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Kinetics of Polymerization of Malononitrile under Hydrogen Pressure

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Abstract

The kinetic study of the polymerization of malononitrile to a dimer, 1,1,3-tricyano-2-amino-1-propene, and a trimer, 1-(aminovinyl)-3-dicyanomethyl-4,5-dicyano-pyrazole, under hydrogen pressure with a Pt-on-alumina catalyst revealed that (1) the reaction was of zero order with respect to malononitrile, of first order with respect to the catalyst and to the initial hydrogen pressure, (2) the products distribution indicated by the dimer fraction (selectivity) was invariable irrespective of conversion but decreased slightly with an increased temperature, and (3) the temperature dependency of the reaction rate was expressed as 20.5 kcal/mol in terms of apparent activation energy.

If the temperature susceptibility of the selectivity is disregarded, the reaction rates in mol/1/min up to 50% conversion and 60 kg/cm² I.H.P. are shown as follows:

$$R_{(\mathrm{malononitrile})} = 9.3\times10^{7}\times e^{-20,500/RT}\times P_{\mathrm{IH}}\times W_{\mathrm{cat}}$$
$$R_{(\mathrm{dimer})} = 7.4\times10^{7}\times e^{-20,500/RT}\times P_{\mathrm{IH}}\times W_{\mathrm{cat}}$$
$$R_{(\mathrm{trimer})} = 1.85\times10^{7}\times e^{-20,500/RT}\times P_{\mathrm{IH}}\times W_{\mathrm{cat}}$$

The zero-order kinetics with respect to malononitrile arises from the invariability of the concentrations of the reaction participants under Gibbs' phase rule, as long as a gas, a liquid and two solid polymer phases are present, and is supported by the constancy of the selectivities.

Introduction

We have pointed out in a previous paper[1], that malononitrile does not undergo hydrogenation at all, but polymerizes, under hydrogen pressure and in the presence of catalyst(s)—Pt, Pd, Rh, Cu, Ni and Co—, to a dimer 1,1,3-tricyano-2-amino-1-propene and to a trimer, 1-(aminovinyl)-3-dicyanomethyl-4,5-dicyano-pyrazole.

Since, in principle, the hydrogenation of malononitrile, but not necessarily its polymerization, is affected by an increase of hydrogen pressure, we were much interested in the behavior of hydrogen pressures upon the reaction. On the other hand, in practice, the dimer has been drawing attention by its biological action to RNA[2],[3],[4],[5], and the trimer is a pyrazole which can most easily be made. We felt, therefore, some kinetic investigations should be made.

The catalyst used throughout this paper was 0.5% Pt-on-alumina which had been proven to have a moderate activity suited for kinetic measurements.

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Experimental Section

The experimental details were similar to those described in the previous paper unless otherwise mentioned.

Malononitrile (extra reagent grade, a Wako Junyaku product) and a Pt catalyst (0.5% Pt on alumina, an Engelhard product) were used without further treatment.

In an autoclave made of 304 ss, 16 mm in dia. and 20 ml in vol. were placed 5 g of malononitrile, a specified amount of the catalyst and a steel ball for agitation, and hydrogen was introduced up to a specified pressure (initial hydrogen pressure, I.H.P.). The reactor was then immersed in an oil bath maintained at a prescribed temperature (reaction temperature) and shaken vigorously at 200 r.p.m. for a prescribed period of time, and quenched immediately with cold water. It took about four min to arrive at the reaction temperature after immersion, so that the reaction time was subtracted by that amount from the prescribed value. In each run, the I.H.P. was the same as the pressure measured after the reaction was over and the reactor quenched, no foreign substances being formed in the gas phase. The product was solid even at the reaction temperature, from which the unreacted malononitrile was removed by sublimation (up to 70°C at 15 mm Hg). An IR spectrometer (Nippon Bunko) was used for determining the ratio of the dimer (905 cm^{-1}) to the trimer (780 cm^{-1}) at a transmittance in the range of 0.3 to 0.8 by the KBr method. The reduction of the catalyst with hydrogen in advance did not affect the conversion significantly.

Results and Discussion

Conversion of malononitrile vs. τ, a time factor (time in min times catalyst amount in g multiplied by 10^3, divided through by amount of malononitrile charged in g), suggests that, at least up to 50% conversion, the reaction is roughly of zero order with respect to malononitrile, and of first order with respect to the catalyst (Fig. 1). The dependency of the reaction rate upon the I.H.P. shows that the reaction rate increases linearly with pressure up to about 60 $\mathrm{kg/cm^2}$, but at a decelerating rate at higher pressures (Fig. 2). Hydrogenation did not occur at I.H.P.'s up to 115 $\mathrm{kg/cm^2}$ (about 155 $\mathrm{kg/cm^2}$ reaction pressure) at 135°C. The distribution of the product in terms of the dimer weight fraction (selectivity), is practically invariable irrespective of conversion at a constant temperature, but, seemingly, slightly decreases with the increase in temperature (Fig. 3). Finally, the temperature dependency of the reaction based on the malononitrile conversion is given as an Arrhenius plot in Fig. 4, which indicates the apparent activation energy being 20.5 kcal/mol.

If the susceptibility of the selectivities upon temperature is neglected, the rate expressions for the conversion of malononitrile, and the formations of the dimer and of the timer up to 50% conversion and 60 $\mathrm{kg/cm^2}$ I.H.P. are formulated respectively as follows:

$$R_{(\mathrm{malononitrile})} = 9.3\times10^7\times e^{-20{,}500/RT}\times P_{\mathrm{IH}}\times W_{\mathrm{cat}} \tag{1}$$

$$R_{(\mathrm{dimer})} = 7.4\times10^7\times e^{-20{,}500/RT}\times P_{\mathrm{IH}}\times W_{\mathrm{cat}} \tag{2}$$

$$R_{(\mathrm{trimer})} = 1.85 \times 10^{7} \times e^{-20{,}500/RT} \times P_{\mathrm{IH}} \times W_{\mathrm{cat}} \tag{3}$$

The zero-order kinetics with respect to malononitrile will be understood by the following considerations.

The dimer and the trimer are sparingly soluble in hot malononitrile (5.5% and 1.5%, respectively, at 135°C). Whereas the reacting system is, of course, not in chemical equilbirium, the rate of dissolution of the polymers into malononitrile

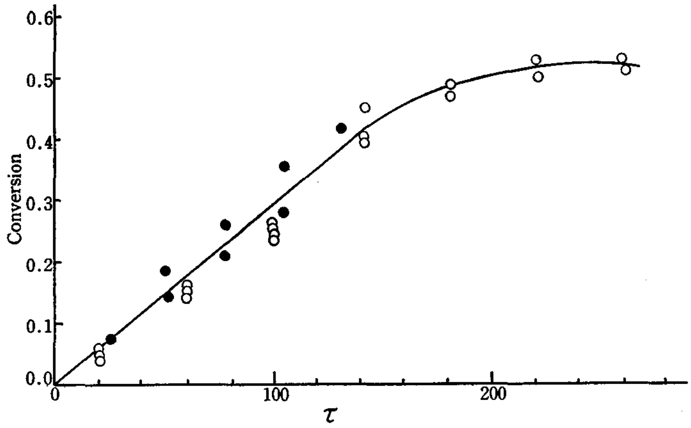


Fig. 1. Conversion of malononitrile vs. time factor, τ, at 130°C and 50 kg/cm² I.H.P., where τ is defined as time in min times amount of catalyst including carrier in g, multipled by 10³, divided through by amount of mlonontrile in g. The solid line up to the conversion of 0.5 shows the calculated value for Eq. (1). ○: Data at varying reaction time using 5 g of malononitrile and 0.02 g of catalyst including carrier. ●: Data at different catalyst amounts for 5 g of malononitrile during reaction time of 26 min.

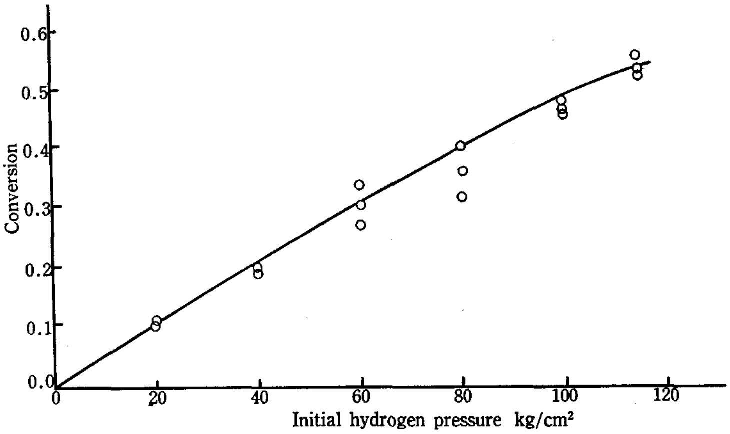


Fig. 2. Effect of initial hydrogen pressure (I.H.P.). The solid line depicts the calculated value for Eq. (1). Malononitrile 5 g, catalyst 0.02 g, 135°C, and 26 min. No hydrogenation has taken place even at 115 kg/cm² I.H.P.

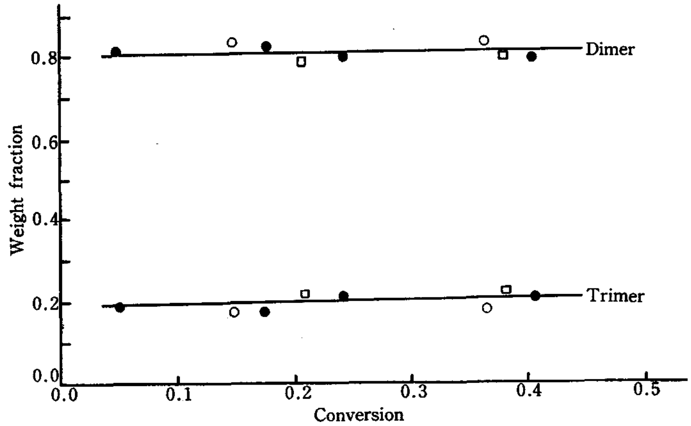


Fig. 3. Distribution of the dimer and the trimer in the product at various temperatures and conversions. The solid line shows the calculated value for Eqs. (2) and (3). ○: At 120°C, ●: at 130°C, and □: at 140°C.

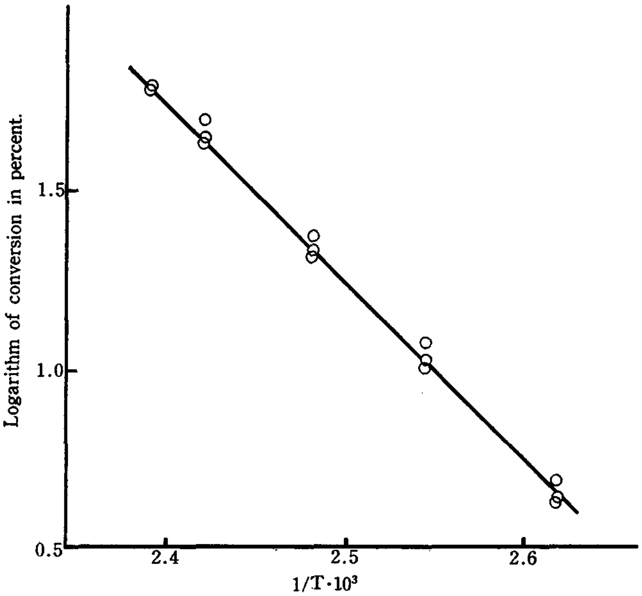
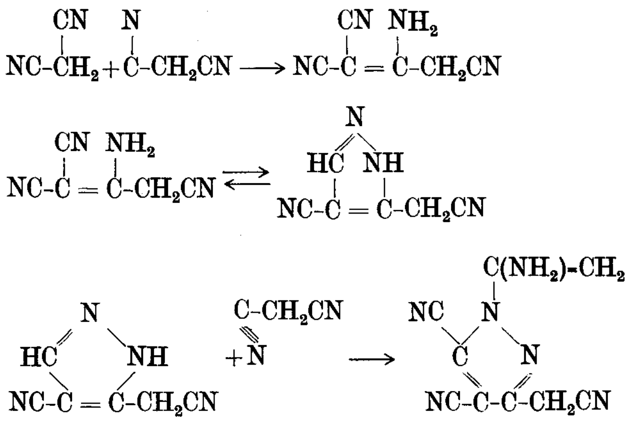


Fig. 4. Effect of temperature on conversion (reaction rate). The solid line corresponds to Eq. (1). Malononitrile 5 g, catalyst 0.02 g, I.H.P. 50 kg/cm², reaction time 26 min.

ought to be much faster than the chemical reaction rate, and consequently, the system can be assumed to be in a quasi phase equilbirium, in which case, if two solid polymer phases appear, Gibbs' phase rule implies that the system is bivariant, because the number of phases is 4 (a gas, a liquid and two solid phases), and the number of components is 4 (hydrogen, malononitrile, the dimer and the trimer). Once the temperature and the pressure are specified, the concentrations of the components remain unaltered regardless of the degree of the conversion, and, in effect, the reaction proceeds at a constant rate, irrespective of the order of the reaction.

Another viewpoint which supports the zero-order kinetics comes from the constancy of the selectivities at a temperature, regardless of the conversion. As described elsewhere[1)], the polymerization of malononitrile is supposed to progress by the following scheme.



$$\mathrm{NC\text{-}\overset{\displaystyle CN}{\overset{|}{C}}H_2 + \overset{\displaystyle N}{\overset{|}{C}}\text{-}CH_2CN \longrightarrow NC\text{-}\overset{\displaystyle CN}{\overset{|}{C}} = \overset{\displaystyle NH_2}{\overset{|}{C}}\text{-}CH_2CN} \tag{4}$$

(5)

(6)

If, for simplicity, we neglect Eq. (5), which is expected to be a rapid reversible reaction in either direction, the above expressions are represented schematically by the following consecutive competitive reactions.

$$A + A \xrightarrow{k_1} B \tag{7}$$

$$B + A \xrightarrow{k_2} C \tag{8}$$

Suppose that the reaction rates are expressed as:

$$-\frac{dA}{dt} = k_1 A^{m_a} + k_2 A^{n_a} B^{n_b} \tag{9}$$

$$\frac{dB}{dt} = 0.5\,k_1 A^{m_a} - k_2 A^{n_a} B^{n_b} \tag{10}$$

$$\frac{dC}{dt} = k_2 A^{n_a} B^{n_b} \tag{11}$$

Eliminating t by dividing Eq. (10) by Eq. (9), we obtain

$$-\frac{dB}{dA} = \frac{0.5\,k_1 A^{m_a} - k_2 A^{n_a} B^{n_b}}{k_1 A^{m_a} + k_2 A^{n_a} B^{n_b}} \tag{12}$$

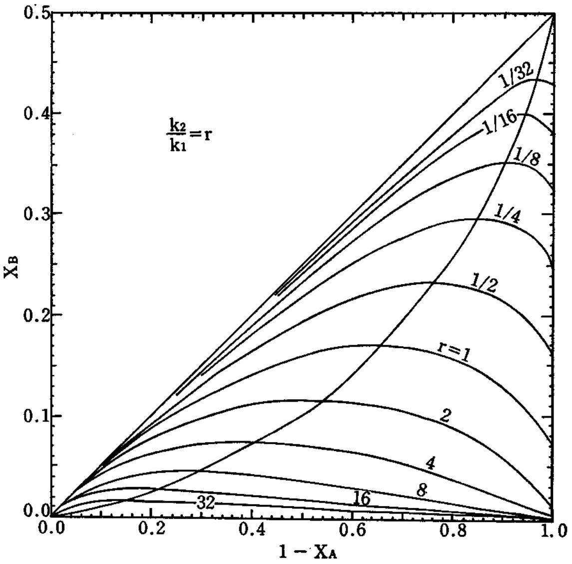


Fig. 5. Trajectories of a consecutive competitive reaction including $A+A\xrightarrow{k_1}B, B+A\xrightarrow{k_2}C$, where $m_a=2$, $n_a=n_b=1$.

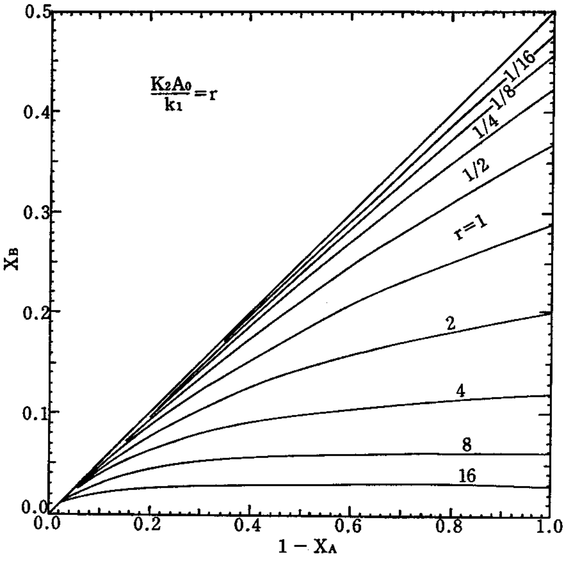


Fig. 6. Trajectories of a consecutive competitive reaction including $A+A\xrightarrow{k_1}B, B+A\xrightarrow{k_2}C$, where $m_a=n_a=n_b=1$.

The reaction trajectories on the (1–X_A) vs. X_B plane in cases where $m_a=2$, $n_a=n_b=1$ and $m_a=n_a=n_b=1$, are given in Figs. 5 and 6, respectively. Eq. (12) implies that (-d B/d A), and accordingly, [$2X_B/(1-X_A)$], i.e. the selectivity, is not constant unless the right hand side of Eq. (12) is constant, this being fulfilled in the present case by the invariability of A and B.

The fact that the reaction obeys the zero-order kinetics as long as two polymer phases are present, simplifies the kinetics appreciably, but contributes little to the reaction mechanism because no information is available therefrom for the order of the reaction.

Of particular interest from a reaction mechanism standpoint, are the facts that the reaction rate increases with an increased I.H.P., and no hydrogenation takes place at least up to an I.H.P. of 115 kg/cm^2, in addition to those described in the previous paper, that little or no polymerization takes place without hydrogen and/or catalyst(s), or with hydrogen and a mere catalyst carrier (activated carbon or alumina), and molecular hydrogen does not take part directly in the reaction, as proven by the use of deuterium[1]. However, at this point, we shall refrain from speculating the mechanism of catalysis and leave it to later studies.

Nomenclature

A, B, C=chemical species or its concentration
A_0=fictitious concentration of A when B and C are absent
m_a, n_a, n_b=order of reaction with respect to respective chemical species
k_1, k_2=rate constant with respect to respective reaction
P_{IH}=initial hydrogen pressure in kg/cm^2
R=reaction rate in mol/l/min
W_{cat}=wt. of catalyst in g including carrier per g of malononitrile
X_A, X_B. X_C= dimensionless concentration made by dividing concentration of chemical species by A_0

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