♣ cis-trans Isomerization in the Synthesis of Fatty Acid Nitriles
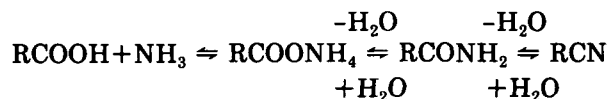
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Isomerization of cis-9-octadecenoic acid and its nitrile was investigated using different catalysts under different experimental conditions during the ammonolysis and dehydration process. It was found that the ratio of cis- to trans-9-octadecene nitrile depends upon the catalyst type and decreases as the process temperature and the reaction time increase and as the catalyst load decreases. Simultaneously, higher amounts of hydrocarbons are formed.

Fatty acid nitriles are important intermediates for the production of primary, secondary and tertiary amines and of cationic surface agents. The quality of these products, widely applied in different branches of indus-try, depends upon the composition of the nitriles. The nitriles are produced from fatty acids in the ammonolysis and dehydration process in the presence of a dehydration catalyst, according to following reaction scheme:

$$RCOOH + NH_3 \overset{-H_2O}{\underset{+H_2O}{\rightleftharpoons}} RCOONH_4 \overset{}{\rightleftharpoons} RCONH_2 \overset{-H_2O}{\underset{+H_2O}{\rightleftharpoons}} RCN$$

These reactions, known since the studies of Ralston et al. (1), can be carried out in a liquid phase as a semi-continuous process or in the gas phase as a continuous one. Using either of the two routes a final product of good quality and with high yield is obtained (2,3). Small amounts of intermediate fatty acids, ammonium soaps and amides are also present. When unsaturated fatty acids are used as the starting reagents, cis-trans isomerization occurs during nitrile synthesis; this is the subject of our work.

EXPERIMENTAL PROCEDURES

Reagents. Oleic acid technical grade. Table 1 contains the chain length distribution as it exists in examined sample analyzed by GLC (4,5), liquid ammonia synthetic 99.9%, from high pressure gas cylinder 0.5 MPa.

Catalysts. Dehydration catalysts. Rhône-Poulenc (6) balls 2-4 mm diameter, and Harshaw Chemical Company rings, 3.5-1.5 mm (3), were used. The characteristics of their porous structure are given in Table 2.

The synthesis of nitriles. The process was carried out continuously in the gas phase. A metal apparatus of 1 dcm³ volume was used according to the general flowsheet in the brochure published by the Harshaw Chemicals Co. (3). The preheated mixed fatty acids and ammonia were charged continuously into a tube reactor filled with the catalyst. The process was carried out at a temperature of 280-360 C, an ammonia excess of 8-12:1 mol/mol and a catalyst load of 100-600 g • dm⁻³ • hr⁻¹. The reaction mixture was collected continuously and cooled. The nitriles were separated from the water layer and analyzed by GLC.

TABLE 1

Chain Length Composition of Oleic Acid (%)

C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	$C_{18=}$	$C_{18==}$	C_{20}	$C_{20=}$
0.1	0.4	2.1	6.3	3.6	75.9	8.4	0.5	0.8

TABLE 2

The Characteristics of the Porous Structure of the Catalysts

Catalysts	Surface area $m^2 \bullet g^{-1}$	Skeletal density $g \bullet cm^{-3}$	Particle density $g \bullet cm^{-1}$	Pore volume $cm^3 \bullet g^{-1}$	Average pore radius nm
Rhône Poulenc					
SCS 9	12.16	3.79	1.31	0.49	300
SCS 79	89.54	3.13	1.04	0.63	14.2
SCS 100	94.96	3.45	1.15	0.55	11.7
SCM 250	231.88	3.18	1.09	0.60	5.2
SCS 250	277.79	3.17	1.15	0.55	3.6
Harshaw					
Al-3996-R	180.0	3.43	0.55	0.64	13.6

TABLE 3

The Influence of the Al_2O_3 Catalysts Upon the Content of cis- and trans-Isomers Percent

| Catalyst	Temperature 320 C						Temperature 340 C					
	100 g•dm⁻³•hr⁻¹			200 g•dm⁻³•hr⁻¹			100 g•dm⁻³•hr⁻¹			200 g•dm⁻³•hr⁻¹		
	Hydrocarbons	trans-	cis-	Hydrocarbons	trans-	cis-	Hydrocarbons	trans-	cis-	Hydrocarbons	trans-	cis-
SCS 9	1.1	6.3	68.5	0.2	5.3	69.0	1.3	6.8	67.4	0.2	6.2	69.1
SCS 79	1.6	29.1	47.0	0.5	20.7	54.3	2.6	37.0	36.1	0.8	20.4	54.7
SCS 100	1.8	47.5	26.2	0.8	29.0	46.2	2.7	47.4	25.3	0.9	26.2	47.8
SCM 250	2.7	49.7	23.2	1.0	32.2	42.3	5.2	47.7	22.6	1.2	40.3	44.1
SCS 250	6.2	47.0	20.8	1.1	33.7	40.8	12.3	37.5	10.1	2.1	46.0	25.1
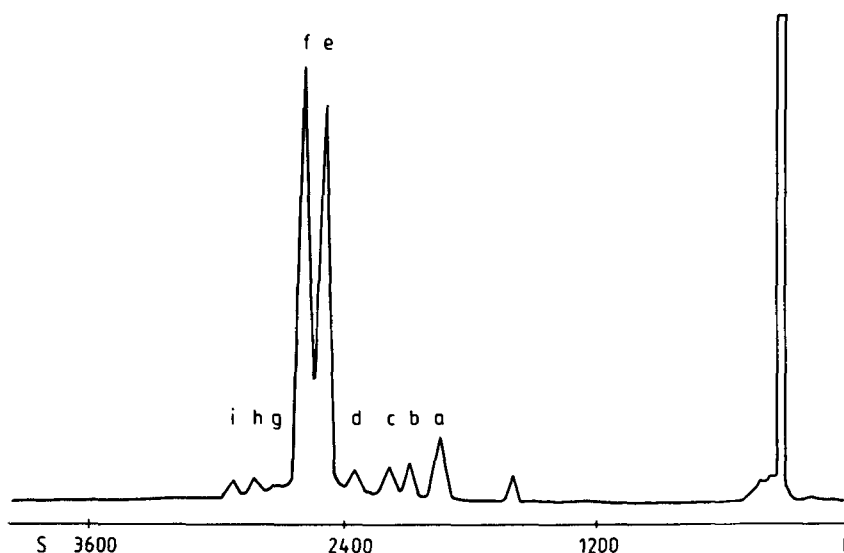
FIG. 1. Chromatogram of reaction products. a, Hexadecane nitrile; b, *trans*-9-hexadecene nitrile; c, *cis*-9-hexadecene nitrile; d, octadecane nitrile; e, *trans*-9-octadecene nitrile; f, *cis*-9-octadecene nitrile; g, eicosane nitrile; h, *cis*-9-eicosene nitrile; i, *cis*-9-eicosene nitrile.

ANALYTICAL METHODS

Gas chromatography. A gas chromatograph with a flame ionization detector was used. A stainless steel column of 2 m length and 3 mm i.d. was filled with W-NAW Chromosorb 80-100 mesh impregnated with 15% OV-275 silicon resin. The separated components were identified by comparison of their retention times with those of accessible standards. Quantitative determination was done using normalization, assuming correction factors as being 1 for all the components.

Potentiometric titration. The contents of fatty acid and ammonia soaps were determined by potentiometric titration (7).

RESULTS AND DISCUSSION

An exemplary chromatogram of the reaction product is shown in Figure 1. The *cis*- and *trans*- isomers were separated and pairs of geometric isomers (peaks e and f, b and c, h and i) are seen on the chromatograms. To study the effect of the catalyst type to be used on the isomers' level in the obtained products, the ammonolysis of oleic acid was carried out continuously in the presence of various dehydration catalysts produced by the Rhône-Poulenc Co. The results obtained, shown in Table 3, prove that, in each instance, the *cis*-9-octadecen nitrile obtained is accompanied by its geometric isomer, i.e., *tris*-9-octadecen nitrile. When shifting from the SCS 9 catalyst to SCS 250, an increased amount of the *trans*-isomer is observed. Similarly, the proportion of hydrocarbons in the products increases in the same sequence. For the SCS 9 catalyst, the content of the *trans*- isomer remains at a steady level of 5-7%, but for the SCM 250 and SCS 250 catalysts it amounts to 30-50% and is greatly influenced by the process temperature and the catalyst load.

For the catalysts investigated the *cis*- and *trans*-isomer rate in the products varies within limits from 10:1 to 1:4, depending on the process conditions. For the 3996R catalyst the content of the *cis*-isomer decreases from ca. 70% to 20% as the temperature increases from 280 C to 360 C (Fig. 2), while the content of the *trans* isomer increases first to 38% but, above 340 C, it decreases to 30%. This is caused by subsequent destruction reactions, which take place and lead to the
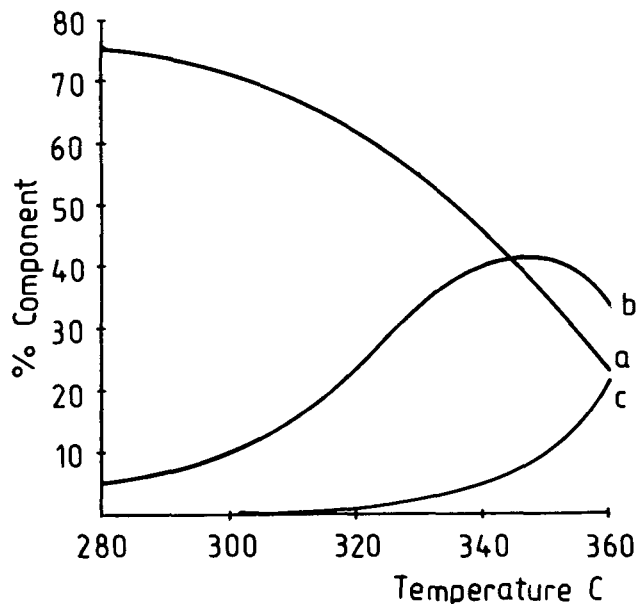

FIG. 2. The influence of the process temperature upon the contents of a, *cis*-9-octadecene nitrile; b, *trans*-9-octadecene nitrile; c, hydrocarbons. Catalyst, Al-3996-R; weight, hourly space velocity, 200 g•dm³•hr⁻¹. Excess NH₃, 8:1, mol/mol.

formation of hydrocarbons. The shape of the curves obtained suggests that mainly *trans*-isomers are degraded. The content of the *cis*-isomer increases with the increase in the catalyst load, and consequently with the decrease in mean residence time of the reagents in the reactor (Fig. 3,4). Simultaneously, the content of the hydrocarbons, decreases significantly. This effect disappears for higher catalyst loads and especially above 400 g•dm⁻³•hr⁻¹. Because the decrease of the catalyst load is also accompanied by a decrease in reaction time, a decrease in the *trans*-isomer content, also should be expected. However, this was observed only at 320 C. At higher temperatures, a well-marked maximum point for the load of 200 g•dm⁻³•hr⁻¹ was obtained. This supports the earlier conclusion that the hydrocarbons

present in the products are formed mainly from the *trans*-isomers. Thus, if the process is carried out at high temperatures and with low catalyst loads, the product can contain small amounts of the *trans*-isomers but quite large amounts of undesirable hydrocarbons.

Isomerization can occur during each of the subsequent steps of the process. This means that the initial fatty acids, their intermediate derivatives, i.e., ammonium soaps or amides, or even the final nitriles, can isomerize to the appropriate *trans*-isomers.

Nitrile isomerization is demonstrated in Figures 5 and 6, which show contents of *cis*- and *trans*-isomers after succeeding passes of the nitriles through the reactor filled with the catalyst. At 320 C after the first pass, the product contains 68% *cis*-9-octadecene nitrile,
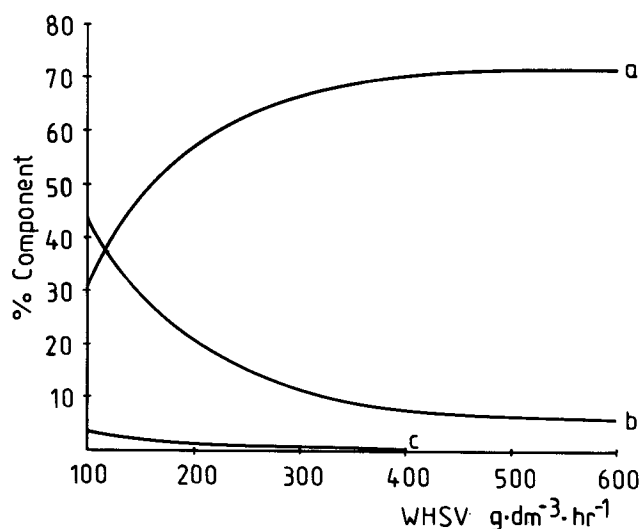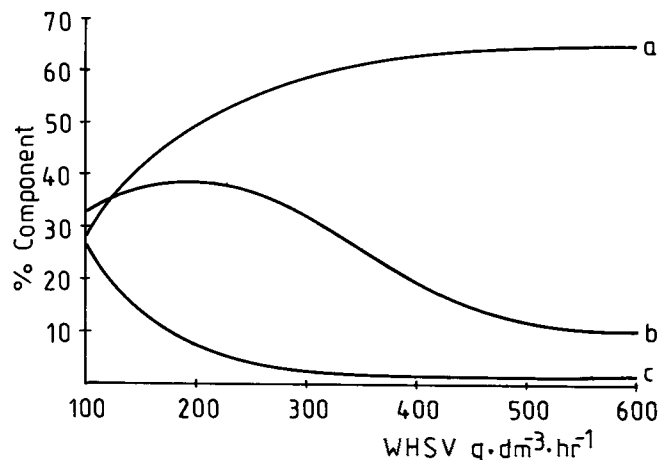

FIG. 3. The influence of the catalyst load upon the contents of the products. a, *cis*-9-octadecene nitrile; b, *trans*-9-octadecene nitrile; c, hydrocarbons. Catalyst, Al-3996-R; temperature, 320 C; excess NH₃, 8:1, mol/mol.
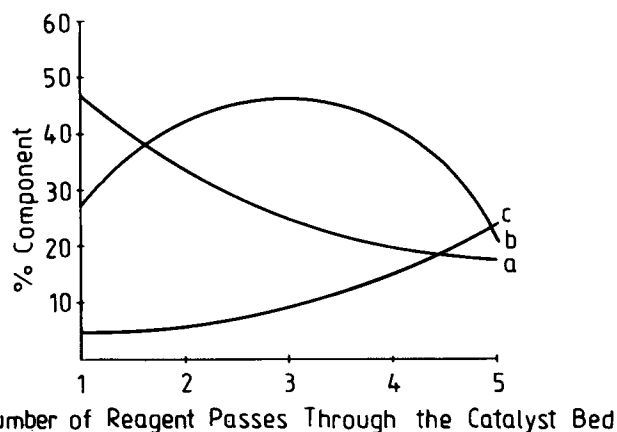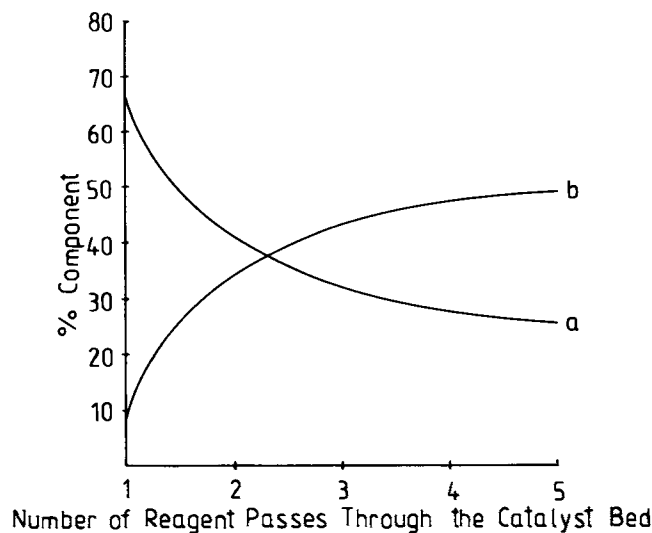

FIG. 5. The influence of the number of reagent passes through the catalyst bed. a, *cis*-9-octadecene nitrile; b, *trans*-9-octadecene nitrile; c, hydrocarbons. Catalyst, Al-3996-R; temperature 320 C; excess NH₃, 12:1, mol/mol. Weight, hourly space velocity, 250 g•dm⁻³•hr⁻¹.

FIG. 4. The influence of the catalyst load upon the contents of the products. a, *cis*-9-octadecene nitrile; b, *trans*-9-octadecene nitrile; c, hydrocarbons. Catalyst, Al-3996-R; temperature, 340 C; excess NH₃, 8:1, mol/mol.

FIG. 6. The influence of the number of reagent passes through the catalyst bed. a, *cis*-9-octadecene nitrile; b, *trans*-9-octadecene nitrile. Catalyst, Al-3996-R; temperature, 340 C; excess NH₃, 8:1. Weight, hourly space velocity, 200 g•dm⁻³•hr⁻¹.

the content of which decreases with each subsequent pass. Simultaneously, the content of *trans*-9-octadecene nitrile increases. Thus, after five succeeding passes the contents of *cis*- and *trans*- isomers are 25.4% and 49.8%, respectively. At 340 C the content of the *cis*-isomer also decreases after each subsequent pass, but the maximum of the *trans*-isomer content is observed after three passes, which is caused by subsequent degradation of the *trans*-isomer to hydrocarbons. This means that any unnecessary increase in reaction time does not change the conversion of fatty acids to nitrile (practically full conversion is obtained) but the increase changes the rate of *cis* to *trans*-isomerization which can influence the use properties of the final products. Higher amounts of hydrocarbons also can be formed at higher temperatures and low catalyst loads, which can decrease the yield of the product and its use properties.

Now, it is difficult to explain the mechanism of hydrocarbon formation. Hydrocarbons are degradation products, and they contain different homologues having fewer carbon atoms than the initial fatty acids. The shape of the kinetic curves really suggests that hydrocarbons are formed mainly from *trans*-isomers. However, it does not rule out the possibility that they may also be formed from *cis*-isomers, but at relatively low rates.

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