Kinetic Investigation of the Raney Copper Catalysed Hydration of Acrylonitrile to Acrylamine

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The Raney copper catalysed hydration of acrylonitrile to acrylamide was investigated in one- and two-phase liquid reaction systems. Kinetic data are reported which support the theory that hydration is taking place in the acrylonitrile phase as well as in the aqueous phase. A complex mechanism is proposed in which acrylonitrile and water both are activated for reaction by coordination to the catalyst surface.

A catalytic process for the hydration of acrylonitrile (AN) to acrylamide using metallic copper as the catalyst in a liquid phase system was recently developed.[1] By using a heterogeneous catalyst of the Raney copper type, a very selective hydration of the nitrile function is achieved and the basis for a new process was obtained which shows significant technological advantages over the conventional sulfuric acid method.[2]

It was observed that the kinetics of this important catalytic reaction conveniently could be studied using a dilatometric method. We now wish to report on the mechanism of the hydration reaction based on kinetic evidence, with special emphasis on data related to the initial rate of reaction at low temperatures, $50-70\,°C$.

EXPERIMENTAL

Reagents. AN (purity better than 99 %) and acrylamide (purity better than 98 %) from Fluka AG, Buchs SG were used without further purification. The catalyst used was

American Grace quality Raney copper with a specific surface area of $10.2 \, m^2 \, g^{-1}$ (BET method).

Procedure and analysis. A dilatometric method was developed in order to determine the rate of reaction. A dilatometer of about 65 ml capacity, composed of a round-bottom reaction flask and a detachable capillary section, was immersed in a thermostat controlled to $\pm 0.05\,°C$. The reaction mixture was agitated by means of a Teflon-coated magnet and the rate of reaction was determined to be independent of the rate agitation in the homogeneous as well as in the two-phase liquid systems. A slurry of catalyst in water was initially charged to the reaction flask. The water was removed by vacuum distillation around room temperature. The flask was filled with argon (99.99 %) and the weight of the catalyst determined. The desired amount of distilled water was charged and the reaction flask was connected to the graduated capillary. The dilatometer was placed in the thermostat at desired reaction temperature. After 15 min, the required amount of AN at the same temperature was added and the zero time was recorded. The change in volume with time was followed and the percentage conversion was calculated on the basis of standard volume/conversion curves. A typical standard curve is shown in Fig. 1 which demonstrates the significant volume change taking place during the reaction. A number of typical reaction mixtures were worked up for product analysis. The only product detected in all cases was pure acrylamide with physical properties (m.p. and IR spectrum) identical to those of the commercial product.

RESULTS AND DISCUSSION

Due to the fact that AN has a limited solubility in water,[3] it is necessary to distinguish between two different types of systems: (i)

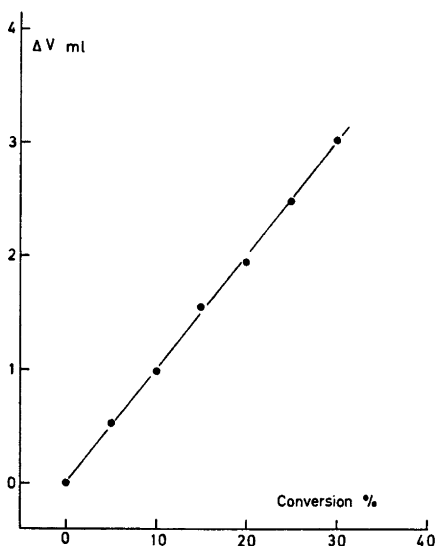* Present address: Chemistry Dept., Faculty of Science, Mansoura University, Mansoura, Egypt.

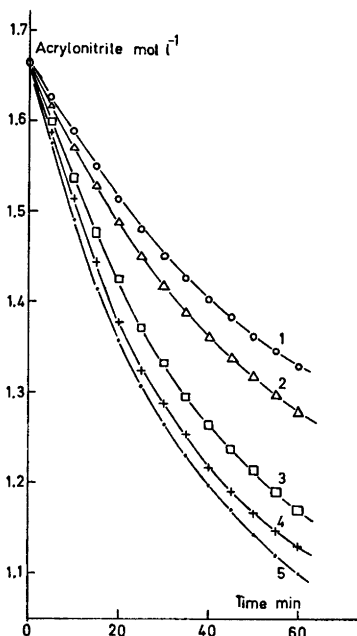*Fig. 1.* Standard curve for a system containing 38.66 wt % acrylonitrile at 70 °C.

Homogeneous liquid phase systems containing AN at a concentration level below the solubility limit in water, and (ii) two-phase systems composed of one organic phase and one aqueous phase.

(i) *Homogeneous liquid phase systems.* The hydration of AN to acrylamide was investigated at an initial AN concentration of 1.667 M and a reaction temperature of 70 °C using different concentrations of Raney copper catalyst within the range between 115 and 250 g l^{-1}. The time/conversion results obtained are reported in Fig. 2. Based on the initial rate of reaction, it was determined that the hydration follows first-order kinetics with respect to the concentration of catalyst (Fig. 3, curve 4) as well as the initial concentration of AN. The rate of reaction (r_1) under these conditions is accordingly given by eqn. 1.

$$r_1 = k_1'[H_2O][Cu][AN] = k_1[Cu][AN] \tag{1}$$

The pseudo second-order rate constant, k_1, for the hydration reaction taking place in the aqueous medium at 70 °C was computed: $k_1 = (2.45 \pm 0.10) \times 10^{-3}$ l h^{-1} g^{-1}.

(ii) *Two-phase systems.* Three different systems containing AN above the solubility limit

Fig. 2. Time/conversion curves for the homogeneous liquid phase system at 70 °C containing different concentrations of catalyst: 115.00 g l^{-1} (1), 147.03 g l^{-1} (2), 201.21 g l^{-1} (3), 229.71 g l^{-1} (4) and 252.38 g l^{-1} (5).
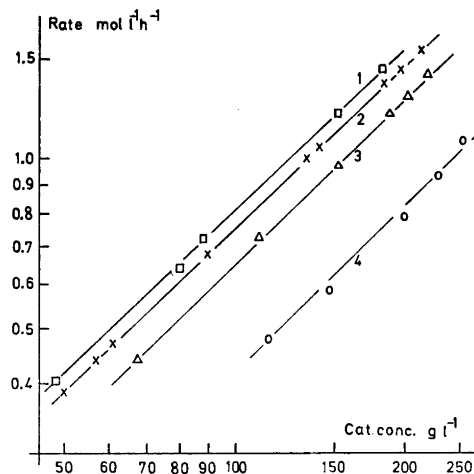

Fig. 3. Relationship between the initial rate of reaction and the concentration of catalyst (log/log) for systems containing different amounts of acrylonitrile: 60.82 wt % (of liquid charge) (1), 38.66 wt % (2), 18.47 wt % (3) and 1.667 mol l^{-1} (homogeneous) (4).

Table 1. The average rate constant for the hydration taking place in the acrylonitrile phase at 70 °C.

Acrylonitrile % by wt.	$10^3 k_2$ 1 h^{-1} g^{-1}	Average value
18.47	2.42	
38.66	2.42	2.43
60.82	2.46	

(18.47, 38.66 and 60.82 % by wt. AN at start) were investigated. The dependencies between the initial rate of hydration and the concentration of the catalyst (log/log) are shown in Fig. 3, curves 1 – 3, and clearly indicate a first-order reaction with respect to the concentration of catalyst. Based on the experimental observation that the rate of reaction was found to be independent of the rate of agitation, it is assumed that the catalyst is equally distributed in both phases. The fact that higher rates are obtained in the systems containing increasing amounts of AN indicates that the hydration is taking place in both phases, the organic as well as the aqueous one. The overall rate of reaction in the system (r) is given by eqn. 2, which contains one pseudo second-order rate term relating to each of the two independent reactions.

$$r = \frac{k_1[Cu][AN]_s V_{H_2O} + k_2[Cu][H_2O]_s V_{AN}}{V_{H_2O} + V_{AN}} \quad (2)$$

The concentration of AN in the water phase, [AN]$_s$, and the concentration of water in the AN phase, [H$_2$O]$_s$, are constant and given by the solubility of the two compounds. At 70 °C, [AN]$_s$ = 1.850 M and [H$_2$O]$_s$ = 4.032 M according to the literature.[3] V_{H_2O} and V_{AN} represent the volumes of the aqueous and the AN phases. Using these values, the rate constant k_2 for the hydration reaction taking place in the AN phase was computed. It was found to be independent of the amount of AN in the system (Table 1) and determined to be 2.43 × 10^{-3} 1 h^{-1} g^{-1}. The homogeneous liquid phase system (containing less than 1.58 M AN) and the two-phase system (containing 38.66 % by wt. AN) were investigated at 50 °C using five different catalyst concentrations within the range of 130 to 290 g l^{-1}. The pseudo second-order rate constants, k_1(50 °C) and
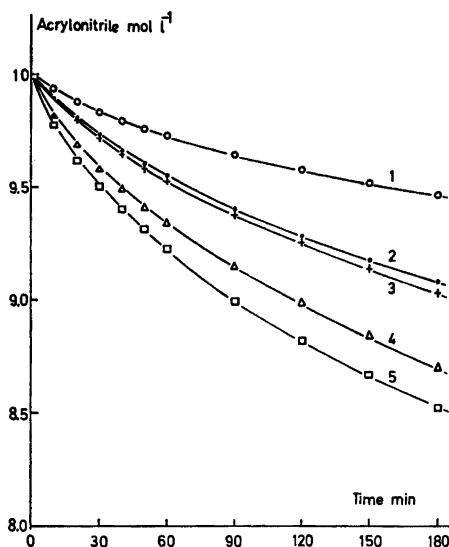

Fig. 4. Time/conversion curves for a two-phase system at 70 °C. Catalyst concentrations: 48.34 g l^{-1} (1), 79.85 g l^{-1} (2), 87. 85 g l^{-1} (3), 152.03 g l^{-1} (4) and 181.04 g l^{-1} (5).

k_2(50 °C) were determined to be (1.07 ± 0.10) × 10^{-3} 1 h^{-1} g^{-1} and (1.03 ± 0.10) × 10^{-3} 1 h^{-1} g^{-1}, respectively. The Arrhenius activation energy, E_A, was then calculated for the hydration reaction taking place in the aqueous as well as in the AN phase. (Temperature range 50 to 70 °C). Within the experimental error, it was found to have the same value, E_A = 37.7 ± 0.8 kJ mol^{-1}, for both reactions.

From the initial rate (eqn. 2) it may be concluded that the rate of hydration should remain constant during an experiment and be independent of the AN conversion as long as two phases are present in the system, unless the rate of reaction is influenced by the acrylamide product formed in the reaction. In order to test this point a series of long-term experiments were carried out using the 60.82 % by wt. AN system. The time/conversion data obtained are reported in Fig. 4. It is concluded that the rate of reaction is influenced by the reaction product formed. Preliminary results obtained from doping experiments also bear out this assumption, and make it necessary to take the presence of acrylamide into account when the mechanism of the hydration is discussed.

Furthermore, it was found that the hydration of propionitrile to propionamide is catalysed in the same way as the hydration of AN. Based on this fact, the presence of olefinic complexes as critical intermediates in the catalytic process may be ruled out. The most likely pathway for the activation of AN thus appears to be the coordination of AN with the copper catalyst *via* the nitrile group. A reaction mechanism in which complexed AN reacts with free water molecules would, however, based on the electronic structure shown in complex B, Scheme 1, lead to the co-production of 3-hydroxypropionitrile (Michael addition). The fact that only very small amounts of this product are formed is clearly in disagreement with such a mechanism.

The strong catalytic effect observed in this system and the high selectivities obtained to give the acrylamide reaction product, favour a mechanism in which AN as well as water are activated by the catalyst. Such a mechanism is outlined in Scheme 1. The inhibitory effect

The activation of water is formulated in accordance with a Lewis acid type mechanism. It is possible that small amounts of hydrated alumina left on the surface during the procedure of preparing the Raney copper catalyst play an important role in this activation step. This aspect of the catalytic process will be made the subject for future investigations.

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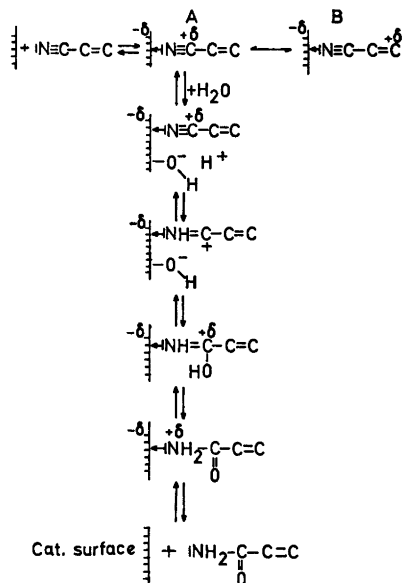
Scheme 1. The mechanism of hydration of acrylonitrile.

of acrylamide is explained, based on the effect that is competes with AN and H_2O with respect to occupation of the active sites on the catalyst surface.