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Kinetics and Mechanism of the Reactions of Butenenitrile with Imidazoles

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The reaction kinetics of 3- and 2-butenenitriles with 2-alkylimidazoles were studied by using NMR, and a mechanism consistent with the results is proposed. The imidazoles were active in isomerizing 3-butenenitrile to 2-butenenitrile, and then reacted only with the 2-butenenitrile to give the corresponding 1-(2-cyano-1-methylethyl)imidazoles. These consecutive reactions, isomerization and cyanoethylation, are second-order over all. For example, in the reaction of 3-butenenitrile with imidazole, the rate measurements of the isomerization at various temperatures, ranging from 30 to 90 °C, afforded the activation parameters of $E_a=$ 14.6 kcal/mol and $\Delta S^*=-35.3$ cal/degree. On the other hand, in the case of 2-butenenitrile with imidazole, the measurements of the cyanoethylation at 60—100 °C gave these parameters; $E_a=15.3$ kcal/mol and $\Delta S^*=-45.7$ cal/degree. In this case, the rates of the isomerization ($k_1=6.0\times10^{-6}$ l/mol s at 60 °C) are approximately ten times larger than those of the cyanoethylation ($k_2=0.53\times10^{-6}$). A mechanism is discussed on the basis of their NMR spectral and kinetic data.

Recently, in our previous paper, the kinetic data on the reaction of acrylonitrile with imidazole have been reported.[1] By means of the NMR method, factors governing the points of the cyanoethylation and the polymerization of acrylonitrile are well understood. The studies have now been extended to unsaturated nitriles with a view to obtaining a clear picture of the reaction.

In this paper, we wish to describe the kinetics of the reactions of 3- and 2-butenenitriles (3-BN and 2-BN) with imidazole (Im), 2-ethylimidazole (EtIm), and 2-isopropylimidazole (*i*-PrIm) respectively, and their possible mechanism.

Experimental

Measurements. All the boiling and melting points are uncorrected. The NMR spectra were obtained at 60 MHz with a Japan Electron Optics Model JNM-3H-60 spectrometer at room temperature. The chemical shifts were reported in ppm downfield from the internal TMS (δ). The IR spectra were recorded on a Shimadzu Model 27-G grating spectrophotometer on a KBr disk for the solid materials or on a NaCl plate for the liquid ones. The GLC analysis was carried out on a Shimadzu gas chromatograph, Model GC-5AP$_3$T, using a 3.00-m column packed with silicone HV grease (20-wt%). The percentage composition of the product was estimated by means of the relative peak areas (uncorrected). A constant-temperature bath with a temperature control of ±0.1 °C was employed.

Materials. Im, EtIm, and *i*-PrIm were recrystallized from benzene several times; mps, 88—89, 83—84, and 133—134.5 °C respectively. Imidazole-1-*d*[2] and 3-BN (bp 118—121 °C)[3] were prepared by the reported methods. 2-BN (bp 115—118 °C) was of a reagent quality and was used without further purification. In all the materials, the purities were determined by means of NMR and GLC analyses.

Kinetic Measurements. The reactions of the imidazoles with 3- or 2-BN were carried out in sealed tubes. The rate of the appearance of the product was followed by using NMR.[1] In a typical preparation, about 1.5 g of Im was placed in a 10-ml volumetric flask and weighed. Then the volume was quickly made up to 10 ml with the nitrile. This solution was transferred into ten separate tubes and sealed. The first NMR analysis was performed as soon as feasible after the sample preparation. The sealed tubes were shaken at a constant temperature for a given time. The rate measurements were then performed by means of the NMR method.[1] Each experiment was repeated in order to check the reproducibility.

Reaction Products. After the reaction had been completed, the reaction mixture collected from each run was treated and purified by the method reported previously.[1] The physical properties of the corresponding 1-(2-cyano-1-methylethyl)imidazoles thus obtained may be shown as follows:

Product 1. 1-(2-Cyano-1-methylethyl)imidazole (**1**); bp 128 °C/0.9 Torr. Picrate; mp 125.0—126.0 °C, Found: C, 42.73; H, 3.23; N, 23.25%. Calcd for $C_{13}H_{12}N_6O_7$: C, 42.84; H, 3.32; N, 23.08%. IR (C≡N) : 2254 cm^{-1}. NMR (CH_2Cl_2) : δ 1.53 (d, 3H, CH_3), 2.82 (d, 2H, $-CH_2CN$), 4.53 (sextet, 1H, $N{>}CH$), 6.97—7.05 (2H, ring-proton), 7.53 (s, 1H, ring).

Product 2. 1-(2-Cyano-1-methylethyl)-2-ethylimidazole (**2**); bp 105 °C/0.4 Torr. Picrate; mp 152.0—153.0 °C, Found: C, 46.16; H, 3.90; N, 22.03%. Calcd for $C_{15}H_{16}N_6O_7$: C, 45.92; H, 4.11; N, 21.42%. IR (C≡N): 2257 cm^{-1}. NMR (CH_2Cl_2) : δ 1.51 (d, 3H, CH_3), 2.81 (d, 2H, $-CH_2CN$), 4.54 (sextet, 1H, $N{>}CH$), 1.29 and 2.70 (t, 3H ; q, 2H, 2-C_2H_5), 6.90 and 7.02 (2H, ring).

Product 3. 1-(2-Cyano-1-methylethyl)-2-isopropylimidazole (**3**); mp 51.0—53.0 °C. Picrate ; mp 151.5—152.5 °C. Found: C, 47.41; H, 4.35; N, 20.95%. Calcd for $C_{16}H_{18}N_6O_7$: C, 47.27; H, 4.46; N, 20.68%. IR (C≡N) : 2248 cm^{-1}. NMR (CH_2Cl_2) : δ 1.54 (d, 3H, CH_3), 2.77 (d, 2H, $-CH_2CN$), 4.56 (sextet, 1H, $N{>}CH$), 1.24 and 1.32 (d, d, 3H, 3H, 2CH_3 of *i*-Pr), 3.01 (septet, 1H, ${>}CH$ of *i*-Pr), 6.88—6.95 (2H, ring).

Results and Discussion

Reactions. In the reaction between Im and 3-BN, the changes in the NMR spectra with the time are shown in Fig. 1. One-proton and two-proton singlets due to the ring protons of Im appear at 7.3 and 8.0 ppm respectively. In the earlier period of the reaction, the new singals of the methyl and olefinic protons due to 2-BN, the product of the isomerization, began to appear in the regions of 2.0—2.2 and 6.5—6.9 ppm respectively (after 60 min, in Fig. 1). Their intensities increased with the reaction time. After a considerable amount of 2-BN had been produced (900 min), the signals of Compound **1** appeared at 1.8 (CH_3), 3.1 ($-CH_2CN$), and 4.9 ppm ($N{>}CH$) respectively. Therefore, the progress of the reaction

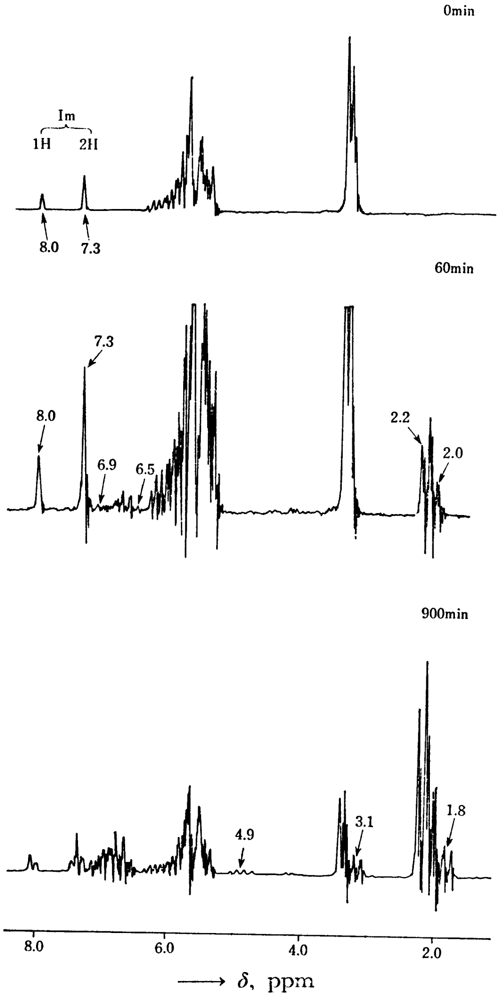


Fig. 1. Changes of the NMR spectra with reaction time, in the reaction of Im (1.325 mol/l) with 3-BN (11.396 mol/l) at 77 °C. After 900 min, the conversion of 3-BN to 2-BN was 67.4%.
3-BN, NMR (CCl_4): δ 3.23—3.38 (2H, CH_2) and 5.27—6.28 (3H, H_2C=CH-).
2-BN, NMR (CCl_4): δ 1.98—2.23 (3H, CH_3), and 5.44—5.74 and 6.47—7.18 ppm (2H, -CH=CH-).

was followed by observing the rates of the appearances of the signals of 2-BN and Compound **1**.

In this reaction at 90 °C, the time-conversion curves of the above two products and the plots of the NH shift and its content at the reaction time are shown in Fig. 2.

From these observations, it is clear that 3-BN is first converted to 2-BN in the presence of Im, and that then 2-BN reacts with Im to give Compound **1**. That is, Im is active in isomerizing 3-BN to 2-BN. It is also easily observable in Fig. 2 that the isomerization proceeds much faster than the cyanoethylation and that, during the proceeding of the isomerization, the NH signal moves downfield.

On the other hand, it was observed by means of the NMR method that, in the reaction of Im with 2-BN, Compound **1** was the sole product. Figure 3 shows both the conversion and NH shift curves in this reaction. The two curves show a similar tendency. The NH signal moves upfield with an increase in the yield of Compound **1**. On the contrary, in the isomerization (Fig. 2) the NH signal moves downfield. Thus, the reactions of the imidazoles with 2-BN yielded the corresponding 1-(2-cyano-1-methylethyl) imidazoles (**1**, **2**, and **3**).

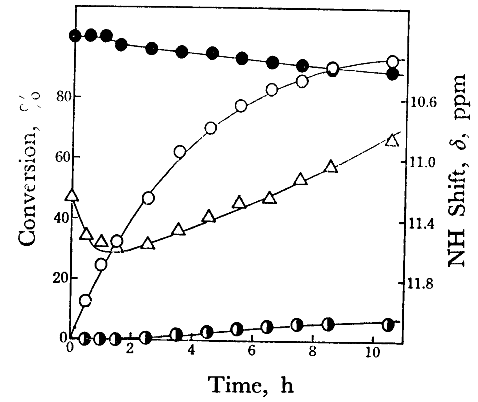


Fig. 2. Time-conversions and NH shift curves in the reaction of Im (1.679 mol/l) with 3-BN (11.110 mol/l) at 90 °C.
○: Conversion of isomerization, 3-BN to 2-BN;
◐: conversion for compound **1**;
△: NH shift; ●: NH content, %.

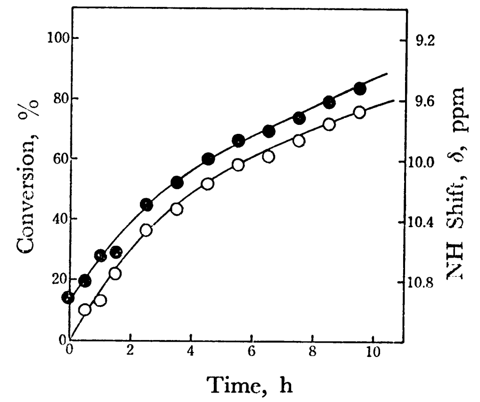
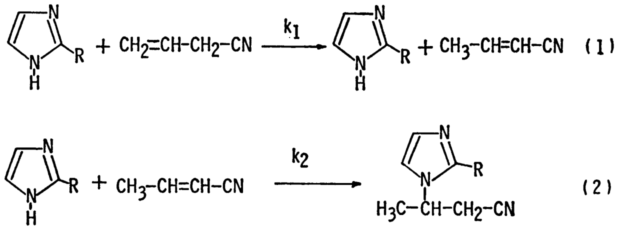


Fig. 3. Time-conversion and NH shift curves in the reaction of Im (1.736 mol/l) with 2-BN (10.800 mol/l) at 90 °C.
○: Conversion; ●: NH shift.

Rates. From the above observations, this consecutive reaction can be represented as follows:



The isomerizaation (Eq. 1) was monitored by the NMR method to trace a time-conversion curve and may be expressed as:

$$d(2\text{-BN})/dt = k_1(3\text{-BN})^m(\text{Im})^n \quad (3)$$

When this process is carried out with an excess of 3-BN, the changes in the concentration of Im are

Table 1. Reaction rates[a] and activation parameters for the isomerization of 3-BN to 2-BN

Temp, °C	30	35	40	45	50	60	70	77	80	90	E_a[b]	ΔS^* [c]
Im	0.8	1.1	1.7	2.3	3.0	6.0	11.8	15.8	28.2	45.2	14.6	−35.3
EtIm					16.2	34.7	68.8		134.0		16.2	−35.1
i-PrIm						39.8		103.0		273.0	15.5	−37.1

a) Calculated by the least-squares method, $k_1 \times 10^6$ l/mol s. b) Activation energy, kcal/mol. c) Calculated at 70 °C, cal/degree.

Table 2. Reaction rates and activation parameters for the cyanoethylation of 2-BN with imidazoles

Imidazoles	$K_2 \times 10^6$ l/mol s (Temperature, °C)						kcal/mol E_a	ΔS^* cal/degree
Im	0.53 (60)	1.3 (70)	1.9 (80)	4.0 (90)	6.5 (100)		15.3	−45.7
EtIm	4.3 (110)	5.4 (120)	7.5 (130)	10.0 (140)			9.2	−63.6
i-PrIm	0.61 (100)	1.2 (120)	2.1 (140)	2.3 (150)	2.7 (160)	2.8 (170)	7.8	−70.1

negligible. Therefore, the apparent rate of the isomerization depends only on the concentration of 3-BN. Consequently, Eq. 3 can be written as:

$$\mathrm{d(2\text{-}BN)/d}t = k_{\mathrm{obsd}}(\mathrm{3\text{-}BN})^m \qquad (4)$$

The orders, *m* and *n*, are determined by the initial-rates (V_0) method.[4] In fact, when the (3-BN) or (Im) concentrations are kept constant and the (Im) or (3-BN) concentrations (C_0) are varied, the plots of log V_0 against log C_0 are linear and their slopes are $m = 1.01$ and $n = 0.96$. That is, the orders are assumed to be 1.0. Consequently, we can rearrange Eqs. 3 and 4 by substituting the above values and can rewrite the equations as follows:

$$\mathrm{d(2\text{-}BN)/d}t = k_1(\mathrm{3\text{-}BN})(\mathrm{Im}) \qquad (5)$$

$$= k_{\mathrm{obsd}}(\mathrm{3\text{-}BN}) \qquad (6)$$

All the runs, carried out with an excess of 3-BN, gave excellent pseudo first-order kinetics to at least 70% completion. The rates were measured at various temperatures between 30 and 90 °C. The rate constants, k_1, derived for the isomerization and their activation parameters in the reactions of the imidazoles with 3-BN are listed in Table 1. In the case of 2-methylimidazole, it was difficult to get an accurate value because of its low solubility in the reaction mixture. As is obvious from the table, the rate constants increase with the change in R in the order of ethyl and isopropyl, while the values of E_a and ΔS^* are almost constant.

On the other hand, the reactions of the imidazoles with 2-BN were found to follow second-order rate equations[1]:

$$\mathrm{d(product)/d}t = k_2(\mathrm{2\text{-}BN})(\mathrm{Im}) \qquad (7)$$

The values of the second-order rate constants, k_2, were obtained by a method reported previously.[1] Table 2 shows the rate constants at various temperatures, along with the values of the activation parameters. Small E_a values and large negative ΔS^* values are observed. In general, such facts indicate that the reaction involves a strongly polarized and/or crowded transition state. In this case, the above fact implies that not only a polar effect, but also a steric effect of R, is a controlling factor. Furthermore, the plot of E_a *vs.* ΔS^* for R of H, C_2H_5, and *i*-Pr shows a good compensation effect.

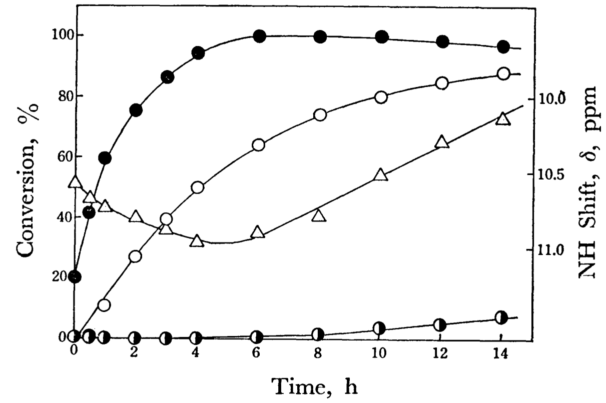
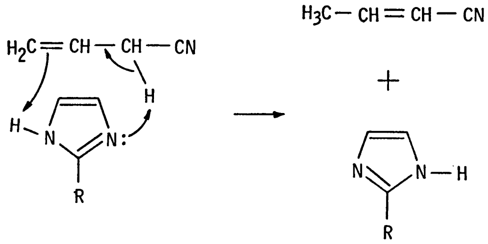


Fig. 4. Time-conversions and NH shift curves in the reaction of imidazole-1-d_1 (1.702 mol/l) with 3-BN (11.090 mol/l) at 70 °C.
○: Conversion of isomerization, 3-BN to 2-BN;
◑: conversion for compound **1**;
△: NH shift; ●: NH content, %.

Possible Reaction Mechanism. *(A) Isomerization.* To elucidate the mechanism, the reaction of imidazole-1-*d*, containing up to 19.2% NH, with 3-BN was performed by monitoring the NMR method. Plots of NH shift, its content, and the conversions against the reaction time are shown in Fig. 4. In the beginning of the reaction, the NH content of imidazole-*d* was 20%; it then increased with an increase in the reaction time. When its content approached 100%, the NH signal began to move upfield and the formation of Compound **1** was observed. The curves of the NH shifts and the conversions in Fig. 4, are identical with those illustrated in Fig. 2. As can be seen in both Figs. 2 and 4, the NH shift in each lowest field appeared at approximately 11 ppm. These phenomena support the idea that either the hydrogen of NH in the Im molecule is bonded to another molecule, probably the 3-BN molecule, by a very weak bond such as a hydrogen bond, or, since the bonding energy of NH falls, the distance is sufficiently stretched. On the other hand, a hydrogen atom of the methylene group in the 3-BN molecule is activated by the $-$I-effect of the CN group.

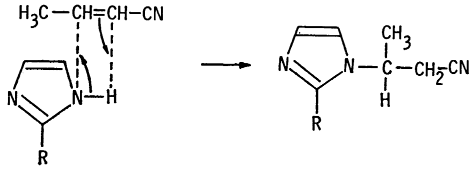
We also attempted the reactions of pyrrole, pyrazole, and imidazole nitrate with 3-BN under the same conditions. However, no products could thus be obtained.

These considerations lead us to believe that the following reaction mechanism holds:



A. Isomerization mechanism

(B) Cyanoethylation. In the reaction of Im with acrylonitrile, we have already reported the value for the activation energy, $E_a = 12.0$ kcal/mol. In this work, the activation energy of the reaction of Im with 2-BN was 15.3 kcal/mol. This result suggests that the reaction of 2-BN with Im is somewhat more difficult than that of acrylonitrile. This may be due to the $+$I-effect of the metyl group in 2-BN. As can be seen in Fig. 3, the NH signal appears at around 11 ppm in the beginning of the reaction. On the basis of the results mentioned above and other considerations,[1] a possible mechanism for the cyanoethylation can be described as follows:



B. Cyanoethylation mechanism

We wish to thank the Shikoku Fine Chemicals Co., Ltd., for the supply of the imidazoles.

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