ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. IV. THE ACTION ON CYCLOHEXANOL AND ITS DERIVATIVES.

By **Harushige INOUE.**

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Chavanne and Roelan(1) have observed that cyclohexanol, by the contact action of alumina, was decomposed at 160° into cyclohexene and water, and the same chemical reaction of the alcohol was also noticed by Bouveault(2) when clay was used as a catalyst at 300°. Japanese acid earth behaves as a catalyst, as mentioned in the previous articles of this subject,(3) in a some-

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(1) Chavanne and Roelan, *Chem. Zentr.*, 80 (1909) I, 73.

(2) Bouveault, *Bull. Soc. Chim.*, [4] 3 (1908), 118.

(3) Inoue, this journal, 1 (1926), 157, 177 & 197.

what different way from alumina, clay or silica which were regarded as the principal constituents of the Japanese acid earth, and the present research was undertaken in the expectation of getting some different results, in some respects, from those mentioned by Chavanne and Roelan, and also by Bouveault.

The cyclohexanol used in the experiment, was prepared from pure phenol by catalytic reduction with reduced nickel and pure hydrogen under 20 atmospheric pressures at 180°, which shows: b.p. 135° under 84.6 mm.; m.p. below 18°; $d_{20}^{20}=0.9547$; $n_D^{20}=1.4650$.

Cyclohexanol(1) was passed with air, or CO_2 on the catalyst heated at 200° and 330° respectively, and the reaction product, which consisted of oily and water layers, was fractionated after being dried with anhydrous sodium sulphate as usual, and each fraction was determined its density and the index of refraction and the results are shown in Tables 1–4.

TABLE 1.

50.9 gr. of cyclohexanol yielded 23.4 gr. oil ($d^{20}=0.8143$) at 200°, in an atmosphere of air.

Fraction	Yield gr.	d_{20}^{20}	n_D^{20}
80–82°	12.2	0.7971	1.44476
82–84°.5	4.7	0.8007	1.44070
85–90°	1.7	0.8045	—
above 90°	3.3	0.8942	1.48078

TABLE 2.

52 gr. of cyclohexanol yielded 26 gr. oil ($d^{20}=0.8362$) at 200°, in an atmosphere of CO_2.

Fraction	Yield gr.	d_{20}^{20}	n_D^{20}
80–82°	6.6	0.7941	1.43622
82–84°.5	10.3	0.7962	1.43772
85–90°	0.7	0.8059	1.44165
90–225°	1.4	0.8774	1.47215
Residue	3.3	0.9044	1.48881

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(1) Inoue, *J. Soc. Chem. Ind. Japan*, 27 (1924), 553.

TABLE 3.

51.4 gr. of cyclohexanol yielded 32.6 gr. oil ($d^{20}=0.8123$) at 330°, in an atmosphere of air.

Fraction	Yield gr.	d_{20}^{20}	n_D^{20}
71–73°	3.2	0.7512	1.41177
73–75°	8.1	0.7536	1.41321
75–80°	3.3	0.7563	1.41510
80–93°	1.6	0.7741	1.42140
93–215°	3.9	0.8896	1.55273
Residue	6.6	0.9644	1.56521

TABLE 4.

49.7 gr. of cyclohexanol yielded 32.8 gr. oil ($d^{20}=0.8065$) at 330°, in an atmosphere of CO_2.

Fraction	Yield gr.	d_{20}^{20}	n_D^{20}
71–73°	2.2	0.7492	1.41282
73–75°	11.5	0.7518	1.41326
75–80°	3.6	0.7558	1.41510
80–93°	1.5	0.7678	1.42370
93–215°	3.7	0.8975	1.50522
Residue	6.4	0.9646	1.55198

As will be seen in Tables 1 and 2 the fractions with b.p. 80–82°, and b.p. 82–84°.5 which are main parts of the reaction product obtained at 200°, as indicated by the physical constants, seem to composed of the cyclohexene resulting by the dehydration of cyclohexanol, which was confirmed by isolating adipic acid (m.p. 153–154°), from the oxidation product of the fractions with nitric acid following the directions denoted by Markonikoff.(1)

While the reaction product resulting at 330°, consisted principally of the fraction with b.p. 73–75° which agrees in density and index of refraction with methyl-cyclopentane isolated by Markonikoff(2) from the low-boiling fractions of Caucasian petroleum, and also by Young(3) from American oil. For the confirmation of the fraction, it was subjected to the oxidation with nitric acid according to the directions of Aschan,(4) and acetic and succinic acids with a

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(1) Markonikoff, *Ann.*, **302** (1899), 27.
(2) Markonikoff, *Ber.*, **30** (1897), 1223.
(3) Young, *J. Chem. Soc.*, 73 (1898), 906.
(4) Aschan, *Ber.*, 31 (1898), 1804.

neutral substance of camphor-like odour, m.p. 176–178°, and of unknown chemical nature, were isolated from the reaction product, and the two acids were confirmed by the characteristic odour and melting point determination (m. p. 183°) respectively.

The formation of methyl-cyclopentane from cyclohexanol, by the contact action of the acid earth at 330°, with decrease in the carbon ring C_6 to C_5, is completely analogous to the so-called rearrangement, the "retropinacoline rearrangement," suggested by Tiffeneau,(1) of alcohols of the cyclohexane series. Such conversion of the cyclohexane ring into the cyclopentane ring was carried out previously by Markonikoff(2) with amino cyclohexane and hydrogen iodide, and by Zelinski(3) with iodocyclohexane.

The assumption of an intermediate formation of cyclohexene, in the way, from cyclohexanol to methyl-cyclopentane, was examined experimentally by transforming the former compound isolated from the reaction product which was obtained by passing cyclohexanol on the earth at 200°, into methyl-cyclopentane.

From 40.8 gr. of the fraction (b.p. 82–84°) mentioned in Table 1, by passing on the earth heated at 330°, 29 gr. of oil ($d_{20}^{20}=0.7942$), 0.5 gr. of ethylene, and 1.2 gr. of water were obtained. The oily reaction product was fractionated into the following 6 portions, and each fraction was studied for density and index of refraction.

TABLE 5.

Fraction	Yield gr.	d_{20}^{20}	n_D^{20}
70–73°	3.8	0.7464	1.41044
73–75°	3.4	0.7533	1.41301
75–77°	4.3	0.7567	1.41441
77–100°	2.9	0.7613	1.41790
120–130°	1.1	0.8123	1.45577
Residue	6.3	0.9387	1.54107

The fraction of b.p. 73–75° was confirmed to be mostly composed of methyl cyclopentane from the measurement of its physical constants. Higher boiling fractions were assumed, from their physical constants, to be composed of polymerized forms of cyclohexene.

When, however, 50 gr. of cyclohexane were treated under the same conditions as cyclohexene, no appreciable change took place, as will be shown in the results of fractionations of the product.

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(1) Tiffeneau, *Ann.*, **405** (1914), 129.
(2) Markonikoff, *Ber.*, **31** (1898). 1223.
(3) Zelinski, *Ber.*, **30** (1899), 388.

TABLE 6.

Fraction	Yield gr.	d_{20}^{20}
78–80°.7	32.7	0.7753
81–82°	6.2	0.7780
82–85°	8.9	0.7785

It is probable that hexamethylene, by the catalytic action of the Japanese acid earth, rearranges itself, at least in part, to form the more stable pentamethylene, even in case of these compounds in which one or more of the hydrogen atoms of the nucleus is replaced by a methyl group, or other long paraffine side-chains; and it is reasonable to suppose that these compounds would react in a manner analogous to that of the mother alcohol itself, since methyl cyclohexanone and menthone behave in a similar way as cyclohexanone toward lead peroxide and sulphuric acid.(1)

To demonstrate the above speculation, methyl cyclohexanol (1 : 2) prepared from o-cresol by catalytic reduction with reduced nickel and hydrogen at 180° (b.p. 167–170°; $d_{20}^{20}=0.9330$; $d_0^0=0.9473$; $n_D^{20}=1.45998$), was passed over the earth heated at 250° and 350° respectively, and the following results were obtained.

When 150 gr. of the alcohol treated at 250°, in presence of the catalyst, 94.0 gr. of oil, 21.3 gr. of water and some gaseous substance were obtained, and the former was divided into the following 11 portions after fractional distillation 10 times.

TABLE 7.

No.	Fraction	Yield gr.	d_0^0	d_{20}^{20}	d_0^{20}	n_α^{20}	n_D^{20}	n_γ^{20}	Methyl cyclohexene, % (by Br-value.)
1	to 86°	2.7	0.7948	0.7783	0.7771	1.42658	1.42940	1.44115	—
2	86–90°	2.9	0.7998	0.7846	0.7835	1.42940	1.43211	1.44331	—
3	90–95°	4.2	0.8018	0.7859	0.7847	1.43090	1.43362	1.44498	90.55
4	95–99°	7.7	0.8039	0.7877	0.7866	1.43242	1.43512	1.44675	95.49
5	99–102°	11.4	0.8047	0.7902	0.7891	1.43383	1.43652	1.44841	98.45
6	102–105°	13.4	0.8082	0.7925	0.7913	1.43565	1.43843	1.45059	99.33
7	105–110°	13.8	0.8135	0.7983	0.7974	1.43847	1.44125	1.45362	about. 100
8	110–115°	1.6	0.8228	0.8085	0.8074	1.44248	1.44451	—	—
9	115–120°	1.4	0.8279	0.8133	0.8121	1.44300	1.44597	—	—
10	120–170°	1.0	0.8645	0.8497	0.8485	1.44812	1.45092	—	—
11	Residue	16.2	—	—	—	—	—	—	—

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(1) O. Wallach, Mathilde Gerhardt and W. Jessen, *J. Chem. Soc.*, **110** (1916), 487.

The fraction of b.p. 90–95° was confirmed as composed of methyl cyclohexenes by its physical constants, elementary analysis (C=86.58; H=13.32%) and also by the bromine-test, and other fractions with b.p. from 95–99° to 105–110° were also ascertained, in a similar manner to that of the third fraction, to consist of methyl cyclohexenes.

The occurrence of methyl-cyclohexene in the fractions mentioned above, was demonstrated by transforming the hydrocarbons present in the fractions with b.p. 99–102° and 102–105° with conc. nitric acid into an acidic sudstance with a m.p. of 152–153°, which shows no lowering of its melting point when mixed with pure adipic acid.

When 150 gr. of the methyl-cyclohexanol were passed over the catalyst heated at 350°, 118.4 gr. of oil ($d_0^{20}=0.8174$; $n_D^{20}=1.46145$) and 26.5 gr. water were obtained, and the oily substance was treated, to isolate some derivatives of cyclopentane formed from methyl-cyclohexanol by contact action of the catalyst, with conc. sulphuric acid to remove the unsaturated hydrocarbons formed from the alcohol, from the saturated ones which occur in the oil. The saturated hydrocarbons which remained, escaped from the reaction of the conc. sulphuric acid, were composed of 25 gr. of a liquid whose boiling point was 80–120°, and 12.4 gr. of another one of higher boiling point. The latter was divided into two fractions by steam distillation, namely 6.4 gr. of volatile ($d_0^{20}=0.8806$) and 3.6 gr. of non-volatile part.

25 gr. of the fraction with b.p. 80–120° were fractionated 10 times, and were divided into the following 8 fractions, each fraction was studied for its density and for the index of refraction and the results are shown in Table 8.

TABLE 8.

No.	Fraction	Yield gr.	d	d_{20}^{20}	d_0^{20}	n_α^{20}	n_D^{20}	n_γ^{20}	Molecular dispersion
1	85–90°	1.7	0.7656	0.7498	0.7488	1.41050	1.41212	1.42163	—
2	90–92°	1.4	0.7716	0.7552	0.7541	1.41311	1.41515	1.42460	0.83
3	92–94°	1.3	0.7747	0.7589	0.7578	1.41482	1.41680	—	—
4	94–96°	2.4	0.7763	0.7612	0.7601	1.41592	1.41810	1.42763	—
5	96–98°	5.2	0.7789	0.7634	0.7623	1.41723	1.41940	1.42884	—
6	98–101°	7.7	0.7815	0.7665	0.7654	1.41833	1.42050	1.43008	0.78
7	101–104°	1.9	0.7850	0.7694	0.7683	1.42034	1.42250	—	—
8	Residue	0.9	—	—	—	—	—	—	—

As will be seen in the above table, the fraction of b.p. 90–92° was noticed to be composed of dimethyl cyclopentane from its physical constants (index of refraction, density and dispersion), and this was also confirmed by elementary analysis: C=85.12; H=15.02, C_7H_{14} requires C=85.71;

H=14.29%. Thus, the occurrence of dimethyl cyclopentane in the reaction product, due to the contact isomerisation of methyl cyclohexene, was demonstrated. The fraction with b.p. 98–101°, to our interest, was learned to be composed of methyl cyclohexane so far studied for its density, index of refraction and dispersion, and also for its elementary composition (C=85.53; H=14.62; C_7H_{14} requires C=85.71; H=14.29%). For identification, it was subjected to contact oxidation by passing it on reduced nickel heated at 350° and toluene was obtained. This hydrocarbon was regarded as originating the contact action of conc. sulphuric acid on methyl cyclohexene, which was used in the previous treatment to clear the unsaturated hydrocarbons from the saturated ones, since methyl cyclohexene, according to Maquenne's report,(1) was actually transformed by the contact action of the acid into methyl cyclohexane.

In order to get more precise knowledge of the formation of methyl cyclohexane from methyl cyclohexene during the treatment, and also the occurrence of its isomeric dimethyl cyclopentane and methyl cyclohexenes in the reaction product, 150 gr. of the alcohol were treated with the earth heated at 350°, in a similar manner as the previous example. 112.4 gr. of oily product (d^0_0=0.8363) were obtained, which was then subjected to fractional distillation 10 times without treatment with sulphuric acid and the following 11 portions were obtained.

TABLE 9.

No.	Fraction	Yield gr.	d^0_0	d^{20}_{20}	d^{20}_0	n^{20}_α	n^{20}_D	n^{20}_γ	Methyl cyclohexene % (by Br-value)
1	75–78°	2.7	0.7659	0.7489	0.7481	1.41352	1.41610	1.42656	—
2	78–82°	3.6	0.7792	0.7610	0.7602	1.41844	1.42095	—	—
3	82–89°	4.3	0.7847	0.7677	0.7669	1.42135	1.42390	1.43489	22.10
4	89–92°	5.2	0.7879	0.7720	0.7712	1.42401	1.42670	1.43734	—
5	92–95°	7.2	0.7930	0.7760	0.7753	1.42668	1.42930	—	—
6	95–99°	7.8	0.7961	0.7793	0.7784	1.42909	1.43191	1.44331	82.95
7	99–102°	16.1	0.8067	0.7901	0.7893	1.43585	1.43863	—	98.25
8	102–105°	14.6	0.8134	0.7976	0.7967	1.44109	1.44416	1.45716	99.87
9	105–110°	16.5	0.8224	0.8060	0.8051	1.44671	1.44987	1.46366	about 100
10	110–120°	2.0	0.8361	0.8191	0.8182	1.45463	1.45807	1.47274	—
11	Residue	21.6	—	—	—	—	—	—	—

The reaction product, from its physical constants, elementary analysis and also the bromine value measured following the directions of

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(1) Maquenne, *Bull. Soc. Chim.*, [3] 9 (1893), 129.

McIlhiney,⁽¹⁾ was considered to be composed of 20% dimethyl cyclopentane and 40% methyl cyclohexene. The fraction with b.p. 99–102°, after being confirmed to be composed of methyl cyclohexene but not cyclohexane, was subjected to oxidation with conc. nitric acid, and oxalic, succinic, adipic (this being the main product) and β-methyl adipic acids were isolated from the reaction product, and also were ascertained by the determination of the melting point.

From the above investigations, it is evident that methyl cyclohexanol, when heated at 250° in presence of the Japanese acid earth, yields methyl cyclohexene as main reaction product, while at 350° the reaction proceeded to form dimethyl cyclopentane from some part of the methyl cyclohexene, but the isomerisation of hexamethylene to pentamethylene hydrocarbon takes place usually under high pressure. Further course of the reaction involved is not clear, but the products are olefines of low molecular weight and polymers of the unsaturated hydrocarbons.

Thus, the contact isomerisation of hydrocarbons of the polymethylene series, besides promoting the actions of dehydration and polymerisation, was forced to denote a special feature of the contact actions of the Japanese acid earth.

Tokyo Imperial Industrial Laboratory,
Hatagaya, Tokyo.

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(1) McIlhiney, *J. Soc. Chem. Ind.*, 13 (1894), 668.