BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 557—558 (1971)

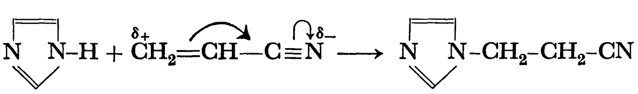
Kinetics of the Reaction of Imidazole with Acrylonitrile by Using NMR

Fukiko YAMADA and Yasuyoshi FUJIMOTO

Department of Applied Chemistry, Faculty of Engineering, Kansai Universtiy, Senriyama, Osaka

(Received June 6, 1970)

Imoto and his co-workers[1] recently reported that acrylonitrile (AN) polymerized in the system of imidazole (Im) and carbon tetrachloride (CCl_4) and that the polymerization proceeded through the radical mechanism. On the other hand, Sawa and Okamura[2] confirmed that, in the presence of the catalyst, potassium hydroxide, the Im derivatives reacted with AN at 100°C to give the corresponding 1-(β-cyanoethyl)-imidazoles. In the latter case, the cyanoethylation appears to proceed through the following ionic mechanism:



The work reported here was carried out in order to study the kinetics of the ionic reaction and to ascertain how the polymerization can be initiated when CCl_4 is present in the reaction system.

Experimental

Measurements. The NMR spectra were obtained at 60 MHz with a Japan Electron Optics Model JNM 3H-60 spectrometer. The chemical shifts are reported in ppm downfield from the internal TMS (δ). A constant-temperature water bath was employed; it was equipped with an immersion heating element that afforded a temperature control of ±0.1°C.

Materials. The AN, Im, and CCl_4 were purified by the reported methods.[1,3] All the reagents used were of an analytical grade.

The Reactions. (*1*) *Cyanoethylation*: The reaction between Im and AN with or without CCl_4 was carried out in sealed tubes. The rate of the disappearance of Im was followed by the NMR method. After the reaction had been completed, the evaporation of the remaining AN at room temperature afforded an oily product that was then purified by means of column chromatography on silica-gel, using methylene chloride as the eluent; this yielded pure 1-(β-cyanoethyl)imidazole (CEIm). NMR, δ, (in CH_2Cl_2): 7.6 (singlet, 1H), 7.0 (doublet, 2H), 4.2 (triplet, 2H), and 2.8 (triplet, 2H). IR absorption (C≡N) at 2258 cm^{-1}. Mol wt (by mass spectrometry), 121. Picrate, mp 121°C (lit,[2] mp 120—121°C), Found N, 23.76%; Calcd for $C_{12}H_{10}N_6O_7$: N, 24.00%.

(2) *Polymerization*: The polymerization of AN in the system of Im and CCl_4 was carried out in sealed tubes in the dark. Definite amounts of AN, Im, and CCl_4 were charged in separate test tubes, cooled in a bath of dry ice and methanol, and sealed in a vacuum. The sealed tubes were then shaken at 25°C for a given time. The rate of the disappearance of Im was followed by the NMR method. After the polymerization had been initiated, the polymer produced was precipitated in the system. Each ingredient was then freed from the precipitate, and the filtrate was examined by the NMR method. The precipitate was washed with methanol. The molecular weight of the polymer obtained for 29 hr at 25°C was found to be 7.20×10^7 by the viscometric method in the dimethylformamide solution.[3]

Results and Discussion

Cyanoethylation. In the reaction between Im and AN with CCl_4, the changes in the NMR spectra with the reaction time are shown in Fig. 1. The one-proton and two-proton singlets due to the ring protons of Im appear at 7.7 and 7.1 ppm respectively. In the earlier period of the reaction, the new methylene signals due to the reaction product, CEIm, began to appear at 4.2 and 2.8 ppm respectively, and their intensities increased with the reaction time. The proton numbers of the methylene signals can be evaluated by comparing the data of the integrated signals with those of the signals due to the Im ring protons, which were unchanged by the reaction. The conversion of the cyanoethylation based on the initial concentration of Im can, therefore, be obtained by means of the integrated data of these signals. The time-conversion curve is shown in Fig. 2. From these data, the reactions between Im and AN with or without CCl_4 were found to follow a second-order rate equation:

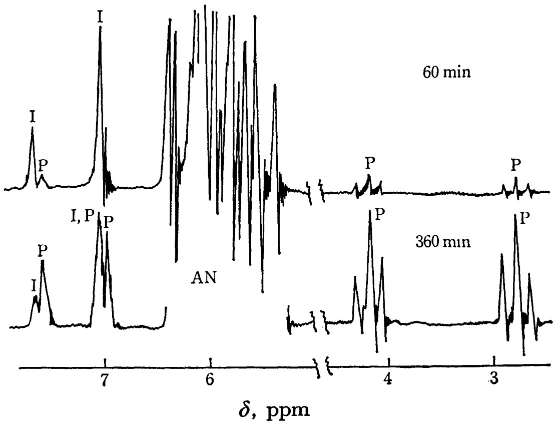


Fig. 1. Changes of the NMR spectra with reaction time at 25°C. Peaks marked AN, I, and P belong to acrylonitrile, imidazole, and the product, respectively.

$$dx/dt = k(a-x)(b-x)$$

giving;

$$\log_{10} b(a-x)/a(b-x) = kt(a-b)/2.303$$

where;

---

[1] M. Imoto, K. Takemoto, T. Otsuki, N. Ueda, S. Tahara, and H. Azuma, *Makromol. Chem.*, **110**, 37 (1967).

[2] N. Sawa and S. Okamura, *Nippon Kagaku Zasshi.*, **90**, 704 (1969).

[3] M. Imoto, K. Takemoto, and H. Sutoh, *Makromol. Chem.*, **110**, 31 (1967).

a = the initial concentration of AN
and b = the initial concentration of Im

The values of the second-order rate constants, k, were obtained graphically by plotting $\log_{10} b(a-x)/a(b-x)$ against t, the slope of the line being $k(a-b)/2.303$. The points obtained fell on good straight lines. The rate constants for the reactions between Im and AN with or without CCl_4 at 25°C are presented in Table 1.

Table 2 shows the rate constants for the reaction at different temperatures, along with the values of the activation energy as evaluated from the slope of the Arrhenius plots.

Table 1. Second-order rate constants for the reaction of Im with AN at 25°C

Run	(AN/Im), mol ratio	CCl_4, mol/l	$k \times 10^4$, l/mol·min
1	6.8	0.88	3.7
2	8.2	2.00	3.7
3	9.2	2.01	3.7
4	6.0	3.65	3.6
5	5.7	4.12	3.7
6	3.4	——	5.2
7	6.9	——	4.6, 4.9, 5.0
8	9.8	——	4.9
9	13.4	——	4.6

Table 2. Reaction rates and the energy of activation for the reaction of Im with AN in CCl_4

Temperature °C	10	20	25	30	40
$k \times 10^4$, l/mol·min	1.2	2.8	3.6	4.6	9.0
E, kcal/mol			12.0		

As is shown in Table 1, in the absence of CCl_4 the rates were slightly increased over those of the reactions in CCl_4. In runs 1 and 5, the mol ratios of Im : AN : CCl_4 are 1 : 7 : 0.5 and 1 : 6 : 3. When the CCl_4 content in the system exceeds the latter ratio, they do not blend with each other. Under the conditions shown in Table 1, the rate is unaffected by the concentration of CCl_4.

Polymerization of AN. As can be seen in Fig. 2, the polymerization of AN was carried out at 25°C in the system of Im and CCl_4. The cyanoethylation of Im had also occurred in the reaction system before the radical polymerization, and the rate constant of the cyanoethylation was found to be 3.7×10^{-4} l/mol·min, which was the same as that of the reaction without polymerization in the presence of air.

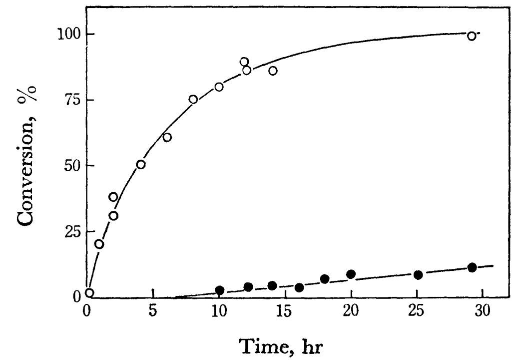
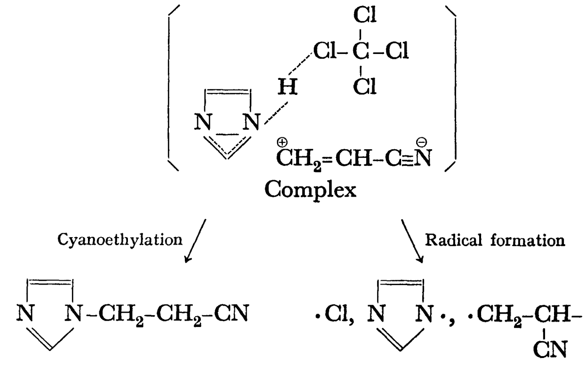


Fig. 2. Time-conversion curves in the system of Im-AN-CCl_4 (mol ratio, 1:6:2.5) at 25°C.
○: Conversion of cyanoethylation is based on the initial concentration of Im.
●: Conversion of polymerization is based on the initial concentration of AN.

Possible Formation Mechanism. On the basis of the results mentioned above and other considerations,[1-3] a possible reaction mechanism for the polymerization and the cyanoethylation can be described as follows:



The above complex may be expected to be formed by the participation of Im, AN, and CCl_4 in the initial step of the reaction.

We wish to thank the Toho Rayon Co. Ltd., for the supply of imidazole.