ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. III. THE ACTION ON PRIMARY ALIPHATIC ALCOHOLS.

By **Harushige INOUE.**

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Sabatier⁽¹⁾ and his co-workers have already described the dehydration of some primary alcohols by the catalytic action of alumina and other metallic oxides, and the experiments were reported by Ipatiew,⁽²⁾ especially with regard to the formation of ethers and hydrocarbons of the olefine series from alcohols in presence of alumina, at different temperatures. The present experiment, therefore, was attempted by the writer to find some relation in the catalytic behavior on some aliphatic alcohols, between Japanese acid earth and alumina.

1. **Methyl Alcohol.** Forty gr. of methyl alcohol purified with lime, b.p. 65–66°, was passed on Japanese acid earth heated at 150°, 200°, 250°, 300°, 350° and 500° respectively at a rate of 14.4 c.c. per hour with a current of air or carbon dioxide gas. Of the reaction products, the qualitative and quantitative determinations of the gaseous substances were made by absorbing with bromine water, and also by the combustion method as usual, and of the liquid one by physical and chemical properties after fractional distillation. The results are shown in the following table.

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(1) Sabatier and Mailhe, *Bull. Soc. Chim.*, (4), 1 (1907), 137, 341, 524 & 773.

(2) Ipatiew, *Ber.*, 36 (1903), 1993.

TABLE 1.

Temp.	Gas	Alcohol & water		Gaseous subst.		Para-form-aldehyde
		gr.	d_{20}^{20}	C_2H_4 (%)	CO (%)	
150°	Air	20	0.8592	0.71	4.86	
	CO_2	30	0.8250	1.29	9.77	
200°	Air	13	0.9603			
250°	Air	13	0.9520	1.09	5.83	
	CO_2	25	0.8512	0.33	0.91	
300°	Air	17	0.9535	6.96	7.41	Trace
350°	Air	21	0.9772	28.05	4.03	0.03 (m.p. 157°)
	CO_2	27	0.9601	12.55	0.36	—
500°	Air	23	0.9905	26.73	5.20	0.06

The occurrence of formaldehyde and of its polymer para-aldehyde in the reaction product was confirmed by the characteristic odour and by the physical properties (m.p. 157–160°). The formation of ethylene, as is seen in the table, is favorable with high temperature, and the yield of carbon monoxide is greater in presence of air than in carbon dioxide.

The same experiment which was undertaken on methyl alcohol, has been extended to ethyl alcohol, isobutyl (b.p. 108°; $d_{15}^{15}=0.8075$) and isoamyl alcohol (b.p. 130–132°; $d_{15}^{15}=0.8189$; $[\alpha]^{18}=2°19'$), and the latter one, as will be seen from its physical constants, contains some active amyl alcohol as an impurity.

2. **Ethyl Alcohol.** Ethyl alcohol purified with silver oxide,(1) was examined by the same was as the case of methyl alcohol.

TABLE 2.

Alcohol gr.	Temp.	Vel. of alcohol c.c./h.	Alcohol & water gr.	Ether %	Ester %	Aldehyde %	C_2H_4 %
40	150°	21.26	25.27	5.73	14.73	about 1	1.72
„	200°	21.26	—	12.31	—	29.27	38.50
„	200°	51.87	11.40	53.02	—	2–3	15.30
„	250°	53.40	—	21.36	—	—	51.61
„	350°	17.83	—	—	—	—	95.71

The yield of ethylene from the alcohol, depends not only upon the rate of passing on catalyst, but on the reaction temperature. The formation of ether, which is due to the dehydration of alcohol as in the case of ethylene-formation, shows a maximum in yield at 200°. The oxidation of alcohol to aldehyde, the polymerisation of the oxidized substance into para-aldehyde (b.p. 120–124°) and the formation of ethyl acetate due to the dismutation of the aldehyde, were confirmed to occur simultaneously by the isolation of these reaction products in a fairly pure state.

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(1) Dulap, *J. Am. Chem. Soc.*, **28** (1906), 395.

3. Isobutyl Alcohol. In the case of isobutyl alcohol, isobutylene and β-butylene are the main reaction products as mentioned by Ipatiew⁽¹⁾ and Senderens⁽²⁾ in the catalytic action of alumina on the alcohol, and dibutyl ether (b.p. 140.9°; $d^{15}_{15}=0.7685$) and di-isobutylene (b.p. =110–113°; $d^{15}_{15}=0.7347$) were confirmed to occur in the reaction product by determining the physical constants of the corresponding fractions mentioned in the following table.

TABLE 3.

Temp.	Vel. of alcohol c.c./h.	Butylenes %	Liquid reaction products.	
			ice cooled gr.	water cooled gr.
150°	15	19.58	0.027 (0.11%)	4.807
250°	”	57.25	0.229 (0.97%)	1.934
350°	”	64.96		1.196

Temp.	Fraction	Yield gr.	d^{20}_{20}	n^{20}_{D}	Remark
150°	to 82°	2.9	0.7472	1.39619	
	103–105°	1.1	0.7840	1.39221	
	105–107°	0.7	0.7852	1.39932	
	107–140°	0.5	0.7794	1.40108	
	140–145°	0.3	0.7639	1.42310	Mostly di-butyl ether
	145–150°	0.9	0.7674	1.43287	
	above 200°	1.2	0.7829	1.43783	
250°	60–62°	1 drop			
	62–85°	—			
	85–110°	6 drops			
	110–113.5°	0.7	0.7344	1.41500	Di-isobutylene
	114–181°	0.6	0.7994	1.45287	
	Residue	0.3			
350°	to 90°	—			
	90–110°	0.2	0.7724	1.43887	
	Residue	0.5	0.8298	1.44326	

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(1) Ipatiew, *Ber.*, **36** (1903), **1993**.

(2) Senderens, *Bull. Soc. Chim.*, (4), **1** (1907), 692.

4. Isoamyl Alcohol. With amyl alcohol, as will be seen in Table 4, amylenes (isopropyl ethylene, methyl-ethyl-ethylene and trimethyl-ethylene), diamyl ether and diamylenes were confirmed to occur as usual in the lower fractions of the reaction product, and the yield of these substances tends to increase with the reaction temperature.

TABLE 4.

Temp.	Fraction	Yield gr.	d_{15}^{15}	n_D^{20}	Remark
150°	40–45°	0.7	0.6438(0°)	1.35836	Amylenes
	45–50°	0.9	—	1.35978	
	50–57°	1.1	0.7320(0°)		
	59–65°	1.1	0.7450(0°)		
	65–70°	1.4	0.7411(0°)	1.37639	
	70–75°	1.2	0.7444(0°)	1.37397	
	75–115°	0.2	0.7874(0°)		
	115–125°	0.3	0.8109(0°)		Diamylenes & amyl alcohol
	125–130°	10.8	0.8012	1.40867	
	130–135°	3.6	0.8027	1.40727	
	135–137°	5.7	0.7988	1.40925	
	170–175°	2.0	0.7783	1.41232	Diamyl ethers
	175–180°	1.3	0.7757	1.41331	
	180–185°	2.2	0.7875	1.41580	
	to 220°	2.2	0.7872	1.43341	
200°	28–33°	1.0		1.37252	Amylenes
	33–37°	2.0		1.37518	
	125–135°	1.4	0.7664	1.41820	Diamylenes & amyl alcohol
	150–160°	2.5	0.7743	1.42120	
	160–170°	0.5	0.7557	1.42440	Diamyl ethers
	170–177°	0.6	0.7693	1.45287	
	above 180°	2.9	0.8101		

TABLE 4. (Continued)

Temp.	Fraction	Yield gr.	d_{15}^{15}	n_D^{20}	Remark
250°	28–33°	2.0	0.6606	1.37667	Amylenes
	33–37°	3.4	0.6659	1.37931	
	37–90°	10 drops			
	90–100°	0.6	0.7658		
	120°(±1°)	0.4	0.7828		Diamylenes & amyl alcohol
	125–150°	0.7	0.7818		
	150–160°	1.2	0.7868	1.45797	
	160–200°	0.8	0.8168	1.48968	
	200–210°	0.6	0.8679	1.51153	
300°	28–33°	1.9	0.6646	1.37683	Amylenes
	33–37°	5.6	0.6672	1.37931	
	37–40°	1.2	0.6745	1.38186	
	40–110°	1 drop			
	110–120°	0.4	0.7618	1.42940	Diamylenes
	120–150°	3 drops			
	150–160°	1.1	0.8050	1.45507	
	Residue	1.3	0.8893	1.50831	
350°	28–33°	3.0	0.6590	1.37509	Amylenes
	33–37°	4.0	0.6700	1.37742	
	37–40°	1.3	0.6721	1.38243	
	40–110°	5 drops			
	110–120°	0.6	0.7848	1.44195	
	120–130°	4 drops			Diamylenes
	130–140°	1.1	0.8238	1.46949	
	140–142°	0.9	0.9010	1.49871	
500°	20–40°	1.0	0.5835		Amylenes
	40–140°	13 drops			
	140–144°	1.2	0.8720	1.49871	Diamylenes

By the contact action of Japanese acid earth, primary alcohols of the aliphatic series yield unsaturated hydrocarbons and ethers as in the case of the catalytic action of alumina, and also aldehydes and esters. Both the dehydration of alcohols and the polymerisation of unsaturated hydrocarbons and aldehydes, as we noticed in the present research, resulted in excellent yields at high temperature. The oxidation of alcohols and the dismutation of the oxidized substance, which occur with this catalyst but not with alumina, are favorable at low temperatures.

Tokyo Imperial Industrial Laboratory,
Hatagaya, Tokyo.