

Nucleophilic Addition to Acetylenes in Superbasic Catalytic Systems: X.* Catalytic Effect of Alkali Metal Hydroxides in the Vinylation of 1-Heptanol

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Abstract—The catalytic activity of alkali metal hydroxides in base-catalyzed addition of 1-heptanol to acetylene depends on the alkali metal nature and degree of hydration of its hydroxide. In a closed system, the catalytic activity of alkali metal hydroxides decreases in the series $2\text{KOH}\cdot\text{H}_2\text{O} > \text{RbOH}\cdot\text{H}_2\text{O} > \text{CsOH}\cdot\text{H}_2\text{O} > \text{NaOH}$. The corresponding series for a flow system is as follows: $\text{RbOH}\cdot\text{H}_2\text{O} > \text{CsOH}\cdot\text{H}_2\text{O} > 2\text{KOH}\cdot\text{H}_2\text{O} > \text{NaOH} > \text{KOH}\cdot\text{H}_2\text{O}$. The difference is explained by participation of the catalyst in side reactions with both 1-heptanol and acetylene. Addition of dimethyl sulfoxide to the catalytic system accelerates the vinylation process.

Direct vinylation, i.e., addition of hydroxy compounds to acetylene in the presence of base catalysts, was thoroughly studied by Favorskii [2], Shostakovskii [3], and Reppe [4]. This reaction can be regarded as the most universal method for preparation of vinyl ethers. The procedure is convenient for large-scale applications due to accessibility of starting compounds, high yields of the target products, and single-stage process. Syntheses of vinyl ethers and numerous studies of their structure and reactivity have been reviewed in a number of publications [5–9].

Despite vast information on the vinylation process, studies on its kinetic parameters are likely to be limited to those published in [9–13]. Among these, only Otsuka *et al.* [13] examined the nature of metal cation in the alkoxide on the rate of vinylation. Using isobutyl alcohol as an example, it was shown that the rate of vinylation decreases in the following series of cations: $\text{K}^+ (1.00) > \text{Rb}^+ (0.83) > \text{Na}^+ (0.76) > \text{Li}^+ (0.10) > \text{C}_6\text{H}_5\text{CH}_2\text{N}^+(\text{CH}_3)_3 (0.00)$.

Side processes accompanying vinylation of alcohols and hydroxy compounds as a whole also remain

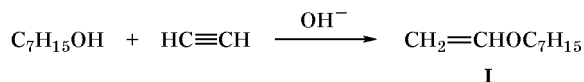
insufficiently studied. Such processes are polymerization of acetylene [7], formation of acetals [5, 7], evolution of hydrogen, formation of carboxylic acid salts, [5–7, 12], etc. The formation of alkali metal carboxylates was often explained by the presence of water [6, 7] which is capable of reacting with acetylene to form acetates and hydrogen [14–16]; however, this does not explain formation of other salts. Moreover, inhibitory effect of water on the vinylation is known [6, 7, 13, 17]; the mechanism of water effect was interpreted in terms of decrease in the basicity of the system [6, 7] or (what is equivalent) decrease in the concentration of RO^- [13].

The present communication gives the results obtained by studying the effect of alkaline catalyst and water on the rate of vinylation of 1-heptanol with acetylene under atmospheric pressure; specific features of the main and side processes are discussed.

The choice of 1-heptanol as model substrate was dictated by its high boiling point and high boiling point of the vinylation product, heptyl vinyl ether (**I**), which make it possible to perform the reaction in the temperature range from 150 to 166°C. The process was performed in both closed and flow systems under

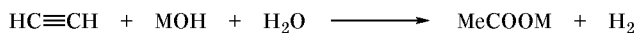
* For communication IX, see [1].

an acetylene pressure equal to atmospheric. In the closed system we measured the rate of absorption of acetylene by 1-heptanol in the presence of 10 mol % of commercial alkali metal hydroxides: NaOH, 2KOH·H₂O (according to the titration data, potassium hydroxide contained 15% of water, which corresponds exactly to the formula 2KOH·H₂O), RbOH·H₂O, and CsOH·H₂O; lithium hydroxide did not catalyze vinylation of 1-heptanol with acetylene even under pressure.



In the presence of the above listed alkali metal hydroxides absorption of acetylene begins only at about 160°C. Figure 1 shows acetylene absorption curves at 164–166°C. It is seen that in the series of hydrated hydroxides 2KOH·H₂O, RbOH·H₂O, and CsOH·H₂O, the rate of acetylene absorption decreases as the size of the cation increases. This may be due to the presence of an additional amount of water which is introduced into the system with the monohydrates RbOH·H₂O and CsOH·H₂O. The presence of water reduces not only the basicity of the system [6, 7] but also partial pressure of acetylene. Sodium hydroxide is the least active catalyst despite it contains no hydrate water.

In all cases the yield of ether **I** determined by GLC was lower than that calculated from the amount of absorbed acetylene, and the conversion of 1-heptanol (without taking into account possible formation of alkoxide) is greater than the yield of vinyl ether **I** (Table 1). These data indicate the occurrence of side reactions involving acetylene and 1-heptanol. On the other hand, titration of the final reaction mixtures (after dilution with water) showed that the catalyst undergoes some transformations which give rise to salts of organic acids (Table 1). Insofar as water is always present in the system (it is liberated upon formation of alkoxides), such a reaction may be the known formation of acetates from alkali, water, and acetylene [14–16]:



Another possible process is the Dumas–Stass reaction leading to alkali metal heptanoates from 1-heptanol and alkali [18]:

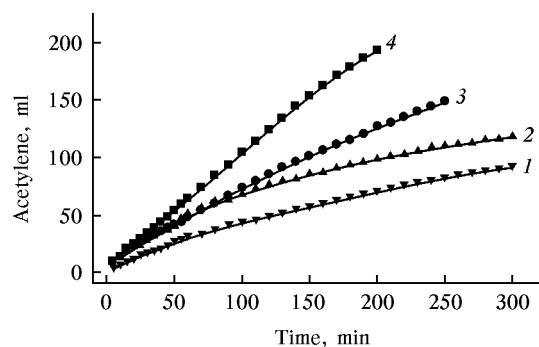
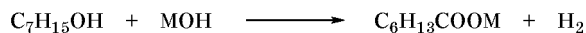
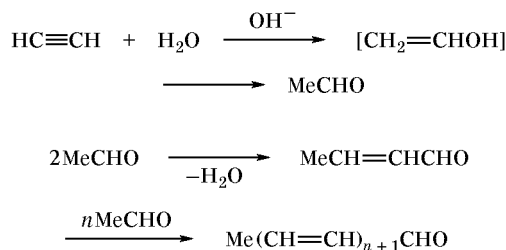


Fig. 1. Absorption of acetylene in the vinylation of 1-heptanol in the presence of alkali metal hydroxides (closed system, 164–166°C): (1) NaOH, (2) CsOH·H₂O, (3) RbOH·H₂O, (4) 2KOH·H₂O.

Assuming that the difference between the conversion of 1-heptanol and the yield of **I** is the result of formation of alkali metal heptanoates, we calculated the conversion of alkali into heptanoate, which turned out to be 6–7% (Table 1). The difference between the conversion of alkali into all salts and heptanoate is its conversion into acetate. Since acetates are formed with participation of acetylene, the required amount of acetylene can be calculated from the amount of acetates. Table 1 gives the conversions of acetylene into acetates. The overall conversion of acetylene into acetate and vinyl ether **I** is complete only when CsOH·H₂O and RbOH·H₂O are used as catalyst. With 2KOH·H₂O and NaOH, the conversion is less than 100%, suggesting the occurrence of other side processes. We observed no polymerization of acetylene (with formation of a dark insoluble powder of polyacetylene); therefore, we can presume that acetylene is consumed for the formation of acetaldehyde and polymers derived therefrom:



We can conclude that the vinylation of alcohols with acetylene is accompanied by side formation of salts via both Dumas–Stass reaction and reaction of acetylene with alkali and water. The two processes release hydrogen which, together with water vapor, reduces partial pressure of acetylene in the gas phase. We can thus explain the higher rate of acetylene

Table 1. Vinylation of 1-heptanol with acetylene (atmospheric pressure, closed system, 10 mol % of alkali metal hydroxide, 164–166°C)

Catalyst	Time, h	Yield of I, ^a %	Conversion of heptanol, %	Absorption of acetylene, mmol	Conversion of acetylene, %		Conversion of catalyst, %	
					into I	into MeCO ₂ M	into MeCO ₂ M	into C ₆ H ₁₃ CO ₂ M
NaOH	5.0	3.0	3.7	4.1	73	15	6	7
2KOH·H ₂ O	3.3	4.9	5.5	8.4	58	15	13	6
RbOH·H ₂ O	4.2	5.7	6.3	6.5	88	17	11	6
CsOH·H ₂ O	7.0	4.2	4.9	5.8	72	28	16	7

^a Yield of ether I calculated on the 1-heptanol taken.

absorption in the catalysis by 2KOH·H₂O not only by the lower concentration of water in the liquid and gas phases but also by the lower activity of potassium hydroxide, as compared to cesium and rubidium hydroxides, in side salt formation reactions accompanied by evolution of hydrogen. Presumably, the higher rate of acetylene absorption in the presence of rubidium hydroxide compared to cesium hydroxide, fast reduction of the rate of acetylene absorption in the presence of CsOH·H₂O, and its slow reduction in the presence of sodium hydroxide can be interpreted in a similar way.

The vinylation of 1-heptanol in a flow system was carried out by passing acetylene at a rate of ~2 l/h through a solution of alkali metal hydroxide in 1-heptanol, heated to 164–166°C. Unlike the closed system, partial pressure of acetylene in a flow system does not depend on the amount of liberated hydrogen, and the order of the kinetic curves changes (Fig. 2). The activity of alkali metal hydroxides falls in the

series RbOH·H₂O > CsOH·H₂O > 2KOH·H₂O > NaOH > KOH·H₂O.

Despite lower concentration of water, 2KOH·H₂O is less active in the vinylation than cesium and rubidium hydroxide monohydrates. On addition of water to an amount corresponding to the monohydrate, the rate of vinylation sharply decreases and becomes even lower than the rate of vinylation in the presence of NaOH. Under these conditions, rubidium hydroxide monohydrate turned out to be more active than cesium hydroxide monohydrate (Fig. 2), which is consistent with the data obtained in the vinylation of 1-heptanol in the closed system (Table 1; cf. yields of I in the presence of RbOH·H₂O and CsOH·H₂O).

The yield of ether I and the conversion of the substrate into products (except for alkoxides) in the presence of each alkali metal hydroxide were calculated from the concentrations of I and 1-heptanol in the reaction mixture after passing acetylene over a period of 7 h. The conversion of MOH into the corresponding metal carboxylates was determined by titration of the reaction mixtures strongly diluted with water. The conversions of alkali into heptanoate and acetate were then calculated separately. The results are collected in Table 2. It is seen that the main process responsible for consumption of alkali is formation of acetates. It was surprising that the yields of ether I in the flow system were lower than in the closed system. A possible reason is faster consumption of alkali (cf. Tables 1 and 2) due to unlimited supply of acetylene into the mixture and hence faster formation of acetates.

It is known [17, 19–23] that addition of nucleophiles to acetylene is strongly accelerated in catalytic media including highly basic reagents. The most convenient and universal are systems like alkali metal hydroxide–polar aprotic solvent (such as DMSO, HMPA, etc.). Higher reaction rate makes it possible

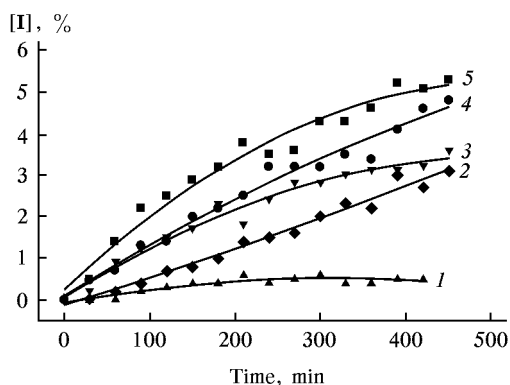


Fig. 2. Change of the concentration of ether I with time in the vinylation of 1-heptanol with acetylene in the presence of alkali metal hydroxides (flow system, 164–166°C): (1) KOH·H₂O, (2) NaOH, (3) 2KOH·H₂O, (4) CsOH·H₂O, (5) RbOH·H₂O.

Table 2. Vinylation of 1-heptanol with acetylene (atmospheric pressure, flow system, 10 mol % of alkali metal hydroxide, 164–166°C, 7 h)

Catalyst	Yield of ether I, %	Conversion of heptanol, %	Conversion of catalyst, %	
			into MeCO ₂ M	into C ₆ H ₁₃ CO ₂ M
NaOH	2.1	2.6	5	16
2KOH·H ₂ O	2.5	4.2	17	9
KOH·H ₂ O	0.4	1.0	6	24
RbOH·H ₂ O	3.9	3.9	0	29
CsOH·H ₂ O	3.4	3.8	4	28

to perform the process under milder conditions. Also, we can expect that lowering the temperature will slow down side processes which accompany the vinylation and deactivate the catalyst.

Taking into account the high activity of cesium hydroxide in side formation of metal carboxylates, we brought 1-heptanol into reaction with acetylene under atmospheric pressure in the presence of commercial cesium hydroxide. The latter was taken in an amount of 20 mol % with respect to 1-heptanol. The amount of dimethyl sulfoxide ensured formation of a 1 M solution of 1-heptanol, in keeping with the conditions developed in [24] for vinylation of alcohols. Acetylene was passed through a solution at a flow rate of about 2 l/h.

Under these conditions (temperature 50°C) the reaction was slow but nevertheless faster than the vinylation of 1-heptanol in the presence of 10 mol % of CsOH·H₂O at 165°C (Fig. 3). Unfortunately, even under such mild conditions the conversion of cesium hydroxide into cesium carboxylates was greater than 20%, according to the potentiometric titration data.

EXPERIMENTAL

The reaction mixtures were analyzed by GLC using an LKhM-80 chromatograph; thermal conductivity detector, carrier gas helium (flow rate 2 l/h), 3000 × 3-mm column, stationary phase 1% of polyethylene glycol 20000 on NaCl (0.16–0.25 mm), oven temperature 100°C. Alkali metal hydroxides, heptanoates, and acetates were quantitated by potentiometric titration of dilute aqueous solutions. The titration was performed at 20°C using an EV-74 universal ionometer equipped with glass and silver chloride electrodes; 0.1 N HClO₄ was used as titrant.

1-Heptanol, RbOH·H₂O, and CsOH·H₂O were of pure grade; DMSO, LiOH, and NaOH were of

chemically pure grade; and KOH was of analytical grade (it contained 15% of hydrate water, according to the titration data). 1-Heptanol and DMSO were distilled prior to use. Commercial acetylene (from gas cylinder) was purified as described in [25].

Vinylation of 1-heptanol with acetylene under atmospheric pressure in a closed system. The system was a 50-ml three-necked round-bottomed flask equipped with a thermometer, a stopper for acetylene outlet (when purging the system), and an acetylene burette which was connected to a vessel filled with a saturated solution of magnesium sulfate. Acetylene from the burette passed through a Tishchenko bottle filled with pelleted KOH into the reaction flask through a gas-inlet tube whose end was above the surface of the reaction mixture. The flask was heated on an oil bath, and the mixture was stirred using a magnetic stirrer.

The flask was charged with 11.6 g (0.1 mol) of 1-heptanol and 0.01 mol of alkali metal hydroxide, the

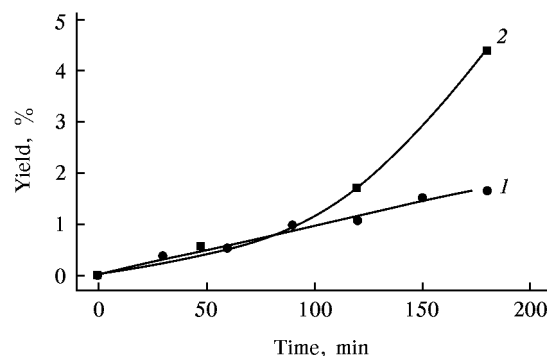


Fig. 3. Change of the yield of ether I with time in the vinylation of 1-heptanol with acetylene in the presence of cesium hydroxide monohydrate without a solvent and in DMSO (flow system): (1) CsOH·H₂O, 165°C; (2) CsOH·H₂O–DMSO, 50°C.

system was purged with acetylene, and the mixture was slowly heated to a required temperature (alkali metal hydroxide dissolved fairly rapidly). The absorption of acetylene was monitored following the level of the magnesium sulfate solution transferred to the burette as acetylene was consumed. The resulting acetylene absorption curves are shown in Fig. 1.

When the reaction was complete, the mixture was analyzed by GLC using ~0.5 g of tridecane as internal standard. The yield of ether **I** was calculated from the GLC data. The mixture was then diluted with water to a volume of 500 ml (aqueous phase) under thorough stirring. The organic layer was separated, and the concentrations of alkali metal hydroxide and carboxylates in the aqueous phase were determined by titration. The results are given in Table 1.

Vinylation of 1-heptanol with acetylene under atmospheric pressure in a flow system. A 50-ml flask equipped with a thermometer, reflux condenser, and gas-inlet tube (immersed into the liquid) was charged with 11.6 g (0.1 mol) of 1-heptanol, 0.01 mol of alkali metal hydroxide, and ~0.5 g (precisely weighed) of tridecane as internal standard for GLC analysis. The mixture was heated on an oil bath under stirring with a magnetic stirrer. Alkali metal hydroxides rapidly dissolved on heating. The mixture was heated to 164–166°C, and acetylene was passed at a flow rate of about 2 l/h. Samples of the mixture were withdrawn every 30 min using a long pipette and were analyzed by GLC. The results (kinetic curves for formation of vinyl ether **I**) are shown in Fig. 2. A considerable dispersion of points is explained by the low concentration of the product, which gives rise to large errors in the treatment of chromatographic data. The concentrations of alkali metal hydroxide, acetate, and heptanoate were determined by potentiometric titration as described above for the closed system (Table 2).

Vinylation of 1-heptanol with acetylene under atmospheric pressure in a flow system in the presence of CsOH·H₂O–DMSO. A 100-ml flask equipped with a thermometer, reflux condenser, and gas-inlet tube (immersed into the liquid) was charged with 5.8 g (0.05 mol) of 1-heptanol, 1.7 g (0.01 mol) of CsOH·H₂O, and 50 ml of DMSO (the latter was also used as internal standard for GLC analysis). Acetylene was passed at a rate of 2 l/h over a period of 3 h through the mixture heated to 50°C; the mixture was analyzed by GLC as described above. The results are given in Fig. 3. The yield of ether **I** calculated from the GLC data was 0.3 g (4.2%).

Potentiometric titration of the reaction mixture (after dilution with water) revealed a 22% conversion of cesium hydroxide into the corresponding carboxylates.

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