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An Acid–Base Catalysis in the Selective Decomposition of Carboxylic Acids

Recently many heterogeneous acid–base catalyses have been studied with increasing emphasis on the relation with solid acidity (*1,2*). The rates of these reactions are accelerated specifically, the extent of promotion being affected by the quantity and the strength of the solid acidity. We report here a novel heterogeneous decomposition reaction of carboxylic acids. The reaction is catalyzed by relatively strong solid acids, the products being carbon monoxide and olefins with one carbon atom less than the original carboxylic acid. Several studies on the decomposition reaction of C_3 to C_5 aliphatic carboxylic acids were carried out for elucidating the reaction mechanism. Commercially available guaranteed grade carboxylic acids were used without further purification. Examples of catalysts with solid acidity were several commercial catalysts: SiO_2 (Nikki Co., N-608), SiO_2–Al_2O_3 (N-631H, 24% Al_2O_3), solid phosphoric acid supported on diatomaceous earth (N-501) and γ-Al_2O_3 (Mizusawa Kagaku Co., Neobead-D5). Heteropoly tungstic acids, as additional examples, were supported from aqueous solution on the pelleted diatomaceous earth. The catalysts grained to 10–20 mesh size were placed in a continuous flow reactor and heated in a stream of a carrier gas at the reaction temperature for more than 1 hr. Pure nitrogen or 2% oxygen diluted by nitrogen was used as the carrier gas, and the products were analyzed by titration and by gas chromatography. The effect of oxygen on the selectivity was not observed except for high temperature reaction on the heteropoly acid catalysts, where the consecutive oxidation reduced the selectivity of the products. No quantitative analysis of water produced in the reaction was made. The formation of hydrogen was not detected gas chromatographically. Selectivity is defined hereafter as the percent mol of the product per mol of the reactant converted. Some results of the decomposition of secondary, tertiary and primary carboxylic acids are summarized in Table 1. *dl*-Methylethylacetic acid (MEAA) was decomposed readily at about 200–300°C by several solid acid catalysts. The main products were carbon monoxide and normal butenes. Small amounts of 2-methylpropene were also detected in the effluent. Isobutyric acid (IBAC) was decomposed into carbon monoxide and propene with a little more difficulty than the former, i.e., conversion of the former at 240°C was 46.9% while that of the latter was 36% (extrapolated) under nearly the same condition with the same catalyst ($H_3PW_{12}O_{40}$).

Pivaric acid (trimethylacetic acid, TMAA) was decomposed quite easily over the heteropoly acid catalyst into carbon monoxide and 2-methylpropene. Only a trace of methacrolein was detected in the product.

Propionic acid was decomposed with difficulty over the heteropoly acid catalyst, and the selectivity to carbon monoxide and ethylene was significantly lower than in the case of secondary or tertiary carboxylic acids mentioned above. The decomposition was detectable only above 280°C, and a higher selectivity was observed in an oxygen-deficient atmosphere. Both butyric and valeric acids were inactive on this catalyst below 300°C.

The results in Table 1 support clearly

TABLE 1

DECOMPOSITION OF CARBOXYLIC ACIDS ON SOLID ACID CATALYSTS

		Conversion	Selectivity (%)		Composition of olefins[b] (%)			
Catalysts	Acid[a]	acid (%)	CO	Olefins	1-	*trans*-2	*cis*-2	Iso
$H_3PW_{12}O_{40}$	MEAA	46.9	99.2	97.9	10.9	55.9	30.2	3.0
	IBAC	36	100	97	100	0	0	0
	TMAA	100	94.1	90.5	0	0	0	100
	PRAC	18.3	68.6	29.6	100	0	0	0
	PRAC[c]	13.2	68.8	54.7	100	0	0	0
$H_4SiW_{12}O_{40}$	IBAC	37.5	100	97	100	0	0	0
H_3PO_4	MEAA	49.9	77.5	38.4	6.5	61.2	25.8	6.5
SiO_2-Al_2O_3	MEAA	13.4	100	84.1	11.3	63.9	24.9	0.0
	MEAA[d]	0.6	23	65	21.5	56.9	21.5	0.0
SiO_2	MEAA	0	0	0				
γ-Al_2O_3	TMAA	0	0	0				

[a] Notation of carboxylic acids: MEAA for *dl*-methylethylacetic acid at 240°C, IBAC for isobutyric acid at 240°C. TMAA for trimethylacetic acid at 230°C, and PRAC for propionic acid at 350°C.

[b] Notation of olefins: 1- for 1-butene from MEAA, propene from IBAC and ethylene from PRAC, *trans*-2 and *cis*-2 for the corresponding 2-butenes, iso for 2-methylpropene, respectively.

[c] No oxygen feed in the reaction gas.

[d] Steam added 15 times mol of MEAA. Reaction conditions: acid/O_2/N_2 = 1:1:48 volume ratio; GHSV, 800; reaction temperature is indicated in footnote *a*.

the carbonium ion mechanism, since the tertiary acid is the most reactive and the primary acid is the most stable. Among the secondary carboxylic acids, MEAA was more reactive than IBAC. These reactivities are in accord with those of the carbonium ions produced from the alkyl group of the carboxylic acids. The small amount of 2-methylpropene formed in the decomposition of MEAA can be well explained by the methyl group shift in the aliphatic carbonium ions (*2*). The reaction is discussed below on the basis of this mechanism.

Solid phosphoric acid, heteropoly acids ($H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$) and silica–alumina exhibited a remarkable activity in the acid decomposition reaction, while alumina and silica were almost inactive, as shown in Table 1. Among the inactive catalysts, alumina is a typical Lewis acid with very weak Brønsted acidity. The differences both in the type and the strength of the solid acidity apparently explain the present observation. The Brønsted acidity is considered to be a driving force of the reaction, while the acid strength is a controlling factor of the catalytic activity. Although no measurements of the solid acidity were made in the present study, their Brønsted acid strength is generally accepted (*2*) to be in the order,

$$SiO_2\text{–}Al_2O_3,\ H_3PW_{12}O_{40} \text{ and } H_4SiW_{12}O_{40},\ H_3PO_4 \gg SiO_2,$$

which is in qualitative accordance with the high activity of the former group of catalysts and the low activity of silica.

The above discussion supports the reaction scheme shown in Fig. 1. In this mechanism, the carboxylic acid is protonated first to form an adsorbed complex A. This protonation occurs on the strong Brønsted acid site of the catalyst surface. The complex A liberates water to form another complex B which then decomposes into a

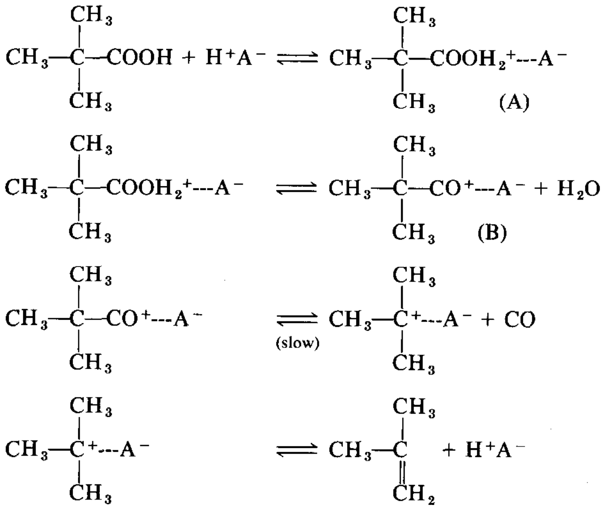

FIG. 1. Mechanism of the decomposition of the carboxylic acids on solid acid catalysts, using trimethylacetic acid as an example.

carbonium ion and carbon monoxide. The water added in the reaction medium will be adsorbed on the catalyst surface and shift the equilibrium of the second step to the left, which is in good agreement with the steam inhibition effect in the decomposition of MEAA on silica–alumina (Table 1). The carbonium ion from the intermediate complex B dissociates a proton to form olefins. It is generally accepted that the isomerization of olefins proceeds via their carbonium ions (*1*), so that those from the decomposition of carboxylic acids are apt to be isomerized. Using the theoretical thermodynamic parameters of Aston *et al.* (*3*), the equilibrium composition of normal butenes at 240°C is estimated to be 11.6% 1-butene, 58.4% *trans*- and 30.0% *cis*-2-butenes. The composition of normal butenes in Table 1 obtained from the reaction of MEAA is thus remarkably close to that of the thermodynamic equilibrium state.

If this mechanism is applied to the decomposition of an ester, the protonated complex A will be changed to the complex B by liberating alcohol, so that the ester will be hydrolyzed during the decomposition to give the complex B which is in equilibrium with the mother carboxylic acid. Actually the result of the reaction of ethyl isobutyrate (Table 2) on the heteropoly acid catalysts suggested the heterogeneous hydrolysis of the ester.

The mechanism described in Fig. 1 can be regarded as a reversed scheme of the Koch reaction (*4*,*5*), which has been known only as a homogeneous catalysis by H_2SO_4, BF_3–H_2O, and several other acids. The highest reactivity of tertiary carboxylic acids and the highest resistivity of the primary acids are directly related to the feasibility of formation of the corresponding carbonium ions. The third step of the scheme in Fig. 1 is accordingly inferred to be the rate-determining step of the overall reaction. The liberation of IBAC during the decomposition of isobutyrate ester also indicates that this is not a fast step. The first protonation and the second dehydration steps cannot be the rate-

TABLE 2

DECOMPOSITION OF ETHYL ISOBUTYRATE OVER $H_3PW_{12}O_{40}$ CATALYST[a]

Conversion	%	Selectivity	%
Ethyl isobutyrate	99.4	Carbon monoxide	81.2
		Propene	70.9
		Ethylene	99.6
		Isobutyric acid	24.6

[a] Reaction conditions: ester/O_2/N_2 = 1 : 1 : 48 volume ratio; GHSV, 800; reaction temperature at 250°C.

determining step since these are common to all the reactants. The difference between the dissociation constants of the aliphatic carboxylic acids are known to be small ($pK_a = 4.7$ to 5.0). As was cited already, however, the Brønsted acidity of the catalysts was found to be an important factor in the reaction. It is quite probable that there is a threshold for the acid strength (H_0^T) and an optimum acidity for the selective and effective decomposition of the carboxylic acid, which, however, is beyond the scope of this preliminary study. On the other hand, application of this novel reaction to aliphatic and alicyclic carboxylic acids promises a new route to some specific olefin syntheses.

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