

## 6. THE ALKYLATION AND KETONIC DECOMPOSITION OF ACETOACETIC AND PRENYLACETOACETIC ESTERS

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We have previously studied the alkylation of acetoacetic ester (AAE) by 1-chloro-3-methyl-2-butene [prenyl chloride (PC)] in the presence of aqueous 50% KOH and a catalytic amount of triethylbenzylammonium chloride (TEBAC) [1, 2]. A number of consecutive parallel reactions proceed in this system leading to the formation of the monoprenyl (I) and diprenyl (II) derivatives of AAE, 2-methyl-2-hepten-6-one (MH), and other compounds. In order to understand the mechanism of these processes and optimize the conditions for industrial syntheses, the relative reactivity of the starting, intermediate, and final products of the reaction in the two-phase catalytic system must be studied. The initial rates of the reactions studied under identical conditions, i.e., at identical temperatures in the presence of the same alkaline reagent (50% aq. KOH) and catalyst (TEBAC) and equal initial reagent concentrations, may serve as a criterion of relative reactivity. In this work, the initial rates of alkylation of AAE and (I) and of the ketonic decomposition of AAE, (I), and (II) were studied in the presence of 50% aq. KOH and TEBAC.

## EXPERIMENTAL

The characteristics of the reagents, kinetic run techniques, and analytical methods are given in our previous work [1]. Benzene or toluene was used as the solvent. The volume of the organic phase was 25 ml. The condensing agent was 10 g 50% aq. KOH and the phase-transition catalyst was 0.23 g TEBAC. The experimental temperature was 40°C. The initial rate was determined by the Newton-Gregory method [3].

Ketonic Decomposition of Acetoacetic Ester and (I). To a mixture of the condensing agent and TEBAC, 0.72 mole/liter AAE or (I) in toluene (25 ml) was added and eight probes were selected. After stirring of the organic and aqueous phases, an abundant white precipitate separated and the concentration of AAE or (I) dropped. The formation of the corresponding ketone (acetone or MH) was observed. The initial rate of consumption of AAE or (I) and also of the formation of acetone and MH are given in Table 1.

A number of runs were performed in benzene at 40°C to determine the concentration of (I) consumed in the formation of the potassium salt of prenylacetoacetic acid with 0.3 mole/liter initial concentration of (I). The runs differed in duration. The concentrations of (I) and MH in the organic layer were determined in the course of the runs. After completion of the runs, the entire reaction mass was treated with 10% aq. HCl, the organic products were extracted with ether, and analyzed by gas-liquid chromatography (GLC). An increase in the amount of MH relative to the analytical data of the final run probe was found. The increase in the MH concentration was related to the potassium prenylacetoacetate. The concentration of (I) converted to the potassium derivative of (V) was calculated using the equation:  $C = C_0 - C_1 - C_{MH} - C_{Ksalt}$ , where  $C_1$  is the current concentration of (I),  $C_{MH}$  is the current concentration of MH, and  $C_{Ksalt}$  is the current concentration of (I) converted into the potassium salt of (I). These results are presented in Fig. 2. The potassium salt concentration increased as follows: 15 min) 0, 30 min) 0.042, 120 min) 0.039, and 240 min) 0.08 relative units.

There is no ketonic decomposition in the reaction of diprenylacetoacetic ester (II) in toluene in the presence of 10 g 50% aq. KOH and 0.23 g TEBAC. The initial rate of consumption of (II) is  $2.46 \cdot 10^{-5}$  mole/liter·sec; decomposition products were not identified.

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TABLE 1. Initial Reaction Rate of Formation of Acetone during Decarboxylation of AAE ( $W_{ac}$ ), Formation of MH during Decarboxylation of (I) ( $W_{MH}$ ), Acidic Decomposition of (II) ( $W_{ad}$ ), and Monoalkylation of AAE ( $W_{\Sigma}$ ) and (I) ( $W_{II}$ ) (40°C, toluene, initial concentrations 0.8 mole/liter, organic phase 25 ml, 10 g 50% aqueous KOH, 0.23 g TEBAC)

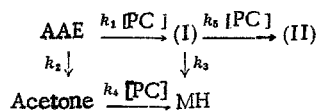
Process	Rate, mole/liter·sec·10 <sup>5</sup>
Decarboxylation of AAE	$W_{ac}=0,335$
Decarboxylation of (I)	$W_{mh}=4,49$
Acidic decomposition of (II)	$W_{ad}=2,45$
Alkylation of AAE	$W_{\Sigma}=50,43$
Alkylation of (I)	$W_{II}=99,3$

Alkylation of Acetoacetic Ester in the Presence of 10 g 50% aq. KOH and 0.23 g TEBAC, The major products in the reaction of equimolar solutions of AAE and PC in toluene (0.8 mole/liter) at 40°C in the presence of the condensing agent are (I), (II), and MH. The kinetic curves for the formation of these products are given in Fig. 3. Calculation of the initial rates shows that the initial rate for the formation is  $5.5 \cdot 10^{-5}$  mole/liter·sec for (I),  $11.8 \cdot 10^{-5}$  mole/liter·sec for MH, and  $33.1 \cdot 10^{-5}$  mole/liter·sec for (II). The initial rate of monoalkylation was evaluated as  $W_{\Sigma} = W_I + W_{II} + W_{MH}$  (see Table 1).

Alkylation of (I) in the Presence of 10 g 50% aq. KOH and 0.23 g TEBAC at 40°C. The initial concentrations of (I) and PC were 0.8 mole/liter and toluene served as the solvent. Only (II) was formed in the course of the reaction. The initial rate of formation for (II) is given in Table 1.

#### RESULTS AND DISCUSSION

Four compounds may be alkylated in the reaction of AAE with PC in the presence of 50% aq. KOH and TEBAC: AAE, with the formation of (I) which may be converted to (II); acetone, which is formed in the ketonic decomposition of AAE, will give MH; and, finally, MH also may be alkylated yielding diisopentenylacetone (DIPA). We did not find the formation of DIPA [1] and shall not consider this reaction. MH may be formed by two pathways: 1) ketonic decomposition of AAE to acetone and the alkylation of acetone by PC and 2) AAE is alkylated by PC to (I) and ketonic decomposition of (I) leads to MH:



The total rate of formation of MH in the alkylation of AAE is  $11.8 \cdot 10^{-5}$  mole/liter·sec. The rate constants determined in special experiments under identical conditions are:

$$\begin{aligned}
 k_1 [\text{PC}] &= W_{\Sigma} / [\text{AAE}]_0 = 63 \cdot 10^{-5} \text{sec}^{-1}, k_3 = W_{MH} / [\text{I}]_0 = 5.83 \cdot 10^{-5} \text{sec}^{-1} \\
 k_2 &= W_{ac} / [\text{AAE}]_0 = 0.49 \cdot 10^{-5} \text{sec}^{-1}, k_4 [\text{PC}] = 0.375 \cdot 10^{-5} \text{sec}^{-1}
 \end{aligned}$$

The term  $k_4$  was calculated from our previous data [4] and converted to standard conditions:  $[\text{PC}] = 0.8$  mole/liter. Thus, the rate constants of the first pathway are significantly lower than the rate constants of the steps of the second pathway.

Contribution of the first pathway should be considered if the current concentration of (I) in the reaction system is lower than the concentration of acetone. However, despite the alkylation of (I) which proceeds under these conditions with a rate  $33.1 \cdot 10^{-5}$  mole/liter·sec,

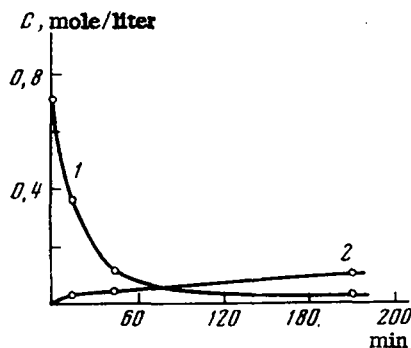


Fig. 1

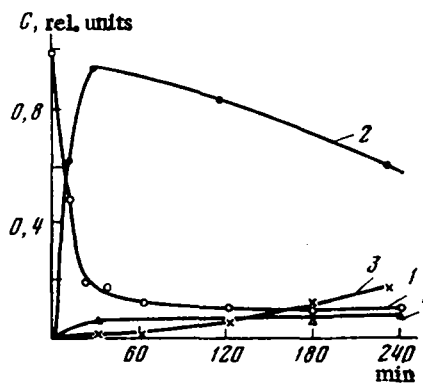


Fig. 2

Fig. 1. Kinetic curves for the consumption of (I) (1) and the formation of MH (2) at 40°C in toluene, with  $[I] = 0.8$  mole/liter, aqueous phase 10 g 50% aq. KOH and 0.23 g TEBAC.

Fig. 2. Kinetic curves for the consumption of (I) (1) and formation of the potassium derivative of (I) (2), MH (3), and potassium prenylacetoacetate (4). The concentrations are given in relative units. The conditions were the same as for Fig. 1.

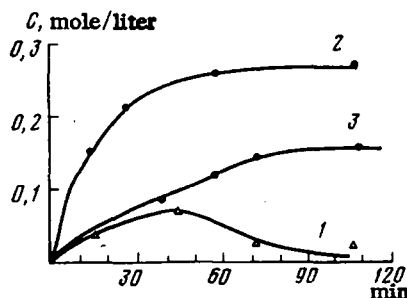


Fig. 3. Kinetic curves for the formation of (I) (1), (II) (2), and MH (3) in the reaction of AAE with PC for the same conditions as in Figs. 1 and 2;  $[AAE] = [PC] = 0.8$  mole/liter.

the concentration of (I) is 30 times greater than the acetone concentration. Thus, we may assume that MH is formed mainly by the second pathway involving the formation of (I) and its ketonic decomposition. This conclusion is in accord with our previous work [1].

Direct determination of the rate of alkylation of AAE and (I) under identical conditions shows that (I) is twice as reactive in the alkylation reaction despite lesser kinetic and thermodynamic acidity [5]. This finding is explained by inclusion of the reversible step of formation of the potassium (and triethylbenzylammonium) derivative of AAE or (I) and their reaction with PC in the alkylation. Since (I) is a weaker acid than AAE, then the equilibrium concentration of (I) should be lower than that of AAE. However, the anion of (I) will be more nucleophilic such that the rate constant of its reaction with PC will be higher, which determines the overall rates of their alkylation.

In the presence of 50% aq. KOH but without PC, the ketonic decomposition of AAE and of (I) takes place and the decomposition of (I) proceeds with a significantly greater rate. On the other hand, consumption of AAE or (I) is observed, which significantly exceeds the accumulation of acetone or MH in the reaction system. Thus, for example, 50% of (I) disappears in only 15 min but only 4.2% MH is formed. In analyzing the organic layer in the run with AAE, this compound is rapidly and almost completely consumed, while acetone and ethanol appear in the reaction products only after 2.5 h in small amounts ( $W_0 = 0.35 \cdot 10^{-5}$  mole/liter  $\cdot$  sec). The major product in the reaction of AAE or (I) with KOH is apparently the potassium derivative which forms a precipitate. In the reaction of AAE with (I), the precipitate partially dissolves after 20-30 min. The free ester may undergo alkaline hydrolysis. The thermodynamic reaction products are potassium acetoacetate or potassium prenylacetoacetate and

ethanol. Thus, the dissolution of the precipitate in the run with (I) is a consequence of the formation of potassium prenylacetoacetate. The concentration of the potassium salt in the reaction of (I) steadily increases while the concentration of the potassium derivative of (I) initially increases and then decreases. The potassium salt of the acid formed is in equilibrium with the corresponding acid, whose decarboxylation leads to MH (see Fig. 2). Thus, a number of parallel and consecutive reactions occur in the ketonic decomposition of AAE or (I): 1) the formation of the potassium derivative (enolization), 2) hydrolysis of the free ester with the formation of the equilibrium potassium salt-acid mixture, and 3) decarboxylation of the acid and formation of the ketone. The difference in the rates of ketonic decomposition for AAE and (I) may be explained as follows. The potassium derivative of AAE is formed more rapidly ( $W_0 = 182.5 \cdot 10^{-5}$  mole/liter $\cdot$ sec for an initial concentration 0.72 mole/liter) than the potassium derivative of (I) ( $W_0 = 62.5$  moles/liter $\cdot$ sec. for  $[(I)] = 0.72$  mole/liter), which is in accord with their kinetic acidities. The equilibrium concentration of the latter is also lower [5]. As a result, the concentration of the free ester is greater in the reaction with (I) than for AAE and thus, the hydrolysis of (I) proceeds at a greater rate despite the lesser reactivity of (I) in the hydrolysis reaction [6]. The rate of decarboxylation of the ketoacids decreases with decreasing electron density on the oxygen atom of the keto group since this does not favor nucleophilic attack on a proton. The introduction of an alkyl (electron-donor) group in the position  $\alpha$  to the  $C=O$  group leads to a redistribution of electron density in the molecule and facilitates decarboxylation [7]. Thus, the differences in the rates of ketonic decomposition are the result of a difference in the steady-state concentrations of free ketoacids and in the rate constants for their decarboxylation.

Ester (II) cannot form metal derivatives and, indeed, does not give a precipitate or the product of the ketonic decomposition of (II), namely, DIPA. The observed consumption of (II) in the presence of 50% aq. KOH and TEBAC is the result of side reactions which were not studied [ $W_0 = 2.5 \cdot 10^{-5}$  mole/liter $\cdot$ sec for 0.8 mole/liter initial concentration of (II)]. These side reactions apparently also proceed in the formation of (II) in the reaction of AAE with PC.

#### CONCLUSIONS

1. We measured the initial rates for the major reactions proceeding in a catalytic two-phase system in the alkylation of acetoacetic ester (AAE) by 1-chloro-3-methyl-2-butene and it was shown that the formation of methylheptenone occurs in the decarboxylation of prenylacetoacetic ester (I) and not as a result of the alkylation of acetone formed from AAE,

2. The initial rates of alkylation and ketonic decomposition of AAE and (I) were measured and substituted AAE was found more active in these reactions,

3. The potassium derivatives of the ketoesters and the potassium salts of the ketoacids are formed in the reaction of 50% aq. KOH with AAE and (I),

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