

COMMUNICATIONS TO THE EDITOR

ISO- AND NORMAL BUTYL ALCOHOLS FROM CARBIDE.

Sir :

In my recent article¹⁾ which appeared in this journal, I showed that the presence of calcium carbide enlarged the scope of organic syntheses enormously. In the present communication, I should like to show thermodynamically that the presence of the carbide likewise is of great significance and interest in the synthesis of iso- and normal butyl alcohols which is verified experimentally. Moreover, the methods of preparing the alcohols in the presence of the carbide are new and they have not been heretofore mentioned in the literature.

Thermodynamic calculations show that the presence of the carbide increases the free energy of reaction from 20 to 60 kcal. at 300°C., as shown in the accompanying Table.

Reaction at 300°C	ΔF cal./mole alcohol
I. From CO + H ₂ .	
$4\text{CO} + 8\text{H}_2 = \text{iso-C}_4\text{H}_9\text{OH} + 3\text{H}_2\text{O}$	-19800
$4\text{CO} + 8\text{H}_2 + 3\text{CaC}_2 = \text{iso-C}_4\text{H}_9\text{OH} + 3\text{C}_2\text{H}_2(\text{polym.}) + 3\text{CaO}$	-83400
II. From Ethyl Alcohol.	
$2\text{C}_2\text{H}_5\text{OH} = \text{n-C}_4\text{H}_9\text{OH} + \text{H}_2\text{O}$	-8800
$2\text{C}_2\text{H}_5\text{OH} + \text{CaC}_2 = \text{n-C}_4\text{H}_9\text{OH} + \text{C}_2\text{H}_2(\text{polym.}) + \text{CaO}$	-30000
III. From Methyl Alcohol.	
$4\text{CH}_3\text{OH} = \text{iso-C}_4\text{H}_9\text{OH} + 3\text{H}_2\text{O}$	-49800
$4\text{CH}_3\text{OH} + 3\text{CaC}_2 = \text{iso-C}_4\text{H}_9\text{OH} + 3\text{C}_2\text{H}_2(\text{polym.}) + 3\text{CaO}$	-113400
IV. From Methanol + Ethanol.	
$2\text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{OH} = \text{iso-C}_4\text{H}_9\text{OH} + 2\text{H}_2\text{O}$	-20700
$2\text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{OH} + 2\text{CaC}_2 = \text{iso-C}_4\text{H}_9\text{OH} + \text{aC}_2\text{H}_2(\text{polym.}) + 2\text{CaO}$	-63100

Each reaction will be described briefly.

Reaction I. Besides the carbide a methanol catalyst is present. Iso-butyl alcohol is chiefly produced. The reaction temperature was from 300 to 400°C; the pressure was about 200 kg/cm².

Reaction II. While in the absence of the carbide a suitable catalyst is essential, in the presence of which a catalyst is entirely dispensed with. In the latter case mainly normal butanol is produced. In the presence of a methanol catalyst along with the carbide, some iso-alcohol is also formed.

Reactions III and IV. In the presence of the carbide, whether or not a catalyst is used, the butyl alcohols are formed. The larger the relative amount of methanol the greater is the

1) R. Negishi, O. Kimura, and O. Kamiike, This Journal, 15, 31 (1941).

proportion of iso-butyl alcohol obtained.

In all these reactions the butanols produced constituted from 20 to 30% of the total liquid products (free of water). In reactions II, III, and IV the reaction temperature and the pressure were, respectively, 350°C and 50 kg/cm².

In a forthcoming paper which will appear in this journal, I shall enlarge upon the thermodynamic considerations and also give more detailed experimental results.

*The Central Laboratory,
South Manchuria Railway Company,
Dairen.*

R. NEGISHI

(Received July 21, 1941)