Ketonization of Fatty Methyl Esters over Sn-Ce-Rh-O Catalyst

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ABSTRACT: A mixture of methyl esters of fatty acids obtained by transesterification of nonerucic rape oil was ketonized. The starting material, diluted with methanol, was converted at atmospheric pressure over a catalyst that contained Sn, Ce, and Rh oxides in a molar ratio of 90:9:1. At a temperature of 385°C ketones were obtained with a total yield of 63% at the 96% conversion of starting material. The reported experiments prove that catalysts other than iron that are active in ketonization of primary alcohols can be successfully used in ketonization of esters of fatty acids. The kind of diluent used plays a crucial role in the conversion.

Paper no. J9683 in *JAOCS 78*, 533–535 (May 2001).

KEY WORDS: Fatty methyl esters, ketonization, oxide catalyst, transesterification, utilization of fatty wastes, waste fats.

The increasing focus on protection of the natural environment has forced industry to look for new raw material bases. Renewable resources from agricultural products or their waste materials provide a possible alternative solution to this problem (1). Studies on the production and application of biofuels (2,3) and biodegradable lubricants (4) as well as other industrial applications of vegetable oils, animal fats, and their recycled forms have been carried out recently. There have been a number of attempts to use (mainly) methyl esters of fatty acids obtained from agriculuturally derived oils as fuel for diesel engines. Mixtures of methyl esters of fatty acids provide a basis for a whole range of biodegradable surface-active agents (5,6) such as sulfated and ethoxylated fatty alcohols, sulfonated and ethoxylated methyl esters, alkylamides, and alkylamines. Fatty acid esters are also a major raw material in the production of fatty alcohols *via* hydrogenolysis (7,8). These esters are produced from vegetable oils and animal fats by esterification of fatty acids and by transesterification of triglycerides, usually with the use of methanol (9) or other alcohols (10). Environmentally harmful fats generated as waste products potentially can provide a cheap and renewable raw material base.

Esters can also be transformed into ketones by means of a reaction carried out at 350–400°C over heterogeneous catalysts such as iron catalyst according to the following general equation (11):

$$3RCOOCH_2R' \xrightarrow{Fe} RCOR + RCOR' + R'COR' + 3CO + 3H_2 \quad [1]$$

Long-chain esters can also be used as substrates. Earlier attempts at ketonization of long-chain esters over iron catalyst (12) showed the possibility of obtaining two long carbon-chain ketones with a high yield and without harmful by-products as opposed to other methods of obtaining such ketones (13). Apart from the ketonization of secondary alcohols, the common method for forming long-chain ketones is the pyrogenic decomposition of barium salts of the fatty acids or passage of vapors of the fatty acids over catalysts such as cerium or thorium oxides at 400–500°C. No other solutions are readily available in the literature (14).

The ketonization of esters considered here proceeds in a continuous mode in the gas phase at atmospheric or reduced pressures in the presence of an inert diluent. The conversion of methyl laurate to 12-tricosanone (with 56% yield) is an example of the reaction carried out under such conditions. In this way a mixture of methyl esters of fatty acids can be processed into a mixture of ketones with long carbon chains.

The addition of long carbon-chain ketones to waxes and surface coating compositions as a means of changing the melting point is generally known (13). They can also be easily converted into long-chain amines (15), which are suitable substrates for the production of a new generation of highly efficient biodegradable gemini surfactants having two lipophilic chains (16). One method for transforming long-chain amines into gemini surfactants involves the use of saccharides, which are also natural renewable raw materials (17). Amines react easily with, oxidized saccharides (e.g., gluconic acid) to form stable amides, and they can be condensed with reducing saccharides in the reaction leading to aminoglycosides.

EXPERIMENTAL PROCEDURES

The methyl esters fraction for ketonization was obtained from nonerucic rape oil refined by the Institute of Heavy Organic Synthesis "Blachownia," Kędzierzyn-Koźle, Poland (ICSO). According to the technology developed by ICSO (18–20) the esters obtained were selectively hydrogenated without any changes in the carboxyl group even when low-quality fats were used.

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The methyl esters fraction supplied by ICSO (iodine number, 0.1 I_2/100 g, saponification number 1884 mg KOH/g; melting point ≈ 40°C) contained mainly octadecanoic acid methyl ester (87.0%). Other fractional components were methyl esters of acids $C_{12:0}$ (0.2%), $C_{14:0}$ (0.2%), $C_{16:0}$ (7.1%), $C_{18:1}$ (0.4%), $C_{20:0}$ (2.8%), and $C_{22:0}$ (2.3%).

Our earlier attempts at the ketonization of long-chain esters over an iron catalyst (11,12) demonstrated the possibility of obtaining ketones with two long carbon chains at a high rate of efficiency and without generation of harmful by-products.

This paper focuses on the attempts to apply another catalyst, Sn-Ce-Rh-O (21), which is active in the ketonization of primary alcohols. This catalyst is obtained by precipitating hydrated oxides with an ammonia solution from the solution of tin (IV) chloride and ammonia-cerium nitrate, collecting the precipitate, and, after drying it, impregnating it with rhodium (III) chloride and calcining it. The Sn-Ce-Rh-O catalyst contained tin(IV), cerium(IV), and rhodium(III) oxides in a molar ratio of 90:9:1. The material was of rutile structure and was characterized by homogeneous distribution of the above catalyst components.

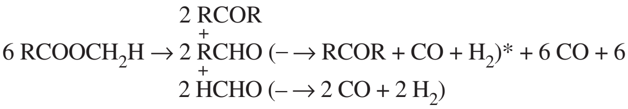
The ketonization of the methyl ester fraction was carried out in an electrically heated quartz flow reactor of 10-mm inner diameter and a fixed bed containing a 2.0 cm^3 amount of catalyst (=*W*) having a granule size of 0.6–1.2 mm. The methyl ester fraction was diluted with methanol or *n*-hexane, at a ratio of 70 g of ester in 100 g of diluent, and heated. After reaching the predetermined temperature it was passed through the catalyst bed at a flow ratio *F* of 3.0 cm^3/h. Products of the reaction were collected directly below the catalyst bed and identified by gas chromatography, mass spectroscopy, and other physicochemical methods. The gaseous products (H_2, CO, and low molecular weight hydrocarbons) formed during the process were not collected and analyzed.

RESULTS AND DISCUSSION

The ketonization reaction was studied in the temperature range of 340–400°C. The applied raw material was diluted with methanol. Depending on the temperature, ketonization of the methyl ester fraction produced a liquid or semiliquid mixture of ketones and hydrocarbons. At the optimal temperature of 385°C (Table 1) and 96% conversion, the total ketone yield was 63% including 47% 18-pentatriacontanone, 3% 16-hentriacontanone, 6% methyl ketones, and 7% other ketones. The collected product contained 14% hydrocarbons (mainly saturated and unsaturated C_{18}).

Dependence of the ketonization process on temperature and load was fairly typical. The ketonization was initiated at 350°C. Alcohols and aldehydes appeared temporarily at lower temperatures as intermediate components. Above the optimal temperature of 385°C the amount of ketones decreased rapidly, resulting in an increase in the amount of degradation products. Influence of the load on the conversion rate was considerably less. At 90% conversion a decrease in temperature by 10°C required the increase in the *W/F* ratio by two times. This corresponded with the same decrease in the flow rate or increase in the amount of the catalyst.

According to Equation 1, in the case of methyl esters $RCOOCH_3$, only one ketone, RCOR, should be obtained due to the loss of one atom of carbon at the alcohol side of the ester:



$$6\,\mathrm{RCOOCH_2H} \rightarrow \begin{array}{l} 2\,\mathrm{RCOR} \\ + \\ 2\,\mathrm{RCHO}\,(-\rightarrow \mathrm{RCOR} + \mathrm{CO} + \mathrm{H_2})^* + 6\,\mathrm{CO} + 6\,\mathrm{H_2} \\ + \\ 2\,\mathrm{HCHO}\,(-\rightarrow 2\,\mathrm{CO} + 2\,\mathrm{H_2}) \end{array} \qquad [2]$$

Therefore,

$$3\,\mathrm{RCOOCH_2H} \rightarrow 3/2\,\mathrm{RCOR} + 9/2\,\mathrm{CO} + 9/2\,\mathrm{H_2} \qquad [3]$$

Note that the asterisk (*) represents the Tishchenko reaction:

$$2\,\mathrm{RCHO} \rightarrow \mathrm{RCOOCH_2R} \qquad [4]$$
$$\mathrm{RCOOCH_2R} \rightarrow \mathrm{RCOR} + \mathrm{CO} + \mathrm{H_2} \qquad [5]$$

However, the product also contains a considerable amount of methyl ketones, which means that the conversion does not have to proceed only according to the suggested scheme. Other rearrangements are also possible.

The substitution of the diluent methanol with an apparently equally inert *n*-hexane resulted in considerably poorer performance. With a similar level of conversion, the content of ketones in the products fell below 40%, while the amount of saturated and unsaturated hydrocarbons increased. C_{18} hy-

TABLE 1
Results of Ketonization of Methyl Esters Fraction: Conversion and Yields of Liquid Products

Reaction temperature (°C)	Contact time (h)	Conversion (%)	Liquid products (%)					
			$C_{17}H_{35}COC_{17}H_{35}$	$C_{15}H_{31}COC_{15}H_{31}$	$CH_3COC_{17}H_{35}$ + $CH_3COC_{15}H_{31}$	Other ketones	Hydrocarbons	Others
375	0.67	90	43	2	5	6	12	11
385	0.67	96	47	3	6	7	14	6
375	1.33	96	35	1	8	7	18	9
390	0.67	98	40	1	9	8	18	6

drocarbons were no longer dominant, and hydrocarbons with all possible numbers of carbon atoms below 18 were detected. The final product was dark as opposed to the light yellow product obtained with the use of methanol.

ACKNOWLEDGMENT

This work was supported by the Polish State Committee for Scientific Research, Grant No. 3T09B07219.

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[Received June 29, 2000; accepted February 8, 2001]