis of aldehydes is induced by small amounts of oxygen, and their decomposition probably takes place at the same time as oxidation. Cullis [9] has shown that the aldehydes oxidize much more rapidly than the corresponding hydrocarbons and that the acids are formed almost entirely by the oxidation of the higher aldehydes. The present results show, however, that the amount of total acids produced is only about one-tenth of the amount of total aldehydes, but the rough correspondence between the relative proportions of individual acids and of individual aldehydes with the same number of carbon atoms supports the view that the acids result from the further oxidation of the aldehydes although this may only proceed to a small extent. The yield of acids will depend largely upon the relative extent to which oxidation and pyrolysis of the aldehydes occurs, since the acids themselves are not readily oxidized. It may be seen from tables 1 and 2 that the lower molecular weight aldehydes and acids predominate and this may be due to degradation rather than oxidation of the higher molecular-weight aldehydes.

TABLE 2.—OXIDATION OF METHYLCYCLOHEXANE WITH STOICHIOMETRIC HYDROCARBON/OXYGEN RATIO

	temp. of oxidation			
	330° C		380° C	
products	mole/mole of hydrocarbon introduced	% of total carbonyl	mole/mole of hydrocarbon introduced	% of total carbonyl
aldehydes				
HCHO	0·058	12·9	0·052	13·8
CH_3CHO	0·256	57·2	0·221	58·7
C_2H_5CHO	0·050	11·3	0·033	8·8
C_3H_7CHO	—	—	0·007	1·8
total aldehydes	0·364	81·3	0·313	83·1
ketones *	0·084	18·7	0·064	16·9
		% of total acids		% of total acids
acids				
HCOOH	0·008	32·0	0·013	22·4
CH_3COOH	0·013	52·0	0·041	69·8
C_2H_5COOH	0·004	16·0	0·003	4·8
C_3H_7COOH	—	—	0·002	3·1
total acids	0·025	100·0	0·059	100·0

* Individual ketones identified in products: temperature of oxidation *ca.* 330° C, acetone, methyl ethyl ketone; temperature of oxidation *ca.* 380° C, acetone, methyl ethyl ketone, methyl *n*-propyl ketone, di-*n*-propyl ketone. Fractional distillation suggested the presence of methylcyclohexanones in the aqueous layer of oxidation products from the 330° C experiments.

TABLE 3.—INDIVIDUAL ALDEHYDES AS A PERCENTAGE OF TOTAL ALDEHYDES

products	oxidation of *n*-heptane at 310° C		oxidation of methylcyclohexane	
	experiment A	experiment B	at 330° C	at 380° C
HCHO	15·8	15·9	16·0	16·7
CH_3CHO	73·6	72·0	70·2	70·6
C_2H_5CHO	8·4	9·8	13·8	10·6
C_3H_7CHO	1·3	1·2	—	2·2
C_4H_9CHO	0·8	1·0	—	—

Fig. 1 shows the X-ray spectrograms of the 2:4-dinitrophenylhydrazones of several ketones present in the oxidation products compared with those of known ketones.

It is not proposed to discuss these experimental results further in the present paper. A brief discussion of the results of the methylcyclohexane oxidation has already been published.[10]

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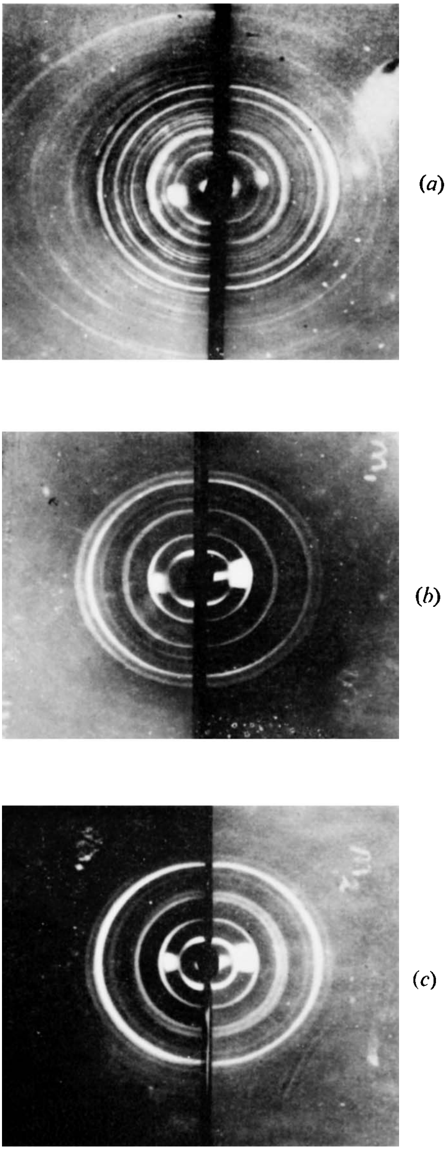

FIG. 1.

[*To face page* 1197.