Elimination Reaction on Solid Acid Catalysts. IV.* A δ_R LFER Study of the Esterification of Alcohols with Carboxylic Acids over Solid Acid Catalysts

Isao Mochida, Yasuhide Anju, Akio Kato, and Tetsuro Seiyama
Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka

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The esterification between eight alcohols and seven carboxylic acids was studied over sodium-poisoned silica-alumina at 250°, using a microcatalytic gas chromatographic technique, in order to elucidate the mechanism of the esterification on a solid acid catalyst on the basis of a LFER (Linear Free-Energy Relationships) approach. Alcohols showed fairly close reactivities for the esterification with acetic acid, whereas, for the olefin formation by intramolecular dehydration and ethylether formation with ethanol, their reactivity varied very much according to the kind of alcohol. In contrast, the reactivities of carboxylic acids for the esterification varied with the structure and were correlated with E_s, Newman's steric-effect parameter, as was observed in the homogeneous acid catalysis, although the reactivity difference under the present conditions was small indeed. It is probably due to the elevated reaction temperature. No ethylacetate, but only thiolacetate, was found in the reaction of acetic acid with ethanethiol. From these facts, it may be concluded that the esterification over a solid acid catalyst may proceed through the attack of an oxonium ion from a carboxylic acid on an adsorbed alcohol, in the manner similar to that in the homogeneous acid-catalyzed esterification.

In a previous paper,[1] two possible mechanistic schemes for the esterification of ethanol with acetic acid were discussed:

$$\text{Mechanism 1: } C_2H_5^+ + CH_3C(OH)_2^+ \longrightarrow CH_3C(O)OC_2H_5 + 2H^+$$

$$\text{Mechanism 2: } CH_3C(OH)_2^+ + C_2H_5OH_2^+ \longrightarrow CH_3C(O)OC_2H_5 + H_3O^+ + H^+$$

One is the attack of the ethyl carbonium ion originating from ethanol on the oxygen atom of the adsorbed acetic acid (Mechanism 1), while the other is that of the oxonium ion from acetic acid on the adsorbed ethanol (Mechanism 2). The δ_C effect (the effect of the nature of the catalyst on the reaction rate),[2] poisoning effect, the kinetic study and a comparison with the dehydration of ethanol on the same catalyst[1,3] all indicate that Mechanism 2 is more probable in the heterogeneous esterification as well as in the homogeneous one.

A study of the dependence of the reactivity upon the reactant structure may give further information about the proposed reaction mechanism. Newman[4] argued the importance of the steric factors of carboxylic acids in homogeneous reactions on the basis of such an approach. In the present study, the mechanism of the esterification on the solid acid catalyst was considered on the basis of the δ_R (the effect of the nature of the reactants on the reaction rate) LFER,[2] using eight alcohols and seven carboxylic acids. A discussion from the same viewpoint was made of the comparisons between the esterifications and the dehydrations of these alcohls. The discrimination between the above two reaction mechanisms may be possible by determining the origin of the ethereal oxygen of the ester. For this purpose, the esterification of ethanethiol with acetic acid may be an adequate system if a common reaction mechanism can be assumed for both alcohols and thiols. An esterification of ethanethiol with acetic acid was, then, studied on the solid acid catalyst. Such a study was attempted in the homogeneous reactions, and the attack of the oxonium ion from benzoic acid was established.[5]

Experimental

Reagents. The alcohols in Table 1 were obtained from the Wako Junyaku Co. The carboxylic acids were obtained from the Tokyo Kasei Co. The ethanethiol was obtained from Nakarai Chemicals, Ltd. All of them were of a E.P. grade except for the ethanol, which was of a G.R. grade.

Catalysts. The catalysts in this work were silica-alumina (13% Al_2O_3) of Japan Cat., a cracking catalyst of the Shokubai Kasei Co. (abbreviated to SA), and the same catalyst impregnated with 0.4 meq Na/g(abbreviated to SA–Na). They were calcined at 550° for 8 hr in the atmosphere.

TABLE 1. THE RATES OF ACETATE FORMATION AND MIXED ETHER FORMATION WITH VARIOUS ALCOHOLS
Catalyst: SA-Na, 1-5 mg
Reaction temperature: 250°C.

No.	Alcohol (ROH)	Rate of acetate formation (mmol·m*l*/g·min)[a]	Rate of mixed ether formation (mmol·m*l*/g·min)[b]
1	Methanol	6.6	—
2	Ethanol	6.3	—
3	*n*-Propanol	8.0	0.12
4	*n*-Butanol	8.2	0.17
5	Isobutanol	7.8	0.19
6	Isopropanol	5.5	1.50
7	*s*-Butanol	8.3	1.56
8	*t*-Butanol	14.0	24.0

a) $ROH + CH_3COOH \longrightarrow CH_3COOR + H_2O$
b) $ROH + C_2H_5OH \longrightarrow C_2H_5OR + H_2O$

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* Part III: I. Mochida, A. Kato, and T. Seiyama, *J. Catalysis*, in press.

[1] I. Mochida, Y. Anju, A. Kato, and T. Seiyama, *J. Catalysis*, in press.

[2] I. Mochida and Y. Yoneda, *ibid.*, **7**, 386, 393, **8**, 223 (1967).

[3] I. Mochida, Y. Anju, A. Kato, and T. Seiyama, This Bulletin, **43**, 2245 (1970).

[4] M. S. Newman, "Steric Effects in Organic Chemistry," ed. by M. S. Newman, Wiley (1956), p. 206.

[5] L. S. Pratt and E. E. Reid, *J. Amer. Chem. Soc.*, **37**, 1932 (1915).

Apparatus and Procedures. For esterifications of alcohols with carboxylic acids and dehydrations of the mixed alcohols, the reaction temperature was 250°C. For the condensation reaction of ethanethiol with acetic acid, it was 300°C. The rates were calculated from the conversion measured by means of the microcatalytic gas-chromatographic technique.[1,3,6] Polyethylene glycol(PEG 1500) was used in an analytical column except in the esterifications of 2-ethyl-*n*-butyric acid and isovaleric acid with ethanol. In these cases, Tween 80+20% H_3PO_4 was used. A carboxylic acid and an alcohol were mixed in equimolar quantities. A fixed quantity (3.4×10^{-2} mmol) of the homogeneous mixture was injected in every run. The conversions of alcohols were kept below 10% except for *tert*-butanol. The same procedure was used for the reaction of mixed alcohols. The rate was expressed by the unit of mmol·m*l*/g·min. The details of the experiments were described in previous papers.[1,3)

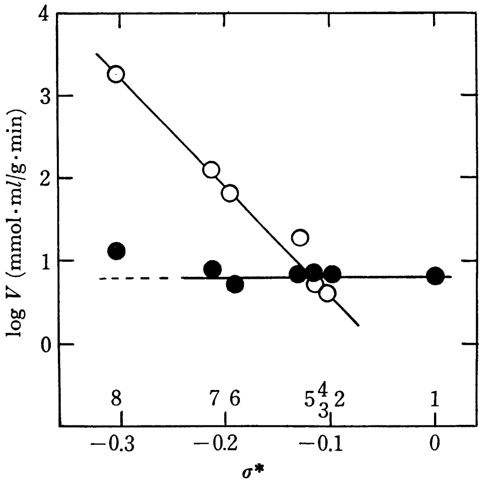

Fig. 1. Reactivities of alcohols as a function of σ*.
Catalyst: SA–Na, 1—5 mg. Reaction temperature: 250°C. Flow rate: 90 m*l*/min. Numbers refer to the reagents designated in Table 1.
○, olefin formation; ●, esterification

Results and Discussion

δ_R *Effect as to Alcohols.* The mixture of an alcohol and an acetic acid gave an olefin and an ester without an ether on SA–Na at 250°C. The reactivities of eight alcohols, ROH, are compared in Fig. 1, where the rates of esterification and dehydration into olefin are plotted against Taft's σ* for the R group. The σ* values are defined as measures of the inductive electron-withdrawing power of an atom or group of atoms in a molecule. The values of σ* were taken from the literature.[7] The reactivities of alcohols for the intramolecular dehydration to olefin varied very much amoung the alcohols, whereas those for esterification remained fairly constant. The large dependence of the dehydration rate upon σ* may mean that the electron-releasing ability of the alkyl group is important in the intramolecular dehydration. Such results have also been reported in the absence of acetic acid.[8] The reactive alcohols tend to proceed into their intramolecular dehydration rather than into their intermolecular esterification, as has been observed in the metal sulfate supported by silica gel.[9] This fact may be understood if we remember that the intermediate from the alcohol with a high tendency to give the carbonium ion is too reactive to stay on the catalyst for the ester formation without being converted into olefin. The distinct difference in the reactivity tendencies suggests different rate-detarmining steps for these intra- and intermolecular reactions.

The ether formations through intermolecular reactions between ethanol and various alcohols were measured on SA–Na at 250°C. The rates are compared with those of acetate formations through the intermolecular reactions of alcohols with acetic acid in Table 1. For primary and secondary alcohols, the rates of the esterifications were much larger than those of the ethyl-ether formations.

The rates of ether formation with ethanol increase in this order of the ease of the formation of the corresponding carbonium ion from alcohols: primary <secondary<tertiary. This indicates a carbonium ion mechanism for the ether formation, in which ethanol is attacked by the carbonium ion from higher alcohol. If the esterification proceeds through a mechanism accompanying carbonium ions from alcohols, the ether formation will be faster than the esterification because more basic ethanol will have a larger susceptibility to the carbonium ion than that of acetic acid. The rates observed, however, do not agree with this expectation for primary and secondary alcohols. Therefore, the carbonium ion formation from alcohols

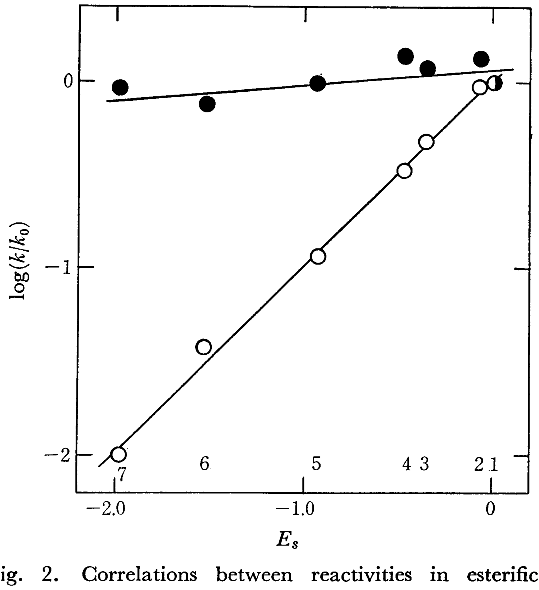

Fig. 2. Correlations between reactivities in esterification and E_s of carboxylic acids.
●, the rates in this work (Catalyst: SA–Na, 3—5 mg, Reaction temperature: 250°C. Flow rate: 90 m*l*/min)
○, rate constants in homogeneous acid-catalyzed reactions at 40°C. Data are taken from Newman (12). Numbers refer to the following reagents: 1, acetic acid, 2, propionic acid; 3, *n*-butyric acid; 4, isobutyric acid; 5, isovaleric acid; 6, pivalic acid; 7, 2-ethyl-*n*-butyric acid

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[6] R. J. Kokes, H. Tobin, and P. H. Emmett, *J. Amer. Chem. Soc.*, **77**, 5860 (1955).

[7] R. W. Taft, Ref. 4, p. 619.

[8] H. Adkins and P. P. Perkins, *J. Amer. Chem. Soc.*, **53**, 1520 (1931).

[9] I. Mochida, A. Kato, and T. Seiyama, *J. Catalysis*, in press.

Table 2. Dependence of the esterification reactivity on the structure of carboxylic acid

Reaction temperature (°C)	s[a)]	Numbers of carboxylic acids used for analysis
20	1.03 ± 0.01	16
30	0.99 ± 0.01	17
40	0.93 ± 0.03	19

a) $\log(k/k_0) = s\ E_s$, where k and k_0 are the rate constants of esterification of ethanol with carboxylic acid and acetic acid, respectively.
Kinetic data were obtained from Ref. 12.

should be abandoned and Mechanism 2 seems more probable for the esterification.

For *tert*-butanol, the rate of mixed-ether formation was larger than that of esterification. A different mechanism should be supposed for the esterification of *tert*-butanol in the heterogeneous reaction as well as in the homogeneous reaction.[10]

δ_R *Effect as to Carboxylic Acids.* The rates of the esterifications of ethanol with some carboxylic acids on SA–Na at 250°C are shown in Fig. 2 as a function of E_s,[11] which is thought to represent the steric factor of the substituent. Newman[12] proposed a sixtet rule for the reactivities of carboxylic acids in the homogeneous esterification, and stressed the importance of the steric factor in this reaction. The analysis of his data at 20, 30, and 40°C showed good correlations with the E_s of the carboxylic acid as is shown in Table 2 and Fig. 2. Large differences in the reactivities were observed. In the heterogeneous catalysis of the present study, a linear correlation was also found, as is shown in Fig. 2, although the kind of carboxylic acids has a smaller effect on the reactivity for esterification. The dependency of the esterification rate on the structure of carboxylic acids decrease with an increase in the reaction temperature in the homogeneous reaction, as may be seen in Table 2. Thus, the smaller reactivity differences among carboxylic acids in the present study may be explained by the reduction of the steric-effect at the higher reaction temperatures. It is interesting that the steric effect was small at the reaction of 250°C in spite of the expectation that the effect might be large on the solid catalyst surface. At any rate, such results do not conflict with Mechanism 2 and suggest, rather, the continuity of the reaction mechanism in homogeneous and heterogeneous acid-catalyzed reactions.

Reaction of Acetic Acid and Ethanethiol. It has been known that the thiol reacts with benzoic acid to produce thiol benzoate in an acidic medium.[5] Whether or not the ester thus produced contains the sulfur atom may give information on the mechanism of esterifications. In the reaction of acetic acid with ethanethiol on SA at 300°C, no ethylacetate except thiol acetate was found by the use of the gas chromatograph.[13] The further identification of thiol acetate was done by means of IR and MS analyses of the trapped sample. The existence of ethylthioacetate without ethylacetate in the product may support Mechanism 2; in this case, the carbon atom of the carbonyl group in the acetic acid, which is positively polarized, may attack the sulfur atom of thiol. The fact that the reactivity of thiol is lower than that of ethanol may be easily deduced by the above reaction mechanism because of the small basicity of the sulfur atom, as estimated from the value of electronegativity.[14] In fact, the reactivity of thiol was only a tenth of that of ethanol.

All the above results suggest that the esterification over the solid acid catalyst may proceed through an attack of the oxonium ion from carboxylic acid on an adsorbed alcohol, in a manner similar to that in the homogeneous acid-catalyzed esterification.

Our thanks are due to Professor Yukio Yoneda of the University of Tokyo for generously providing us with a program of the least-square means. The electronic computaion was carried out on a FACOM 230–60 of the Computer Center of Kyushu University. We are also grateful to Mr. Hozumi Futada for his analysis by means of a Mass Spectrometer.

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[10] L. F. Fieser and M. Fieser, "Introduction to Organic Chemistry," Heath and Company (1957), p. 139.

[11] R. W. Taft, Ref. 4, p. 598.

[12] M. S. Newman, Ref. 4, p. 205.

[13] Only thiol acetate and ethyldisulfide were detected. The latter might be produced from unreacted thiol by the catalytic action of the copper metal of the analytical column.

[14] L. Pauling, "The Nature of the Chemical Bond," Corenl University Press, Ithaca, New York (1960), p. 90.