

ADDITION OF SECONDARY AMINO GROUP TO DOUBLE BOND OF ACRYLATES

Jiří HORÁLEK^a, Emil KREJCAR^a and Jaroslav CHURÁČEK^b

^a Research Institute of Synthetic Resins and Lacquers, 532 07 Pardubice and

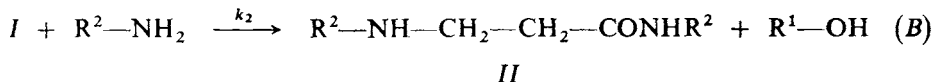
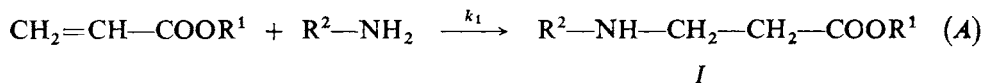
^b Institute of Chemical Technology, 532 10 Pardubice

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The near IR region spectroscopy has been used to follow the addition reactions of the secondary amino groups of tert-butyl 3-butylaminopropanoate, N,N'-dibutyl-3-aminopropanamide, and dibutylamine to tert-butyl acrylate. The additions are bimolecular reactions of the second order. The respective rate constants found for the above-mentioned compounds are $3.54 \cdot 10^{-6}$, $2.34 \cdot 10^{-5}$, and $3.18 \cdot 10^{-6} \text{ l mol}^{-1} \text{ s}^{-1}$. The secondary amidic groups increase the nucleophilicity of secondary amino group and hence also the rate of the addition reaction.

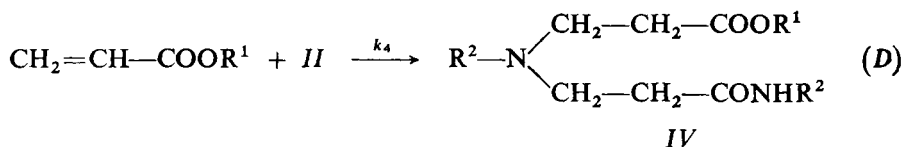
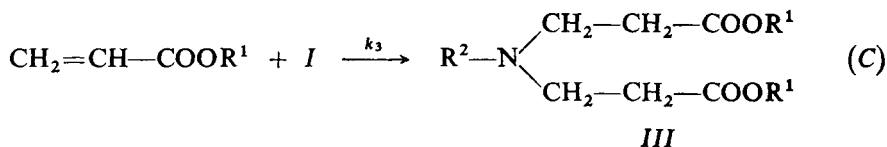
Investigation of addition reactions of primary amines to the double bond of acrylate esters, which form the basis of some technologically important curing reaction types for modified epoxide mixtures, revealed (refs¹⁻⁵) that secondary amino groups can participate in the reaction, too. If these systems also involve aminolysis, then the reaction order and rate constant are not easily determined, because the system represents two parallel reactions, each of them being a consecutive competitive reaction. Hence, our intention is to deal with the addition reactions of the secondary amino groups of the intermediates to the double bond of the starting acrylate which can take place in these systems.

It can be expected that a reaction of primary amine with acrylate will produce the following amino derivatives:



The I/II product ratio in the nucleophilic addition represents a result of a whole set of partial factors (the components ratio and structure, basicity of the nucleophilic agent, polarity of the medium, catalysts, etc.). The aminolysis of an acrylate is sufficiently fast only in the presence of primary amino groups; after their consump-

tion by the addition to the acrylate double bond the aminolysis abruptly decelerates and gradually ceases⁶. Subsequently, there can occur the addition of the secondary amino group of N-alkyl- β -alanine ester (*I*) and/or N,N'-dialkyl-3-aminopropanamide (*II*) to the double bond of the starting acrylate according to the following scheme:



With regard to the mechanism indicated we followed the reactions of double bond in the acrylate with secondary amino group of the intermediates *I* and *II* by NIR spectroscopy using the absorption bands at 6 530 and 6 150 cm^{-1} corresponding to the first overtones of the stretching vibrations of secondary amino group ($2\nu(\text{N}-\text{H})$) and of terminal methylene group ($2\nu(\text{H}-\text{C}=\text{C})$), respectively (refs⁷⁻⁹).

EXPERIMENTAL

The starting aminoester (*I*, $\text{R}^1 = \text{t-C}_4\text{H}_9$, $\text{R}^2 = \text{n-C}_4\text{H}_9$) was prepared by the nucleophilic addition of 1-butanamine (Janssen Chimica, Belgium, 99%, d^{20}_4 0.740, n^{20}_D 1.4015) to the double bond of tert-butyl acrylate (Fluka AG, Switzerland, 99%, d^{20}_4 0.883, n^{20}_D 1.410) (ref.¹⁰). The aminoamide (*II*, $\text{R}^1 = \text{R}^2 = \text{n-C}_4\text{H}_9$) was obtained by 1 h boiling of 1-butanamine with methyl acrylate at the molar ratio of 2.5 : 1. The excess 1-butanamine and the methanol released were distilled off in vacuum. The further reaction products *III* and *IV* were prepared by the reactions of the aminoester *I* and aminoamide *II*, respectively, with the acrylate at the molar ratio of 1 : 1.5 in aqueous ethanolic solution. After 1 h boiling, the unreacted components and the solvents were distilled off in vacuum. Purity of all the substances given was checked by ¹H and ¹³C NMR spectroscopy (Bruker AM 400 spectrometer; deuteriochloroform as the solvent). An increased intensity of the spectral curve (scale = 8) showed the presence of impurities below 2%. The physical constants of the individual reaction products obtained from tert-butyl acrylate and 1-butanamine are given in Table I.

The reaction of the acrylate double bond with the amino group of aminoester *I* or aminoamide *II* was followed without solvent. Both components were always mixed in the ratio of 1 : 1 in a tempered (25°C) quartz cell (0.2 cm). NIR spectra were recorded at definite time intervals in the range from 8 000 to 4 500 cm^{-1} using a CF 4 NIR spectrophotometer (Optica Milano). The absorption bands followed were evaluated by means of the base tangent line method. The conversion of both the secondary amino groups and double bonds was calculated from Eq. (1)

$$x = (A_0 - A_t)/A_0, \quad (1)$$

where A_0 means the initial absorption at 6 530 and 6 150 cm^{-1} , respectively, and A_t are the corresponding absorptions during the reaction course.

RESULTS AND DISCUSSION

In the preliminary experiments using NIR spectroscopy we followed the different reactivity of acidic hydrogen atoms of amino groups of a series of primary or secondary amines reacting with the terminal methylene group of the α,β -unsaturated monomer. These preliminary studies showed that the addition of amino group of secondary amines much more depends on the structure of the alkyl group in the amine as compared with that of the primary amines. Table II documents the influence of steric hindrance of alkyl groups which co-determines the reactivity of amines in the reactions studied. The findings presented were then applied to the solution of the problem of effect of structure of intermediates containing secondary

TABLE I
Physical constants of the addition products I–IV

Constant	I	II	III	IV
Density d^{20} , g/cm^3	0.8800	0.9234	0.9831	0.9545
Refractive index n_D^{20}	1.4268	1.4583	1.4333	1.4572

TABLE II
Reactivities of selected primary and secondary amines to the double bond of tert-butyl acrylate

Primary amine	Reaction course ^a	Secondary amine	Reaction course ^a
Propylamine	+++	Dipropylamine	+
Isopropylamine	+++	Dibutylamine	+
Cyclopropylamine	+++	Diisopropylamine	—
Butylamine	+++	N-Ethylcyclohexylamine	—
Tert-butylamine	++	N-Isopropylcyclohexylamine	—
Neopentylamine	+++	Dicyclohexylamine	—

^a +++ means positive already at the first spectral measurement immediately after mixing the components (a distinct decrease of the absorption bands due to double bonds); ++ means positive test after 2 h standing at 25°C; + means positive test after 6 h standing at 25°C; — means a negative test.

amino groups on the course of the isolated second step of the consecutive competitive reaction of primary amines with acrylates.

Two types of intermediates containing a secondary amino group can be formed in the reaction of 1-butanamine with tert-butyl acrylate, viz. tert-butyl 3-butylamino-propanoate and N,N'-dibutyl-3-aminopropanamide. As their analytical concentration is not constant during the reaction of 1-butanamine with tert-butyl acrylate, the 1 : 1 molar ratio of the components was chosen for easier interpretation of results of the kinetic measurements. The NIR spectra of the model reaction products *III* and *IV* showed that these substances exhibit no distinct absorption in the spectral region investigated and, hence, do not interfere with analytical determination of secondary amino groups and double bonds.

Figure 1 shows the time dependence of the conversion of secondary amino groups of both intermediates in the reaction with tert-butyl acrylate without solvent. For comparison, the figure also gives the conversion of secondary amino groups in the reaction of dibutylamine with tert-butyl acrylate without solvent.

Comparison of the time dependences of conversion of secondary amino groups shows that the reactivity of double bond with secondary amino group decreases in the series: aminoamide *II* \gg secondary amine $>$ aminoester *I*. In all the cases the conversion of double bonds is, within the experimental error of 2–5% rel., identical with that of secondary amino groups. No aminolysis of ester group with secondary amino group was observed in the systems investigated. The reaction order was determined by the method of partial reaction time¹¹. All the three reactions

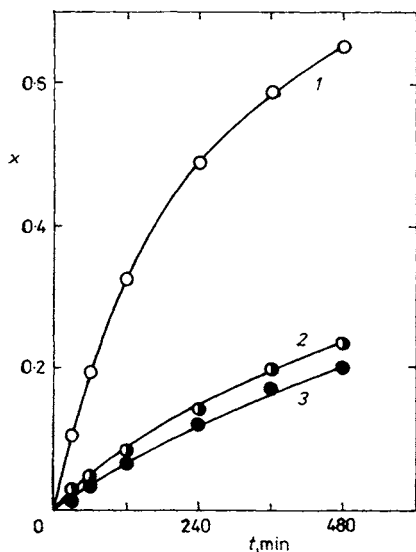


FIG. 1
The time dependence of conversion of secondary amino groups; 1 aminoamide *II*, 2 dibutylamine, 3 aminoester *I*

given were found to be bimolecular reactions of overall second order. The rate constants were determined graphically and numerically. In all the three cases the fundamental equation was fulfilled for the stoichiometric ratio of the components in the second order reactions. The values of rate constants and half-lives are given in Table III.

The way of realization of the addition reaction in the systems studied ensures the independence of relative order of nucleophilicity of the secondary amino group with regard to the reaction conditions and the substrate type. The solvation effects do not make themselves felt here either. The nucleophilicity of these reagents containing the same central atom increases with increasing basicity (the effect of alkyl groups). The slightly electron-withdrawing character of the ester group in the aminoester *I* somewhat decreases the reactivity of the secondary amino group. On the other hand, the slightly basic character of amidic group in the aminoamide *II* distinctly increases the reactivity of the secondary amino group as compared with dibutylamine (which only contains "neutral" butyl groups). In addition, the interaction of the lone electron pair at the amidic nitrogen atom with the electron system of the oxygen atom in the ester carbonyl group of the starting acrylate also favours the suitable orientation of reaction centres of both the reacting components.

From these facts it follows that in the systems in which a side aminolysis reaction is possible the tertiary amino group will predominantly be formed by the reaction of the starting acrylate with aminoamide *II*. If an unsaturated monomer is used as additive to a macromolecular compound (e.g. epoxide resin), the tertiary nitrogen atom can act as a catalyst of anionic polymerization, whereby the curing process and, hence, also mechanico-physical properties of the final product are unfavourably affected.

TABLE III

The rate constant and half-life values of the reactions of secondary amino groups with the double bond of tert-butyl acrylate (mol. ratio 1 : 1, temperature 25°C)

Compound	Initial conc. l mol ⁻¹	Graphically		Numerically	
		$k_i \cdot 10^6$ l mol ⁻¹ s ⁻¹	$\tau_{1/2} \cdot 10^{-5}$ s	$k_i \cdot 10^6$ l mol ⁻¹ s ⁻¹	$\tau_{1/2} \cdot 10^{-5}$ s
Aminoester <i>I</i> (k_k)	2.680	3.60	1.036	3.54	1.054
Aminoamide <i>II</i> (k_{kk})	2.688	23.20	0.160	23.40	0.159
Dibutylamine	3.430	3.21	0.908	3.18	0.917

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