# *A Kinetic Study of Addition Reaction of Vinyl Ether with Carboxylic Acids*

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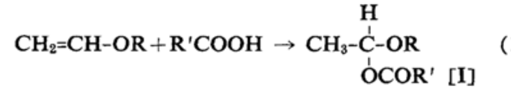
The addition reactions of vinyl ethers with carboxylic acids have been known to give hemiacetal esters (I) in high yields in the presence of a catalytic amount of strong acids, such as hydrochloric acid, sulfuric acid and phosphoric acid.



$$CH_2{=}CH\text{-}OR + R'COOH \rightarrow CH_3\text{-}\overset{\displaystyle H}{\underset{\displaystyle OCOR'}{C}}\text{-}OR \quad [I] \qquad (1)$$

There are numerous publications in the literature on the addition reactions of vinyl ethers with compounds containing active hydrogen, such as alcohols, phenols and carboxylic acids[1-4]; however, there have been no papers published on the kinetic study of the reactions of vinyl ethers except on their hydrolysis[5,6].

In the present investigation, the rates of the addition reaction of *n*-butyl vinyl ether with carboxylic acids in dioxane and toluene have been measured in order to study the mechanism of the addition reactions.

## Experimental

**Materials.**—*n*-Butyl vinyl ether was obtained from commercial source and purified as follows; the vinyl ether was washed several times with equal volumes of water containing a small amount of sodium carbonate, dried over potassium hydroxide and distilled from metallic sodium through a 30 cm. long column, b. p. 93.0~94.0°C.

Carboxylic acids were also obtained from a commercial source and purified by distillation or recrystallization. Melting points or boiling points and p*K*a of the carboxylic acids used are listed in Table. I.

**Solvent.**—Dioxane (b. p. 101.3°C), toluene (b. p. 111°C) and anisole (b. p. 154°C) were purified by being stored over metallic sodium wire and being distilled from metallic sodium.

**General Kinetic Method.**—In a 50 ml. volumetric flask a solution of *n*-butyl vinyl ether in dioxane was prepared which was exactly 3.00 mol./l. with respect to the vinyl ether. The exact molarity of the solution was determined by iodometry[7]. Similarly, a solution of the corresponding carboxylic acids of appropriate concentration was prepared.

As a typical run, 20 ml. of the carboxylic acid

TABLE I. LIST OF CARBOXYLIC ACIDS USED

| Acid | B. p. | $pK_a^{25°C}$ | Acid | M. p. | $pK_a^{25°C}$ |
|---|---|---|---|---|---|
| Acetic | 118.5 | 4.76 | Benzoic acid | 121.7 | 4.17 |
| Propionic | 141.0 | 4.88 | *o*-$NO_2$- | 148 | 2.21 |
| *n*-Butyric | 162.5 | 4.82 | *o*-Br- | 149 | 2.82 |
| *n*-Valeric | 187.0 | 4.81 | *o*-Cl- | 141 | 2.89 |
| *n*-Caproic | 205.0 | 4.85 | *m*-$NO_2$- | 142 | 3.46 |
| Monochloroacetic | 189.5 | 2.81 | *m*-$CH_3$- | 111 | 4.28 |
| | | | *p*-$NO_2$- | 240 | 3.40 |
| | | | *p*-$CH_3O$- | 184 | 4.49 |
| | | | 3.5, Di-$NO_2$- | 205 | 2.80 |

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[1] N. A. Gershtein and M. F. Shostakovskii, *Zhur. Obshchei Khim.* (*J. Gen. Chem.*), **21**, 1452 (1951); *Chem. Abstr.*, **46**, **3001** (**1952**).

[2] M. Levas, *Ann. chim.* (*Paris*), **7**, 697 (1952).

[3] C. E. Schildknecht, A. O. Zoss and C. Mckinly, *Ind. Eng. Chem.*, **39**, 180 (1947).

[4] W. Reppe, *Ann.*, **601**, 81 (1956).

[5] A. Zahorka und K. Weimann, *Monatsh.* **71**, 229 (1938).

[6] E. N. Prolezhava, E. S. Shapiro and M. F. Shostakovskii, *Zhur. Obshchei Khim.* (*J. Gen. Chem.*), **18**, 1663 (1948); *Chem. Abstr.*, **43**, 3272 (1949).

[7] S. Siggia and R. L. Edsberg, *Anal. Chem.*, **20**, 762 (1948).

solution was placed in a 30 ml. reaction tube, and immersed in a thermostat for 20 min. to obtain a constant temperature. To start the reaction, 5 ml. of the vinyl ether solution was pipetted into the carboxylic acid solution. Two milliliter aliquots of this solution were withdrawn from time to time by means of a pipet and put into the mixture of 15 ml. of standard 0.1 N iodine solution and 15 ml. of methanol in a 100 ml. erlenmyer flask. After the mixture was stirred for 5 min., the excess iodine was titrated with standard 0.1 N sodium thiosulfate solution.

When toluene or anisole was used as the solvent, 0.5 N iodine solution and a large excess of methanol were used to make the titrating mixture homogeneous.

## Results and Discussion

Fig. 1 shows plots of percentage reaction against time (min.) for the reaction of *n*-butyl vinyl ether and monochloroacetic acid in dioxane at 60.0°C with various initial concentrations of reactants. The order of the reaction was determined by van't Hoff's initial rate method, and 0.95±0.1 order with respect to vinyl ether and 2.05±0.1 order with respect to carboxylic acid are obtained. Hence, the kinetic equation of the reaction is expressed by

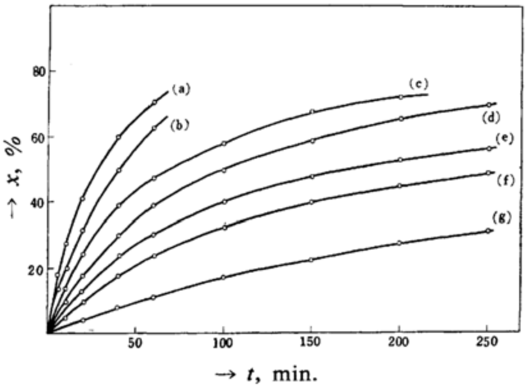


Fig. 1. The addition reactions of *n*-butyl vinyl ether with monochloroacetic acid in dioxane at 60°C.
The plots of percentage reaction *x* against time by various concentration:

| Run | a) | b) | c) | d) | e) | f) | g) |
|---|---|---|---|---|---|---|---|
| *n*-Butyl vinyl ether, mol./l. | 0.6 | 0.5 | 1.2 | 1.0 | 0.6 | 0.5 | 0.3 |
| Monochloro-acetic acid mol./l. | 1.2 | 1.0 | 0.6 | 0.5 | 0.6 | 0.5 | 0.3 |

$$-\frac{dC}{dt}=kAB^2 \tag{2}$$

where the symbols *A*, *B* and *C* represent the concentrations of vinyl ether, carboxylic acid and product, respectively.

Eq. 2 may be integrated to give Eq. 3 or 4.

For $A_0 \neq B_0$,

$$2.303\log\frac{A_0(B_0-C)}{B_0(A_0-C)}+\frac{B_0-A_0}{B_0}-\frac{B_0-A_0}{B_0-C}=(B_0-A_0)^2kt \tag{3}$$

For $A_0=B_0$, $$\frac{2A_0C-C^2}{(A_0-C)^2}=2A_0^2kt \tag{4}$$

where $A_0$ and $B_0$ represent the initial concentrations of vinyl ether and carboxylic acid, respectively.

For individual runs with varvious initial concentrations shown in Fig. 1, the third order rate constants were calculated by the Eq. 3 or 4 at appropriate percentage reaction. The rate constants are determined along the abovementioned way in such a large range of reaction, i. e. from 10% to 60% completion. Table II shows these rate constants and leads to the fact that these constants are very close together in magnitude (the average value of the rate constant is $4.06\times10^{-4}$ mol$^{-2}$ sec$^{-1}$).

Similarly, the third order rate constants of the reaction of *n*-butyl vinyl ether with aliphatic and aromatic carboxylic acids are obtained (Tables III and IV). The plots of the logarithm of the rate constants vs. threciprocal absolute temperature gave satisfactory straight lines from which activation energies and entropies of activation were obtained (Table IV).

The effects of the substituents of carboxylic acids on this addition reaction are noted as follows:

(1) The rate increases as the acidity of carboxylic acid increases.

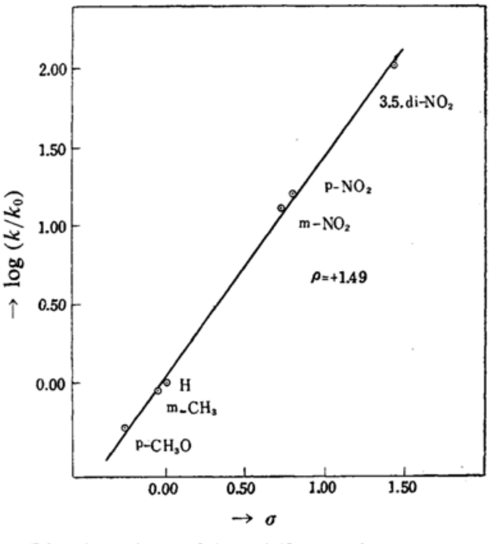


Fig. 2. Plots of log ($k/k_0$) against the Hammett σ-values.

TABLE II. THE RATE CONSTANTS FOR THE ADDITION REACTION OF *n*-BUTYL VINYL ETHER WITH MONOCLOROACETIC ACID IN DIOXANE AT 60°C

| Run | Initial concentration (mol./l.) V. E. | ClAcOH | $k\times10^{-4}$ mol$^{-2}$ sec$^{-1}$ $x$ (%)=10 | 20 | 30 | 40 | 50 | 60 | 70 | Average |
|---|---|---|---|---|---|---|---|---|---|---|
| a | 0.6 | 1.2 | — | 4.11 | 4.05 | 3.97 | 4.15 | 4.12 | 3.95 | 4.06 |
| b | 0.5 | 1.0 | — | 4.08 | 3.99 | 3.93 | 4.02 | 4.10 | — | 4.02 |
| c | 1.2 | 0.6 | — | 4.02 | 4.05 | 4.08 | 4.00 | 3.99 | 4.12 | 4.04 |
| d | 1.0 | 0.5 | — | 3.98 | 3.85 | 4.05 | 4.03 | 3.90 | — | 3.96 |
| e | 0.6 | 0.6 | 4.20 | 4.09 | 4.22 | 4.03 | 3.97 | — | — | 4.10 |
| f | 0.5 | 0.5 | 4.11 | 4.08 | 4.15 | 4.23 | 4.17 | — | — | 4.15 |
| g | 0.3 | 0.3 | 3.98 | 4.08 | 4.07 | — | — | — | — | 4.05 |
| | | | | | | | | | Average | 4.06 |

TABLE III. THE RATE CONSTANTS, THE ACTIVATION ENERGIES AND THE ENTROPIES OF ACTIVATION OF THE ADDITION REACTIONS OF *n*-BUTYL VINYL ETHER WITH CARBOXYLIC ACIDS IN DIOXANE

| Carboxylic acid | $k\times10^{-5}$ mol$^{-2}$ sec$^{-1}$ 70°C | 60°C | 50°C | 40°C | 30°C | $E$ (kcal.) | $-\Delta S^{\neq}$ (e. u.) |
|---|---|---|---|---|---|---|---|
| Acetic | 0.99 | 0.46 | 0.20 | — | — | 16.5 | 33.0 |
| Monochloroacetic | — | 40.6 | 18.5 | 8.69 | 3.95 | 15.6 | 27.4 |
| Benzoic | 3.14 | 1.48 | 0.73 | 0.32 | — | 16.2 | 32.2 |
| 3.5, Di-$NO_2$- | — | 190.0 | 97.5 | 51.1 | — | 13.9 | 29.9 |
| *o*-$NO_2$- | — | 150.0 | 67.5 | 32.5 | 15.3 | 14.7 | 27.5 |
| *m*-$NO_2$- | — | 20.0 | 10.1 | 4.80 | 2.20 | 14.8 | 31.4 |
| *p*-$NO_2$- | 43.8 | 23.3 | 10.9 | — | — | 14.7 | 31.2 |
| *m*-$CH_3$- | 2.84 | 1.37 | 0.62 | 0.29 | — | 16.2 | 32.3 |
| *p*-$CH_3O$- | 1.83 | 0.79 | 0.34 | — | — | 17.5 | 29.5 |
| *o*-Br- | 31.2 | 15.0 | 7.40 | 3.75 | — | 15.1 | 31.0 |
| *o*-Cl- | 26.0 | 13.0 | 6.65 | 3.15 | — | 15.4 | 32.5 |

TABLE IV. THE RATE CONSTANTS OF THE ADDITION REACTION OF *n*-BUTYL VINYL ETHER WITH ALIPHATIC CARBOXYLIC ACIDS IN TOLUENE AT 60°C

| Carboxylic acid | Acetic | Propionic | *n*-Butyric | *n*-Valeric | *n*-Caproic |
|---|---|---|---|---|---|
| $k\times10^{-5}$ mol$^{-2}$ sec$^{-1}$ | 8.70 | 3.66 | 3.05 | 1.67 | 1.01 |

(2) The effect of substituents in meta and para substituted benzoic acids nearly follows the Hammett equation. As shown in Fig. 2, $\log k$ is approximately a linear function of the substituent constants $\sigma$ given by Hammett[8], and the gradient of the plots gave a value for the reaction constant $\rho$ of $+1.49$.

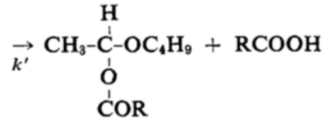
(3) In ortho substituted benzoic acids, the reaction is not so fast as expected from their acidities, which may be attributed to the steric hindrance of the ortho substituents.

(4) In fatty acids, the rate decreases as the length of carbon chain increases.

These results lead to the conclusion that the reaction takes place in two stages, namely the initial formation of an intermediate complex in equilibrium with vinyl ether and carboxylic acid and followed by the reaction of the complex with another carboxylic acid via rate determining step.

$$CH_2{=}CH\text{-}OC_4H_9 + RCOOH \underset{K}{\rightleftarrows} [RCOOH\cdots CH_2{=}CH\text{-}OC_4H_9] \quad (5)$$

Complex + RCOOH



$$\xrightarrow[k']{} CH_3\text{-}\overset{\displaystyle H}{\underset{\displaystyle \underset{COR}{O}}{C}}\text{-}OC_4H_9 + RCOOH \quad (6)$$

For the first stage, the concentration of the complex is found to be

$$[\text{Complex}] = K[CH_2{=}CH\text{-}OC_4H_9]\,[RCOOH] \quad (7)$$

where $K$ is the equilibrium constant of this stage.

For the second stage, the rate of formation of the product is given by

$$\frac{d[\text{product}]}{dt} = k'\,[\text{complex}]\,[RCOOH] \quad (8)$$

where $k'$ is the rate constant of this stage.

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[8] L. P. Hammett, "Physical Organic Chmistry", McGraw-Hill Book Co., Inc., New York, N. Y. (1941), p. 188.

The over-all kinetic equation, therefore, expressed as

$$\frac{\mathrm{d}\,[\text{product}]}{\mathrm{d}t}=k'K\,[\mathrm{CH_2{=}CH{-}OC_4H_9}]\,[\mathrm{RCOOH}]^2 \tag{9}$$

It is natural to consider that $K$ is directly proportional to $K_a$, the dissociation constant of the carboxylic acid used. Since a linear Hammett relation is observed, the experimental rate constant $k$ becomes directly proportional to $K_a$,

$$K \propto K_a \quad \text{and} \quad k=k'K \tag{10}$$

The results show that $k'$, the rate constant of the second stage, is not largely influenced by nucleophilic nature of carboxylic acid.

This two-stage mechanism was further ascertained by the following experiments.

Eq. 11 is given, when two kinds of carboxylic acids are reacted competitively with vinyl ether in a kinetic run,

$$-\frac{\mathrm{d}A}{\mathrm{d}t}=k_1AB_1^2+k_2AB_1B_2+k_3AB_2^2 \tag{11}$$

where $A$ is the concentration of *n*-butyl vinyl ether, $B_1$ and $B_2$ are those of two carboxylic acids, respectively.

Fig. 3 shows plots of percentage reaction against time (min.) for the competitive reaction of vinyl ether (0.6 mol./l.) with monochloroacetic acid $B_1$ (0.6 mol./l.) and acetic acid $B_2$ (0.6 mol./l.) in dioxane at 60°C.

From Eq. 11 by use of rate constants, $k_1==4.06\times10^{-4}\ \mathrm{mol^{-2}sec^{-1}}$ and $k_3=4.6\times10^{-6}\mathrm{mol^{-2}\ sec^{-1}}$, which have been obtained in the separate experiment listed in Table III, the value of $k_2$ can be estimated graphically by initial rate given in Fig. 3. It is $4.0\times10^{-4}\ \mathrm{mol^{-2}\ sec^{-1}}$ and the kinetic equation can be expressed as follows.

$$-\frac{\mathrm{d}A}{\mathrm{d}t}=4.07\times10^{-4}AB_1^2+4.0\times10^{-4}AB_1B_2+4.6\times10^{-6}AB_2^2 \tag{12}$$

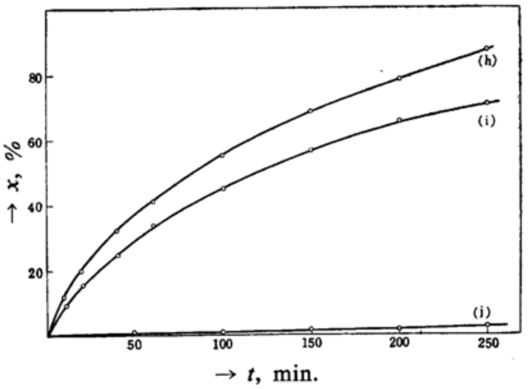
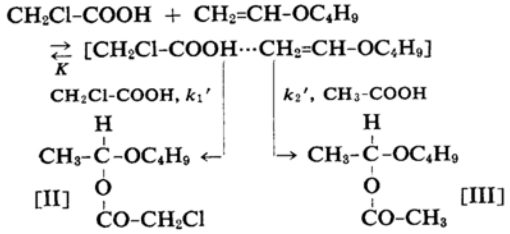


Fig. 3. The competitive addition reactions of *n*-butyl ether with two carboxylic acids in dioxane at 60°C.

The plots of percentage reaction $x$ against time;

| Run | h) | i) | j) |
|---|---|---|---|
| *n*-Butyl vinyl ether, mol./l. | 0.6 | 0.5 | 0.5 |
| Monochloroacetic acid mol./l. | 0.6 | 0.5 | — |
| Acetic acid, mol./l. | 0.6 | 0.5 | 0.5 |



$$\mathrm{CH_2Cl{-}COOH + CH_2{=}CH{-}OC_4H_9 \underset{K}{\rightleftarrows} [CH_2Cl{-}COOH\cdots CH_2{=}CH{-}OC_4H_9]}$$

$$\mathrm{CH_2Cl{-}COOH},\ k_1' \qquad k_2',\ \mathrm{CH_3{-}COOH}$$

$$[\mathrm{II}]\ \mathrm{CH_3{-}\overset{\displaystyle H}{\underset{\underset{\displaystyle CO{-}CH_2Cl}{\displaystyle O}}{C}}{-}OC_4H_9} \longleftarrow \qquad \longrightarrow \mathrm{CH_3{-}\overset{\displaystyle H}{\underset{\underset{\displaystyle CO{-}CH_3}{\displaystyle O}}{C}}{-}OC_4H_9}\ [\mathrm{III}]$$

By the separate experiment, it was ascertained that the ratio of the formation of II and III was 4 : 3. Since $k_1$ and $k_2$ are nearly the same values, this gives further experimental support for the above mentioned consideration that the first step, the formation of the complex from vinyl ether and carboxylic acid, is a dominant factor in this reaction and the rates of second step, $k_1'$ and $k_2'$, are nearly equal.

The reaction of *n*-butyl vinyl ether with acetic acid is accelerated by a catalytic amount of phosphoric acid. In a similar fashion as described in the case of the above mentioned competitive reaction of two carboxylic acids, Eq. 11 is also available to this reaction when $A$, $B_1$ and $B_2$ represent the concentrations of the vinyl ether, phosphoric acid and the acetic acid, respectively. Since $B_1$ and $k_3$, the rate constant of self catalyzed reaction of acetic acid, are very small values, both the first term, $k_1\ AB_1^2$, and the third term, $k_3\ AB_2^2$, are small compared with the second term, $k_2AB_1B_2$. Then, the kinetic equation is given as follows;

$$-\frac{\mathrm{d}A}{\mathrm{d}t}=k_2AB_1B_2 \tag{13}$$

Fig. 4 shows plots of $\log\{(200-x)/(100-x)\}$ (where $x$ represents percentage reaction of the vinyl ether) against time for the reaction of *n*-butyl vinyl ether (initial concentration 0.6 mol./l.) and acetic acid (initial concentration 1.2 mol./l.) in dioxane at 50°C with various concentrations of phosphoric acid, a—e.

The rates of reaction increase linearly as the concentration of phosphoric acid increases, and second order plots have a sufficiently straight lines from which the rate constants $k_2$ have been obtained (Table IV). It was confirmed that the reaction is a general acid catalyzed reaction similar to the results obtaind in the case of hydrolysis of vinyl ether[5,6].

TABLE V. THE RATE CONSTANTS OF THE ADDITION REACTION OF *n*-BUTYL VINYL ETHER WITH MONOCHLOROACETIC ACID IN VARIOUS SOLVENTS AT 30°C

| Solvent | $k$, $mol^{-2} sec^{-1}$ | Solvent | $k$, $mol^{-2} sec^{-1}$ |
|---|---|---|---|
| Dioxane | $3.95\times10^{-5}$ | Toluene 5+dioxane 1 | $9.1\times10^{-3}$ |
| Anisole | $1.34\times10^{-3}$ | Toluene 2+dioxane 1 | $2.1\times10^{-3}$ |
| Toluene | $2.08\times10^{-2}$ | Toluene 1+dioxane 2 | $0.7\times10^{-3}$ |
| | | Toluene 11+ether 1 | $3.3\times10^{-3}$ |

TABLE VI. THE RATE CONSTANTS OF THE ADDITION REACTION OF *n*-BUTYL VINYL ETHER WITH ACETIC ACID IN THE PRESENCE OF A CATALYTIC AMOUNT OF PHOSPHORIC ACID IN DIOXANE AT 50°C

| Run | $[H_3PO_4]$, mol./l. | $k'[H_3PO_4]$, $mol^{-1} sec^{-1}$ | $k'$, $mol^{-2} sec^{-1}$ |
|---|---|---|---|
| a | $4.8\times10^{-4}$ | $1.50\times10^{-5}$ | $3.1\times10^{-1}$ |
| b | 9.6 〃 | 2.60 〃 | 2.7 〃 |
| c | 13.8 〃 | 4.40 〃 | 3.0 〃 |
| d | 24.0 〃 | 8.15 〃 | 3.4 〃 |
| e | 48.0 〃 | 15.8 〃 | 3.3 〃 |

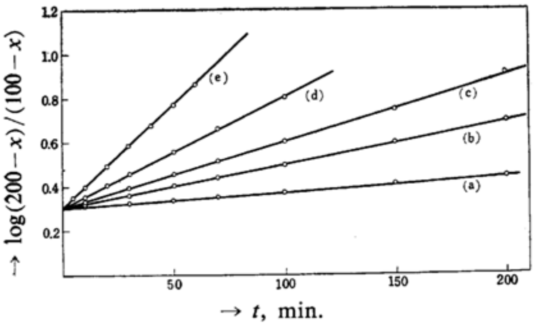
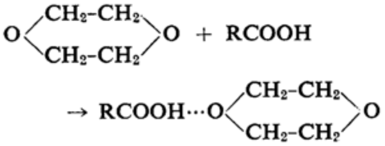


Fig. 4. The addition reaction of *n*-butyl vinyl ether with acetic acid in the presence of a catalytic amount of phosphoric acid in dioxane at 50°C.

In addition, the rates of this reaction are remarkably influenced by the nature of the solvent used. Table V shows the rate constants of the reaction of chloroacetic acid with *n*-butyl vinyl ether in dioxane, anisole and toluene at 30°C. In toluene the reaction is faster by 520 times than in dioxane. In anisole the reaction is not so fast as in toluene but still it is faster by 34 times than in dioxane. It was also observed that the addition of a small amount of dioxane or diethyl ether to toluene solution retards the reaction considerably.

Possible formation of complex from carboxylic acid and solvent containing ether linkage such as dioxane, competes with the formation of the above-mentioned complex from vinyl ether and carboxylic acid, and decreases the concentration of the latter which is the necessary intermediate to form the product, hemiacetal ester. This is a reason why the reaction is very slow in dioxane.



$$CH_2{=}CH\text{-}OC_4H_9 + RCOOH$$
$$\rightarrow RCOOH\cdots CH_2{=}CH\text{-}OC_4H_9$$

## Summary

The rate constants, the activation energies and the entropies of activation of the addition reactions of *n*-butyl vinyl ether with carboxylic acids in dioxane, anisole and toluene were determined. It was found that the reaction is first order with respect to vinyl ether and second order with respect to carboxylic acid, and the rate of the reaction increases as the acidity of carboxylic acid increases and a linear Hammett relation is observed in the reaction of meta and para substituted benzoic acids. In the presence of a catalytic amount of phosphoric acid, the rate increases linearly with its concentration. The addition involves two stages, namely the initial formation of intermediate complex from vinyl ether and carboxylic acid, followed by the reaction of the complex with another carboxylic acid. In addition, the solvent effect has been clarified and a general acid catalyzed reaction has been discussed in view of these results.

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