

## Linear Relationship between Activity of a New Ru-catalyst and Acidity of Substituted Benzoic Acids in the Dimerization of Acrylonitrile

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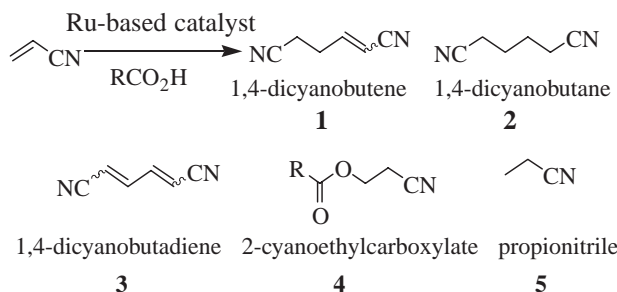
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(Received November 7, 2005; CL-051381; E-mail: 25988u@ube-ind.co.jp)

A new type of catalyst system using ruthenium and carboxylic acid is useful for the tail-to-tail dimerization of acrylonitrile, proceeding without the formation of undesired by-product propionitrile. Carboxylic acids having  $pK_a$  3.5–5 are suitable as co-catalysts for the dimerization of acrylonitrile. The relationship between the logarithm of the relative rate in the dimer formation and the  $pK_a$  of *m*- and *p*-substituted benzoic acids (Brønsted plot) was linear ( $R^2 = 0.946$ ) with a slope of  $-0.199$ . The role of the carboxylic acids can be considered to be effective protonation in the protonolysis of the carbon–ruthenium bond of an intermediate Ru complex.

The regioselective tail-to-tail dimerization of acrylonitrile (AN) has provided an attractive alternative route toward the formation of hexamethylenediamine, which is one of the monomers used in the production of Nylon-6,6.<sup>1,2</sup> Ruthenium-based catalysts are important candidates for this reaction due to the high reactivity [the catalyst turnover number (TON) has been about 1000] and the high selectivity for the linear dimers **1**–**3**.<sup>3,4</sup> Komiya and his co-workers found that zero-valent ruthenium complexes are effective catalyst precursors for the tail-to-tail dimerization of AN. In their Ru-catalytic system, the inevitable use of hydrogen as an extra agent to keep the reaction catalytic resulted in the formation of a large amount of propionitrile **5** as an undesirable by-product.<sup>3i</sup>

Recently, we found that the catalytic system of  $[RuCl_2(DMSO)_4]/CH_3CH_2COONa/DMSO/carboxylic\ acid$  gives linear dimers of AN (TON = 1206) without the formation of **5** (Scheme 1).<sup>5</sup>



Scheme 1.

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. Reported herein are the results. Table 1 shows TON values for the Ru-catalyzed dimerization of AN at 150 °C for 6 h in the presence of various substituted benzoic acids. Products were analyzed by gas chromatography.

**Table 1.** TON for dimerization of acrylonitrile at 150 °C for 6 h in the presence of substituted benzoic acids<sup>a</sup>

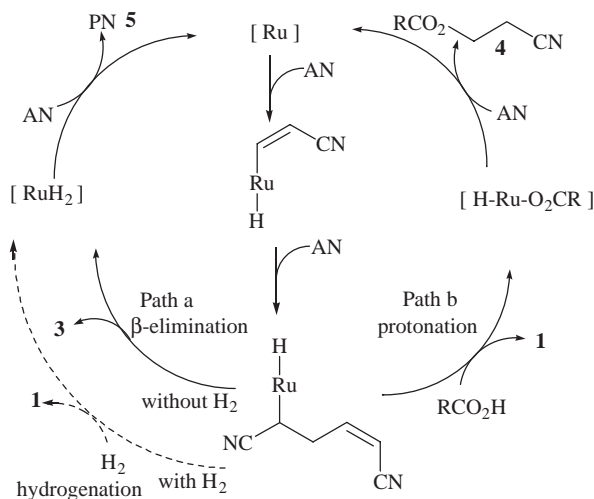
Carboxylic acid	$pK_a$	TON <sup>b</sup>
PhCO <sub>2</sub> H	4.20 <sup>c</sup>	636
<i>p</i> -Substituted benzoic acid		
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	3.83 <sup>c</sup>	616
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	4.24 <sup>c</sup>	355
<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	4.47 <sup>c</sup>	346
<i>m</i> -Substituted benzoic acid		
<i>m</i> -NCC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	3.60 <sup>c</sup>	778
<i>m</i> -ClC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	3.99 <sup>c</sup>	705
<i>m</i> -MeOC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	4.09 <sup>c</sup>	443
<i>m</i> -MeC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	4.34 <sup>c</sup>	379
<i>o</i> -Substituted benzoic acid		
<i>o</i> -PhCOC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	3.54 <sup>d</sup>	960
<i>o</i> -MeC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	3.91 <sup>c</sup>	442
<i>o</i> -MeOC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	4.09 <sup>c</sup>	195

<sup>a</sup>Reaction conditions: AN 283 mmol, anisole (internal standard for gas chromatography) 18.5 mmol, DMSO 6.4 mmol,  $RuCl_2(DMSO)_4$  0.0381 mmol, sodium propionate 0.306 mmol, acid 5.70 mmol, 150 °C, and 6 h. <sup>b</sup>TON =  $[2 \times (\text{combined mol of dimers } \mathbf{1-3})]/[\text{mol of Ru}]$ . <sup>c</sup> $pK_a$  values taken from Ref. 6. <sup>d</sup> $pK_a$  values taken from Ref. 7.

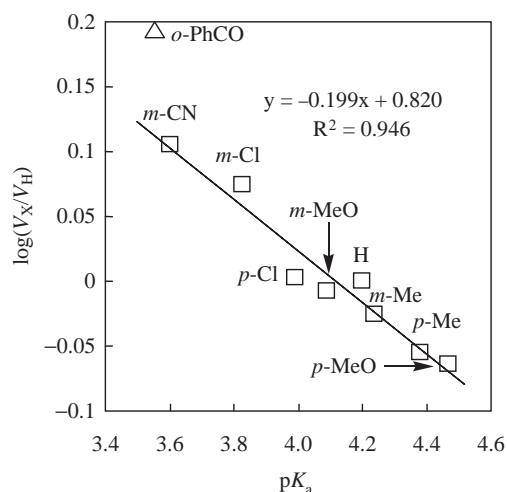
The main product was 1,4-dicyanobutene.

The TON in the catalyzed reactions by *m*- and *p*-substituted benzoic acids increased with smaller  $pK_a$  (stronger acid). The effective acidity of carboxylic acids for optimal TON is around  $pK_a$  3.5 and the use of *o*-benzoylbenzoic acid as the co-catalyst gave rise to the highest TON of all the carboxylic acids examined in the present experiments. Phenol as well as *p*-toluene sulfonic acid and trifluoroacetic acid were ineffective as co-catalysts for the dimerization.<sup>8</sup> It can be assumed that the active Ru-catalyst for the dimerization is produced in the presence of carboxylic acids of  $pK_a = 3.5-5$ , while in the presence of strong acids such as sulfonic acid and trifluoroacetic acid, such active catalysts either are not formed or are destroyed. A plausible mechanism containing both the hydrogenation and the protonation steps is shown in Scheme 2.<sup>5</sup>

The reaction at 120 °C proceeded for 24 h at the same rate without deactivation of catalyst. The relationship between the logarithm of  $V_X/V_H$  [ $V_X$ : dimer production per second (mmol/s) for *m*- and *p*-substituted benzoic acids,  $V_H$ : dimer production per second (mmol/s) for benzoic acid] and the  $pK_a$  of carboxylic acids is shown in Figure 1. The plots for *m*- and *p*-substituted benzoic acids showed a good linear correlation 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



Scheme 2.



**Figure 1.** Relationship between  $\log(V_X/V_H)$  and  $pK_a$  of substituted benzoic acids at 120 °C.  $\square$ : *m*- and *p*-substituted benzoic acid,  $\triangle$ : *o*-benzoylbenzoic acid.

supposed that proton-transfer in the protonolysis process is rate-determining. The small value for the slope ( $-0.199$ ) in the Brønsted relationship suggests that the protonolysis step has a very early transition state. The deviation of the plot for *o*-benzoylbenzoic acid from the fitted line is probably related to favorable steric factors in the protonation step.

Further investigations on the mechanism, reaction conditions and the catalysts in the acrylonitrile dimerization are in progress.

We thank Dr. S. Murai, Professor Emeritus of Osaka University, and Dr. K. Ohkata, Professor of Hiroshima University, for their valuable discussions and suggestions. We also thank Dr. Satoshi Kojima for reading the manuscript and making several helpful suggestions.

## References and Notes

- 1 a) G. W. Parshall S. D. Ittel, *Applied Homogeneous Catalysis*, 2nd ed., Wiley-Interscience, New York, **1992**, p. 242. b) K. Weissmehl, H.-J. Arpe, *Industrial Organic Chemistry*,

2nd ed., Verlag Chemie, Weinheim, Germany, **1993**. c) R. J. McKinney, U.S. Patent 4504674, **1985**.

- 2 a) J. M. Thomas, R. Raja, G. Sankar, R. G. Bell, *Acc. Chem. Res.* **2001**, *34*, 191. b) W. Niu, K. M. Draths, J. W. Frost, *Biotechnol. Prog.* **2002**, *18*, 201. c) G. Kiss, *Chem. Rev.* **2001**, *101*, 3435.
- 3 a) A. Misono, Y. Uchida, M. Hidai, H. Kanai, *Chem. Commun.* **1967**, 357. b) J. D. McClure, R. Owyang, L. H. Slaugh, *J. Organomet. Chem.* **1968**, *12*, 8. c) E. Billig, C. B. Strow, R. L. Pruett, *Chem. Commun.* **1968**, 1307. d) A. Misono, Y. Uchida, M. Hidai, I. Inomata, *Chem. Commun.* **1968**, 704. e) A. Misono, Y. Uchida, M. Hidai, H. Shinohara, Y. Watanabe, *Bull. Chem. Soc. Jpn.* **1968**, *41*, 396. f) W. Strohmeier, A. Kaiser, *J. Organomet. Chem.* **1976**, *114*, 273. g) D. T. Tsou, J. D. Burrington, E. A. Maher, R. K. Grasselli, *J. Mol. Catal.* **1985**, *30*, 219. h) D. T. Tsou, J. D. Burrington, E. A. Maher, R. K. Grasselli, *J. Mol. Catal.* **1983**, *22*, 29. i) A. Fukuoka, T. Nagano, S. Furuta, M. Yoshizawa, M. Hirano, S. Komiya, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1409.
- 4 a) Rhone-Poulenc, Neth. Appl. 6603115, **1966**; *Chem. Abstr.* **1967**, *66*, 85483. b) H. Shinohara, Y. Watanabe, T. Suzuki, Jpn. Kokai Tokyo Koho 24585, **1969**; *Chem. Abstr.* **1970**, *72*, 42849. c) W. H. Knoth, U.S. Patent 3538133, **1970**; *Chem. Abstr.* **1971**, *74*, 6970. d) G. W. Godin, Ger. Offen 2019907, **1971**; *Chem. Abstr.* **1971**, *75*, 19734. e) P. F. Todd, Ger. Patent 2,446,641, **1975**; *Chem. Abstr.* **1975**, *83*, 27639. f) R. K. Grasselli, J. D. Burrington, F. A. Pesa, H. F. Hardman, Eur. Pat. Appl. EP 72231, **1983**; *Chem. Abstr.* **1983**, *99*, 139364. g) S. Murai, K. Oodan, R. Sugise, M. Shirai, T. Shimakawa, Jpn. Kokai Tokyo Koho 09531, **1994**; *Chem. Abstr.* **1994**, *120*, 191146. h) T. Yorisue, S. Kanejima, Jpn. Kokai Tokyo Koho 245539, **1996**; *Chem. Abstr.* **1996**, *126*, 7712. i) Y. Suzuki, Y. Kiso, PCT Int. Appl. WO 1531, **1997**; *Chem. Abstr.* **1997**, *126*, 157193. j) H. Yasuda, Jpn. Kokai Tokyo Koho 03544, **1999**; *Chem. Abstr.* **1999**, *130*, 168018.
- 5 K. Kashiwagi, R. Sugise, T. Shimakawa, T. Matsuura, M. Shirai, F. Kakiuchi, S. Murai, *Organometallics* **1997**, *16*, 2233. Previously, we reported some results of lesser production of 2-cyanoethyl carboxylate than that of 1,4-dicyanobutene. The production of the equimolar amount of 1,4-dicyanobutene and 2-cyanoethyl carboxylate was needed for the mechanism shown in Scheme 2. Therefore, we proposed the different mechanism previously. But we found subsequently the regeneration of carboxylic acid and AN from 2-cyanoethyl carboxylate under the dimerization conditions. This results make possible to explain the production of 2-cyanoethyl carboxylate lesser than that of 1,4-dicyanobutene, thus we propose the mechanism (Path b) corresponding to that under H<sub>2</sub> pressure (Path a) this time. An alternative possibility, which is shown in Ref. 5, is not shown in Scheme 2 for simplicity. Further investigation on this reaction is in progress.
- 6 E. A. Braude, F. C. Nachod, *Determination of Organic Structures by Physical Methods*, Academic Press, New York, **1955**, p. 567.
- 7 G. B. Bray, J. E. Doppy, S. R. C. Hughers, *J. Chem. Soc.* **1957**, 265.
- 8 The dimer of AN was not formed at all when *p*-toluene sulfonic acid and trifluoroacetic acid were used as the acid. Phenol gave the same results as in the case of the absence of hydrogen and carboxylic acid. The Ru-catalyzed dimerization of AN in the absence of hydrogen and carboxylic acid proceeded to afford a small amount of 1,4-dicyanobutadiene **3** as the major dimer.