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REACTION BEHAVIOR OF ALKANES WITH CARBON MONOXIDE IN A HF-SbF_5 SOLUTION

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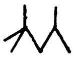
The reaction of alkanes with carbon monoxide in a HF-SbF_5 solution at 30 °C under atmospheric pressure gave significantly different results from those in the Koch-Haaf reaction of alkenes and alcohols in usual strong acids. The results demonstrated that alkanes react very easily under these conditions with preferential formation of secondary carboxylic acids when the alkane has less than six carbon atoms, while a formation of β-scission products occurs, exclusively, with more than seven carbon atoms.

Paatz and Weisgerber reported that the reactions of isopentane, methylcyclopentane or cyclohexane with carbon monoxide in the presence of HF-SbF_5 at room temperature under atmospheric pressure gave C_6 or C_7 acids along with some ketones.1) The reaction is of substantial interest, particularly because of the mild conditions under which alkanes undergo the reaction. However , to date , no extensive studies of the reaction have been reported except for our previous report which dealt with the reaction of 2,2,4-trimethyl pentane.2) We have therefore been studying the details about the reaction of alkanes with various skeletal structures in order to clarify their reaction behavior in super acidic media, and here we wish to report some of these results with acyclic alkanes.

A solution of HF-SbF_5 (ca 20 ml) was placed into a three necked 100-ml Kel-F reaction vessel under sufficient stirring at an appropriate temperature. Then 5～20 mmol of an alkane was added dropwise for 45 min into the acid solution followed by an introduction of carbon monoxide. The reaction mixture was then allowed to stand at 30 °C for 1 hr. The resulting solution was hydrolyzed with ice-water, and carboxylic acids obtained after being worked up according to the usual manner2) were esterified with diazomethane and identified by means of GLC, GC-mass, IR and NMR spectrometry comparing with authentic samples. Representative results thus obtained are listed in Table 1.

The reaction of branched alkanes can be considered to be readily initiated by protolysis3) at tertiary C-H bond to give tertiary carbenium ions, which in turn undergo skeletal isomerizations via secondary carbenium ions. The substantial formation of secondary carboxylic acids can be explained by the speculation that the secondary carbenium ions thus formed are present either in high concentration or to have sufficient long life time in a HF-SbF_5 solution for a reaction with carbon monoxide, although there are few reports in which the secondary carbenium ions were detected spectroscopically, in super acidic media .3b) In straight chain alkanes, the protolysis at C-C bonds gives fragment cations which form carboxylic acids with lower number of carbon atoms together with the products stemming from the protolysis at sec-C-H bonds in the substrate. Alkanes having seven or more carbon atoms, with different skeletal structures, after protolysis at their C-H bonds afford carbenium ions which undergo exclusive β-cleavage to give fragment carbenium ions and olefins.

Table 1. Reaction of Alkanes with CO[a]

Substrate	Total[b] Yield %	Product[c] Distribution %										
		C_3 Acid	C_4 Acid	C_5 Acids			C_6 Acids			C_7 Acids		C_8 Acids
					tert-	sec-		tert-	sec-	tert-	sec-	
	55	some	some	4	67	33	95	38	62	trace		—
	53	3	26	14	27	73	57	39	61	trace		—
	61	—	some	3	67	33	3	40	60	94 29	71	—
	69	2	10	18	13	87	5	39	61	65 33	67	some
	57	—	some	10	80	20	15	40	60	75 35	65	—
	80	some	47	48	90	10	5	38	62	some		some
	102	—	—	100	100	0	—			—		—
	90	some	6	87	90	10	7	38	62	some		some
	61	some	34	31	87	13	33	38	62	2		some

a) React. time. 1hr, React. temp. 30°C, Alkane 20 mmol, SbF_5/alkane = 2 mole ratio, HF/SbF_5 = 5 mole ratio b) Based on alkane used c) Details of skeletal structures will be reported in the future.

Such carbenium ions then react with carbon monoxide followed by treatment with water to yield corresponding carboxylic acids with four∼six carbon atoms. Although it was reported that copper(I) carbonyl catalysts in FSO_3H-SbF_5 promoted the reaction of alkanes with carbon monoxide under atmospheric pressure due to the high solubility of carbon monoxide in such acid media,[4] the yield of carboxylic acids in the reaction in a HF-SbF_5 solution was greatly diminished by the presence of copper(I) carbonyl catalyst.[5]

The distinguishing marks of carboxylation reaction in a HF-SbF_5 solution are as followes. The carboxylation reaction proceeds more readily than in the Koch-Haaf reaction, in which alkenes and alcohols are only carboxylated at high temperature and pressure or high concentration of carbon monoxide by use of copper(I) carbonyl catalyst in the usual strong acids such as H_2SO_4 etc In the present reaction, secondary carboxylic acids are obtained as major products, whereas tertiary carboxylic acids are exclusively produced, even from non-branched alkenes or alcohols in the Koch-Haaf carboxylation reaction.[6] Exclusive formation of β-cleavage products in the reaction of alkanes with seven or more carbon atoms is not observed in the case of alkenes or alcohols under the Koch-Haaf conditions.[6,7]

References
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5) Isopentane gave carboxylic acids in a total yield of 3% or less in $Cu(CO)_n^+$–HF-SbF_5 solution under the same conditions described in Table 1.
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