BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2993—2995 (1969)

The Reaction of Alcohols and Hydrocarbons in a Silent Electric Discharge. II. The Reaction of 2-Propanol with Ethylene—The Effects of the Reaction Conditions*[1]

Teruo HIRAKI

Institute of Commodities, Faculty of Economics, Kagawa University, Takamatsu-shi

(Received August 18, 1968)

It has been established that the α-C-alkylations of primary and secondary alcohols result from their peroxide-,[1)] light-,[2)] and gamma-rays-induced[3)] reactions with olefins. However, no detailed study of the reaction of alcohol with olefin under a silent discharge has been reported.

A previous study[4)] of the decomposition of 2-propanol under a silent discharge showed that an α-hydrogen atom in 2-propanol is replaced by alkyl groups. The present study was undertaken to ascertain whether or not a chain telomerization occurs in the reaction of 2-propanol and ethylene by a silent discharge, and to establish the difference in the chemical behavior of 2-propanol between that in the presence of ethylene and that in its absence. The author wishes to report some observations on the ethylene effects on the reaction of 2-propanol, and to report that no 2-methyl-2-hexanol (1 : 2 telomer) or higher telomers, derived from a 2-propanol-ethylene mixture excited by light, peroxide or γ-rays, were formed by the silent discharge.

Experimental

Materials. The 2-propanol was purified and the packing material was prepared by the methods described in a previous paper.[4)] Commercial ethylene was used without purification. No impurity was found in either reagent by gas chromatography using columns of PEG-6000 and of activated charcoal respectively.

Apparatus and Procedure. The apparatus and the procedure were similar to those previously reported,[4)] except that the reaction was carried out in the presence of ethylene. All the experiments were performed using a flow system. Ethylene coming from a reservoir was passed through a solid sodium hydroxide tube in order to remove any water, and was then introduced into a discharge tube with gaseous 2-propanol. The ethylene flow rate was measured by a calibrated flowmeter.

The reaction products coming through the tube were separated into a condensable part and non-condensable gases by three traps cooled at 0°C. The voltage was stepped up by a transformer (capacity: 15 kV) to give the required value.

Analyses. The non-condensable gases were identified by comparing their retention times on a gas chromatogram with those of authentic samples (Columns of activated charcoal, hexamethylphosphoramide, and molecular sieve-13X were used). The condensable products were identified by gas chromatography (column, tricresyl phosphate, PEG-6000 and silicone DC-550 at 120°C; carrier gas, He) as well as by derivatization.[5)]

---

*1 The major part of these research results were presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967.

1) W. H. Urry, F. W. Stacey, E. S. Huyser and O. O. Juveland, *J. Am. Chem. Soc.*, **76**, 450 (1954); E. V. Kirkland, *Ind. Eng. Chem.*, **52**, 397 (1960).

2) W. H. Urry, F. W. Stacey, O. O. Juveland and C. H. McDonnell, *J. Am. Chem. Soc.*, **75**, 250 (1953).

3) K. Hirota and M. Hatada, This Bulletin, **34**, 1644 (1961); T. Kurihara and H. Hotta, *ibid.*, **37**, 1448 (1964).

4) T. Hiraki, *ibid.*, **42**, 470 (1969).

5) The 3,5-dinitrobenzoates of 2-methyl-2-butanol and *dl*-2-pentanol were prepared according to the procedure of Shriner *et al.*; R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley & Sons, New York (1956), p. 212.

TABLE 1. INFLUENCE OF ETHYLENE ADDITION ON THE DISCHARGE REACTION OF 2-PROPANOL

Run No.		1	2	3	4	12	13
Packing		None*				$Cu(OH)_2$**	
Second. voltage, kV		15	15	15	13.5	15	15
Second. current, mA		3.0	2.8	4.9	4.7	1.2	0.9
Temp. of discharge tube, °C		85	85	32	32	85	85
Residence time, hr		6	4.5	6	9	5	4
Materials							
2-Propanol	amount, g	38.63	36.99	39.24	38.78	38.95	38.56
	velocity, g/hr	6.44	8.22	6.54	4.31	7.79	9.65
Ethylene	volume, *l*	13.32	0	13.20	0	13.10	0
	velocity, *l*/hr	2.22	0	2.20	0	2.62	0
Molar ratio (C_2H_4/*i*-PrOH)		0.93	0	0.90	0	0.89	0
Amount of liquid products, g		1.72	2.10	0.12	0.20	1.31	1.68
Conversion, %***		4.46	5.68	0.31	0.52	3.36	4.36
Composition of liquid products, %****							
Acetone		23.4	50.6	10.9	24.3	83.5	29.9
Acetaldehyde		17.7	16.7	2.2	0.3	4.3	5.9
2-Methyl-2-butanol		9.6	0.6	18.8	2.2	2.1	0.3
2-Methyl-2-propanol		2.4	2.0	7.8	9.3	1.1	4.5
dl-2-Butanol		7.2	6.9	10.5	3.7	0.8	3.0
dl-2-Pentanol		6.4	1.2	0	0	0.9	0.4
Methyl vinyl ketone		2.8	2.8	4.4	1.2	1.7	9.6
Hydrocarbons		23.9	13.9	7.4	53.0	4.8	43.9
The others		6.6	5.3	38.0	6.0	0.8	2.5

* Siemens ozonizer was used.

** A 5 g of $Cu(OH)_2$ was filled in a glass filter.

*** The conversion efficiency was given by (grams of reaction product per grams of 2-propanol used)×100.

**** The yields of each compound produced were given by (grams of each compound per grams of total reaction product)×100.

Results and Discussion

Influence of Ethylene Addition on the Discharge Reaction of 2-Propanol. *a) With a Siemens Tube.* The main liquid products of the reaction in the Siemens ozonizer were acetone, acetaldehyde, 2-methyl-2-butanol, *dl*-2-butanol, *dl*-2-pentanol, and hydrocarbons (Run No. 1). The percentage compositions of these products shown in the tables are the averages of three experiments; the fluctuations in the yields of these compounds were less than 1%. The gaseous products were C_1-C_4-hydrocarbons, carbon monoxide, and hydrogen; they were not determined quantitatively. An unidentified brown solid was deposited on the glass wall.

All the compounds, except the deposit, had also been formed in the silent discharge-induced reaction of 2-propanol without ethylene.[4] However, the distribution of the products was different from that in the reaction without ethylene: (1) The acetone yield decreased greatly in the presence of ethylene, while the yields of 2-methyl-2-butanol, *dl*-2-pentanol, and hydrocarbons increased. These findings suggest that there is a close relationship between the formations of acetone and of these alcohols.

The radicals from 2-propanol in the silent discharge are mainly $(CH_3)_2\dot{C}OH$, $CH_3CHOH\dot{C}H_2$ and $\dot{C}H_3$, as has been described in the previous paper.[4] Acetone can be formed by the elimination of a hydrogen atom from the $(CH_3)_2\dot{C}OH$ and $CH_3CHOH\dot{C}H_2$ radicals, while 2-methyl-2-butanol and *dl*-2-pentanol can be formed by adding these radicals to ethylene. Thus, the decrease in acetone in the presence of ethylene seems to be due to the latter addition reaction. A similar mechanism has also been observed in the light-[2] and γ-ray-induced[3] reactions.

The possible combination reaction of the $(CH_3)_2\dot{C}OH$ radical with the $\dot{C}_2H_5$ radical which might explain 2-methyl-2-butanol has been discarded, since little or no *n*-butane, which would indicate the presence of $\dot{C}_2H_5$ radicals, was observed.

(2) The yield of *dl*-2-butanol was scarcely affected by the presence of ethylene. Possible ways of this production are thought to be as follows:

TABLE 2. TEMPERATURE DEPENDENCE OF THE YIELD

Run No. / Packing	10	11	12	14
		$Cu(OH)_2$**		
Second. voltage, kV	0	15	15	15
Second. current, mA	0	1.4	1.2	1.0
Temp. of discharge tube, °C	150	150	85	28
Residence time, hr	5	5	5	5
Materials				
2-Propanol amount, g	39.02	37.55	38.95	39.21
2-Propanol velocity, g/hr	7.80	7.51	7.79	7.84
Ethylene volume, *l*	14.00	12.20	13.10	13.68
Ethylene velocity, *l*/hr	2.80	2.44	2.62	2.74
Molar ratio (C_2H_4/*i*-PrOH)	0.96	0.87	0.89	0.93
Amount of liquid products, g	11.30	7.67	1.31	0.02
Conversion, %***	28.96	20.42	3.36	0.05
Composition of liquid products, %****				
Acetone	97.0	83.7	83.5	43.6
Acetaldehyde	0	1.7	4.3	5.1
2-Methyl-2-butanol	0	0.5	2.1	10.3
2-Methyl-2-propanol	0	0	1.1	Trace
dl-2-Butanol	0	0.1	0.8	Trace
dl-2-Pentanol	0	0	0.9	7.7
Methyl vinyl ketone	0	0	1.7	0
Hydrocarbons	1.3	13.5	4.8	7.7
The others	1.7	0.5	0.8	25.6

$$CH_3\dot{C}HOH + CH_2{=}CH_2 \rightarrow CH_3CHOH\dot{C}_2H_4 \xrightarrow{i\text{-PrOH}} CH_3CHOHC_2H_5 \quad (A)$$

$$CH_3CHOH\dot{C}H_2 + \dot{C}H_3 \rightarrow CH_3CHOHC_2H_5 \quad (B)$$

Thus, reaction B may be thought to be retarded in the presence of ethylene and reaction A, to be facilitated, because ethylene may act as a free radical scavenger; the reverse is the production of *dl*-2-butanol in the reaction without ethylene.

b) With a Special Tube. When the reaction of 2-propanol with ethylene was carried out in a special discharge tube filled with $Cu(OH)_2$ (Run No. 12), as compared with the reaction without ethylene (Run No. 13), the following differences were noticed in the liquid products: (1) the acetone yield increased remarkably, and (2) the yields of 2-methyl-2-propanol, methyl vinyl ketone, and hydrocarbons decreased. A similar tendency was observed when a reduced copper tube[4] was used.

Thomas *et al.*[6] showed that, in the decomposition of ethylene under a silent discharge, the products most frequently identified were hydrogen, acetylene, and a liquid.

In the present work the hydrogen thus produced may turn $Cu(OH)_2$ into some effective catalyst for the dehydrogenation of 2-propanol.[7] For this reason, the acetone yield might increase in the presence of ethylene.

Thomas *et al.*[6] have also shown that acetylene and hydrogen are formed through the vinyl radical, and that the radical could give 1-butene and 1,3-butadiene. These C_4-hydrocarbons were observed little in the reaction of 2-propanol with ethylene (Run No. 12), though some were obtained in the reaction without ethylene (Run No. 13). Thus, it is thought that most of the vinyl radicals produced decompose immediately to form C_2H_2 and H_2 when there is a high flow rate of ethylene in the presence of $Cu(OH)_2$. For this reason, the methyl vinyl ketone yield might decrease in the reaction with ethylene.

Temperature Dependence of the Yield. As may be seen from Run No. 10 in Table 2, the reaction of 2-propanol with ethylene at 150°C without an electrical field afforded a great quantity of acetone. Similar results were also observed in the silent-discharge-induced reaction at 150°C (Run No. 11). Thus, at such a high temperature, it may be said that the dehydrogenation to give acetone occurred preferably to an interaction of 2-propanol and ethylene induced by the discharge.

The author wishes to express his thanks to Professor Tamon Matsuura, Hiroshima University, and to Professor Kazuaki Kawamoto, Kagawa University, for their kind advice.

6) C. L. Thomas, G. Egloff and J. C. Morrell, *Chem. Revs.*, **28**, 1 (1941).

7) Sabatier showed that $Cu(OH)_2$ treated with hydrogen was an effective catalyst for the dehydrogenation of alcohols; P. Sabatier, *Compt. rend.*, **172**, 733 (1921).