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Nucleophilic Addition to Acetylenes in Superbasic Catalytic Systems: XI.* Transformations of Alkali Metal Hydroxides during Vinylation of 1-Heptanol with Acetylene under Elevated Pressure

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Abstract—Base-catalyzed addition of 1-heptanol to acetylene under elevated pressure of the latter is accompanied by side processes including formation of carboxylic acid salts (alkali metal heptanoates and acetates) with liberation of hydrogen and acetylene polymerization. The rate of acetylene absorption depends on the alkali metal nature and falls down in the series $CsOH \cdot H_2O \geq RbOH \cdot H_2O > 2KOH \cdot H_2O > NaOH > LiOH$. Approximately the same order is observed for variation of the rate of deactivation of the catalyst owing to its transformation into metal carboxylate. Dehydration of the catalyst accelerates both vinylation and acetylene polymerization.

In the preceding communication [1] we reported the results of our study of the vinylation of 1-heptanol with acetylene under atmospheric pressure in the presence of alkali metal hydroxides. We also estimated the role of the alkali metal cation in the main and side processes. It was reasonable to continue the work in this line by studying vinylation of 1-heptanol with acetylene under elevated pressure in the presence of the same catalysts.

The reactions were carried out in a 1-l rotating steel high-pressure reactor. Acetylene was supplied into the reactor at an initial pressure of 12–17 atm, and the mixture was heated to a required temperature (110–150°C). By the end of the process, the reaction mixture was usually a two-phase system consisting of a liquid and solid fractions. The amount of the latter depended on the initial concentration of the catalyst. The precipitate was washed with acetone to remove adsorbed liquid products and with diethyl ether to remove tars and was examined by spectral methods (IR and ^{1}H NMR), potentiometric titration in aqueous medium, and elemental analysis.

The liquid parts of the reaction mixtures and acetone washings (after removal of acetone) were subjected to fractional distillation, and fractions thus obtained were analyzed by GLC; the yield of 1-heptyl vinyl ether and the conversion of 1-heptanol were calculated. The still residues were analyzed by titration to determine the concentration of alkali metal hydroxide and metal carboxylates.

Our results show (Table 1) that the conversion of 1-heptanol, the yield of 1-heptyl vinyl ether, and the selectivity of vinylation (initial acetylene pressure 12–14 atm, 150°C, 5 h) depend on the nature and concentration of alkali metal hydroxide (LiOH, NaOH, $2KOH \cdot H_2O$, $RbOH \cdot H_2O$, or $CsOH \cdot H_2O$; initial concentration 5–20 mol %). Lithium hydroxide turned out to be a poor catalyst even at a concentration of 20 mol %; the reaction mixture contained only traces of 1-heptyl vinyl ether. These data are consistent with both published data [2] and our previous results. In the presence of the other alkali metal hydroxides at a concentration of 20 mol % the conversion of 1-heptanol attained 96–100%, and the yields of 1-heptyl vinyl ether were approximately similar but not quantitative (61–68%; Table 1). This means that

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[*] For communication X, see [1].

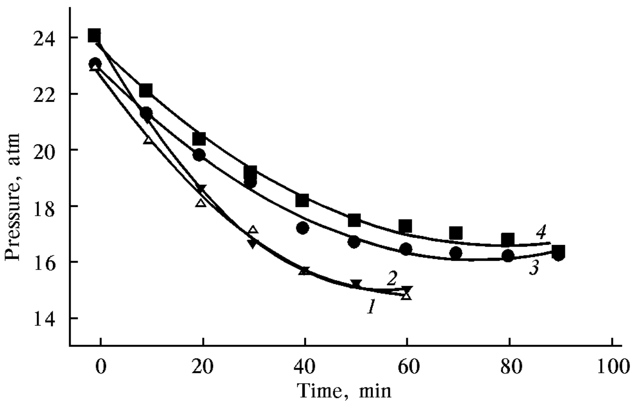


Fig. 1. Kinetic curves for acetylene absorption in the vinylation of 1-heptanol (substrate amount 0.4 mol, initial acetylene pressure 17 atm at room temperature, 150°C) in the presence of 10 mol % of (*1*) $RbOH \cdot H_2O$, (*2*) $CsOH \cdot H_2O$, (*3*) $2KOH \cdot H_2O$, and (*4*) NaOH.

the vinylation process is accompanied by side reactions involving either the initial reactants or final products, or both.

Reduction of the concentration of NaOH and $2KOH \cdot H_2O$ to 10 mol % did not change the yield of the product and reaction selectivity to an appreciable extent; both these parameters remained in the range from 61 to 69%. In the presence of the same amount of $RbOH \cdot H_2O$ or $CsOH \cdot H_2O$ the yield of 1-heptyl vinyl ether increases by 7–18%, and the selectivity of its formation attains 76–81%, the conversion of 1-heptanol remaining unchanged (Table 1). Further reduction of the catalyst concentration (down to 5 mol %) is favorable only in the case of potassium hydroxide: the yield of 1-heptyl vinyl ether increases to 70%, and the selectivity, to 78%. With the other alkali metal hydroxides taken at the same concentration, the yield of the target product was lower, while the selectivity of its formation almost did not change (Table 1).

Table 1. Base-catalyzed vinylation of 1-heptanol with acetylene (substrate amount 0.15 mol, initial acetylene pressure 12–14 atm at room temperature, 150°C, 5 h)

Catalyst, mol %	Substrate conversion, %	Yield of 1-heptyl vinyl ether, %	Selectivity, %
LiOH, 20	20	<2	<10
NaOH, 20	96	64	67
NaOH, 10	89	61	69
NaOH, 5	76	50	66
$2KOH \cdot H_2O$, 20	100	61	61
$2KOH \cdot H_2O$, 10	96	63	66
$2KOH \cdot H_2O$, 5	90	70	78
$RbOH \cdot H_2O$, 20	100	68	68
$RbOH \cdot H_2O$, 10	99	75	76
$RbOH \cdot H_2O$, 5	73	57	78
$CsOH \cdot H_2O$, 20	100	64	64
$CsOH \cdot H_2O$, 10	99	80	81
$CsOH \cdot H_2O$, 5	90	73	81

The rate of vinylation of 1-heptanol was estimated by the rate of acetylene absorption, i.e., by the reduction of the overall pressure in the reactor under the assumption that the absorbed acetylene is primarily consumed for the formation of 1-heptyl vinyl ether. The reactor was charged with 1-heptanol, alkali metal hydroxide as catalyst (10 mol % with respect to the substrate), and acetylene was supplied at an initial pressure of 17 atm. As the temperature rose, the pressure increased and attained the maximal value (23–24 atm) at about 110°C. During a certain period, the pressure remained constant and began to fall down 3–5 min before a required temperature was reached (150°C). This moment was assumed to be the initial one, and the pressure was then measured every 10 min (Fig. 1). As follows from the acetylene absorption curves shown in Fig. 1, the rates of vinylation of 1-heptanol in the presence of $RbOH \cdot H_2O$ and $CsOH \cdot H_2O$ are approximately similar: the initial rates are 0.25 and 0.30 mol l min^{-1}, respectively. An analogous pattern is observed for $2KOH \cdot H_2O$ and NaOH: the initial rates are equal to 0.18 mol l min^{-1} (Fig. 1, curves *3* and *4*). However, the curves for the first pair come to a plateau in less than 1 h, whereas the corresponding period for $2KOH \cdot H_2O$ and NaOH is longer by a factor of 1.5.

Table 2 summarizes the yields of 1-heptyl vinyl ether, substrate conversions, and reaction selectivities for vinylation of 1-heptanol with acetylene at 150°C in the presence of various alkali metal hydroxides. Comparison of the yields of the target product shows that cesium and rubidium hydroxides are clearly superior to the other catalysts: 81–86% against ~70% for sodium and potassium hydroxides. However, their advantage becomes less obvious when the activity of alkali metal hydroxides is estimated by the selectivity of formation of 1-heptyl vinyl ether. The data in Tables 1 and 2 indicate that, after intense acetylene absorption has ceased, heating of the reaction mixture leads to decrease of the yield of 1-heptyl vinyl ether and hence of the reaction selectivity. This means that the target product undergoes further transformations.

The vinylation of 1-heptanol at 100–115°C was found to proceed at a relatively low rate, regardless

Table 2. Vinylation of 1-heptanol (0.4 mol) with acetylene (initial pressure 17 atm at room temperature) at 150°C in the presence of 10 mol % of alkali metal hydroxide

Catalyst	Time, h	Yield of 1-heptyl vinyl ether, %	Conversion of 1-heptanol, %	Selectivity, %
NaOH	1.5	72	84	86
$2KOH \cdot H_2O$	1.5	69	85	81
$RbOH \cdot H_2O$	1.0	81	97	83
$CsOH \cdot H_2O$	1.0	86	98	88

of the catalyst nature. The rate of vinylation in the presence of sodium hydroxide sharply decreases (the pressure in the reactor fell down by only 1 atm in 2 h), and it was necessary to heat the reaction mixture at 130°C for an additional 2 h in order to attain the same acetylene conversion as in experiments with $2KOH \cdot H_2O$ and $RbOH \cdot H_2O$ as catalyst (Table 3). The best conversion of 1-heptanol, as well as the yield of 1-heptyl vinyl ether, was obtained with the use of cesium hydroxide monohydrate as catalyst (Table 3).

On the other hand, even under so mild temperature conditions deactivation of the catalyst was observed. Potentiometric titration of the precipitates and still residues obtained after fractional distillation of the reactions mixtures showed that in 4 h (reaction time) 25% of sodium or potassium hydroxide and up to 50% of rubidium or cesium hydroxide was converted into the corresponding carboxylic acid salts, alkali metal heptanoates [3] or acetates [4–6] (Table 3).

The basicity of the medium and the activity of reacting anions can be enhanced by binding of alkali metal cations with polyethers containing OCH_2CH_2O fragments, e.g., crown ethers or polyethylene glycols [6, 7]. Figure 2 shows the effect of addition of 1 mol % of polyethylene glycol (PEG, molecular weight 400) on the vinylation of 1-heptanol catalyzed by potassium hydroxide (curve *1*). This curve is steeper that the curve for acetylene absorption obtained under analogous conditions but in the absence of PEG-400 (Fig. 2, curve *2*). However, in both cases the yields of 1-heptyl vinyl ether were almost similar (60% and 61%); therefore, increased acetylene absorption in the presence of PEG is likely to result from vinylation of polyethylene glycol itself; it is known [6] that PEG reacts with acetylene more readily than do aliphatic alcohols. Nevertheless, we presume that addition of larger amounts of polyethylene glycol or other crown ether-like activating species will inrease the rate of vinylation of 1-heptanol.

Water is known to inhibit vinylation thus reducing the yield of vinyl ethers [6]. On the other hand, alkali metal alkoxides are more efficient catalysts than the corresponding hydroxides in nucleophilic addition of alcohols to acetylene [8]. Taking the above into account, we made an attempt to increase the selectivity and efficiency of vinylation by carrying out the reaction in anhydrous medium.

We failed to remove crystallization water from cesium hydroxide as an azeotropic mixture with octane or toluene (without 1-heptanol). By heating a mixture of $CsOH \cdot H_2O$ with 1-heptanol and excess octane under stirring at 130–140°C with a Dean–Stark trap we succeeded in removing about 70% of water (calculated on the hydrate water and that released in the formation of cesium 1-heptanolate) as an azeotropic mixture with octane. The resulting suspension was heated under acetylene pressure. The reaction was accompanied by fast absorption of acetylene and evolution of heat; the mixture spontaneously warmed up from 125 to 150°C in several minutes. In this case the amount of absorbed acetylene was greater by a factor of 1.8 than that required for complete vinylation of the alcohol; this is explained by anionic polymerization of acetylene. Despite the relatively short reaction time (~10 min) and active acetylene

Table 3. Base-catalyzed vinylation of 1-heptanol with acetylene at 110–115°C (initial acetylene pressure 12–13 atm at room temperature, 4 h) in the presence of alkali metal hydroxides (10 mol %)

Catalyst	Yield of 1-heptyl vinyl ether, %	Conversion of 1-heptanol, %	Conversion of catalyst, %
NaOH[a]	33	45	25
$2KOH \cdot H_2O$	27	37	25
$RbOH \cdot H_2O$	22	32	45
$CsOH \cdot H_2O$	31	44	50

[a] The reaction mixture was heated first for 2 h at 110–115°C and then for 2 h at 130°C.

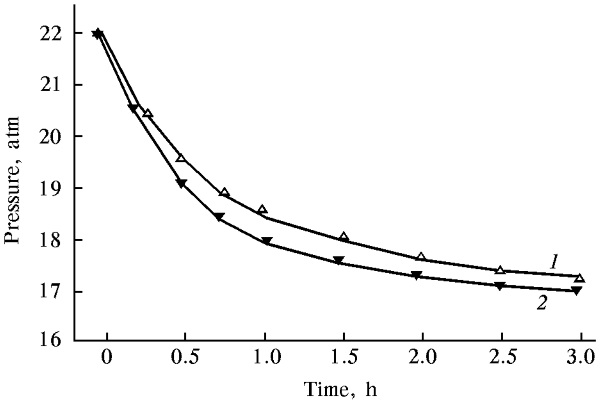


Fig. 2. Kinetic curves for acetylene absorption in the vinylation of 1-heptanol (0.3 mol) with acetylene (initial acetylene pressure 16 atm at room temperature, 130°C) (*1*) in the presence of 10 mol % of $2KOH \cdot H_2O$ and (*2*) in the presence of 10 mol % of $2KOH \cdot H_2O$ and 1 mol % of polyethylene glycol (molecular weight 400).

polymerization, the yield of 1-heptyl vinyl ether was 85%, and the conversion of 1-heptanol attained 98%; these results are comparable with those obtained in the vinylation of 1-heptanol at 150°C in 1 h in the presence of cesium hydroxide (Table 2).

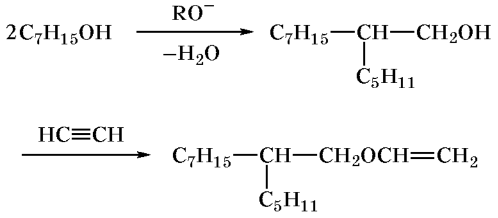
Chromatographic analysis of the liquid part of the reaction mixture showed the presence of three major components: water, 1-heptyl vinyl ether, and 1-heptanol; also, traces of a volatile substance were detected, assumingly of 1-heptene or heptane. When the reaction was performed with dehydrated cesium hydroxide, an additional high-boiling fraction, bp 104–120°C (2 mm), was isolated. Its amount was 5 wt % of the total amount of products; according to the GLC data, it contained 4 main components and 6 components in trace amounts. Among these, we unambiguously identified expected 1,1-di(heptyloxy)-ethane $CH_3CH(OC_7H_{15}\text{-}n)_2$, whose yield was 1.2% on the 1-heptanol taken. The other components were characterized by IR spectra. The presence of the following absorption bands, ν, cm^{-1}: 1197, 1607 w, 1634 sh, and 1644 v.s (stretching vibrations of the C–O and C=C bonds in vinyloxy group), suggests that one of the high-boiling components is vinyl ether formed as a result of initial condensation of 1-heptanol according to Guerbet [9] (Scheme 1).

Table 4. Transformations of alkali metal hydroxides during vinylation of 1-heptanol with acetylene (initial pressure 14–17 atm at room temperature, 150°C, 5 h)

Catalyst, mol %	Hydroxide conversion, %	Carboxylate fraction, %	
		heptanoate	acetate
LiOH, 20	50	Traces	~100
NaOH, 20	88	48	52
NaOH, 10	94	80	20
NaOH, 5	91	79	21
$2KOH \cdot H_2O$, 20	99	50	50
$2KOH \cdot H_2O$, 10	95	56	44
$2KOH \cdot H_2O$, 5	94	48	52
$2KOH \cdot H_2O$, 20[a]	72	~100	Traces
$RbOH \cdot H_2O$, 20	99	35	65
$RbOH \cdot H_2O$, 10	95	40	60
$RbOH \cdot H_2O$, 5	92	40	60
$RbOH \cdot H_2O$, 20[a]	51	~100	Traces
$CsOH \cdot H_2O$, 20	99	26	74
$CsOH \cdot H_2O$, 10	98	43	57
$CsOH \cdot H_2O$, 5	96	37	63

[a] Without acetylene.

Scheme 1.



$$2C_7H_{15}OH \xrightarrow[-H_2O]{RO^-} C_7H_{15}\text{—}\underset{\substack{|\\ C_5H_{11}}}{CH}\text{—}CH_2OH \xrightarrow{HC\equiv CH} C_7H_{15}\text{—}\underset{\substack{|\\ C_5H_{11}}}{CH}\text{—}CH_2OCH{=}CH_2$$

2-Pentylnonyl vinyl ether is likely to be formed in the reactions performed under different conditions, for the IR spectra of the extracts of the still residues contained similar absorption bands; however, its amounts were even smaller. No hydroxy compounds were found in the above mixture of high-boiling components: the IR spectra lacked the corresponding absorption bands.

The amount of the solid fraction of the reaction mixture depends on the nature and concentration of alkali metal hydroxide. In the reactions with NaOH, the solid fraction was a light yellow powder whose weight was 15, 7, or 3% of the total weight of the reaction mixture with an initial NaOH concentration of 20, 10, and 5 mol %, respectively. With rubidium and cesium hydroxide monohydrates at concentrations of 20 and 10 mol % the dark brown powders constituted 15–25 wt % of the mixture. Approximately the same amount of the solid fraction was obtained in experiments with 20 mol % of $2KOH \cdot H_2O$; reduction of the concentration of the latter to 10 mol % leads to a more than twofold decrease of the amount of the solid fraction which becomes light brown. In experiments with 5 mol % of the catalyst, almost no solid products were formed. In these cases, the transformations of alkali metal hydroxides were deduced from analysis of the still residues which remained after distillation of liquid products. A homogeneous reaction mixture was also obtained in experiments with lithium hydroxide as catalyst.

The results of titration of the solid fractions and still residues showed that the activity of alkali metal hydroxides during the process increases in the series $LiOH < NaOH < 2KOH \cdot H_2O \le RbOH \cdot H_2O \approx CsOH \cdot H_2O$ (Table 4). Rubidium and cesium hydroxides are almost completely converted into carboxylic acid salts. In the IR spectra of the solid fractions, as well as of the still residues obtained after vacuum distillation of 1-heptyl vinyl ether and 1-heptanol, we observed characteristic absorption bands of COO^- group at about 1400 and 1560 cm^{-1} [10] and a set of bands in the region 2800–2900 cm^{-1} (ν C–H). Their intensity and resolution change from one experiment to another, but the general pattern was the same for all alkali metal hydroxides used.

Primary and secondary alcohols are known [9] to lose hydrogen on heating above 200°C in the presence of sodium or potassium hydroxide; as a result, carboxylic acid salts are formed (Dumas–Stas reaction). We have found that all alkali metal hydroxides, except for LiOH, react with 1-heptanol under the vinylation conditions, yielding alkali metal heptanoates:

$$C_7H_{15}OH + MOH \longrightarrow C_6H_{13}COOM + H_2$$

In fact, heptanoic acid was isolated by acidification of aqueous solutions of the solid fractions. Dehydrogenation of 1-heptanol with potassium and rubidium hydroxides in the absence of acetylene (see Tabl. 4, note [a]) also occurs. Here, potassium hydroxide is more active than RbOH (according to the tritration data, the ratio hydroxide–heptanoate was 1:3 and 1:1, respectively. Moreover, the vinylation process is accompanied by known formation of acetates from acetylene, alkali metal hydroxide, and water [11–13]:

$$HC{\equiv}CH + MOH + H_2O \longrightarrow MeCOOM + H_2$$

The presence of alkali metal acetates in the solid fraction was confirmed by the ^1H NMR spectra which contain a signal at δ 1.90 ppm (CH_3COO^-). Insofar as the acidity constants of the resulting carboxylic acids are very similar, it was possible to determine only the overall concentration of salts by potentiometric titration. An approximate ratio of alkali metal acetates and heptanoates can be estimated on the basis of the NMR signal intensities (solvent D_2O). In the reactions catalyzed by NaOH, i.e., when the system contains a little of water, sodium heptanoate is preferentially formed. In the presence of $2KOH \cdot H_2O$ approximately equal amounts of CH_3COOK and $C_6H_{15}COOK$ are obtained. Rubidium and cesium hydroxides monohydrates are converted mainly into the corresponding acetates.

Apart from metal hydroxides and carboxylates, the solid fractions contained a small amount (less than 10 wt %) of tars (the corresponding part of the solid fraction is soluble in ether) and a colored insoluble polymer. The latter can be isolated by dissolution in water of the precipitate preliminarily washed with acetone and ether. Especially large amounts of the polymeric product were obtained in reactions with 20 mol % of potassium, rubidium, and cesium hydroxides (35–40 wt % of the overall amount of the solid fraction). The polymer contains up to 80% of carbon, ~10% of hydrogen, oxygen, and ash; obviously, it is polyacetylene. Insignificant polymerization of acetylene is known [6] to accompany vinylation in all cases. The contribution of acetylene polymerization increases by the moment of complete transformation of 1-heptanol which, as follows from Fig. 1 and Table 2, comes very soon when cesium or rubidium hydroxide is used as catalyst. Therefore, these catalysts, as well as potassium hydroxide at a concentration of 20 mol %, promote formation of polyacetylene in considerable amounts.

EXPERIMENTAL

The IR spectra were recorded in the range from 400 to 4000 cm^{-1} on a Specord 75IR spectrometer from samples prepared as thin films or KBr pellets. The ^1H NMR spectra were obtained on a Jeol FX-90Q instrument (90 MHz) at room temperature using D_2O as solvent and DSS as internal reference or $CDCl_3$ as solvent and HMDS as internal reference. The reaction mixtures were analyzed by GLC on an LKhM-80 chromatograph equipped with a thermal conductivity detector; carrier gas helium (flow rate 2 l/h); 3000 × 3-mm column packed with 1% of polyethylene glycol 20000 on NaCl (0.16–0.25 mm).

The concentrations of alkali metal hydroxides, heptanoates, and acetates in the reaction mixtures were determined by potentiometric titration of dilute aqueous solutions at 20°C using a universal EV-74 ionometer equipped with glass and silver chloride electrodes; the titrant was 0.1 N $HClO_4$.

1-Heptanol, $RbOH \cdot H_2O$, and $CsOH \cdot H_2O$ were of pure grade, LiOH and NaOH were of chemically pure grade, and KOH was of analytical grade (according to the titration data); commercial potassium hydroxide of analytical grade contained 14% of water, which exactly corresponds to the formula $2KOH \cdot H_2O$; 1-heptanol was distilled prior to use.

General procedure for vinylation of 1-heptanol with acetylene under elevated pressure. A 1-l rotating high-pressure reactor was charged with 1-heptanol and alkali metal hydroxide (5, 10, or 20 mol % with respect to 1-heptanol), and acetylene was supplied from a cylinder at an initial pressure of 12–17 atm. The mixture was heated to a required temperature, and the pressure in the reactor was monitored using a manometer (Figs. 1, 2). By the end of the process, the mixture was a two-phase system consisting of a liquid fraction and a solid precipitate. The precipitate was filtered off, washed in succession with acetone and ether, and dried until constant weight under reduced pressure. The precipitate was examined by spectral methods (IR and ^{1}H NMR), aqueous potentiometric titration, and elemental analysis. These data were used to calculate the concentrations of metal hydroxides and carboxylates. The amount of tars was determined by evaporation of the ether washings.

The liquid fraction, as well as the acetone washings (after removal of the solvent), was distilled under reduced pressure (10–20 mm). The distillate was analyzed by GLC to determine the yield of 1-heptyl vinyl ether and conversion of 1-heptanol (Tables 1–4). The still residue was diluted with water, and the amounts of alkali metal hydroxide and carboxylates were determined and summed up with the amounts obtained by analysis of the solid fraction of the reaction mixture (see above; Table 4).

1-Heptyl vinyl ether, bp 59–60°C (12 mm), n_D^{20} = 1.4226. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.41 d.d (1H, =CHO), 4.15 d.d and 3.92 d.d (2H, CH_2=, J_{cis} = 6.8, J_{trans} = 14.3, ^2J = 1.8 Hz), 3.65 t (2H, OCH_2, ^3J = 6.4 Hz), 1.63–1.33 m (10H, CH_2), 0.89 t (3H, CH_3, ^3J = 5.2 Hz). IR spectrum (film), cm^{-1}: 810 (ω CH_2=), 963 (ω CH=), 1207 (ν C–O), 1320 (δ CH=), 1379 (δ CH_2=), 1609, 1635, 1650 (νC=C), 3048, 3079 (ν CH=), 3119 (ν CH_2=).

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