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The Reaction of Amino Alcohols with Acrylates

By Naoya OGATA* and Tomohiko ASAHARA

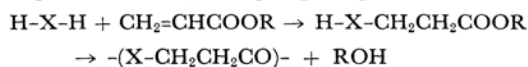
Basic Research Laboratories, Toyo Rayon Co., Ltd., Tebiro, Kamakura

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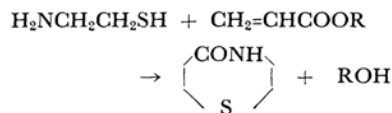
The addition reaction of amino alcohols with acrylates were studied. The addition takes place at the amino group of amino alcohol, producing *N*-(hydroxyalkyl)- β -alanine in a good yield. The reaction rate becomes slower as the ester group of acrylate becomes larger, and phenyl acrylate gives a polymer as soon as it is mixed with ethanolamine. The rates of the addition reaction with acrylate are in the following order: $\text{NH}_2\text{CH}_2\text{CH}_2\text{OH} > \text{CH}_3\text{NHCH}_2\text{CH}_2\text{OH} \gg \text{RNH}_2 > \text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$.

It is well known (the Michael reaction) that a conjugated system of the $\text{C}=\text{C}-\text{C}=\text{O}$ type, such as an α, β -unsaturated carbonyl compound, adds a compound with an active hydrogen group in the presence of the base.

When a compound with two active hydrogen groups reacts with acrylates, the product could be a new monomer for polymer materials, since a further polycondensation between the remaining group and carboxylate group is possible:



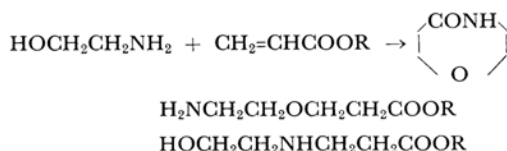
It is reported¹⁾ that β -aminoethyl mercaptane reacts with acrylates as is shown below to give a thialactam:



If an amino alcohol is used in place of β -aminoethyl mercaptane, the following products would be formed in the system:

* Present address: Dept. of Chem., Sophia Univ., Chiyoda-ku, Tokyo.

1) F. Jacob and P. Schlack, *Chem. Ber.*, **96**, 88 (1963).



Therefore, kinetic studies on the Michael-type reaction between amino alcohols and acrylates have been carried out. They will be described below.

Experimental

Reagents.—Commercial amino alcohols and acrylates were dried in the presence of calcium hydride and distilled by means of a Shibata fractional distillation column.

Reaction.—Amino alcohols and acrylates were dissolved in solvents at given concentrations, and the solutions were mixed at a given temperature, with or without an alkali alkoxide. The reaction rates were followed by the gas chromatographic method, using a polyethyleneglycol 6000 column. After the evaporation of the solvents, the products were distilled under a high vacuum and the products were characterized by an elementary analysis and by a study of their infrared and 100 Mc. NMR spectra.

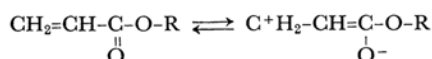
Results and Discussion

Reaction with Amino Alcohols.—The reaction rates of amino alcohols with acrylates were

measured in tetrahydrofuran in the absence of an alkali alkoxide at 0, 20 and 50°C. In each case, the reactions were completed within 10 hr. at 20°C and unchanged acrylates were found in the system only in amounts of 1 to 2%.

The rates apparently followed a second-order reaction; the rate constants are summarized in Table I. In the case of methyl acrylate, the rate constant decreased at the initial stage of the reaction and an auto-catalytic effect was apparently observed. The rate constants in Table I for methyl acrylate are extrapolated values at $t=0$ for the linear part.

It may be seen from Table I that the rate constants decreased with the size of ester groups in the following order: $-\text{CH}_3 > -\text{C}_2\text{H}_5 > n\text{C}_4\text{H}_9$. The effect of alkyl groups on the addition reaction may be ascribed to the increasing $-I$ effect, which may reduce the carbonium ion character of the β -carbon atom and, hence, may prevent a nucleophilic attack of the amino group.



When phenyl acrylate and ethanolamine were mixed in tetrahydrofuran at a concentration of 0.1 mol./l., the reaction rate was too rapid to measure and a polymer was precipitated as soon as they were mixed. A theoretical amount of phenol was found, and neither phenyl acrylate nor ethanolamine remained in the system. The

TABLE I. RATE CONSTANTS* OF THE REACTION OF AMINO ALCOHOLS AND ACRYLATES

Amino alcohol	Acrylate	0°C	20°C	50°C
Ethanolamine	$-\text{CH}_3$	3.9×10^{-2}	9.0×10^{-2}	4.7×10^{-2}
	$-\text{C}_2\text{H}_5$	1.3×10^{-2}	2.4×10^{-2}	4.3×10^{-2}
	$-n\text{C}_4\text{H}_9$	0.8×10^{-2}	1.8×10^{-2}	2.6×10^{-2}
	$-\text{C}_6\text{H}_5$		(reacted immediately)	
N-Methyl ethanolamine	$-\text{CH}_3$	—	5.0×10^{-2}	—
Diethanolamine	$-\text{C}_2\text{H}_5$	—	9.0×10^{-2}	—
Propanolamine	$-\text{CH}_3$	—	4.0×10^{-2}	—
	$-\text{C}_2\text{H}_5$	—	2.0×10^{-2}	—

* Concentration is 1 mol./l. of tetrahydrofuran, unit; min^{-1}

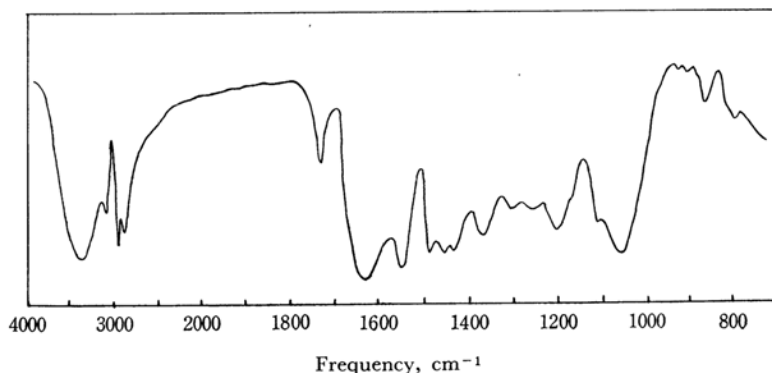


Fig. 1. Infrared spectrum of the polymer from phenyl acrylate and ethanolamine.

analytical data of this polymer were as follows: C=49.0%, H=8.5%, N=7.9%, M. W.=500. The infrared spectrum of the polymer, shown in Fig. 1, suggests a polyamide structure.

When an amine hydrogen of ethanolamine is replaced by an alkyl group, the rate becomes slower, especially for diethanolamine, the rate constant being one-thousandth that of ethanolamine.

The solvent effect on the addition reaction of ethanolamine and methyl acrylate was measured to be as shown in Table II. Generally speaking, the reaction is faster in a solvent with a higher dielectric constant. This finding suggests that the reaction might proceed through an ionic mechanism.

TABLE II. RATE CONSTANTS* OF THE REACTION OF ETHANOLAMINE AND METHYL ACRYLATE IN VARIOUS SOLVENTS AT 20°C

Solvent	Dielectric constant (20°C)	k_1 , min ⁻¹
Methanol	3.26	9×10^{-2}
Tetrahydrofurane	—	7×10^{-2}
Acetonitrile	38.8	4×10^{-2}
Dimethylformamide	36.6	4×10^{-2}
Pyridine	12.3	3×10^{-2}
Dioxane	2.2	2×10^{-2}

* Concentration is 1 mol./l.

Reactions with Amines or Alcohol.—When an amino alcohol is added to an acrylate, there are two reaction sites, namely, an amino and a hydroxy group. Therefore, the rates of the addition reaction of simple amine or alcohol to ethyl acrylate were compared; they are summarized in Table III.

TABLE III. RATE CONSTANTS* OF THE REACTION OF AMINE OR ALCOHOL WITH ETHYL ACRYLATE IN TETRAHYDROFURANE AT 20°C

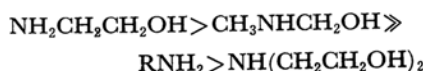
Reactant	pK_a	k_1 , min ⁻¹
Aniline	4.62	0
Benzylamine	9.34	5.0×10^{-5}
Diethanolamine	8.80	9.0×10^{-5}
Allylamine	9.49	1.6×10^{-4}
<i>n</i> -Butylamine	10.59	2.1×10^{-3}
Ethanolamine	9.50	2.4×10^{-2}
Ethanol**	—	1.2×10^{-1}

* Concentration is 1 mol./l.

** In the presence of 5 mol.% of potassium metal.

Aniline does not react at all, even in the presence of 5 mol.% CH_3OK , and, generally, amines with higher pK values react faster. However, ethanolamine, which has almost the same pK value as allylamine, reacts about 150 times as fast as allylamine. The great accelerating effect of the hydroxyethyl group on the reactivity of the amino group

is very interesting; it needs a further investigation. On the other hand, when an amine hydrogen of ethanolamine is further replaced by the hydroxyethyl group, the rate of the addition reaction decreases:



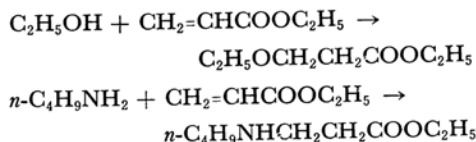
This peculiar behavior of ethanolamine suggests that the reaction involves not only a simple nucleophilic mechanism, but also a more complicated mechanism.

Alcohol does not react at all with ethyl acrylate, while in the presence of 5 mol.% of potassium ethoxide it reacts 5 times as fast as ethanolamine.

The Structure and Properties of the Reaction Products.—*Amine or Alcohol.*—The analytical results of the reaction product on *n*-butyl amine or ethanol with ethyl acrylate are as follows:

	B. p.	M.W.	C, %	H, %	N, %	Yield
<i>n</i> -Butyl amine						
Obs. 70/3 mmHg	173	62.3	6.9	8.1	87	
Calcd. —	173	62.4	7.5	8.1	—	
Ethanol						
Obs. 54/8 mmHg	146	58.3	9.59	—	60	
Calcd. —	146	58.1	9.62	—	—	

The analytical data and infrared spectra of the products support the following reactions:



Amino Alcohol.—The reaction products were polymerized into a sticky polymer by letting them stand at room temperature for several days, though it was necessary to keep them below 0°C. Their analytical results are shown in Table IV.

The infrared spectra of the products showed strong absorptions at 1720, 1200 and 1100 cm^{-1} ; these absorptions were easily assigned to an ester group, as can be seen in Fig. 2. The absorption peak at 3400 cm^{-1} is assigned to a hydroxy group, since no absorption at 1600 cm^{-1} resulting from an amine deformation was found; the strong absorption observed at 1050 cm^{-1} was assigned to a hydroxy deformation band. The infrared spectrum of the reaction product of *N*-methyl ethanolamine also showed the existence of a hydroxy group.

The qualitative analysis of the reaction products gave strong support for the existence of a secondary amine. The NMR spectra of the products are shown in Fig. 3. In the case of the methyl ester, a sharp peak at 6.2 τ and a broad peak at 6.53 τ can be assigned to $-\text{OCH}_3$ and OH or $-\text{NH}_2$ respectively. As the absorption strengths of 6.31, 7.03, 7.24 and 7.43 τ are almost identical, there

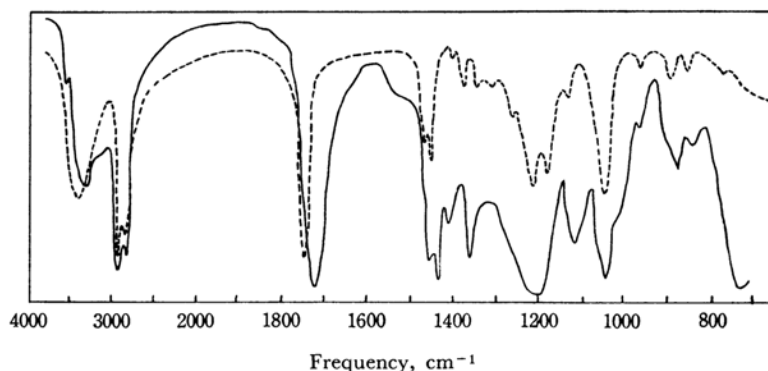


Fig. 2. Infrared spectra of the reaction products.

— Ethanolamine and methyl acrylate

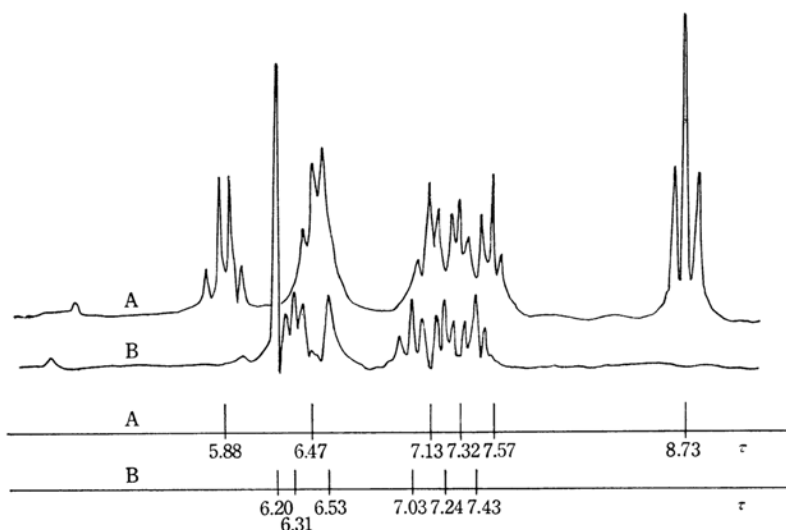
--- *N*-Methyl ethanolamine and ethyl acrylate

Fig. 3. NMR Spectra of the reaction products.

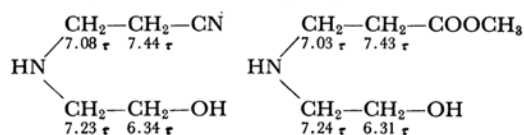
TABLE IV. ANALYTICAL RESULTS OF THE REACTION PRODUCTS OF AMINO ALCOHOL AND ACRYLATES

Amino alcohol	Acrylate	B.p. °C/ mmHg	M.p. °C	M. W.		Base, mol./g.		N, %	
				Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
Ethanolamine	-CH ₃	107/3	40	148	148	6.8 × 10 ⁻³	6.8 × 10 ⁻³	8.7	10.0
	-C ₂ H ₅	135/3	28	161	165	6.2 × 10 ⁻³	6.0 × 10 ⁻³	8.7	8.9
	- <i>n</i> C ₄ H ₉	116/1	—	189	188	5.3 × 10 ⁻³	5.1 × 10 ⁻³	7.4	7.6
<i>N</i> -Methyl ethanolamine	-CH ₃	95/4	—	161	162	6.2 × 10 ⁻³	6.2 × 10 ⁻³	8.7	8.8
Propanolamine	-CH ₃	102/2	—	161	227	—	—	8.7	9.8
	-C ₂ H ₅	137/3	—	175	180	—	—	8.0	8.5

are four methylene groups. The chemical shift of -OCH₂ is generally in the range from 5.5 to 6.7 τ ,²⁾ and the peak at 6.31 τ may be assigned to -OCH₂-. The peak at 7.43 τ is assigned to -N-CH₂-, which was split into two peaks by the influence of a functional group at the β -position.

It is known³⁾ that ethanolamine adds to acrylonitrile and the structure of the product is *N*-(β -cyanoethyl)-ethanolamine. The NMR spectrum of this product reconfirms that ethanolamine adds

to an acrylate at the amino group as is shown below:



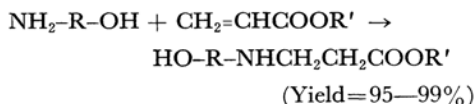
2) K. Nukada, O. Yamamoto, T. Suzuki, M. Takeuchi and M. Ohnishi, *Anal. Chem.*, **35**, 1892 (1963).

3) Y. Ogata, *J. Am. Chem. Soc.*, **78**, 5426 (1956).

Hydroxylamine reacts with acryamide⁴⁾ at the amino group;



From these results, it may be said that the reaction of amino alcohols with acrylates in the absence of a basic catalyst takes place at the amino group, yielding *N*-(hydroxyalkyl)- β -alanine:



As has been stated above, the reaction rate of alcohol with ethyl acrylate in the presence of a potassium catalyst is about 600 times as fast as

that of amine itself, and it is much faster than ethanolamine. The reaction of ethanolamine in the presence of an alkali alkoxide is expected to take place at the hydroxy group of ethanolamine. However, the reaction in the presence of an alkali alkoxide caused a polymerization, yielding a theoretical amount of alcohol; a low-molecular-weight polymer was also precipitated, the analytical data of which showed the same results as in the case of phenyl acrylate, and the polymer was not a homo-polyacrylate. This peculiar reaction, as well as the reaction of phenyl acrylate, will be elucidated in the near future.

The authors wish to express their thanks to Dr. Toshio Hoshino for permission to publish this paper and also to Dr. Kenkichi Nukada for his helpful discussion of the NMR spectra.

4) A. R. Sayigh, *J. Org. Chem.*, **29**, 2042 (1964).