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Vapor-Phase Conversion of Esters into Ketones in the Presence of an Sn-, Ce-, and Rh-Containing Oxide Catalyst

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Abstract—The catalytic conversion of acyclic and cyclic esters into ketones was studied. Based on an analysis of data on the yields of the products of ester conversion, the conclusion was drawn that ketones result from a reaction between two ester molecules with the intermediate formation of a β-ketoester. This reaction is accompanied by the partial thermal decomposition of esters to aldehydes (reverse Tishchenko reaction) with the subsequent condensation.

INTRODUCTION

The catalytic conversion of esters was found several decades ago [1, 2]. An ester with equal numbers of carbon atoms on each side of the ester group ($RCOOCH_2R$) is converted into a symmetric ketone (RCOR) in a vapor phase in the presence of heterogeneous catalysts [3].

If the lengths of carbon chains in the acid and alcohol moieties of an ester are different, published data on the composition of the resulting ketones are ambiguous. It is believed that one of the following reactions takes place:

–The conversion of the acid moiety of an ester into a symmetric ketone with the simultaneous formation of ethylene derivatives at the alcohol moiety of the ester (Kagan reaction) [4];

–the conversion into a ketone (asymmetric) with the loss of a carbon atom from the alcohol moiety of the ester [5];

–the conversion by the Cannizzaro mechanism with the intermediate formation of an acid [6];

–the Claisen–Dieckmann condensation of esters via a β-ketoester [7]; and

–the equivalent participation of moieties on each side of the ester group in a high-temperature reaction like the reverse Tishchenko reaction with the formation of two aldehydes and the subsequent condensation [8].

Many authors related the conversion of esters to the Tishchenko reaction [9–11], which consists in the condensation of two aldehydes to form an ester. This reaction can occur in either the liquid or vapor phase in the presence of heterogeneous catalysts [12]. The Meerwein–Ponndorf–Verley and Oppenauer reactions are of preparative importance, whereas the Tishchenko reaction (which is related to the Cannizzaro reaction) has found commercial application in the production of esters [13–16].

The conversion of esters into ketones is related to the Tishchenko reaction because this reaction becomes reversible at high temperatures [8]. Bork [17] explained the conversion of esters into ketones by ester cleavage to aldehydes, that is, the reverse Tishchenko reaction. In this case, the probability of formation of an asymmetric ketone is twice as high as that for the others.

The conversion of esters into ketones is also related to the conversion of primary alcohols. Examples of the dehydrogenation of these alcohols to aldehydes are well known [18]. Examples of the conversion of primary alcohols into ketones are less known; it is likely that the alcohols undergo dehydrogenation to aldehydes with the subsequent condensation of the aldehydes into esters [19–24]. Isaguliants and Belomestnykh [25] compared the well-studied reactions of primary and secondary alcohols.

Our previous studies were devoted to the conversion of primary alcohols and esters; however, the interpretation of product composition was inadequate. Therefore, we studied the conversion of esters with secondary substituents, which hinder the reaction, into ketones.

EXPERIMENTS

An Sn–Ce–Rh–O catalyst containing Sn(IV), Ce(IV), and Rh(III) oxides in a molar ratio of 90 : 9 : 1 was used in the experiments. The synthesis and properties of this catalyst were previously described in detail [26]. The experiments on ester conversion in the presence of this catalyst were performed in a typical flow setup at atmospheric pressure and 370°C. A quartz reactor 10 mm in i.d. with a catalyst bed volume of 3 cm^3 was used. The catalyst particle size was 0.6–1.2 mm.

Table 1. Product yields in the conversion of $C_4OOisoC_3$ and $C_{10}OOisoC_3$ esters

$C_4OOisoC_3$ (93.0% conversion)		$C_{10}OOisoC_3$ (91.0% conversion)	
product	yield, %	product	yield, %
$C_3^=$	28.0	$C_3^=$	30.0
$C_4^=$, C_4	0.5	$C_{10}^=$, C_{10}	4.0
C_4HO	0.5	$C_{10}HO$	0.5
C_4OH	1.5	$C_{10}OH$	3.0
C_4OOC_4	Traces	$C_{10}OOC_{10}$	Traces
CCOC	7.0	CCOC	5.0
$CCOC_3$	10.0	$CCOC_9$	7.5
C_3COC_3	34.0	C_9COC_9	28.0
C_3COC_6	1.0	–	–
Others	10.5	Others	13.0

Starting reactants were supplied with a delivery pump at a liquid flow rate of 3 cm^3 /h. The reaction products were analyzed by gas chromatography and mass spectrometry. The following starting reactants were used: isopropyl butyrate ($C_4OOisoC_3$), isopropyl caprate ($C_{10}OOisoC_3$), cyclohexyl butyrate (C_4OOCy), butyl cyclohexylformate ($CyCOOC_4$), butyl acetate (C_2OOC_4), and ethyl butyrate (C_4OOC_2). No solvent was used in the course of the reaction.

RESULTS AND DISCUSSION

Under reaction conditions, the conversion of both isopropyl esters ($C_4OOisoC_3$ and $C_{10}OOisoC_3$) resulted in a ketone built from only the acid fragments of the parent esters: 4-heptanone (C_3COC_3) and 10-nonadecanone (C_9COC_9) were formed from $C_4OOisoC_3$ and $C_{10}OOisoC_3$, respectively (Table 1). Acetone and propylene were formed from the alcohol moiety of these esters. The amount of propylene was much greater than that of acetone, although previous experiments on isopropanol conversion in the presence of the given catalyst clearly demonstrated its dehydrogenating properties: the reaction almost exclusively yielded acetone [27]. As a result of this conversion of isopropyl esters, the total yield of ketones was lower than that in the case of the esters of normal alcohols [3]. In the case of normal alcohols, the formation of ketones bearing methyl groups can be easily explained by dealkylation; however, this is not so evident in the case of isopropyl esters. Previously [7], we assumed that esters are converted into ketones via a β-ketoester intermediate. The conversion via a β-ketoester consists in that two ester molecules undergo condensation with the formation of a β-ketoester (reaction (I)) [28, 29]. This is the Claisen–Dieckmann condensation. The degradation of the unstable β-ketoester (reaction (II)) occurs via two paths depending on the amount of hydrogen obtained in the dehydrogenation (reaction (III)) of the alcohols formed in reactions (I) and (II). It is important that in both cases a symmetric ketone RCOR is formed from the acid moieties of two ester molecules and a symmetric ketone R'COR' is formed in a smaller amount from the alcohol moieties of the ester by dehydrogenation (reaction (III)) and condensation (reaction (IV)). The formation of the ketone R'COR' in a smaller amount as compared with RCOR can be explained by the fact that the alcohol moiety of an ester is converted into an alkene (reaction (II)) to a greater extent. This corresponds to the Kagan reaction [4].

$$2RCOOCH_2R' \longrightarrow RCOR_{(-H)}COOCH_2R' + R'CH_2OH, \qquad (I)$$

$$\left.\begin{array}{c} RCOR_{(-H)}COOCH_2R' \longrightarrow RCOR + CO_2 + CH_2{=}R'_{(-H)} \\ \text{or} \\ RCOR_{(-H)}COOCH_2R' + H_2 \longrightarrow RCOR + CO + R'CH_2OH, \end{array}\right\} \qquad (II)$$

$$R'CH_2OH \longrightarrow R'CHO + H_2, \qquad (III)$$

$$R'CHO \longrightarrow (\ldots) \longrightarrow R'COOCH_2R' \longrightarrow (\ldots) \longrightarrow R'COR'. \qquad (IV)$$

The composition of the conversion products of both isopropyl esters corresponds to this mechanism only in part. In this case, isopropanol and acetone are formed in place of $R'CH_2OH$ and R'CHO; however, an alcohol, an aldehyde, and an ester, which are formed from the acid moiety of the ester, were also detected among the products. We repeated the experiment with the use of esters containing cyclohexyl groups on different sides of the ester group (C_4OOCy and $CyCOOC_4$) (Table 2). In the case of C_4OOCy, the results were similar to the results obtained with isopropyl esters. As for the conversion of $CyCOOC_4$, dicyclohexyl ketone (CyCOCy) was detected among the products; however, both C_3COC_3 ketones and asymmetric cyclohexyl propyl ketone

Table 2. Product yields in the conversion of C_4OOCy and $CyCOOC_4$ esters

C_4OOCy (94.0% conversion)		$CyCOOC_4$ (90.0% conversion)	
product	yield, %	product	yield, %
$C_4^=$, C_4	0.5	$C_4^=$, C_4	1.0
$Cy^=$	21.0	$Cy^=$	Traces
C_4HO	0.5	C_4HO	2.0
C_4OH	2.0	C_4OH	3.0
C_4OOC_4	0.5	CyCHO	2.0
$CCOC_3$	5.0	$CyCH_2OH$	3.0
C_3COC_3	38.5	C_4OOC_4	3.0
Cy=O	3.0	C_4OOCCy	7.0
C_3COPh	5.0	CyCOOCCy	6.0
Others	18.0	$CCOC_3$	1.0
–	–	C_3COC_3	10.0
–	–	C_3COCy	25.0
–	–	CyCOCy	11.0
–	–	C_3COC_{10}	3.0
–	–	Others	13.0

Table 3. Product yields in the conversion of C_4OOC_2 and C_2OOC_4 esters

C_4OOC_2 (96.0% conversion)		C_2OOC_4 (97.0% conversion)	
product	yield, %	product	yield, %
$C_2^=$, C_2	24.0	$C_2^=$, C_2	6.0
$C_4^=$, C_4	4.0	$C_4^=$, C_4	20.0
C_2HO	4.0	C_2HO	1.0
C_4HO	1.0	C_4HO	6.0
C_2OH	5.0	C_2OH	1.0
C_4OH	2.0	C_4OH	6.0
C_2OOC_2	Traces	C_2OOC_2	Traces
C_2OOC_4	Traces	C_4OOC_2	Traces
C_4OOC_4	Traces	C_4OOC_4	1.0
CCOC	6.0	CCOC	26.0
$CCOC_3$	15.0	$CCOC_3$	16.0
$CCOC_5$	Traces	$CCOC_5$	2.0
C_3COC_3	30.0	C_3COC_3	5.0
C_3COC_5	Traces	C_3COC_5	–
Others	5.0	Others	7.0

(C_3COCy) were also present in significant amounts. In the products of C_4OOCy conversion, ketones containing cyclohexyl substituents on each side or on one side of the ester group of the molecule were not detected. Note that methyl phenyl ketone C_3COPh was present, which was probably formed by dehydration.

The presence of C_3COC_3 and C_3COCy ketones, as well as an alcohol, an aldehyde, and esters formed from the *n*-butyl group, in the reaction products results from the reverse Tishchenko reaction. It should be remembered that *n*-butanol is also formed via β-ketoesters. Nevertheless, because of the presence of the above ketones, the reaction mechanism cannot be unambiguously determined as a mechanism via β-ketoesters. On the other hand, the occurrence of the reaction by the mechanism of the reverse Tishchenko reaction is also doubtful because of the very low concentration of asymmetric ketone in the reaction products.

Because in the case of the reverse Tishchenko reaction metameric esters are converted into identical products, that is, into two corresponding aldehydes, we used C_2OOC_4 and C_4OOC_2 as the starting materials. The conversions of both metameric esters resulted in the same ketones (Table 3): acetone (CCOC), C_3COC_3, and 2-pentanone ($CCOC_3$). However, these ketones were formed in different proportions. In both cases, the ketone that was formed from the acid moiety was predominant (30 and 26%, respectively). An asymmetric ketone in an amount of 15.0 or 16.0%, respectively, was detected in the products of both reactions. Alcohols, aldehydes, esters, and hydrocarbons were also detected in the reaction products; they were mainly formed from the alcohol moieties of esters. Ketones C_xCOC_x and C_yCOC_y, which were primarily formed by the secondary condensation of ketones and alkenes, were also detected. Thus, based on the quantitative ratios between the reaction products of both of the metameric esters, the reaction of ester conversion into ketones cannot be explained by only one of the mechanisms under consideration.

The results suggest that ketones are formed by a bimolecular reaction of esters. The esters undergo condensation to form an intermediate product and to liberate two alcohol molecules, whereas the acid residues form a ketone with the carbon chain shortened by a carbon atom. The liberated alcohol molecules enter into the subsequent reactions, which afford sequent ketones from the produced esters. The path of ester conversion into ketones from acid residues is shorter and hence more effective than the formation of ketones from alcohol residues. It also follows from an analysis of the quantitative ratios between the reaction products of ester conversion that a transformation via β-ketoesters is accompanied by the partial thermal decomposition of the esters with the subsequent condensation of the resulting aldehydes.

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