

Ruthenium-catalyzed dimerization of acrylonitrile in the presence of carboxylic acids

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Dedicated to the memory of Professor Katsuo Ohkata.

Abstract

A new ruthenium-based catalytic system for the tail-to-tail dimerization of acrylonitrile has been developed. The addition of carboxylic acids effectively increased the selectivity toward linear dimers, while suppressing the formation of propionitrile, an undesired by-product. Thus, under optimized conditions, the selectivity for linear dimers reached 85.8%. The carboxylic acids are considered to be involved in the protonolysis of the ruthenium–carbon bond of precursors to the product dimers. In accordance with this hypothesis, a linear relationship was observed between the logarithm of the relative rate of dimerization and the pK_a value of substituted benzoic acids. It has also been found that the new catalytic system promotes decomposition of 2-cyanoethyl carboxylate, a main Michael addition by-product in the dimerization, to acrylonitrile and the corresponding carboxylic acid under the dimerization conditions. This leads to an increase in the selectivity for linear dimers. A plausible mechanism for the dimerization is proposed.

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1. Introduction

Transition metal-catalyzed dimerization of olefins is useful for synthesizing intermediates for fine and commodity chemicals [1–7]. Considerable attention has been focused on the tail-to-tail dimerization of acrylonitrile (AN), since it provides an attractive alternative route to hexamethylenediamine, one of the monomers used in the production of Nylon-6,6 [8,9].

Previously, we reported that a catalytic system [RuCl₂(DMSO)₄/CH₃CH₂COONa/DMSO/carboxylic acid] effectively promoted tail-to-tail dimerization of AN (TON = 1206) without the formation of propionitrile (PN) and proposed a mechanism involving the protonolysis of the carbon–ruthenium bond of precursors to dimeric products by added carboxylic

acids [10a]. Herein we report on the relationship between the pK_a value of carboxylic acids and catalytic activity. We also describe the catalytic decomposition of 2-cyanoethyl carboxylate (CEC) **4**, a main by-product derived from carboxylic acid, to AN under the dimerization conditions. A part of this work has been reported in preliminary form [10b].

2. Experimental

All reagents were purchased from Wako Pure Chemical Industries, Tokyo Kasei Kogyo, Aldrich, or Ishizu Seiyaku and used without purification. RuCl₂(DMSO)₄ was prepared from RuCl₃·3H₂O and DMSO as reported previously [11]. The yield of dimers **1–3** is defined as follows: yield of dimers **1–3** = 100 × [2 × (combined moles of dimers **1–3**)]/[moles of charged AN]. The selectivity for dimers **1–3** is defined as follows: selectivity of dimers **1–3** = 100 × [2 × (combined moles of dimers **1–3**)]/[moles of converted AN]. The catalyst turnover number (TON) for dimers **1–3** is defined as fol-

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lows: $\text{TON} = [2 \times (\text{combined moles of dimers } \mathbf{1-3}) / (\text{moles of Ru})]$. The yield of **4** is defined based on charged AN: yield of **4** = $100 \times (\text{moles of } \mathbf{4}) / (\text{moles of charged AN})$. The selectivity of **4** is defined based on converted AN: selectivity of **4** = $100 \times (\text{moles of } \mathbf{4}) / (\text{moles of converted AN})$.

2.1. Cyanoethyl propionate **4a**

To a stirred mixture of propionic anhydride (100.6 g, 1.00 mol) and ethylene cyanohydrin (42.6 g, 1.00 mol) was added pyridine (6.00 g, 0.0759 mol) over 10 min at room temperature. The mixture was refluxed for 1 h. Aqueous NH_4Cl was added to the mixture at room temperature. The organic layer was extracted with diethyl ether. The extract was washed with saturated aqueous NaCl and dried over Na_2SO_4 . The solution was evaporated and the residue was purified by vacuum distillation to give 50.4 g (40%) of a colorless oil **4a** (bp 116–117 °C/25 mmHg). IR (neat, cm^{-1}): 2985, 2946, 2255, 1743, 1464, 1421, 1385, 1352, 1275, 1179, 1087, 1037. $^1\text{H NMR}$ (CDCl_3): δ 1.17 (t, $J = 8$ Hz, 3H), 2.40 (q, $J = 8$ Hz, 2H), 2.71 (t, $J = 6$ Hz, 2H), 4.29 (t, $J = 6$ Hz, 2H). Anal. Calcd. for $\text{C}_6\text{H}_9\text{NO}_2$: C, 56.68; H, 7.13; N, 11.02. Found: C, 56.42; H, 7.08; N, 10.89.

2.2. Cyanoethyl *o*-benzoylbenzoate **4b**

A mixture of *o*-benzoylbenzoic acid (5.00 g, 22.1 mmol) and thionyl chloride (3.2 mL) was refluxed for 2 h. The excess thionyl chloride was removed under reduced pressure. Pyridine (4 mL) and ethylene cyanohydrin (1.65 g, 23.2 mmol) were added to the residue and the mixture was stirred overnight. Toluene and water were then added. The extracted organic layer was washed with 2 M hydrochloric acid and a 5% aqueous NaHCO_3 solution and dried over Na_2SO_4 . The solution was evaporated and the residue was purified by silica gel column chromatography. Recrystallization from toluene gave 0.43 g (7%) of a colorless crystal. IR (KBr, cm^{-1}): 2253, 1780, 1725, 1672, 1597, 1580, 1449, 1278, 1136, 1087, 933, 769, 703, 637. $^1\text{H NMR}$ (CDCl_3) δ 2.55 (t, $J = 8$ Hz, 2H), 4.30 (t, $J = 8$ Hz, 2H), 7.4–7.8 (m, 8H), 8.2 (m, 1H). Anal. Calcd. for $\text{C}_{14}\text{H}_{10}\text{O}_3$: C, 74.33%; H, 4.46%. Found: C, 74.40%; H, 4.47%.

2.3. Additive effect of 2-cyanoethyl propionate **4a** on the catalytic dimerization reaction of AN (Table 1; entry 2)

A mixture of AN (15.00 g, 282.7 mmol), $\text{RuCl}_2(\text{DMSO})_4$ (0.184 g, 0.380 mmol), ethylbenzene (4.00 g, 380 mmol: internal standard for gas chromatography), propionic acid (2.52 g, 34.0 mmol), DMSO (0.515 g, 6.60 mmol), $\text{C}_2\text{H}_5\text{CO}_2\text{Na}$ (0.183 g, 1.90 mmol), and 2-cyanoethyl propionate **4a** (4.32 g, 34.0 mmol) was heated under a nitrogen atmosphere to 150 °C and kept at that temperature for 6 h in a 100 mL stainless steel autoclave equipped with a glass insert tube. The obtained mixture was analyzed by gas chromatography on a 10% PEG20M/Chromosorb W(AW-DMCS) column. The conversion of AN was 31.0%. The yields of the products were as follows: *cis*-**1** 9.50%, *trans*-**1** 11.65%, adiponitrile **2** 1.14%, *cis,cis*-**3** 0.51%, *cis,trans*-**3** 1.22%, *trans,trans*-**3** 0.68%, PN **5** 19.4%

(selectivity 6.3%), and 2-cyanoethyl propionate **4a** 3.0% (selectivity 9.6% based on AN). The overall yield of linear dimers **1–3** was 24.7% (TON 184) and the selectivity for linear dimers **1–3** was 79.7%.

The yield of **4a** was defined based on charged AN: yield of **4a** = $100 \times [(\text{moles of } \mathbf{4a}) - (\text{moles of added } \mathbf{4a})] / (\text{moles of charged AN})$. The selectivity of **4a** was defined based on converted AN: selectivity of **4a** = $100 \times [(\text{moles of } \mathbf{4a}) - (\text{moles of added } \mathbf{4a})] / (\text{moles of converted AN})$.

2.4. Dimerization of acrylonitrile (AN) in the presence of carboxylic acids at 150 °C for 6 h (Table 2)

2.4.1. General method

An example of *o*-benzoylbenzoic acid as the carboxylic acid is shown. A mixture of AN 15.00 g (282.7 mmol), anisole (internal standard for gas chromatography) 2.00 g (18.5 mmol), DMSO 0.50 g (6.4 mmol), $\text{RuCl}_2(\text{DMSO})_4$ 0.0185 g (0.0382 mmol), sodium propionate 0.0294 g (0.306 mmol), and *o*-benzoylbenzoic acid 1.29 g (5.70 mmol) was stirred in a 100 mL autoclave with a glass insert tube at 150 °C for 6 h under argon. The obtained mixture was analyzed by gas chromatography on a 10% PEG20M/Chromosorb W(AW-DMCS) column. The conversion of AN was 15.5%. The yields of products were as follows: *cis*-**1** 5.63%, *trans*-**1** 6.27%, adiponitrile **2** 0.20%, *cis,cis*-**3** 0.15%, *cis,trans*-**3** 0.50%, *trans,trans*-**3** 0.25%, PN **5** 0.50% (selectivity 3.2%), and 2-cyanoethyl *o*-benzoylbenzoate **4b** 1.20% (selectivity 7.7%). The overall yield of the linear dimers **1–3** was 13.0% (TON 960) and the selectivity for the linear dimers **1–3** was 83.9%. 2-Cyanoethyl *o*-benzoylbenzoate **4b** was analyzed by gas chromatography on a OV-17/Chromosorb W(AW-DMCS) column.

2.5. Time profile of dimerization of AN at 120 °C

A mixture of AN 15.00 g (282.7 mmol), anisole (internal standard for gas chromatography) 2.00 g (18.5 mmol), DMSO 0.50 g (6.4 mmol), $\text{RuCl}_2(\text{DMSO})_4$ 0.0185 g (0.0382 mmol), sodium propionate 0.0294 g (0.306 mmol), and a carboxylic acid (5.70 mmol) was stirred at room temperature under argon. The obtained mixture was divided 1.2 mL each into 3 mL stainless steel pressure vessels under argon. The dimerization reaction was carried out at 120 °C. The produced dimers **1–3** were analyzed by gas chromatography.

2.6. Ruthenium (II) carboxylate complex $[\text{Ru}(\text{C}_4\text{H}_3\text{SCO}_2)_2(\text{H}_2\text{O})(\text{DMSO})_3]$

A mixture of $\text{RuCl}_2(\text{DMSO})_4$ 0.50 g (1.0 mmol), 2-thiophenecarboxylic acid 1.00 g (7.80 mmol), sodium carbonate 0.60 g (5.7 mmol), and CH_2Cl_2 5 mL was stirred for 1 h at room temperature. Toluene 50 mL and a 5 wt.% aqueous Na_2CO_3 solution were added to the mixture. The organic layer was dried over Na_2SO_4 . The solution was evaporated and a yellow powder 0.4653 g (yield 74%) was obtained. This powder could be purified by recrystallization from CH_2Cl_2 –toluene. IR (KBr, cm^{-1}): 3300–2200, 3013, 2925, 1573, 1525, 1423, 1373, 1333, 1113,

1017. ^1H NMR (CDCl_3) δ 3.2–3.6 (18H), 7.05 (2H), 7.3 (2H), 7.6 (2H), 9.9 (2H). Anal. Calcd. for $\text{C}_{14}\text{H}_{26}\text{O}_8\text{S}_5\text{Ru}$: C, 31.62%; H, 4.31%; O, 21.06%. Found: C, 31.67%; H, 4.26%; O, 21.23%.

2.7. Dimerization of AN using $\text{Ru}(\text{C}_4\text{H}_3\text{SCO}_2)_2(\text{H}_2\text{O})(\text{DMSO})_3$

A mixture of $\text{Ru}(\text{C}_4\text{H}_3\text{SCO}_2)_2(\text{H}_2\text{O})(\text{DMSO})_3$ 0.015 mmol, DMSO 2.56 mmol, 2-thiophenecarboxylic acid 2.26 mmol, anisole 0.800 g (as an internal standard for gas chromatography), and AN 113 mmol was heated at 150°C for 6 h under argon. The conversion of AN was 11.8%. The yields of the products were as follows: DCB **1** 8.94%, DCBD **3** 1.06%, AND **2** 0.12%, 2-cyanoethyl 2-thiophenecarboxylate 0.50%, PN **5** 0.59%. The total yield of the dimers was 10.1% (selectivity 85.8%) with a TON of 762.

A similar result was obtained for the dimerization of AN, when a mixture of $\text{RuCl}_2(\text{DMSO})_4$ 0.015 mmol, and sodium propionate 0.033 mmol was used as catalyst instead of $\text{Ru}(\text{C}_4\text{H}_3\text{SCO}_2)_2(\text{H}_2\text{O})(\text{DMSO})_3$.

2.8. Dimerization of AN in the absence of hydrogen and carboxylic acid

A mixture of AN 15.00 g (282.7 mmol), anisole (internal standard for gas chromatography) 2.00 g (18.5 mmol), DMSO 0.50 g (6.4 mmol), $\text{RuCl}_2(\text{DMSO})_4$ 0.0185 g (0.0382 mmol), and sodium propionate 0.0294 g (0.306 mmol) was stirred in a 100 mL autoclave with a glass insert tube for 6 h at 150°C under argon. The obtained mixture was analyzed by gas chromatography. The conversion of AN was 3.7%. The yields of the products were as follows: *cis*-**1** 0.05%, *trans*-**1** 0.06%, *cis,cis*-**3** 0.31%, *cis,trans*-**3** 0.72%, *trans,trans*-**3** 0.35% and PN **5** 1.58% (selectivity 43%). The overall yield of linear dimers was 1.48% (TON 110) and the selectivity for linear dimers was 40%.

3. Results and discussion

3.1. Additive effect of CEC **4**

We reported previously that the tail-to-tail dimerization of AN by Ru catalysts yielded a mixture of 1,4-dicyanobut-1-ene (*cis*- and *trans*-DCB) **1**, adiponitrile (ADN) **2**, and 1,4-dicyanobuta-1,3-diene (*cis,cis*-, *cis,trans*- and *trans,trans*-

DCBD) **3** along with 2-cyanoethyl carboxylate (CEC) **4** and propionitrile (PN) **5** as by-products (Scheme 1) [10a].

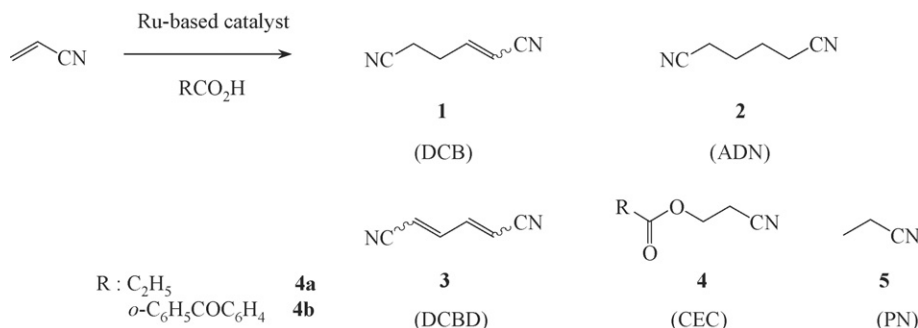
This catalytic system made it possible to avoid the production of PN **5**, which was a main by-product resulting from hydrogenation of the starting material (AN) when the reaction was carried out in the presence of hydrogen. But CEC **4** newly formed as a major undesired by-product by the Michael addition of carboxylic acids to AN.

The β -elimination of carboxylic acids from CEC **4** has been known to occur readily [12]. We have previously found that the quantitative reproduction of AN and carboxylic acid from CEC **4** can be achieved also by ruthenium catalysts [13]. We reckoned that if the reproduction of AN and carboxylic acid from CEC **4** were possible in the dimerization reaction of AN, we would be able to decrease the production of CEC **4**. Thus, we examined the addition of 2-cyanoethyl propionate **4a** into the dimerization reaction mixture at the beginning of the reaction. Table 1 shows the additive effect of **4a**.

The quantity of the formed 2-cyanoethyl propionate **4a** decreased by the addition of 2-cyanoethyl propionate **4a** (entry 2). The selectivity for dimers **1–3** improved dramatically to 79.7%. The conversion of AN became high with an increase in the ruthenium catalyst, but the TON of the Ru catalyst decreased drastically (entries 2–4). In entry 5, no formation of 2-cyanoethyl propionate **4a** was observed. In this case the catalytic conversion of AN to dimers occurred with both the highest selectivity (86.8%) and the highest TON (418) for the dimerization of AN using propionic acid. The dimerization of AN in the presence of carboxylic acid without the production of CEC **4** could be achieved for the first time. When *o*-benzoylbenzoic acid, which was reported to be the favorite carboxylic acid for the dimerization of AN [10], was used, only a minimal additive effect of 2-cyanoethyl *o*-benzoylbenzoate **4b** was observed [14]. It is attributed to the fact that the nucleophilicity of *o*-benzoylbenzoic acid weaker than that of propionic acid lowered the rate of addition of the carboxylic acid to AN. This made the addition comparable with or slower than the rate of the reverse reaction to regenerate the carboxylic acid from CEC **4**.

3.2. Influence of the $\text{p}K_a$ of carboxylic acids in the Ru-catalyzed dimerization of AN

We reported previously that the TON for the dimerization of AN was greatly dependent on the carboxylic acid



Scheme 1. Ru-catalyzed dimerization of acrylonitrile in the presence of carboxylic acids.

Table 1
Additive effect of 2-cyanoethyl propionate **4a** on the dimerization of acrylonitrile (AN)^a

Entry	RuCl ₂ (DMSO) ₄ (mmol)	Temperature (°C)	Conversion of AN (%)	Combined selectivity of dimers 1–3 (%) and (TON)	Selectivity for 2-cyanoethyl propionate 4a (%)
1 ^b	0.38	150	33.0	54.7 (134)	37.0
2	0.38	150	31.0	79.7 (184)	9.6
3 ^c	0.76	150	33.4	85.2 (106)	3.0
4	0.08	150	10.2	73.2 (264)	19.6
5 ^d	0.08	150	13.6	86.8 (418)	0

^a Reaction conditions: AN 282.7 mmol, ethylbenzene 38.0 mmol, propionic acid 34.0 mmol, sodium propionate 1.90 mmol, DMSO 6.60 mmol, 2-cyanoethyl propionate **4a** 34.0 mmol, 150 °C, 6 h.

^b 2-Cyanoethyl propionate **4a** was not added. Propionic acid 68 mmol, sodium propionate 1.14 mmol.

^c Sodium propionate 2.28 mmol.

^d 2-Cyanoethyl propionate **4a** 51.0 mmol.

used and that the carboxylic acid functioned in the protonolysis step [10]. In order to investigate the protonolysis step, we have studied the relationship between catalytic activity and the acidity of carboxylic acids in this catalytic system. In a typical reaction by RuCl₂(DMSO)₄ (0.0382 mmol) and DMSO (6.4 mmol) at 150 °C for 6 h in the presence of sodium propionate (0.306 mmol) and *o*-benzoylbenzoic acid (5.70 mmol) in AN (282.7 mmol), the conversion of AN was 15.5%. The products and their yields were as follows: *cis*-DCB **1** (5.63%), *trans*-DCB **1** (6.27%), ADN **2** (0.20%), *cis,cis*-DCBD **3** (0.15%), *cis,trans*-DCBD **3** (0.50%), *trans,trans*-DCBD **3** (0.25%), PN **5** (0.50%) (selectivity 3.2%), and 2-cyanoethyl *o*-benzoylbenzoate (1.20%) (selectivity 7.7%). The overall yield of linear dimers **1–3** was 13.0% (TON 960) and the selectivity for dimers was 83.9%.

Table 2 shows the TON values for the Ru-catalyzed dimerization of AN at 150 °C for 6 h in the presence of various carboxylic acids. Fig. 1 shows the relationship between TON and p*K*_a values.

The TON in the catalyzed reaction by *m*- and *p*-substituted benzoic acids increased with smaller p*K*_a (in stronger acid), while such a relationship was not observed between the TON and the p*K*_a of aliphatic carboxylic acids. *o*-Benzoylbenzoic acid and anthranilic acid gave high TON in comparison with carboxylic acids of similar p*K*_a. It is probably related to the favorable coordination of a carboxylic acid to ruthenium by substitution in the protonation step. A lot of other bulky *o*-substituted benzoic

acids gave low TON. On the other hand, aliphatic carboxylic acids with bulky alkyl groups gave high TON. The effective acidity of carboxylic acids for optimum TON was around p*K*_a 3–3.5 and the use of *o*-benzoylbenzoic acid as the proton source gave rise to the highest TON in the present experiments. Almost all of the Ru catalyst was deactivated after 6 h under these conditions (150 °C). Thus, even when the dimerization reaction of AN was continued for 9 h, the TON for dimers did not increase.

Phenol as well as *p*-toluenesulfonic acid and trifluoroacetic acid were ineffective as proton sources for the dimerization [19]. Thus we concluded that the active Ru-catalyst for the dimer-

Table 2
TON for the dimerization of acrylonitrile (AN) at 150 °C for 6 h in the presence of various carboxylic acids

Carboxylic acid	p <i>K</i> _a	TON
Aliphatic carboxylic acid		
CH ₃ CO ₂ H	4.76 ^a	193
(CH ₃) ₂ CHCO ₂ H	4.86 ^a	300
C ₂ H ₅ CO ₂ H	4.88 ^a	211
(CH ₃) ₃ CCO ₂ H	5.03 ^a	308
Aromatic carboxylic acid		
C ₆ H ₅ CO ₂ H	4.20 ^b	636
<i>p</i> -Cl-C ₆ H ₄ CO ₂ H	3.83 ^b	616
<i>p</i> -CH ₃ -C ₆ H ₄ CO ₂ H	4.24 ^b	355
<i>p</i> -CH ₃ O-C ₆ H ₄ CO ₂ H	4.47 ^b	346
<i>m</i> -NC-C ₆ H ₄ CO ₂ H	3.60 ^b	778
<i>m</i> -Cl-C ₆ H ₄ CO ₂ H	3.99 ^b	705
<i>m</i> -CH ₃ O-C ₆ H ₄ CO ₂ H	4.09 ^b	443
<i>m</i> -CH ₃ -C ₆ H ₄ CO ₂ H	4.34 ^b	379
<i>o</i> -Cl-C ₆ H ₄ CO ₂ H	2.94 ^b	859
<i>o</i> -F-C ₆ H ₄ CO ₂ H	3.27 ^b	727
<i>o</i> -C ₆ H ₅ CO-C ₆ H ₄ CO ₂ H	3.54 ^c	960
<i>o</i> -CH ₃ -C ₆ H ₄ CO ₂ H	3.91 ^b	442
<i>o</i> -CH ₃ O-C ₆ H ₄ CO ₂ H	4.09 ^b	195
<i>o</i> -H ₂ N-C ₆ H ₄ CO ₂ H	4.98 ^b	470
2,6-Cl ₂ -C ₆ H ₃ CO ₂ H	1.82 ^d	645

Reaction conditions: AN 282.7 mmol, anisole 18.5 mmol, DMSO 6.4 mmol, RuCl₂(DMSO)₄ 0.0382 mmol, sodium propionate 0.306 mmol, acid 5.70 mmol, 150 °C, 6 h.

^a p*K*_a value taken from [15].

^b p*K*_a value taken from [16].

^c p*K*_a value taken from [17].

^d p*K*_a value taken from [18].

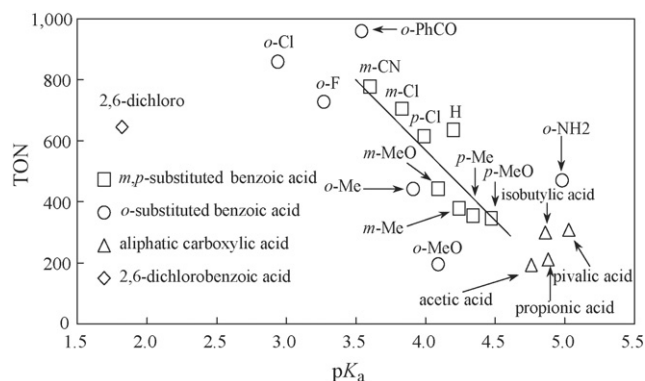


Fig. 1. Relationship between the TON for the dimerization of acrylonitrile and the p*K*_a of carboxylic acids.

Table 3

Time profile of the dimerization of acrylonitrile (AN) in the presence of substituted benzoic acids at 120 °C^a

Substituent	pK _a	TON				
		4 h	9 h	14 h	19 h	24 h
H	4.20	69	147	241	325	402
<i>m</i> -CH ₃	4.24	70	140	230	310	372
<i>p</i> -CH ₃	4.34	65	144	200	304	342
<i>m</i> -CH ₃ O	4.09	72	151	242	306	400
<i>p</i> -CH ₃ O	4.47	71	126	200	298	335
<i>m</i> -Cl	3.83	79	188	305	377	468
<i>p</i> -Cl	3.99	70	153	253	324	397
<i>m</i> -CN	3.60	96	187	326	408	504

4, 9, 14, 19 and 24 h represent reaction time.

^a Reaction conditions: AN 282.7 mmol, anisole 18.5 mmol, DMSO 6.4 mmol, RuCl₂(DMSO)₄ 0.0382 mmol, sodium propionate 0.306 mmol, acid 5.70 mmol.

ization was produced in the presence of only carboxylic acids having pK_a of 1.8–5.0 while such an active catalyst was not formed in the presence of strong acids such as sulfonic acid and trifluoroacetic acid.

Table 3 shows the time profile of the dimerization and the influence of the acidity (pK_a) of the carboxylic acid on the TON of dimerization at 120 °C. The reaction at 120 °C proceeded for 24 h at the same rate without deactivation of the catalyst. The relationship between the logarithm of V_X/V_H (V_X is the dimer production per second (mmol/s) for *m*- and *p*-substituted benzoic acids and V_H is the dimer production per second (mmol/s) for benzoic acid) and the pK_a of the carboxylic acids is shown in Fig. 2. The plots for *m*- and *p*-substituted benzoic acids showed a good linear correlation ($R^2 = 0.946$) with a slope of -0.199 . Since the slope is related to the free energy of activation in the rate-determining step, it could be supposed that proton-transfer in the protonolysis process is rate-determining. The small value for the slope (-0.199) in the Brønsted relationship suggested that the protonolysis step has a very early transition state.

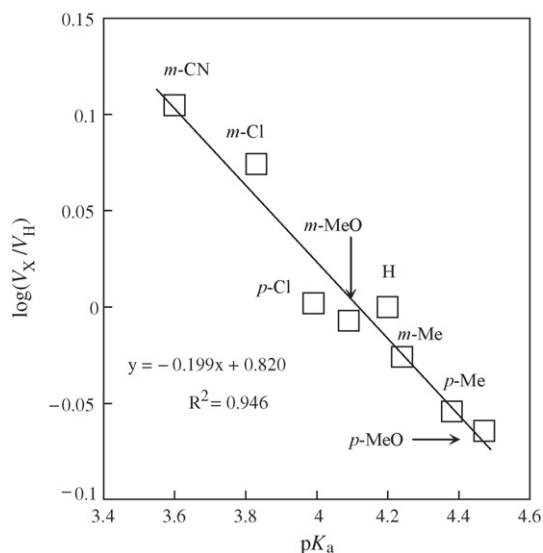


Fig. 2. Relationship between $\log(V_X/V_H)$ and pK_a of *m*- and *p*-substituted benzoic acids at 120 °C.

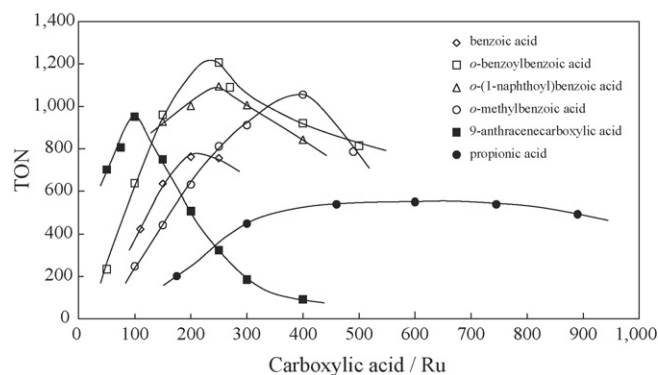


Fig. 3. Relationship between TON for the dimerization of acrylonitrile and the molar ratio of carboxylic acid/Ru.

3.3. Influence of the molar ratio between carboxylic acid and Ru on the TON

The TON for the dimerization of AN depended on the molar ratio between acid and Ru as shown in Fig. 3. The shapes of the maxima varied from sharp peaks to rounded humps and the optimum ratio of carboxylic acid to Ru depended upon the structure of the carboxylic acid. For example, the TON in the presence of 9-anthracenecarboxylic acid went up to its maximum at the acid/Ru ratio of about 100 but beyond this ratio, the TON steadily decreased. The depressed TON for the dimer at high acid/Ru ratio is probably related to the higher degree of deactivation of the catalyst due to higher concentration of the carboxylic acid, which can coordinate to the ruthenium atom and the steric environment around ruthenium.

3.4. Formation of the ruthenium carboxylate complex

Recently, the formation of ruthenium (II) carboxylate from RuCl₂(DMSO)₄ and silver carboxylate has been reported [20]. It could be assumed that the in situ formation of a similar ruthenium carboxylate occurred in the catalytic dimerization of AN, because both a carboxylic acid and a base were needed to activate the ruthenium catalyst. In order to gain support for this assumption, a ruthenium carboxylate complex was synthesized from RuCl₂(DMSO)₄, 2-thiophenecarboxylic acid, and sodium carbonate. This carboxylate complex had the same catalytic activity for dimerization of AN as the catalyst prepared in situ from RuCl₂(DMSO)₄, 2-thiophenecarboxylic acid, and sodium propionate (see Section 2.7).

3.5. Considerations on the reaction mechanism

In all of the previously reported data except that of our catalytic system [3,4], the molar ratio of AN dimers to the by-product PN had not exceeded 1:1 (within the range of experimental error). Furthermore, dimerization in the absence of extra molecular hydrogen has been shown to give a small amount of DCBD **3** as the major dimer with a TON of only 5 [21]. In contrast with these prior results, we have found an efficient Ru-catalytic system for the dimerization of AN in the absence of

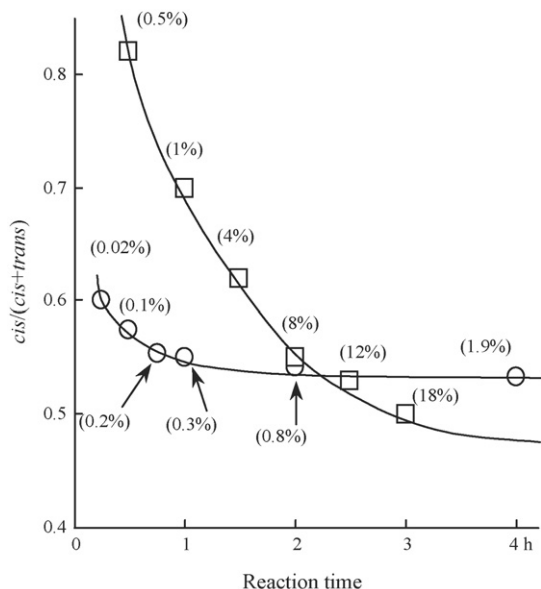


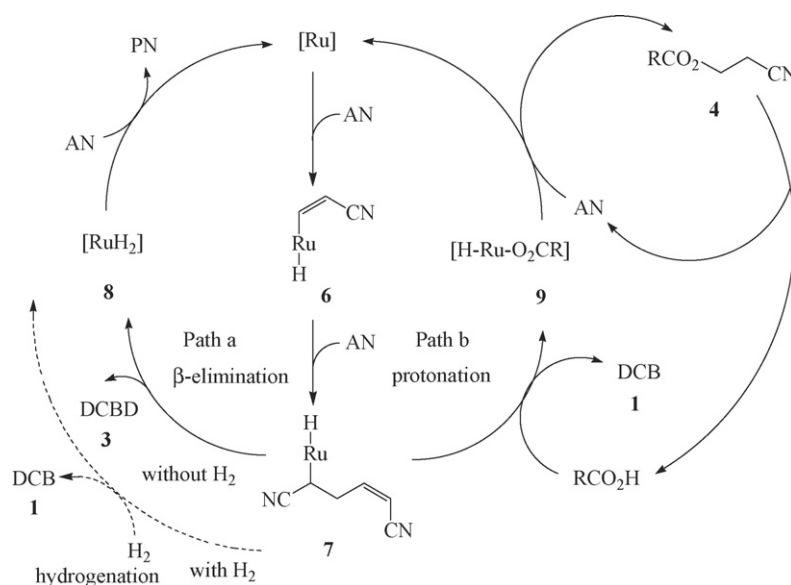
Fig. 4. The ratio of *cis*-1/(*cis*- and *trans*-1) vs. time in the Ru catalyzed dimerization. (□) $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (38 wt.%Ru) 0.75 mmol, AN 456 mmol, and EtOH 60 mL under H_2 20 kg/cm² at 120 °C. (○) $\text{RuCl}_2(\text{DMSO})_4$ 0.085 mmol, sodium propionate 0.255 mmol, propionic acid 20.2 mmol, AN 84.8 mmol at 115 °C. The combined yields of dimers 1–3 are shown in parentheses.

extra hydrogen. In our Ru-based catalytic system, a carboxylic acid was used instead of hydrogen and the *cis* to *trans* ratio of the DCB 1 decreased according to reaction time with the *cis*-isomer being rich at the initial period as in the reaction in the presence of hydrogen (Fig. 4) [10a].

We also investigated the dimerization reaction of AN in the absence of hydrogen and carboxylic acid with our system as a comparison. The reaction using $\text{RuCl}_2(\text{DMSO})_4$ (0.0382 mmol) and sodium propionate (0.306 mmol) in the presence of DMSO (6.4 mmol) in AN (282.7 mmol) was carried out for 6 h at

150 °C. The conversion of AN was 3.70%. The products and the yields were as follows: *cis*-DCB 1 (0.07%), *trans*-DCB 1 (0.08%), *cis,cis*-DCBD 3 (0.44%), *cis,trans*-DCBD 3 (1.02%), *trans,trans*-DCBD 3 (0.49%), PN 5 (1.58%). The overall combined yield of linear dimers 1 and 3 was 1.48% (TON 110) in which the selectivity for DCBD 3 was 92.8%. Thus, even though there was no hydrogen or carboxylic acid, the catalytic cycle of the dimerization of AN proceeded to give DCBD 3 as the major dimer.

Based upon these results, a plausible mechanism for the reaction in the absence of carboxylic acid is proposed as shown in the left half of Scheme 2 in a simplified manner [23]. The carbon–hydrogen bond *cis* to the cyano group in AN is cleaved by [Ru] (oxidative addition) to give 6 [24,25], which undergoes carbometalation with a second AN to give intermediate Ru complex 7. The carbon–ruthenium bond-cleavage in 7 occurs with molecular hydrogen to give dimer 1 either before (this possibility is shown as Path a in Scheme 2) or after (this possibility is not shown in Scheme 2) taking up another molecule of AN, thereby giving rise to the by-product PN (Path a: with H_2). When the carbon–ruthenium bond in 7 is not cleaved by molecular hydrogen, DCBD 3 can be formed by β -hydrogen elimination (Path a: without H_2). In any event, one molecule of AN is consumed to give PN in the process of regenerating the catalyst [Ru], thus imposing a limitation to this system (the molar ratio of AN dimers to PN ≤ 1). A proposed catalytic cycle operative in the presence of carboxylic acids is shown as Path b in Scheme 2 [10b]. The protonolysis of intermediate 7 with carboxylic acids affords 1 along with complex 9 followed by regeneration of the catalyst [Ru]. Previously, we reported that CEC 4 was formed in smaller molar quantity than DCB 1. The production of an equimolar amount of DCB 1 and CEC 4 was needed for the reaction mechanism reported previously [10b]. Therefore, we proposed a different mechanism for the regeneration of the catalyst [Ru] [10a]. But we found, subsequently,



Scheme 2. Plausible mechanism for the dimerization of acrylonitrile (AN) in the presence of carboxylic acids. Alternative possibilities are not shown for simplicity. PN: propionitrile.

that the regeneration of carboxylic acid and AN from CEC **4** under the dimerization conditions occurs [13]. These results make it possible to explain the fact that CEC **4** was formed in smaller molar quantity than DCB **1**. Thus, we propose the mechanism (Path b) corresponding to that under H₂ pressure (Path a). Regeneration of carboxylic acid and AN from CEC **4** makes it possible to use carboxylic acid in smaller quantity than DCB **1**. The alternative possibility involving the AN adduct of **7**, which was speculated previously [10a], is not shown in Scheme 2 for simplicity (see Supplemental data).

Another possibility is via a 2,5-dicyanoruthenacyclopentane intermediate. The coupling reaction of dienes has been reported previously to occur via ruthenacyclopentane intermediates [26]. It was pointed out that the elimination of hydrogen from the ruthenacyclopentane ring was sterically difficult [27]. The ruthenium catalyzed coupling reaction of dienes and enol esters via ruthenacyclopentane intermediates has also been reported [28]. In this reaction *cis*-olefins, which had sterically hindered configurations corresponding to *cis*-DCB in the dimerization of AN, were produced selectively. Reaction mechanisms, which involve the elimination of hydrogen from the ruthenacyclopentane ring, were proposed. But no special reagents such as carboxylic acids or hydrogen were needed to promote the reaction catalytically in this case. Thus, it is different from the dimerization reaction of AN using a ruthenium-based catalyst in the presence of carboxylic acids or hydrogen in our system. In the event, we think that the mechanism shown in Scheme 2 is more plausible than a mechanism involving a 2,5-dicyanoruthenacyclopentane intermediate.

We could not get any information on the reaction mechanism by the use of CH₃CO₂D as the carboxylic acid. ¹H NMR of DCB **1** showed the homogeneous distribution of deuterium in DCB **1**. It is attributed to the fact that active exchange between the hydrogen of DCB **1** and the proton of the carboxylic acid proceeds under dimerization conditions (see Supplemental data).

4. Conclusion

We have examined the ruthenium-catalyzed acrylonitrile tail-to-tail dimerization reaction using various acids. The important features of the catalytic reaction (protonolysis route) are as follows: (1) The catalytic conversion of AN to linear dimers occurred with high selectivity (85.8%), which represents a breakthrough against the intrinsic limit of 66.6% in the conventional hydrogenolysis route. (2) The depressed production of CEC **4** by means of the addition of CEC **4** at the beginning of the reaction lead to the highest selectivity for dimers (86.3%). (3) No branched dimer was formed. (4) Comparable or better TONs compared with previously reported results were obtained. (5) AN can be used as both a reactant and the solvent at the same time, which will be advantageous in a large-scale operation. (6) Carboxylic acids having pK_a of 1.8–5.0 were the only effective proton sources for cleaving the carbon–ruthenium bond of the immediate intermediates to the product dimers. The acidity of the most effective carboxylic acids was around pK_a 3–3.5. (7) The catalytic cycle involves proton transfer in the rate-determining step. (8) Mechanistically, the present reaction

seems to involve the oxidative addition of ruthenium into the C–H bond, which is similar to that observed in ruthenium-catalyzed C–H/olefin coupling [26,29]. This is different from the reaction mechanism of the rhodium-catalyzed dimerization of acrylic ester, which proceeds via the initial hydrometalation of the olefin [6h].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2006.08.077.

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