Hydrogen Exchange and Isotope Effect on the Vinylation of Acetic Acid

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Introduction

As yet few investigations have been made as to the mechanism of the addition of reagent to the carbon triple bond, except that of the hydrogenation of acetylenic hydrocarbons[1]. The present investigation was undertaken to obtain some information about the mechanism of the addition to the triple bond. Vinyl acetate is synthetized by the addition of acetic acid to acetylene. By analogy with the addition of hydrogen halide to olefins it seems likely that the reaction takes place through the following process.

$$\text{(i)}\quad CH{\equiv}CH + H^+ \rightleftarrows CH_2{=}CH^+$$

$$\text{(ii)}\quad CH_2{=}CH^+ + CH_3COO^- \rightarrow CH_2{=}CH{\cdot}OCOCH_3 \qquad (1)$$

The initial step in the addition may be the donation of proton to acetylene by acetic acid to form an intermediate ion, (i), the latter then combining with acetate ion, (ii). This view suggested some ideas to the author, as follows. If (ii) is slow and rate-determining, acetylene may readily exchange its hydrogen with acetic acid in the course of reaction. However, if (i) is the slow step, the hydrogen exchange may hardly take place at all. Under this consideration the experiment of the deuterium exchange between acetylene and acetic acid-*d*, CH_3COOD, was undertaken. In the experiment acetylene and acetic acid-*d* were allowed to react in vapor phase with zinc acetate supported on active charcoal as catalyst at 160°C. In the course of reaction the change of deuterium concentration of acetylene was investigated. It appeared also possible to obtain some useful information about the reaction mechanism by the study of isotope effect on the reaction rate. The reaction rate was measured by a static method, and the effect of deuterium substitution on the reaction rate was studied.

Experimental

Materials.—G. R. glacial acetic acid was dried by vacuum distillation over phosphor pentoxide and used without farther treatment. Acetic acid-*d*, CH_3COOD, was prepared with acetic anhydrate and heavy water heating at 180°C. The heavy

1) G. C. Bond, "Catalysis," III, Reinhold Publishing Corp., New York, N. Y. (1955), p. 109.

water was obtained from Osaka University by courtesy of Prof. T. Titani and Prof. K. Hirota. The deuterium concentration of acetic acid-*d* was analyzed by burning it on cupric oxide and measuring the density of the water with a pressure sensitive buoy[2]. The deuterium concentration of the acetic acid-*d* was 96.2 atom % in hydroxyl hydrogen.

Acetylene was prepared with calcium carbide and water, and purified by the usual method. Dideuteroacetylene was prepared by the distillation of heavy water over calcium carbide following Lind's method[3]. Mass spectrometric analysis of the dideuteroacetylene showed that 8.1% of C_2HD was present, or 96.0 atom % in total deuterium concentration. The isotope analysis of acetylene was made in the Faculty of Science of Osaka University with the Hitachi MR-B type mass spectrometer.

Catalysts.—The zinc acetate catalyst supported on charcoal was prepared as follows. A proper amount of zinc acetate aqueous solution was absorbed into the active charcoal granules, Tsurumi Coal-GVAS, and they were dried at 110°C. Prior to use, the catalyst was evacuated a 170°C. Zinc acetate content of the catalyst used for the exchang experiment was 32% and that used for the isotope effect experiment was 28% in weight respectively.

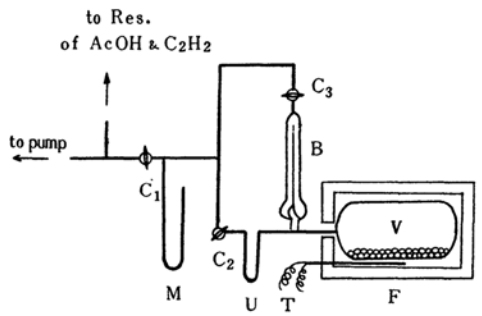


Fig. 1. Apparatus for the study of vinylation of acetic acid.

B	Bourdon gauge	M	manometer
C_1, C_2, C_3	stop cocks	T	thermocouple
		U	U tube
F	heater	V	reaction vessel

Apparatus and Procedure.—The main part of the apparatus is shown in Fig. 1. The glass reaction vessel, V, in which 18 g. of the catalyst had been contained, was evacuated at 160°C. A requisite amount of acetic acid-*d* was distilled into the U tube, U, in front of the reaction vessel, V, while U was cooled in liquid oxygen. Closing the stopcock, C_2, U was then warmed to room temperature, and the acetic acid-*d* was left to be adsorbed in the catalyst completely. Then acetylene was admitted into the reaction vessel through C_2. The succeeding pressure change with the reaction in the vessel was observed with the Bourdon gauge, B. The reaction temperature was kept at 160°C in the range of ±0.5°. After a definite time U was recooled in liquid oxygen, and the reaction was stopped. Acetylene was separated from the condensate in U by fractional distillation between −60° and −183°C. Prior to isotope analysis, acetylene was purified by repeated distillation through the traps at −60°C.

Results

I. Exchange of deuterium between acetylene and acetic acid-*d*.—In every run 0.2 cc. of acetic aid-*d* and about half of the equivalent moles of acetylene were admitted into the reaction vessel. The acetylene were admitted into the reaction vessel. The acetic acid-*d* used in this experiment contained 24.4 atom % of deuterium at the hydroxyl hydrogen. The total pressure was about 110 mmHg. at the start of every run. The results are given in Table I. In the fourth column of the table are shown the mole ratios of C_2HD and C_2H_2 in the acetylene samples, which were taken out in the course of vinylation by the procedure mentioned above. The formation of C_2HD indicated that the hydrogen exchange between acetylene and acetic acid-*d* occurred in the course of vinylation. As to the exchange rate, however, the reproducibility of the rates was hardly sufficient to make any kinetic analysis, for the observed ratios, C_2HD/C_2H_2, were not parallel with reaction time. It appears that the exchange rate increased with reaction time. It appears that the exchange rate increased with repetition of experiment. Some of the runs, which were carried out at 150°C, made no marked difference in the exchange rate to the other

TABLE I
DEUTERIUM EXCHANGE BETWEEN ACETYLENE AND ACETIC ACID-*d*

Run No.	Temp. (°C)	Reaction time (hr.)	C_2HD/C_2H_2
1	160	6	0.060
2	〃	12	0.110
3	〃	12	0.142
4	〃	15	0.191
5	〃	10.5	0.183
6	〃	3	0.170
7	150	3	0.182
8	〃	12	0.172
9	〃	6	0.162
10	〃	9	0.134
11*	160	21	0.094
12*	〃	12	0.108
13*	〃	6	0.182

* With active charcoal only.

2) T. Okamoto and M. Shindo, *J. Chem. Soc. Japan*, **57**, 9 (1936).
3) S. C. Lind, J. C. Jungers and C. H. Schiflett, *J. Am. Chem. Soc.*, **57**, 1032 (1935).

runs, which were carried out at 160°C. The runs from No. 11 to 13 were carried out with the active charcoal only, which contained no zinc acetate. In these runs no vinyl acetate was produced, but the exchange of deuterium occurred in a rate comparable to the other runs as is shown in Table I. The value of C_2HD/C_2H_2 at the exchange equilibrium can be estimated experimentally as about 1.8 from the data in Table I except No. 4, which was carried out under a somewhat different condition.

II. Deuterium isotope effect.—The rate of vinylation of acetic acid on the zinc acetate-charcoal catalyst is of the first order with respect to acetylene pressure[4], and in the presence of a definite and larger amount of acetic acid the reaction rate is approximately given by

$$-\frac{dP_a}{dt}=k_1P_a \qquad (2)$$

where P_a is the partial pressure of acetylene at any time t and k_1 is the first order rate constant. P_a is calculated approximately as the difference

$$P_a=P-P_b' \qquad (3)$$

where P is the total pressure of the reaction system at the time and P_b' is the adsorption equilibrium pressure of acetic acid before the admission of acetylene, or before the initiation of the reaction with acetylene. It has been assumed that in the beginning of reaction the decrease of acetic acid pressure with the reaction progress may be canceled by the increase of pressure of vinyl acetate produced. k_1 can be given by the slope of long P_a curve plotted against time as is shown in Fig. 2, where the results for a typical run are shown. The values of k_1 were used as the measure of deuterium isotope effect on the reaction of rate. Under a definite condition k_1 of the reaction of heavy acetylene and acetic acic-*d* was compared with that of the reaction of normal acetylene and acetic acid. The results at 160°C are given in Table II. In every run 0.27 cc. of acetic acid-*d* was used, and the initial pressure of acetylene was about 100 mmHg. The

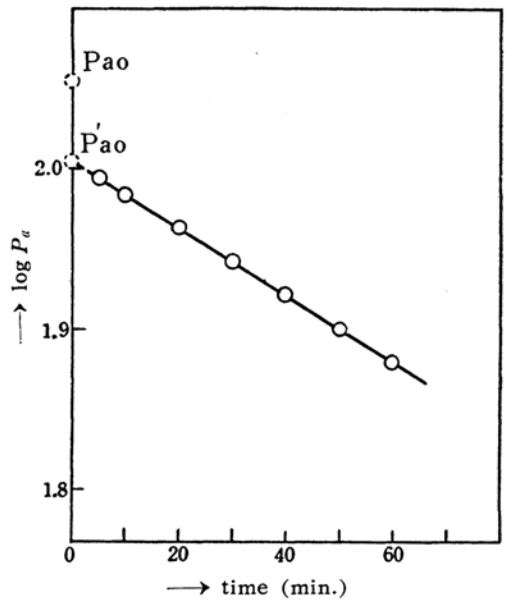


Fig. 2. The reaction rate of vinylation of acetic acid at 160°C.

runs of standard vinylation reaction with normal acetylene and acetic acid were performed before and after each run with the heavy reagents in order to confirm that the catalyst activity was not modified during this experiment. The results showed that the values of k_1 of the standard runs were always within $(3.6\pm0.1)\times10^{-3}$ min.$^{-1}$. In Table II the ratios, k_D/k_H, given in the fourth column are the ratios of k_1 of the reaction between the heavy reactants, of which the deuterium concentrations are given in the first and the second columns, and the k_1 of the reaction with the normal reactants. The ratios were always greater than unity and increased with the deuterium concentration of the reactants. The ratio was 1.6 for the reaction of almost wholly deuterated reactants, 96 atom %, at 160°C.

TABLE II

DEUTERIUM ISOTOPE EFFECT ON VINYLATION OF ACETIC ACID AT 160°C.

Deuterium Conc. atom %		$k_1\times10$	k_D/k_H
Acetylene	Acetic acid (in OH)		
0	0	3.6	
41	24	4.2	1.2
41	44	4.8	1.3
96	96	5.8	1.6

Discussion

Furukawa and Kozasa[5] investigated this vapor phase synthesis of vinyl acetate at

4) In another report*, it has been shown that the rate of vinylation of acetic acid on zinc acetate-charcoal catalyst is given by

$$-\frac{dp_a}{dt}=k\frac{p_a\,p_b}{(1+Kp_b)^2}$$

where p_a and p_b are the partial pressure of acetylene and that of acetic acid respectively. k is the rate constant and K is the equilibrium constant of adsorption of acetic acid on the catalyst.

* N. Yamada, *J. Chem. Soc. Japan (Pure Chem. Sect.)*, **78**, 252 (1957).

200° to 250°C. They noticed that the reaction rate is of the first order with respect to acetylene pressure and independent of acetic acid pressure. They presumed that the rate-determining step of this reaction is the adsorption of acetylene on the catalyst, and suggested that the reaction proceeds through acetylene-zinc acetate complex as intermediate. The author also studied the kinetics of this reaction at 160°C. Then it was concluded that the rate determining step is not the adsorption of acetylene, but is the reaction on the surface of the catalyst. Now the fact of the hydrogen exchange in the course of vinylation favors the above conclusion. If the adsorption was the slowest step and determined the reaction rate, acetylene would have little chance to exchange its hydrogen with acetic acid on the catalyst.

It has been shown that acetylene exchanges its hydrogen with acetic acid in the course of vinylation. This can be explained by accepting the already proposed mechanism (1) as that of the vinylation, and the step (ii) as the slow step. The hydrogen exchange was also found to occur between acetylene and acetic acid on the active charcoal, when no vinyl acetate was produced. If we assume that the exchange reaction on the charcoal proceeds through the same mechanism as that of the exchange on the zinc acetate catalyst, which has been presumed as (1), then the fact may suggest the following. The step (i) can proceed readily both from left to right and reversely, but the step (ii) cannot proceed so readily without zinc acetate catalyst. This argument makes it more probable that the step (ii) must be the rate-determining step.

We can find a great likeness between (1) and the mechanism of specific acid-catalyzed reaction as

$$\text{(i)}\quad S + H^{\cdot} \rightleftarrows SH^{\cdot} \qquad (4)$$
$$\text{(ii)}\quad SH^{\cdot} \rightarrow \text{product}$$

where S is the substrate. It has been found that most acid-catalyzed reactions proceed more readily in D_2O than in H_2O[6]. The isotope effect is caused by the pre-equilibrium (i) of (4). This means that if there is such a pre-equilibrium, the effect of the isotope mass makes the concentration of SD greater than that of SH under comparable conditions. If we find experimentally $k_D > k_H$ in an acid-catalyzed reaction, then an acid-base equilibrium must always be involved in the kinetic scheme. Now it has been found that there is such an isotope effect on vinyl acetate synthetic reaction as $k_D > k_H$.

The isotope effect obtained, $k_D/k_H = 1.6$, is of the same order as those found by other workers for acid-catalyzed reactions, $k_D/k_H = 1.3 \sim 3.0$[6]. It has not yet been fully ascertained whether vinylation reaction of organic acid with zinc acetate catalyst is an acid-catalyzed reaction[7]. However, since in the vinylation one of the reactants is an acid, it is reasonable to suppose that there exists such an acid-base equilibrium as (i) of (1). It should also be noted that usually the addition of reagents to the carbon-carbon triple bond requires a combination of a mercuric salt and a strong acid as catalyst. The fact of the hydrogen exchange between acetylene and acetic acid also favors this consideration. It may be concluded that by analogy to acid-catalyzed reaction the observed deuterium isotope effect supports the mechanism (1) as that of vinylation of acetic acid does.

In the previous papers the author reported the exchange of the acetate group between acetic acid, zinc acetate and vinyl acetate. It was shown that at 150°C acetate group exchange occurred rapidly between acetic acid and zinc acetate[8], but very slowly between acetic acid and vinyl acetate[9], and the exchange was not found between vinyl acetate and zinc acetate[10]. It is presumable that the exchange of the acetate group between acetic acid and zinc acetate proceeds through an intermediate complex as Norris[11] suggested

$$CH_3COOH + Zn(CH_3COO)_2 \rightleftarrows Zn(CH_3COO)_3 \cdot H \qquad (5)$$

In other words the proton of acetic acid may easily transfer to one of the acetate groups of zinc acetate. This may be true also in the vinylation reaction of acetic acid on zinc acetate, and possibly then the transfer of proton from acetic acid to acetylene may also readily occur on the

5) J. Furukawa, H. Kozasa and S. Yamashita, *Chem. High Polymers* (Japan), **9**, 240 (1952).

6) K. B. Wiberg, *Chem. Rev.*, **55**, 718 (1955); R. P. Bell, "Advances in Catalysis," **IV**. Academic Press Inc. New York, N. Y. (1952), p. 184.

7) S. Otsuka, Y. Matumoto and S. Murahashi, *J. Chem. Soc. Japan (Pure Chem. Sect.)*, **75**, 798 (1954); S. Otsuka, ibid., **75**, 1115 (1954).

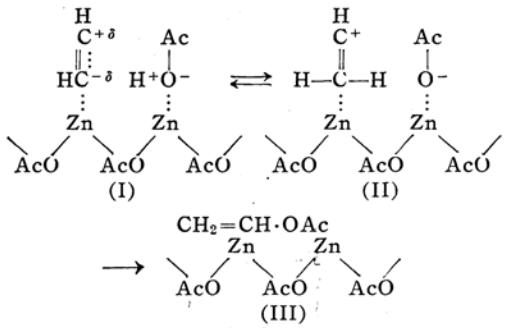
8) N. Yamada K. Suma and T. Takeuchi, ibid., **74**, 1018 (1953).

9) N. Yamada, T. Inokuchi and T. Takeuchi, ibid., **75**, 977 (1954).

10) N. Yamada, T. Inokuchi and T. Takeuchi, ibid., **75**, 1093 (1954).

11) E. A. Evance, J. L. Huston and T. H. Norris, *J. Am. Chem. Soc.*, **74**, 4985 (1952).

catalyst surface. This consideration leads to the more comprehensive picture of the reaction mechanism as shown below



The kinetic study of this reaction[4] supports the mechanism of Hinshelwood type. That is to say, the reaction takes place between the acetylene molecules and the acetic acid molecules adsorbed on adjacent active points of the catalyst, presumably on adjacent zinc atoms. Acetylene an acetic acid may be linked to a zinc atom on the catalyst surface by coordination. It may result in electronic polarization of their molecules as (I) shows. The proton transfer may occur from acetic acid to the acetate ion of zinc acetate (acetate group exchange), or to acetylene (hydrogen exchange and vinylation). The step from (II) to (III) may be irreversible, for the acetate group exchange between vinyl acetate and zinc acetate was not found. As it has been mentioned, hydrogen exchange and isotope effect on the vinylation reaction of acetic acid indicate that the step (I)-(II) should be in pre-equilibrium and the step (II)-(III) should be the rate-determining step.

Summary

The mechanism of vinylation reaction of acetic acid was studied by the use of deuterium. The exchange of deuterium was found to occur between acetylene and acetic acid-*d* on zinc acetate-charcoal catalyst. The deuterium isotope effect of the reaction rate was also found, and the rate ratio, k_D/k_H, was 1.6 at 160°C. A mechanism of the reaction which contains a pre-equilibrium of intermediate ion formation, $CH{\equiv}CH + H^+ \rightleftarrows CH_2{=}CH^+$, $CH_2{=}CH^+ + CH_3COO^- \rightarrow CH_2{=}CH{\cdot}OCOCH_3$, was proposed and discussed.

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