

# Effects of Solvents and the Structure of Amines on the Rates of Reactions of $\alpha,\beta$ -Unsaturated Nitriles and Amides with Secondary Amines

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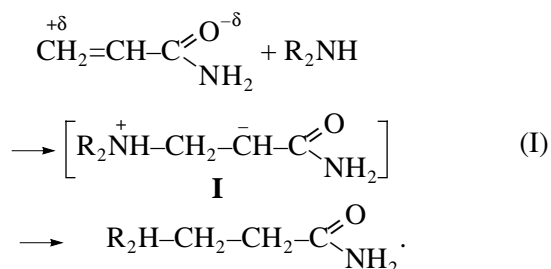
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**Abstract**—The kinetics of reactions between  $\alpha,\beta$ -unsaturated compounds (UCs) (acrylonitrile (AN), acrylamide (AA), and methacrylamide (MAA)) and secondary amines (As) (piperidine, morpholine, diethanolamine, diethylamine, and dipropylamine) in water, as well as in DMF, DMSO, formamide, and 1,4-dioxane for acrylonitrile, was studied. It was found that  $w = k[\text{HC}]_0[\text{A}]_0$  for all of the test pairs. Viscosity, permittivity, and solvation characteristics, such as solvent polarity, nucleophilicity, and electrophilicity, were taken into account in considering the solvent effect on the overall reaction rate. The electrophilicity (acidity) of a medium was found to exert the greatest effect on the reaction rate. It is believed that an increase in the electrophilicity is favorable for the rapid protonation of the UC–amine intermediate complex. The effects of amine basicity, ionization potential, and dipole moment and the steric parameters of substituents in amine molecules on the rates of reactions between the unsaturated compounds and secondary amines were considered.

## INTRODUCTION

The addition reactions of amines at activated  $>\text{C}=\text{C}<$  bonds are widely known as Michael reactions [1]. Despite differences in the reactivity and nature of nucleophilic agents, the addition almost always begins with a nucleophilic attack on the  $\beta$ -carbon atom of a double bond with the formation of an intermediate zwitter-ion:



Two main conclusions can be drawn from published kinetic data. First, the slowest step of the reaction is an attack on the alkene group by a nucleophile followed by the rapid protonation of **I** with the participation of a solvent or another amine molecule. Second, the higher the electrophilicity of the  $\beta$ -carbon atom and the nucleophilicity of the amine, the higher the reaction rate [1–3].

A recently developed area in the kinetics of liquid-phase reactions is the deduction and application of various empirical and semiempirical correlation equations. These equations relate the kinetic parameters of liquid-phase processes, in particular, reaction rate con-

stants, to the parameters that quantitatively characterize the properties of media and reactants.

In this work, we studied the reaction kinetics of several unsaturated compounds (UCs), nitriles and amides, in particular, acrylonitrile, acrylamide, and methacrylamide, with secondary amines (piperidine, morpholine, diethylamine, dipropylamine, and diethanolamine) in water, DMF, DMSO, formamide, and 1,4-dioxane for the quantitative evaluation of the effects of the nature of solvents and amines on the kinetics of these processes.

## EXPERIMENTAL

The starting substances were purified according to published procedures [4]. The reaction rates were measured using two independent techniques: dilatometry and UV spectroscopy. SF-26 and Safas-170 spectrometers were used. In the course of the processes, the concentrations of acrylonitrile, acrylamide, and methacrylamide were determined by measuring the absorbance (*A*) of samples containing acrylonitrile, acrylamide, and methacrylamide at  $\lambda = 210$ , 220, and 220 nm, respectively. In the range  $[\text{UC}]_0 = 5\text{--}30 \times 10^{-5}$  mol/l, an  $A\text{--}[\text{UC}]_0$  calibration curve was plotted. This concentration range was chosen because at  $[\text{UC}]_0 > 30 \times 10^{-5}$  mol/l the reaction products,  $\text{R}_2\text{NH}$ , and unsaturated compounds exhibit absorption in the same spectral region (210–220 nm).

Because the reactions between unsaturated compounds and  $\text{HC}\text{--}\text{R}_2\text{NH}$  occur with a decrease in volume, dilatometry can be applied to determine the reaction rates. For this purpose, the limiting contraction

$\Delta V_{\infty}$  of the reaction solution was determined for each pair of the reactants (at almost complete consumption of the reactants as determined by thin-layer chromatography) at different temperatures and concentrations of the reactants. On this basis,  $\Delta V$ –concentration calibration curves were plotted.

The orders and rate constants of reactions were determined with the use of data on the initial rates ( $w_0$ ). On the condition that  $[UC]_0 = [A]_0$  (A is an amine), the rate constants were also determined by the integral equation  $1/C - 1/C_0 = kt$ .

Note that the reaction rate constants determined by dilatometry and UV spectroscopy in water are in a good agreement. Thus, the rate constant of the reaction between acrylonitrile and morpholine in water was equal to  $2.8 \times 10^{-2}$  or  $3 \times 10^{-2} \text{ l mol}^{-1} \text{ s}^{-1}$ , as determined by dilatometry or UV spectroscopy, respectively. The determination error in rate constants was no higher than 5%.

The rate constants of reactions between acrylonitrile and morpholine in DMF, DMSO, and formamide solutions were determined by only dilatometry because these solvents and the unsaturated compounds exhibit absorption in the same region.

In this work, reaction rate constants in aqueous solutions and water–1,4-dioxane mixtures were determined by only UV spectroscopy. The experiments were performed in the ranges of initial concentrations of the unsaturated compounds and amines of  $10^{-1}$  to 2 mol/l or  $10^{-2}$  to  $10^{-1}$  mol/l for a reaction of acrylonitrile with piperidine.

The consumption of secondary amines and the formation of products were qualitatively determined by thin-layer chromatography. Commercial Silufol UV-254 plates were used. A mixture of 1,4-dioxane, benzene, and an aqueous 25% ammonia solution in the ratio 3 : 3 : 0.5 was used as a mobile phase. Spots were visualized by iodine vapor.

## RESULTS AND DISCUSSION

The rate of reactions between unsaturated compounds and secondary amines remained almost unchanged when the reaction was performed in air or in an inert atmosphere; the reaction rate was also indepen-

dent of the presence of inhibitors of chain-radical reactions. This fact is indicative of the absence of a chain-radical mechanism.

We found that the reaction rate for all of the pairs examined is described by the equation

$$w_0 = k[HC]_0[A]_0 \quad (1)$$

The effect of the structure of unsaturated compounds on the rate of the test reactions is beyond the scope of this article.

Table 3 indicates that the reactivity increases in the order methacrylamide < acrylamide < acrylonitrile. This order is adequately described by the previously proposed [3] correlation equation

$$\log k = a + be/Q, \quad (2)$$

where  $Q$  and  $e$  are the Alfrey–Price parameters [5].

### *Effect of the Nature of the Solvent on the Reaction Rate*

The rate of liquid-phase reactions depends not only on the nature of reacting particles (ion, nonpolar molecule, or dipole) but also on the nature of the solvent. The Michael reaction can be considered as dipole–dipole or dipole–ion interactions. Thus, in these reactions, intermolecular interactions are electrostatic. From this point of view, permittivity ( $\epsilon$ ) can significantly affect the reaction rate. It was found previously [3] that solvents can be arranged in the following order according to their activating effect on the reaction between unsaturated compounds and secondary amines:  $H_2O > DMSO > DMF > 1,4\text{-dioxane}$ . The solvent permittivity gradually increases in this order. The above order of solvents is also valid for the reaction of acrylonitrile and morpholine. However, formamide, whose permittivity is higher than that of water, is out of this order (Table 1). In fact, the solvents can be arranged in the following order in accordance with their activating effect:  $H_2O > \text{formamide} > DMSO > DMF > 1,4\text{-dioxane}$ . That is, permittivity is not the only factor responsible for the reaction rate.

It follows from the above order that water is the best solvent for reactions between unsaturated compounds and secondary amines. This is consistent with published data [2, 8].

**Table 1.** Effect of solvent on the rate constant of the reaction between acrylonitrile and morpholine at 293 K

Solvent characteristics	Solvent				
	$H_2O$	formamide	DMSO	DMF	1,4-dioxane
$\epsilon_{293}$ [6]	80.1	111.5	48.9	36.7	2.2
$n_{293}$ [7]	1.333	1.448	1.478	1.427	1.422
$E_T$ [7]	63.1	56.6	45.0	43.8	36.0
$B$ [7]	123	150	193	159	129
$k, \text{l mol}^{-1} \text{s}^{-1}$	$(3 \pm 0.1) \times 10^{-2}$	$(3.2 \pm 0.1) \times 10^{-3}$	$(1.1 \pm 0.05) \times 10^{-4}$	$(8.5 \pm 0.04) \times 10^{-5}$	$(1 \pm 0.05) \times 10^{-5}$

It is our opinion that other properties of a solvent, namely, its ability to nonspecifically and specifically solvate the reactants, should also be taken into account in determining the role of solvents in the reaction unsaturated compound + secondary amine. Thus, the following interactions can occur in the system unsaturated compound + secondary amine + solvent: alkene–secondary amine [1], amine–solvent [9], and alkene–solvent [10, 11]. The system becomes more complicated with the use of a binary solvent because the physicochemical properties of a solvent mixture ( $\epsilon$ , viscosity  $\eta$ , density, etc.) are usually nonadditive.

We also determined the rate of the reaction unsaturated compound + secondary amine in water–cosolvent (DMSO, DMF, formamide, or 1,4-dioxane) mixtures. Table 2 indicates that, as expected, the rate of the reaction of acrylonitrile with morpholine in water–1,4-dioxane mixtures increased with the molar fraction of water. Similar behavior was also observed in other water–cosolvent mixtures. Note that our kinetic data obtained in mixed solutions are inconsistent with the additivity equation  $k = k_1N_1 + k_2N_2$ , where  $k$  is the rate constant at a given composition of the solvent mixture,  $k_1$  and  $k_2$  are the rate constants in the corresponding neat solvents, and  $N_1$  and  $N_2$  are the molar fractions of the corresponding solvents in the mixture. As can be seen in Table 2, the viscosity of water–dioxane mixtures passes through a maximum, and an associate of the composition 1,4-dioxane  $\cdot$  3H<sub>2</sub>O is formed at the point of maximum. The formation of an associate with the composition DMF  $\cdot$  3H<sub>2</sub>O in a mixture of water and DMF was also observed previously [10]. To study the effect of viscosity on the rate of the Michael reaction, we examined the reaction of acrylonitrile with morpholine in an aqueous 30% glycerol solution. The viscosity of this solution is equal to the viscosity of pure formamide [12] and to the viscosity that corresponds to the point of maximum for the water–DMF mixture [10]. We found that the reaction rates in water and an aqueous 30% glycerol solution were almost the same. Thus, the effect of viscosity on the rate of the Michael reaction can be neglected.

In the general case, the solvent's effect on the reaction rate is difficult to describe adequately with the use of only one characteristic of a solvent because the process of solvation depends on all of the specific and non-

specific effects. They can be included in a multiparametric correlation equation in accordance with the linear free-energy relation.

An equation proposed by Koppel and Palm [13] can be considered as the most general equation. The terms of this equation reflect the effect of nonspecific solvation due to the polarity and polarizability of solvent molecules and the effect of specific solvation due to the electrophilicity and nucleophilicity of the medium.

$$\log k = a_0 + a_1(\epsilon - 1)/(2\epsilon + 1) + a_2(n^2 - 1)/(n^2 + 2) + a_3E_T + a_4B, \quad (3)$$

where  $n$  is the refractive index,  $E_T$  is the electrophilicity according to Dimroth–Reichardt [14],  $B$  is the nucleophilicity according to Palm, and  $a_i$  are parameters.

Entelis and Tiger [7] applied Eq. (3) to establish correlations with the use of a great body of kinetic, spectral, and other data (a total of 70) on solvents. The use of Eq. (3) was also effective in the consideration of the solvent effect on the rate of the reaction secondary amine–*N*-(methylchloromethylene) arene sulfoxide, which was studied by Makitra *et al.* [15].

The number of solvents used in this study is small for the valid solution of Eq. (3) (evaluation of the multiple correlation coefficient, standard deviation, etc.); however, it allowed us to estimate the contributions from  $\epsilon$ ,  $n$ ,  $E_T$ , and  $B$  to the rates of reactions of unsaturated compounds with morpholine.

The solution of Eq. (3) for the reactions of unsaturated compounds with morpholine resulted in the following:

$$\log k = -9.01 - 0.494(\epsilon - 1)/(2\epsilon + 1) - 3.125(n^2 - 1)/(n^2 + 2) + 0.129E_T + 0.002B. \quad (4)$$

As is evident from Eq. (4), solvent electrophilicity is the determining factor. A good correlation between  $\log k$  and  $E_T$  was obtained. We derived the following equation for the reaction of acrylonitrile with morpholine:

$$\log k = (-9.657 \pm 0.168) + (0.128 \pm 0.003)E_T, \quad (5)$$

$$r = 0.999.$$

**Table 2.** Effect of the composition of H<sub>2</sub>O + 1,4-dioxane mixtures on the rate constant of the reaction between acrylonitrile and morpholine at 293 K

Mixture characteristics	Mole fraction of H <sub>2</sub> O								
	0	0.10	0.20	0.35	0.55	0.70	0.80	0.92	1.00
$\epsilon_{293}$ [6]	2.24	2.5	3.19	6.65	12.19	24.0	35.0	54.0	80.1
$\eta_{213}$ , cP	1.00	1.02	1.06	1.17	1.35	1.46	1.40	1.10	0.67
$k$ , l mol <sup>-1</sup> s <sup>-1</sup>	$(1 \pm 0.05) \times 10^{-5}$	$(1.6 \pm 0.1) \times 10^{-5}$	$(4 \pm 0.2) \times 10^{-5}$	$(2.6 \pm 0.1) \times 10^{-4}$	$(7.7 \pm 0.3) \times 10^{-4}$	$(1.8 \pm 0.1) \times 10^{-3}$	$(1 \pm 0.05) \times 10^{-2}$	$(2.4 \pm 0.1) \times 10^{-2}$	$(3.0 \pm 0.1) \times 10^{-2}$

This is likely due to the fact that in this case the solvent plays a double role: a solvating agent and a proton-transferring agent.

Based on published kinetic data [16] for the reaction between acrylonitrile and dimethylhydrazine in alcohols, we also established a correlation between  $\log k$  and  $E_T$  of alcohols.

$$\log k = (-0.994 \pm 0.054) + (0.0555 \pm 0.011)E_T, \quad (6)$$

$$r = 0.933.$$

#### Effect of the Structure of Amine on the Reaction Rate

Table 3 demonstrates that the reactivity of amines increases in the order

Diethanolamine < morpholine < dipropylamine < diethylamine < piperidine.

The effect of the amine structure on the rate of reactions between unsaturated compounds and secondary amines is inadequately explained in the literature. An effort was made to explain the reactivity of aliphatic and aromatic amines with the use of the Taft and Hammett relations, respectively. Thus, using the reaction of acrylonitrile with amines (benzylamine, butylamine, isobutylamine, *tert*-butylamine, and diethylamine) in  $C_6H_5Br$  as an example, Shvets *et al.* [9] obtained a correlation between the reactivity of amines and the Taft function ( $\sigma_R$ ). ElSadany *et al.* found a relationship between the Hammett  $\sigma$  function and the logarithms of the rate constants of benzylideneacetophenone reactions with *p*-methylaniline and *p*-nitroaniline. According to our data, there is no correlation between  $\log k$  and  $\sigma_R$ .

It was noted [1, 23] that the rate of amine addition to olefins increases with increasing basicity of the amine. However, the basicity of amines can be used as a measure of the reactivity in the case when amine molecules with similar volumes are compared, such as piperidine and morpholine.

It was demonstrated [3, 24] by the example of reactions of aliphatic and heterocyclic secondary amines

with unsaturated compounds that no clearly defined correlation takes place between  $\log k$  and  $pK_a$  of amines.

The data given in Table 3 indicate that no correlation takes place between  $\log k$  and  $pK_a$  for all of the amines studied. However, a satisfactory correlation between  $\log k$  and  $pK_a$  for the reactions of acrylamide and acrylonitrile with secondary amines was obtained without considering the data for morpholine. The correlation between  $\log k$  and  $pK_a$  for reactions between methacrylamide and secondary amines was unsatisfactory.

The results of our calculations are given below.

$$\log k_{AA} = -(10.419 \pm 0.754) + (2.199 \pm 0.209)pK_a, \quad (7)$$

$$r = 0.931;$$

$$\log k_{AN} = -(10.771 \pm 2.002) + (0.871 \pm 0.121)pK_a, \quad (8)$$

$$r = 0.955.$$

A clearly defined correlation between  $\log k$  of the reactions of amines with peroxides, electrophiles, and stable radicals and the ionization potentials of amines ( $I$ ) was demonstrated [25, 26]. It was found that  $d \log k / dI < 0$  for radical reactions and  $d \log k / dI > 0$  for nonradical reactions. This regularity was used [3] to establish a correlation between  $\log k$  and  $I$  of amines in the reactions unsaturated compound + secondary amine; in this case,  $d \log k / dI > 0$ , which is typical of nonradical reactions.

The data summarized in Table 3 demonstrate that morpholine is inconsistent with this rule, although the correlation was satisfactory for the other amines. Thus,

$$\log k_{MAA} = (-10.822 \pm 2.040) + (0.763 \pm 0.267)I, \quad (9)$$

$$r = 0.906;$$

$$\log k_{AA} = (-8.236 \pm 0.395) + (0.754 \pm 0.050)I, \quad (10)$$

$$r = 0.997;$$

**Table 3.** Effect of the nature of amine on the rate constant of the reaction between the amine and acrylonitrile ( $k_1$ ), acrylamide ( $k_2$ ), or methacrylamide ( $k_3$ ) in water at 293 K

Amine	Piperidine	Diethylamine	Dipropylamine	Morpholine	Diethanolamine
$k_1, 1 \text{ mol}^{-1} \text{ s}^{-1}$	$(2 \pm 0.1) \times 10^{-1}$	$(3.5 \pm 0.2) \times 10^{-2}$	$(3.2 \pm 0.1) \times 10^{-2}$	$(3 \pm 0.1) \times 10^{-2}$	$(1.00 \pm 0.05) \times 10^{-3}$
$k_2, 1 \text{ mol}^{-1} \text{ s}^{-1}$	$(2.5 \pm 0.1) \times 10^{-2}$	$(4.0 \pm 0.2) \times 10^{-3}$	$(3.7 \pm 0.1) \times 10^{-3}$	$(3.0 \pm 0.1) \times 10^{-3}$	$(2.1 \pm 0.1) \times 10^{-4}$
$k_3, 1 \text{ mol}^{-1} \text{ s}^{-1}$	$(2.0 \pm 0.1) \times 10^{-4}$	$(7.2 \pm 0.3) \times 10^{-6}$	$(5.0 \pm 0.2) \times 10^{-6}$	$(3.7 \pm 0.15) \times 10^{-6}$	$1.0 \times 10^{-6}$
$I, \text{ eV}$ [17, 18]	8.7	7.85	7.76	8.5	6.0
$pK_a$ [19]	11.12	10.93	10.91	8.7	8.88
$E_s$ [20]	-0.51	-0.14	-0.72	-0.51	-0.79
$\mu_{298}$ [21]	1.2	1.2	1.07	1.54	2.81
$\sigma_R$ [20]	-0.18	-0.20	-0.23	0.67	—

$$\log k_{\text{AN}} = (-8.015 \pm 0.850) + (0.082 \pm 0.0107)I, \quad (11)$$

$$r = 1.000.$$

Thus, the basicity and ionization potentials of amines cannot separately characterize the reactivity in reactions with unsaturated compounds.

Taking into account the mechanism of the test reactions, we also attempted to consider the effect of the dipole moment ( $\mu$ ) and the steric factor ( $E_s$ ) (steric parameters of substituents). The  $E_s$  parameter was chosen intentionally because the interaction becomes sterically hindered with an increase in the length and branching of a hydrocarbon chain. The steric factor was considered in detail in [27].

Taking into account the above, we derived the following correlation equations that relate the amine reactivity in reactions with acrylonitrile, acrylamide, and methacrylamide in water to the values of  $I$ ,  $pK_a$ ,  $E_s$ , and  $\mu$  of amines:

$$\log k_{\text{AN}} = -11.26 + 0.77I + 0.31pK_a - 0.12E_s + 0.23\mu \quad (12)$$

$$\log k_{\text{AA}} = -13.17 + 0.77I + 0.37pK_a - 0.18E_s + 0.49\mu \quad (13)$$

$$\log k_{\text{MAA}} = -31.94 + 1.58I + 1.04pK_a - 0.54E_s + 2.3\mu \quad (14)$$

The coefficients of  $I$ ,  $pK_a$ , and  $\mu$  in Eqs. (12)–(14) have a positive sign and the coefficient of  $E_s$  has a negative sign. This fact is consistent with a known mechanism of the above reactions.

It follows from Eqs. (12)–(14) that of the four parameters the ionization potential is most important for amines.

However, the effects of other parameters cannot be neglected based in this conclusion.

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