*A Kinetic Study on the Vinylation of Alcohol**

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Previous interpretations⁽¹⁾ of the vinylation reaction of alcohol are not satisfactory, because few of them are based upon kinetic studies. In the present study, the course of the vinylation was traced under atmospheric pressure using phenylacetylene and benzyl alcohol as reactants, so that inaccuracies inherent in the autoclave reaction were eliminated.

In the first place, it was synthetically ascertained that the acetylene and the alcohol react to give a corresponding vinylation product, styryl benzyl ether, under a condition similar to that in the present kinetic measurement. Secondly, the volumetric analysis of phenylacetylene was examined and modified. Thirdly, dependences of the rate of reaction upon the concentration of phenylacetylene and the activity of the alcoholate were examined. And finally, a possible mechanism of the vinylation is proposed.

Experimental

1. Materials.—Commercial C.P. benzyl alcohol was treated with anhydrous potassium carbonate and rectified at a reduced pressure under nitrogen. A cut boiling at 110–111°/30 mm. was used. Phenylacetylene was prepared from cinnamic acid according to the literature[2]. A cut boiling at 50–51.5°/30 mm. was used.

2. Styryl benzyl ether.—A solution of 2 g. of metallic sodium in 125 g. of benzyl alcohol was placed in a 500-cc. four-necked flask equipped with a stirrer, thermometer, reflux condenser and dropping funnel. The solution was heated to 130°C in an oil bath and 20 g. of phenylacetylene in 50 g. of benzyl alcohol was added. The addition was controlled so that the temperature of the solution did not exceed 135°C. After being stirred at that temperature for two hours, to the solution was added 100 cc. of water and the separated organic layer was extracted with ether. The ether layer was washed with water, dried on anhydrous potassium carbonate, the solvent evaporated and the residue was distilled in vacuo under nitrogen. Thus, besides unreacted phenylacetylene, 23 g. of an oily product (A) boiling at

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1) A review on the vinylation mechanism: S. Murahashi, *J. Soc. Org. Synth. Chem. Japan*, 10, 485 (1952) (in Japanese).

2) H. Gilman, "Organic Syntheses, Collective Vol. I", John Wiley and Sons, Inc., New York, N.Y. (1948), p. 438.

183°/9 mm. was obtained. A small quantity of residue remained in the distillation flask. On being cooled, the adduct (A) solidified into white crystals which showed m.p. 72–73°C on being recrystallized three times from ethanol.

Anal. Found: C, 85.68; H, 6.68; Mol. Wt., 203. Calcd for $C_{15}H_{14}O$: C, 85.71; H, 6.67; Mol. Wt., 210.

3. A Modified Volumetric Analysis of Phenylacetylene.—The principle[3] of the analysis is represented as

$$C_6H_5C{\equiv}CH + Cu^{(+)} = C_6H_5C{\equiv}CCu + H^{(+)} \qquad (1)$$

$$C_6H_5C{\equiv}CCu + Fe^{(3+)} + H_2SO_4 = C_6H_5C{\equiv}CH + CuSO_4 + Fe^{(2+)} + H^{(+)} \qquad (2)$$

$$10Fe^{(2+)} + 2KMnO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10Fe^{(3+)} + 5SO_4^{(2-)} + 8H_2O \qquad (3)$$

1 mol. of $C_6H_5C{\equiv}CH$ (102.13 g.) corresponds to 1 N $KMnO_4$ (31.606 g.).

Since cuprous chloride in saturated ammonium carbonate solution[4] was found to give poor results for the precipitation reagent of phenylacetylene, we applied Ilosvay's method[3] with some modifications to the present analysis.

A solution of 1 g. of $CuSO_4 \cdot 5H_2O$ in 5 cc. of water was added to 5.5 cc. of 10.61 N NH_4OH. Into this deep blue solution, 3 g. of $NH_2OH \cdot HCl$ was dissolved and diluted with water to 50 cc. The blue color disappeared completely in a few minutes[5].

The precipitation of the acetylide was seriously affected by the concentration of NH_4OH. The most suitable pH for the precipitation was found to be 8.6–8.7. To examine the accuracy of the analysis, known quantities (9.039, 4.520, 1.792 and 0.897 ($\times 10^{-4}$ mol.)) of the acetylene in 5 cc. of ethanol were treated with 20 cc. of the cuprous solution. The yellow precipitates of the acetylide were filtered on a glass filter (No. 4). To remove the excess hydroxylamine, the precipitates were washed with water several times until the filtrate did not decolorize one drop of N/10 $KMnO_4$. During these operations, the precipitates should be covered with the mother liquid in order to keep the acetylide from the air oxidation.

For dissolving the precipitates, a solution of ferric sulfate in sulfuric acid was prepared; 100 g. of ferric sulfate[6] was dissolved in 250 g. of sulfuric acid (sp. gr., 1.85), which was diluted with water to 1 l. Twenty cc. of the ferric solution was mixed with 10 to 15 cc. of H_2SO_4, added to the precipitates and was digested for 10 to 20 minutes on a steam bath to complete solution. There was obtained a clear light-green solution involving ferrous ion, which was cooled to the room temperature, and to this was added a few cc. of 85% phosphoric acid[7], and then titrated with N/20 $KMnO_4$. The average of errors for 16 measurements was −0.8% with standard deviation 4.12%.

For the precipitation of the acetylide from benzyl alcohol solution some modifications were required because of the slight solubility of the alcohol in water. Known quantities (10.626, 5.313 and 2.125 ($\times 10^{-4}$ mol.)) of phenylacetylene in 10 to 15 cc. of benzyl alcohol were mixed with 20 to 30 cc. of the precipitating agent under vigorous shaking. The mixing was effected by the addition of some ethanol. When the precipitation was completed, the precipitates were filtered and washed successively with water, aqueous ethanol, and with ethanol and water to remove hydroxylamine and benzyl alcohol. The average of errors for 11 measurements was −0.51% with standard deviation 4.96%.

4. Kinetic Measurement.—The reactions were carried out in test tubes immersed in an oil bath, the temperature of which was controlled to 130± 0.5°C. A typical run of the measurements is as follows:

A 5.4-cc. solution of sodium benzylate in benzyl alcohol was placed in a 15-cc. test tube and heated to 130°C. To this solution, a 5-cc. solution of phenylacetylene in benzyl alcohol was added. The initial concentrations of phenylacetylene, sodium benzylate and benzyl alcohol were 0.001, 0.010 and 0.100 (in mol. ratio), respectively. After a definite time interval, the reaction solution was added to a slight exess 1 N HCl solution to interrupt the reaction. The excess of hydrochloric acid was neutralized with 1 N NaOH using methyl red as indicator and the unreacted phenylacetylene in the mixture was analyzed. In one run, the analysis was done with respect to four to eight test tubes with the reaction time varied.

Results and Discussion

The results obtained are summarized in Table I. The rates of vinylation estimated

TABLE I

REACTION BETWEEN PHENYLACETYLENE* AND BENZYL ALCOHOL IN BENZYL ALCOHOL AT 130±0.5°

Exp. No.	Sodium Benzylate (M)	Sodium Benzylate (a_r)	$k_1 = v/p$ ($\times 10^{-2}$)	$k_2 = k_1/a_r$ ($\times 10^{-2}$)	No. of Tests
1	0.48	2.17	1.34±0.08	0.66	7
2	.72	3.50	2.33±0.03	.67	7
3	.86	4.85	4.36±0.32	.90	7
4	.87	4.93	4.91±0.19	.99	7
5	.97	6.35	5.75±0.07	.91	6
6	1.00	6.97	6.75±0.14	.97	4
7**	1.01	7.01	6.73±0.19	.96	6
8	1.04	7.95	7.28±0.34	.92	4
9	1.13	10.77	9.05±0.14	.84	5
10	1.37	20.35	17.71±0.77	.87	5
			Mean:	0.87±0.08	

* The initial concentration p_o of the acetylene is 0.096 mol./1.

** p_o: 0.048 mol./1.

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[3] L. Ilosvay and N. Ilosva, *Ber.*, **32**, 2697 (1899).

[4] Fr. Hein, A. Meyer, *Z. anal. Chem.*, **72**, 30 (1927).

[5] The solution should be kept from contact with air. In this study, the solution was prepared immediately before the analysis.

[6] The ferric alum solution, which appeared in Hein's paper[4] as the reagent for solution of the acetylide, was not satisfactory, because it was difficult to obtain a clear ferric solution even if sulfuric acid was used in great excess.

[7] F.P. Treadwell, "Lehrbuch der anal. Chem. II. Band", Franz Deuticke, Leipzig (1937), p. 523.

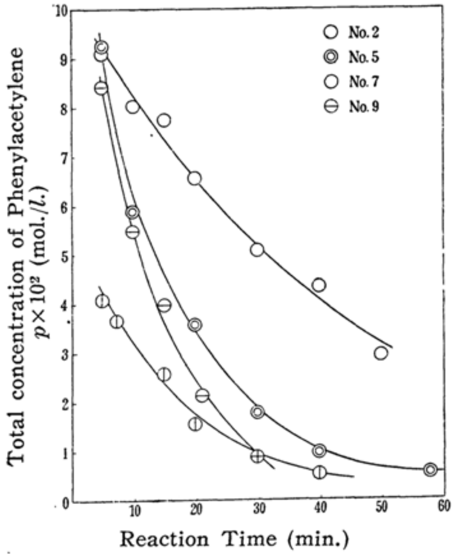

Fig. 1. Typical runs of the reaction with the initial concentration of phenylacetylene 0.096 (mol./l.)[a]. The concentrations of sodium benzylate: 2) 0.72; 5) 0.97; 7) 1.01; 9) 1.13 (mol./l.)

[a] In No. 7, the initial concentration of the acetylene is 0.048 (mol./l.).

from straight line portions of the reaction curves, some examples of which are shown in Fig. 1, were found to be first order with respect to the total concentration of the acetylene as shown in Table I. Thus the rate v is expressed as

$$v=k_1p \tag{4}$$

where p denotes the total concentration of phenylacetylene and k_1 is a constant. From Table I, it can be seen that the constant k_1 is proportional to the relative mean ionic activity[8] a_r of the alcoholate but not to the analytical concentration. Thus Eq. (4) is reduced to Eq. (5):

$$v=k_2pa_r \tag{5}$$

where k_2 is a constant.

If we assume that the addition of the alcoholate ion to the acetylene is the rate determining stage, the rate v of the vinylation is expressed as Eq. (6).

$$v=k_3[\mathrm{RO}^{(-)}][\mathrm{R'C{\equiv}CH}] \tag{6}$$

where k_3 is a constant. In the reaction system, an equilibrium between the alcoholate and the acetylide is present:

$$\mathrm{RO}^{(-)}+\mathrm{R'C{\equiv}CH} \overset{K_1}{\rightleftarrows} \mathrm{ROH}+\mathrm{R'C{\equiv}C}^{(-)} \tag{7}$$

where K_1 is an equilibrium constant, and

$$[\mathrm{RO}^{(-)}]+[\mathrm{R'C{\equiv}C}^{(-)}]=[\mathrm{Na}] \tag{8}$$

$$[\mathrm{R'C{\equiv}CH}]+[\mathrm{R'C{\equiv}C}^{(-)}]\doteq p \tag{9}$$

From Eqs. (6)—(9),

$$v=k_3p[\mathrm{Na}][\mathrm{ROH}]^2/\{[\mathrm{ROH}]+K_1[\mathrm{RO}^{(-)}]\}\{[\mathrm{ROH}]+K_1[\mathrm{R'C{\equiv}CH}]\} \tag{10}$$

Under the present condition, the reaction was carried out in benzyl aclohol in large excess, so that Eq. (10) is reduced to

$$v=k_4p[\mathrm{Na}] \tag{11}$$

where k_4 is a constant. Since the relative mean ionic activity a_r of sodium benzylate is little varied under the condition even if the formation of acetylide is taken into consideration, Eq. (11) is equivalent to Eq. (5)[9]. These results are essentially in accordance with Rigamonti and Bernardi's[10].

In a previous paper[11], we reported a rate expression:

$$v=k[\mathrm{Ac.}]^{1.5}[\mathrm{Na}]^1[\mathrm{Al.}]^{1.4} \tag{12}$$

where Ac. and Al. denote acetylene and ethanol. The reaction was examined with low concentration of sodium alcoholate so that Eq. (10) was transformed to Eq. (13).

$$v=k_3p[\mathrm{Na}][\mathrm{ROH}]/\{[\mathrm{ROH}]+K_1[\mathrm{R'C{\equiv}CH}]\} \tag{13}$$

Equation (12) was interpreted by Eq. (13).

Recently Otsuka[12] found that the dependence of the rate upon the concentration of alcohol or of acetylene decreased, to a degree less than first order, with increasing concentrations of the reactants. He accounted for the kinetic data in terms of a complex formation from acetylene, alcohol and alcoholate. However, there seem to be no experimental evidences for such complex intermediates.

In his experiment, the concentration of the alkali is so small that Eq. (13) still holds well. Considering the order of magnitude of $\mathrm{pK_a}$[13], the tendency of decrease in the reaction order of alcohol or of acetylene is well accounted for by Eq. (13).

Equation (5) may be derived from an alternative mechanism in which an addition between benzyl alcohol and phenylacetylide is assumed as the rate determining step.

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[8] The relative mean ionic activity a_r of the alcoholate in benzyl alcohol was potentiometrically determined according to the Harned method:

a) H.S, Harned and J. C. Hecker, *J. Am. Chem. Soc.*, **55**, 4838 (1933).

b) H.S. Harned and M.A. Cook, ibid., **59**, 496 (1937).

[9] $[\mathrm{Na}]=k_5a_r$

[10] R. Rigamonti and L. Bernardi, *Chime. Ind.* (*Milan*), **34**, 561 (1952); *C.A.*, **47**, 2583b (1953).

[11] A. Onishi, N. Saito and J. Furukawa, *Repts. Chem. Research. Inst., Kyoto Univ.*, **19**, 85 (1949) (in Japanese).

[12] S. Otsuka, presented at the 8th Annual Meeting of the Chemical Society of Japan in Tokyo, April 1, 1955.

[13] For example, $\mathrm{pK_a}$ of phenylacetylene and benzyl alcohol are 21 and 19. J.B. Conant and G.W. Wheland, *J. Am. Chem. Soc.*, **54**, 1212 (1932).

Otsuka[14] found that the rate of vinylation of phenol was much slower than that of alcohol; if a mixture of alcohol and phenol was reacted with acetylene in the presence of alkali, only phenol was vinylated until the latter[15] was completely converted to the vinyl ether. This supports the assumption that alcoholate and acetylene participate in the rate determining step.

Summary

To elucidate the vinylation mechanism, a liquid phase reaction between phenylacetylene and benzyl alcohol was kinetically studied. The reaction was found to proceed along a second order mechanism between the acetylene and the alcoholate. A possible mechanism of the reaction was proposed.

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14) S. Otsuka, private communication.

15) In the reaction mixture, the concentration of $C_2H_5O^{(-)}$ is negligibly small compared with that of $C_6H_5O^{(-)}$.