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Skeletal Rearrangement of Unsaturated Nitriles over Solid-Base Catalysts

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It was found that the skeletal rearrangement of unsaturated nitriles, such as methacrylonitrile to crotononitrile, took place readily over solid-base catalysts at the temperature range of 573 ~ 673 K. MgO and CaO have shown high activity for the reaction, while acidic catalysts are inactive. The product distribution in the arrangement of *trans*-pent-3-enenitrile and the rearrangement of ^{13}C-labeled methacrylonitrile suggested that the reaction path involves an asymmetric anionic intermediate formed by methyl hydrogen abstraction by the surface base site and a subsequent CN-migration. © 1993 Academic Press, Inc.

INTRODUCTION

We have reported that magnesium oxide supported transition metal cations catalyzed the vapour-phase condensation of methanol with saturated ketones, esters, or nitrile to form the corresponding α,β-unsaturated compounds (Eq. (1)) (*1–5*).

$$RCH_2Z + CH_3OH \xrightarrow[M-MgO]{} RC(=CH_2)Z + H_2 + H_2O \quad (1)$$

Z = COR, COOR, CN;

R = Alkyl.

For example, methacrylonitrile is synthesized in the high selectivity (above 95%) by the reaction of propionitrile with methanol over the Mn^{2+} ion-containing magnesium oxide catalyst. In this reaction, small amounts of *cis*- and *trans*-crotononitriles were also formed. These products are the structural isomers of methacrylonitrile which is the main product. Since the above condensation reaction proceeds via base-catalyzed Aldol-type condensation (*5*), the C–C bond formation takes place at the α-position of the reactants, yielding the iso-compound such as methacrylonitrile. Therefore, the formation of crotononitrile in the reaction is unusual from the mechanistic point of view. From separate experiments using methacrylonitrile as a reactant, the formation of crotononitrile in the condensation was, however, easily explained by our new finding that the skeletal rearrangement of methacrylonitrile to crotononitrile readily occurs over solid-base metal oxides (Eq. (2)) (*6*).

$$RCH{=}\underset{CN}{\underset{|}{C}}R' \rightleftharpoons R\underset{CN}{\underset{|}{C}}{=}CHR' \quad (2)$$

In this report we studied reaction mechanism of the skeletal rearrangement of unsaturated nitriles in order to clarify whether the reaction proceeds via alkyl migration or CN-migration and what the role of the solid-base is.

EXPERIMENTAL

Various metal oxide catalysts having acidic or basic properties were tested for the

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reaction. Unless noted otherwise, commercially available metal oxides (SiO_2; Matheson ID gel, SiO_2–Al_2O_3; GL Science N631-L, Si/Al = 6.1, others; Soekawa Rika, 99.9%) were used as catalyst and were heat-treated at 873 K for 2 h under a He gas stream prior to the reaction. For MgO catalysts two others were used besides the commercial oxide; two MgO were prepared by heat-decomposition of magnesium hydroxide (Kanto Kagaku, 99%) and basic magnesium carbonate (Kanto Kagaku, 99%) at 873 K for 2 h under the He gas stream. CaO catalysts besides commercial one were also prepared by heat-decomposition of calcium carbonate (Kanto Kagaku, 99%) or calcium hydroxide (Kanto Kagaku, 99%) under the same heating condition. Surface area was determined by BET method (N_2 adsorption at liquid-N_2 temperature).

Catalytic activity was determined using a pulse reactor connected directly to a gas chromatograph (PEG 1000, 2 m, 343 K), or a conventional fixed bed flow-reactor was employed. Details of the reaction conditions are described in the footnotes of the figures. All organic chemicals were reagent grade and used without further purification. Products were identified by GC-MS and ^{1}H-NMR spectroscopy (270 MHz).

^{13}C-tracer experiments were carried out as follows: 3-wt% Mn^{2+}–MgO was used as a catalyst (wt% is based on the amount of Mn ion). The preparation of the catalyst has been described in our previous paper (*5*). Briefly, commercial MgO was suspended in an aqueous solution of manganese nitrate (Kanto Kagaku, 99%) and then solidified again. The resulting solid was heat-treated under the condition as mentioned above. A mixture of propionitrile and 99% enriched ^{13}C-methanol (partial pressures 4 kPa respectively, remainder He, total flow rate 56 ml min^{-1}) was allowed to react over the catalyst (1 g) at 623 K using a conventional fixed-bed flow reactor. Under the condition, the conversion of propionitrile was 3% and the selectivities to methacrylonitrile and crotononitrile were 72 and 28%, respectively. After fractionating the collected products using a gas chromatograph (PEG 1000, 2 m, 343 K), each separated product was dissolved in $CDCl_3$ with TMS and was subjected to ^{13}C-NMR analysis (67.9 MHz) at room temperature.

RESULTS AND DISCUSSION

Skeletal Rearrangement of Methacrylonitrile to Crotononitrile

Table 1 summarizes the conversion and selectivity data in the rearrangement reaction of methacrylonitrile to crotononitrile over various metal oxide catalysts using the pulse reactor at 593 K. As the gas-phase reaction of this substrate was reported (*7*), the reaction was conducted in the absence of catalyst under the reaction conditions shown in Table 1, but no reaction was observed. Among the catalysts tested, MgO, CaO, and La_2O_3, all of which are well known as strong solid-bases, were found to be particularly active and selective for the rearrangement. The crotononitrile formed was a mixture of *cis*- and *trans*-isomers with a *cis*/*trans* ratio of 6/4, which is the thermodynamic equilibrium composition at the reaction temperature. A trace amount of allyl cyanide was also formed. The total carbon balance was close to 100% in each pulse with the exception of the initial one. The lower activity of La_2O_3 to the CaO or MgO may be due to its low surface area. SrO and Y_2O_3 which also belong to the solid-base group were almost inactive.

With weakly basic oxide catalysts such as ZnO and SnO_2, no reaction occurred. CuO, NiO, Fe_2O_3, MoO_3, and WO_3 were either inactive or decomposed the methacrylonitrile to acetonitrile. In case of the acidic catalysts, Al_2O_3 and/or SiO_2–Al_2O_3, on the other hand, conversions of methacrylonitrile were observed, but no crotononitrile was formed. No products could be collected; it seemed that a polymerization of methacrylonitrile took place over the acidic surface and the products were retained on the catalyst surface. From the above results

TABLE 1

Skeletal Isomerization of Methacrylonitrile over Various Metal Oxide Catalysts[a]

Catalyst	Conversion of methacrylonitrile (%)	Selectivity (%) to	
		Cis-crotononitrile	*Trans*-crotononitrile
MgO	5.5	57.4	42.6
CaO	7.7	59.4	40.6
SrO	0	—	—
La_2O_3	0.5	66.9	33.1
Y_2O_3	0	—	—
ZnO	0	—	—
SnO_2	0	—	—
NiO	0	—	—
CuO	5.4	0	0
Fe_2O_3	0	—	—
MoO_3	0	—	—
WO_3	0	—	—
Al_2O_3	5.7	0	0
SiO_2–Al_2O_3	2.8	0	0

[a] Reaction conditions: reaction temp., 593°C; catalyst weight, 50 mg; pulse size, 1 μl; carrier gas (He), 50 ml min^{-1}.

it is obvious that the skeletal rearrangement of methacrylonitrile was catalyzed by metal oxides which are strongly basic.

We further examined MgO and CaO catalysts prepared by the calcination of $Mg(OH)_2$, basic $MgCO_3$, and $CaCO_3$ at 873 K and the results are shown in Table 2. Clearly, every catalyst showed higher activities than the commercially available oxides simply because of the larger surface area. However, the activity of the MgO catalyst prepared from basic magnesium carbonate was exceptionally high and the selectivity to crotononitrile was slightly low compared with the other MgO catalysts. Since it was confirmed by XRD that the phase of each samples after the heat-treatment was the oxide, the difference of the activity seems to

TABLE 2

Skeletal Rearrangement of Methacrylonitrile over Various MgO and CaO Catalysts[a]

Catalyst			Conversion of methacrylonitrile (%)	Selectivity (%) to crotononitrile	
	Precursor	Surface area (m^2 g^{-1})		*Cis*-	*Trans*-
MgO	Commercial	11	5.5	57.4	42.6
	$Mg(OH)_2$	47	16.0	58.2	41.8
	$MgCO_3$ (basic)	94	72.9	44.3	31.4
CaO	Commercial	—	7.7	59.4	40.6
	$CaCO_3$	65	21.5	40.5	30.6

[a] Reaction conditions were the same as those of Table 1.

be caused by not only surface area but also the nature of surface base site.

Marked deactivation in every pulses was observed for the MgO catalysts prepared from basic magnesium carbonate. This may be due to the poisoning the strong surface base site by the deposition of carbonaceous species because small amounts of acetonitrile and propionitrile, which can be formed from methacrylonitrile decomposition, were detected during elution and also because CO_2 was detected by the injection of enough oxygen into the reactor. After the oxygen exposure, followed by heat-treatment at 873 K in a He stream, the original activity was restored.

We tested the catalytic activity of the MgO catalyst prepared from magnesium carbonate for the skeletal rearrangement of methacrylonitrile using a conventional fixed-bed flow reactor as well. Figure 1 shows the activity and selectivity changes as a function of the reaction time. The conversion of methacrylonitrile decreased drastically at the beginning of the reaction and gradually reached a steady state. The selectivities also changed markedly during this deactivation period and then stabilized.

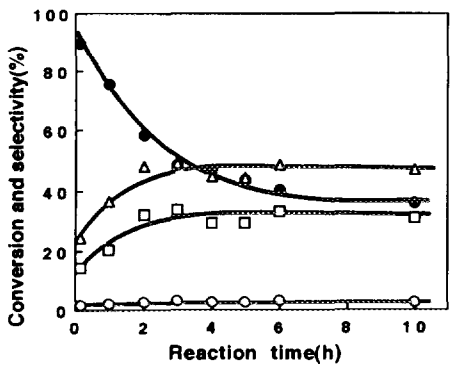


FIG. 1. Changes of the conversion of methacrylonitrile (●) and selectivities to *cis*-crotononitrile (△), *trans*-crotononitrile (□), and allyl cyanide (○) as a function of the reaction time. The skeletal rearrangement of methacrylonitrile was carried out using a flow reactor at 350°C over MgO catalyst (1 g) prepared from basic magnesium carbonate. Partial pressure of methacrylonitrile was 7.7 kPa (remainder He) and total flow rate was 43 ml min^{-1}.

Skeletal Rearrangement of Various Nitriles

In order to examine the reaction pathway for the skeletal rearrangement, we carried out the reactions of isobutyronitrile and 2-phenylpropene using the pulse reactor under the same reaction conditions as shown in Table 1. The MgO catalyst prepared from basic magnesium carbonate was used for the reactions. The reason for selecting isobutyronitrile is to check whether a C=C double bond is needed in the molecule; the reason for selecting 2-phenylpropene is to understand the effect of the substituent group phenyl vs CN. In both cases no reactions were observed; *n*-butyronitrile was not formed during the reaction of isobutyronitrile and the rearrangement of phenylpropene did not occur. Therefore, this type of rearrangement seems to be specific for unsaturated nitriles. These results suggest the possibility that the reaction path involves a anionic intermediate formed by hydrogen abstraction from a methyl group by the surface base site. Furthermore, the anionic intermediate would be formed more easily if the substituent group is more electron withdrawing (such as the CN group).

It would be interesting to know whether the alkyl or the CN group migrate. For this purpose, the rearrangement of *trans*-pent-3-enenitrile was carried out. There are 10 possible product isomers, as shown in Fig. 2. The isomers in group A can be formed via *cis–trans* isomerization and C=C double bond shift. The isomers in group C are possible if *CH_3-migration* takes place. For the isomers in group B, there are two possible paths: *CH_3-migration and CN-migration*. Then one can estimate from the isomer distribution in the reaction of *trans*-pent-3-enenitrile which pathway is used. The reaction data are listed in Table 3. The catalysts used in this experiment were MgO prepared from magnesium carbonate, CaO from $Ca(OH)_2$, and SiO_2 (silica gel).

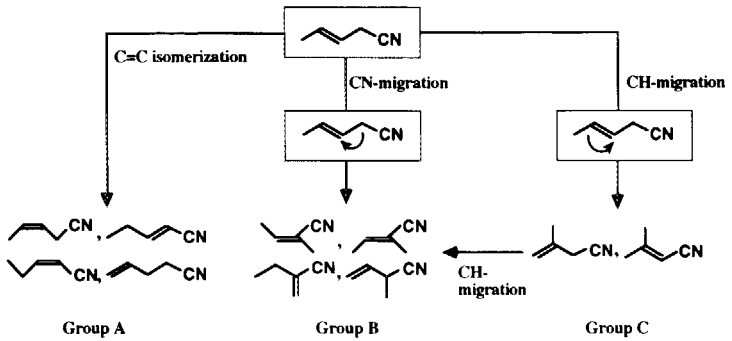
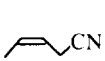
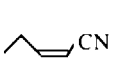
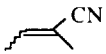
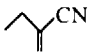
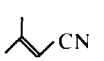
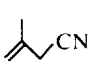


FIG. 2. Possible products of the isomerization of pent-3-enenitrile.

TABLE 3

Skeletal Rearrangement of *Trans*-pent-3-enenitrile (PEN)[a]

Catalyst	Reaction temperature (K)	Conversion of PEN (%)	Selectivity (%) to							
			Group A			Group B		Group C		CH_3CN
										
SiO_2-gel	623	62	3	36	61	0	0	0	0	0
MgO[b]	623	86	2	15	17	13	6	0	0	21
MgO[b]	643	91	1	9	8	20	4	0	0	29
CaO[c]	623	81	2	22	25	6	4	0	0	25

[a] Reaction conditions: catalyst weight, 30 mg; pulse size, 1 μl; carrier gas (He), 30 ml min^{-1}.
[b] Prepared from basic magnesium carbonate heated at 873°C.
[c] Prepared from calcium hydroxide heated at 873°C.

When SiO_2 was used as a catalyst, the products were *trans*- and *cis*-pent-2-enenitriles, and *cis*-pent-3-enenitrile. These products belong to the group A only, revealing that *cis–trans* isomerization and double bond isomerization took place over the SiO_2 catalyst. When *trans*-pent-3-enenitrile was allowed to react over the solid-base catalysts MgO and CaO, the reaction occurred readily with a conversion of more than 80% in each case and produced skeletal rearrangement isomers in addition to the isomers of the group A. All these skeletal isomers are found to belong to group B. Products of group C were not detected. Since the reaction is not selective, as can be seen in Table 3, and many other side reactions such as decomposition and CN-elimination take place at the same time, one may think that the isomers of group C reacted further to give the isomers of group B even if these isomers were formed once via CH_3-migration. To test this, we carried out the reaction of 3-methylbut-2-enenitrile which belongs to group C and has a molecular structure not possible for 1,2 CN-migration. The reaction conditions were same as those of Table 3 and the MgO catalyst prepared from basic magnesium carbonate was used. 3-Methylbut-2-enenitrile was found inactive under the present reaction conditions and no reaction was observed over the MgO catalyst. In addition, if the isomers of group B could form from the isomers of group C, 3-methylbut-2-enenitrile, for example, should exist in the products on thermodynamic grounds. However the result was negative; no 3-methylbut-2-enenitrile was formed. These results, therefore, clearly imply that the skeletal rearrangement proceed via a CN-migration pathway.

^{13}C-Tracer Study by NMR

We carried out ^{13}C-tracer experiments in order to confirm the CN migration mechanism in the skeletal rearrangement over solid-base catalysts. If methacrylonitrile is tagged with ^{13}C atoms both at methyl carbon and at methylene carbon as in Eq. (3), it will be possible to determine which migrations really occur by analyzing whether the carbon bound to CN group of crotononitrile is labeled with ^{13}C or not.

$$CH_3CH_2CN + {}^{13}CH_3OH \rightarrow {}^{13}CH_2{=}C(-{}^{13}CH_3)-CN \quad (3)$$

$$\xrightarrow{\text{CN-migration}} {}^{13}CH_3-CH={}^{13}CH-CN \qquad \xrightarrow{\text{CH-migration}} {}^{13}CH_3-{}^{13}CH=CH-CN$$

We were able to synthesize such ^{13}C-labeled methacrylonitrile by the condensation reaction (Eq. (1)) with propionitrile and ^{13}C-enriched methanol over Mn^{2+}–MgO catalyst and at the same time crotononitrile can be formed from the formed methacrylonitrile by the skeletal rearrangement over the catalyst. Therefore, the purpose will be achieved by the determination of the position of ^{13}C-enriched carbon in crotononitrile which is produced at the same time during the condensation reaction of propionitrile with ^{13}C-methanol.

In this experiment 3-wt% Mn^{2+}–MgO catalyst was used due to the fact that MgO catalyst was inactive for the condensation reaction of propionitrile and methanol (*2*). Since crotononitrile cannot be a primary product of the condensation reaction from the reaction mechanism reason reported previously (*4*, *5*), it seems that the skeletal rearrangement of methacrylonitrile to crotononitrile takes place over the MgO surface even in the presence of Mn ions. Figure 3 shows the ^{13}C-NMR spectrum of the methacrylonitrile produced by the condensation

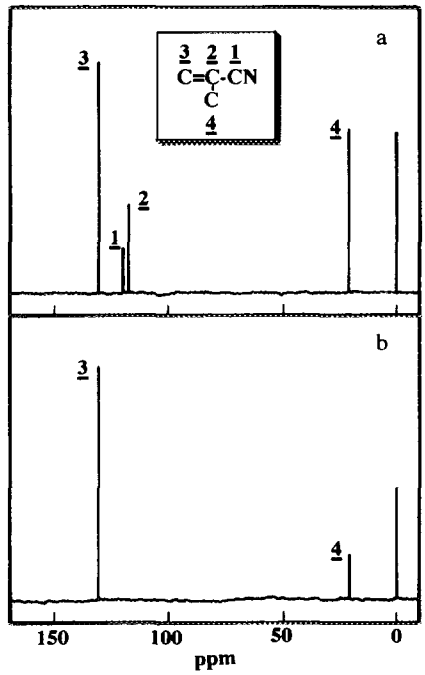


FIG. 3. ^{13}C-NMR spectra (67.9 MHz) of (a) natural-abundance methacrylonitrile and (b) ^{13}C-enriched methacrylonitrile synthesized by the condensation of propionitrile and ^{13}C-methanol.

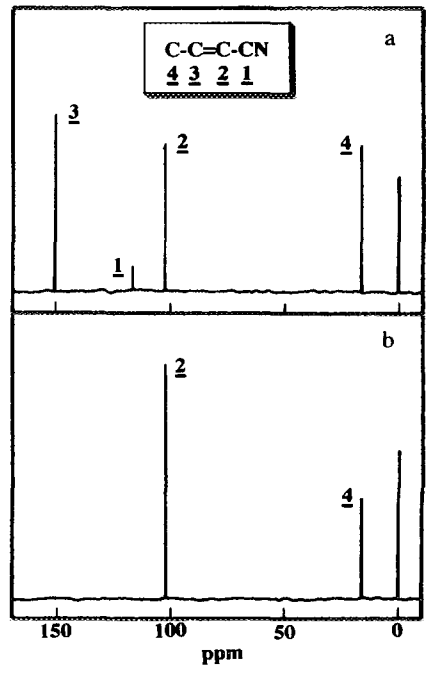
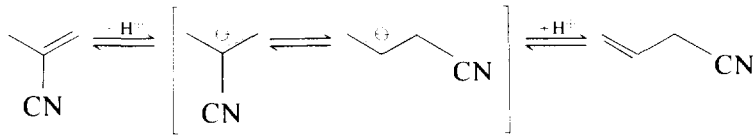


FIG. 4. ^{13}C-NMR spectra (67.9 MHz) of (a) natural-abundance crotononitrile and (b) ^{13}C-enriched crotononitrile formed by the skeletal rearrangement during the condensation of propionitrile and ^{13}C-methanol.

reaction over the Mn^{2+}–MgO catalyst (Fig. 3b) in addition to that of natural-abundance methacrylonitrile (Fig. 3a). Similarly, Fig. 4 shows ^{13}C-NMR spectra of crotononitrile. As expected from the condensation reaction (Eq. (1)), the methacrylonitrile contained ^{13}C atom at both methyl group and methylene group and no ^{13}C atoms were found at the tertiary carbon and CN group. In addition, the peak intensity of methyl carbon is apparently smaller than that of methylene one, compared with the relative intensity of each peaks of natural-abundance methacrylonitrile. This implys that the rate of C=C double bond isomerization of methacrylonitrile is not very large under the conditions of the condensation.

The crotononitrile formed from the skeletal rearrangement of the above mentioned ^{13}C-labeled methacrylonitrile were located at the 2- and 4-positions exclusively (Fig. 4). This can be explained only by a CN-migration mechanism. If the CH_3-migration takes place, then one must observe ^{13}C atoms at the 3-position of crotononitrile. As reported for plasma-induced isomerization of nitriles (*8*), the isomerization mechanism is thought to proceed via a cyclopropane intermediate and a subsequent C–C bond fission of the cyclopropane ring. However, this mechanism gives the same position of ^{13}C atom at the CH_3-migration mechanism, so that it can be also ruled out.

All of the results clearly support the skeletal rearrangement of unsaturated nitriles proceeds via CN-migration. As a consequence, the following reaction scheme can be written:



Hydrogen abstraction takes place first to give anionic intermediate, which could be the slow step of the overall reaction. In this step, the surface basic site plays an important role for abstracting a proton from the reactant. Then the CN group migrates to the terminal carbon. After reprotonation the reaction is completed.

From Fig. 4 one may note that the peak intensity of the C atom at the 4-position is lower than that at the 2-position. If a symmetric, delocalized π-allyl intermediate forms on the catalyst surface, then the peak intensity ratio of two carbons should be the same as that of natural-abundance sample. Therefore, the result indicates that the anionic intermediate is asymmetric and the CN-migration occurs to olefinic carbon dominantly. There seems to be a CN-migration preference caused by adsorption states on the surface.

In conclusion, the skeletal rearrangement of unsaturated nitriles was found to take place over solid-base catalysts. MgO and CaO are particularly active for the reaction, while acidic catalysts are inactive. It is suggested that the reaction path involves an asymmetric anionic intermediate formed by proton abstraction on the methyl group, and then CN-group-migration.

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