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Kinetics of the Carbomethoxylation of Methylacetylene–Allene Mixtures Catalyzed by Palladium Complexes

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Abstract—Pathways leading to the desired product and by-product (copolymer of allene and CO) were determined for the carbomethoxylation of allene–methylacetylene mixtures catalyzed by the $PdCl_2(Ph_3P)_2$–HCl–*ortho*-phenanthroline system. Ratios for the rates of these transformations were found. Allene $\rightleftarrows$ methylacetylene isomerization under carbomethoxylation conditions was observed.

INTRODUCTION

Earlier, the $PdCl_2(Ph_3P)_2$–HCl–*ortho*-phenanthroline system was found to be active in the formation of methyl methacrylate (MMA) from methylacetylene and allene present in the methyleacetylene–allene fraction (MAF) of hydrocarbons. Methyl crotonate (MC), which is an isomer of MMA, and a Pd-containing copolymer of allene and CO are formed as by-products [1, 2]

$$\left.\begin{array}{l} CH_2{=}C{=}CH_2 \\ CH_3{-}C{\equiv}CH \end{array}\right\} + CO + MeOH$$

$$\longrightarrow MMA + MC + (\text{Copolimer or allene and CO})$$

$$MMA/MC = 100 : 0\text{–}16 : 1.$$

In this work, we report the carbomethoxylation kinetics of methylacetylene–allene fractions. Reversible allene $\rightleftarrows$ methylacetylene isomerization is observed under carbomethoxylation conditions. A scheme consistent with experimental data is suggested to describe the transformations occurring in the system.

EXPERIMENTAL

Allene and methylacetylene were carbomethoxylated in a glass reactor (V = 100 ml) placed in a steel autoclave, using a procedure described in [1]. Liquid and gaseous reaction products were analyzed by GLC. Quantitative analysis was performed using an internal standard method as described in [2]. The starting substances were "individual" allene and methylacetylene (MAF_1 and MAF_2), which form as exhaust gases in industrial pyrolysis of gasoline hydrocarbons after concentrating, and an artificial mixture of "individual" allene and methylacetylene. The compositions of the raw materials used for carbomethoxylation are presented in Table 1. The reaction was carried out under vigorous stirring so that the reaction rate was independent of the rotational speed of the stirrer (kinetic control).

It was shown [1, 2] that impurities in the mixtures examined (propylene and unsaturated C_4 hydrocarbons) are inert under carbomethoxylation conditions. Therefore, we will not consider their transformations. All experiments were carried out at 85°C and at a constant CO pressure of 4.0 MPa. The reactant concentrations were $[PdCl_2(Ph_3P)_2] = 1.3 \times 10^{-3}$ mol/l, [phenanthroline] = 4.5×10^{-3} mol/l, [HCl] = 0.73 mol/l, and [allene + methylacetylene] = 0.040 mol/l. The volume of the liquid phase (methanol) was 50 ml. The concentrations of allene and methylacetylene in the liquid phase under operating conditions were determined from the solubilities of these compounds in methanol. The distribution coefficients $\alpha = C_{liq}/C_{gas}$ for allene and methylacetylene were close: $\alpha = 0.1$ at 85°C. Similar solubility data for these compounds are presented in [3].

RESULTS AND DISCUSSION

Analysis of data presented in [1, 2] suggests that the transformation of allene and methylacetylene into MMA + MC and a copolymer proceeds according to Scheme 1.

Direct polymer formation from methylacetylene is ruled out, because earlier data [2] indicate that only allene is directly involved in polymer formation: the yield of the copolymer of allene and CO is proportional to the initial allene concentration, and the copolymer is not formed in 2 h if allene is absent from the initial mixture. Methylacetylene serves as a source of MMA + MC [1]. Allene is another source of MMA + MC: according to balance calculations for the carbomethoxylation of individual allene (Table 2), the number of moles of MMA + MC formed from individual allene is

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† Deceased.

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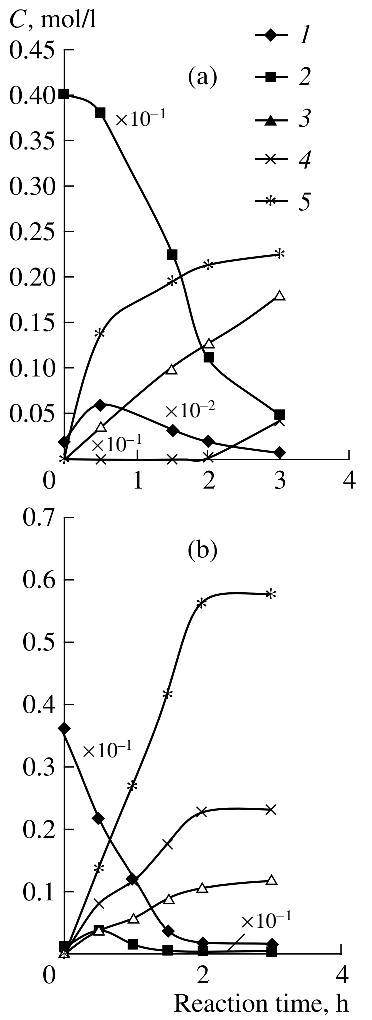

Fig. 1. Typical time dependences of the concentrations of the reactants and reaction products and CO consumption for the carbomethoxylation of (a) individual methylacetylene and (b) individual allene: (*1*) A, (*2*) MA, (*3*) MMA + MC, (*4*) polymer, and (*5*) CO.

larger than the number of moles of acetylene taken for the reaction. However, these data do not elucidate the pathway leading to MMA + MC, which allows the isomerization of allene to methylacetylene with subsequent carbomethoxylation to MMA + MC and/or the direct conversion of allene into MMA + MC:

$$\begin{tikzcd} \text{Allene} \arrow[r, shift left] \arrow[d] \arrow[dr] & \text{Methylacetylene} \arrow[l, shift left] \arrow[d] \\ \text{Polymer} & (\text{MMA} + \text{MC}) \end{tikzcd}$$

Scheme 1.

Allene ⇄ Methylacetylene Isomerization

The kinetic data obtained for the carbomethoxylation of MAF and individual allene and methylacetylene rule out direct allene conversion into MMA + MC.

Using the raw materials whose composition is presented in Table 1, we related the concentrations of the reactants and products to the reaction time (Table 2). The experimental plots obtained for the carbomethoxylation of individual methylacetylene and allene are presented in Fig. 1. The methylacetylene concentration shows a pronounced peak 1.5 h after the beginning of the reaction (Fig. 1b). It is of interest that this peak is observed when raw materials with different allene-to-methylacetylene ratios are used, and that the higher the allene content of the initial mixture, the higher the peak. When individual methylacetylene is used as the raw material, a peak is observed in the allene concentration versus time curve (Fig. 1a). The observed time dependences (Fig. 1) are most likely to be a consequence of reversible allene ⇄ methylacetylene isomerization. In all cases, the rate of allene conversion exceeds the rate of methylacetylene conversion.

The isomerization of methylacetylene to allene is also indicated by the following findings. Figure 2 plots the dependence of the yield of carbomethoxylation products, ([MMA] + [MC])/$[\text{MA}]_0$, on MA conversion ($([\text{MA}]_0 - [\text{MA}]_f)/[\text{MA}]_0$) for different mixtures of allene and methylacetylene. These data demonstrate that the selectivity of MMA + MC formation from methylacetylene (determined as the slope of the plot) is 65.8%. Since the polymer does not form straight from methylacetylene, we infer that 34.2% of the initial methylacetylene isomerizes to allene, which then polymerizes. However, as distinct from the system containing individual allene, which generates a copolymer at a

Table 1. Composition of the original raw materials

Raw materials	Propylene, mol %	Allene, mol %	Methylacetylene, mol %	ΣC_4, mol %
"Individual" allene	0.41	95.9	3.04	0.65
"Individual" methylacetylene	0.40	0.37	99.1	0.13
MAF_1	8.17	60.91	30.68	0.24
MAF_2	15.33	42.39	41.48	0.90
Artificial mixture	0.40	20.00	79.13	0.47

Table 2. Observed and calculated concentrations of products of the carbomethoxylation of allene, methylacetylene, and their mixtures

τ, h	$[A]_0^*$, mol/l	$[MA]_0^*$, mol/l	$[A]_f^*$, mol/l		$[MA]_f^*$, mol/l		[MMA = MC], mol/l	
			experiment	calculation	experiment	calculation	experiment	calculation
MAF_2 ($[A]_0/[MA]_0 = 2$)								
0.5	0.1888	0.0951	0.0896	0.0876	0.0466	0.0483	0.0286	0.0326
1.0	0.2260	0.1138	0.0758	0.0799	0.0496	0.0454	0.0795	0.0671
1.5	0.2264	0.1140	0.0688	0.0638	0.0324	0.0371	0.0921	0.0749
2.0	0.2254	0.1136	0.0640	0.0625	0.0345	0.0364	0.1020	0.0755
MAF_1 ($[A]_0/[MA]_0 = 1$)								
0.5	0.1560	0.1520	0.0918	0.0876	0.0810	0.0848	0.0303	0.0410
1.0	0.1704	0.1668	0.1044	0.1028	0.0986	0.0999	0.0726	0.0487
1.5	0.1932	0.1892	0.0644	0.0633	0.0596	0.0608	0.0972	0.0928
2.0	0.1864	0.1824	0.0386	0.0439	0.0472	0.0420	0.1208	0.1007
Methylacetylene ($[A]_0/[MA]_0 = 0.004$)								
0.5	0.0017	0.4560	0.0059	0.0028	0.4090	0.4127	0.0358	0.0229
1.5	0.0012	0.3200	0.0032	0.0033	0.2242	0.2259	0.0989	0.0501
2.0	0.0015	0.4614	0.0019	0.0027	0.1113	0.1103	0.1259	0.1631
3.0	0.0012	0.3092	0.0065	0.0016	0.0478	0.0499	0.1786	0.1363
Allene ($[A]_0/[MA]_0 = 32$)								
0.2	0.3900	0.0123	0.3556	0.3433	0.0051	0.0172	0.0139	0.0044
0.5	0.3520	0.0111	0.2170	0.2332	0.0374	0.0209	0.0364	0.0177
1.0	0.3560	0.0112	0.1414	0.1342	0.0148	0.0219	0.0386	0.0439
1.5	0.3760	0.0119	0.0372	0.0325	0.0060	0.0106	0.0877	0.0831
2.0	0.3440	0.0108	0.0182	0.0163	0.0043	0.0062	0.1051	0.0814
3.0	0.3780	0.0120	0.0149	0.0128	0.0032	0.0053	0.1181	0.0915
Artificially composed mixture of allene and methylacetylene ($[A]_0/[MA]_0 = 0.2$)								
0.5	0.0820	0.3102	0.0212	0.0190	0.0533	0.0559	0.0358	0.1357
1.0	0.0898	0.2880	0.0168	0.0193	0.0514	0.0488	0.0991	0.1298
1.5	0.0488	0.3120	0.0102	0.0103	0.0467	0.0465	0.1102	0.1333
2.0	0.1426	0.1936	0.0059	0.0097	0.0256	0.0284	0.1221	0.1380
2.0	0.0707	0.2935	0.0093	0.0424	0.0295	0.0733	0.0716	0.0927

Note: τ is the reaction time; $[A]_0$, $[A]_f$ and $[MA]_0$ and $[MA]_f$ are the initial and final concentrations of allene and methylacetylene, respectively, in the liquid phase.

* The concentrations were calculated using a distribution coefficient of 0.1.

constant rate starting at the very beginning of the reaction (the polymer stops forming in ~2 h (Fig. 1b)), the copolymer formation involving methylacetylene occurs at a much lower rate and only after a long induction period of ~2 h (Fig. 1a). The resulting polymeric product is similar in composition to the product formed from allene. Thus, these specific features of the two systems of reactants can be assumed to result from the copolymerization of CO and allene formed from methylacetylene by a fairly slow isomerization.

Kinetic Model for Scheme 1

Preliminary processing of experimental data for Scheme 1 showed that the rate of the direct transformation of allene into MMA was very low compared to the

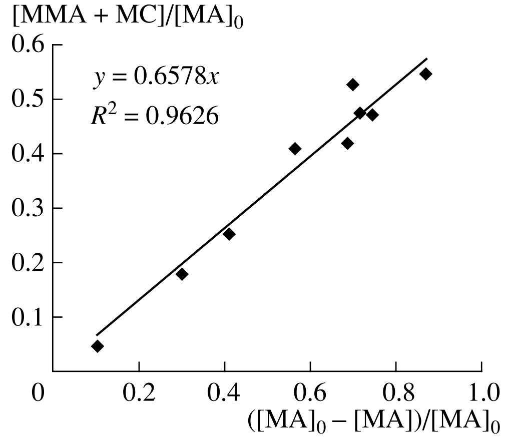

Fig. 2. Yield of MMA and MC versus methylacetylene conversion.

rate of isomerization of allene to methylacetylene. Therefore, the whole scheme of MMA and MC formation was not considered. The complete array of experimental data was processed for the following scheme of transformations:

$$\text{Polymer} \xleftarrow{k_2} \text{Allene} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{Methylacetylene}$$

$$\xrightarrow{k_3} \text{MMA + MC}$$

Scheme 2.

Taking into account that the reaction is first-order with respect to the reactants and using the equations $d[A]/d\tau = -k_{app,1}[A]$ and $d[MA]/d\tau = -k_{app,2}[MA]$ for the transformation rate of allene (A) and methylacetylene (MA), we estimated the rate constants from experimental data obtained by a series of experiments with individual allene and methylacetylene. The apparent constants of consumption of allene ($k_{app,1}$) and methylacetylene ($k_{app,2}$) are $k_{app,1} = 1.247$ h^{-1}, $R_1 = 0.954$; $k_{app,2} = 0.728$ h^{-1}, $R_2 = 0.928$ (R_1 and R_2 are correlation coefficients).

The complete array of experimental data obtained for the starting mixtures of MAF of different compositions (Table 2) was processed using the apparent constants presented above (as a first approximation) and the kinetic equations for Scheme 2:

$$d[A]/d\tau = -(k_1 + k_2)[A] + k_{-1}[MA], \qquad (1)$$

$$d[MA]/d\tau = k_1[A] - (k_1 + k_3)[MA], \qquad (2)$$

$$d[MMA + MC]/d\tau = k_3[MA]. \qquad (3)$$

The rate constant of each reaction in Scheme 2 was determined by minimizing the residual sum of squared differences between the calculated and experimental concentrations of allene, methylacetylene, and MMA + MC (Table 2).

The following rate constants were obtained: $k_1 = 2.5310$ h^{-1}, $k_2 = 15.1064$ h^{-1}, $k_{-1} = 0.5087$ h^{-1}, $k_3 = 0.5953$ h^{-1}, and $K_{equiv} = 4.974$; the standard deviation was 1.28×10^{-2} (K_{equiv} is the equilibrium constant of allene $\rightleftarrows$ methylacetylene isomerization).

According to the equilibrium constant obtained, the calculated equilibrium composition of the allene–methylacetylene gas mixture is 16.7 and 83.3%, respectively (according to [4], these values are 18.1 and 81.9% at 100°C). It is noteworthy that when methylacetylene–allene mixtures of different compositions are used, the final allene/methylacetylene ratio does not achieve an equilibrium value; that is, in the carbomethoxylation of a methylacetylene–allene fraction in the presence of the $PdCl_2(Ph_3P)_2$–*ortho*-phenanthroline–HCl catalytic system, allene $\rightleftarrows$ methylacetylene isomerization occurs, but the composition of the methylacetylene–allene fraction is nonequilibrium. Thus, our data suggest that the most probable carbomethoxylation pathway is the direct carbomethoxylation of methylacetylene to MMA and MC. The isomerization of methylacetylene to allene and the related formation of the polymer from allene and CO are side reactions. The pathway to MMA in allene carbomethoxylation includes the slow direct transformation of allene into MMA with simultaneous allene isomerization to methylacetylene, which turns rather rapidly into MMA.

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