REACTIONS OF PRIMARY ALIPHATIC AND CYCLOALIPHATIC AMINES WITH 1-BUTYL ACRYLATE

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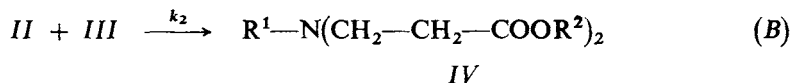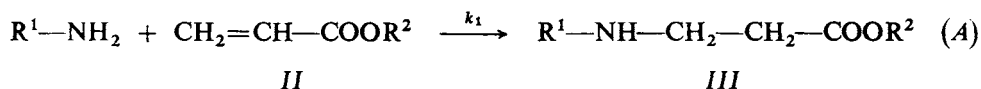*Research Institute of Synthetic Resins and Lacquers, 532 07 Pardubice*

The addition reactions of primary aliphatic and cycloaliphatic amines with 1-butyl acrylate have been investigated by means of near IR spectroscopy. The additions proceed contrary to the Markownikoff rule and are consecutive competitive reactions which can be treated as isolated reactions with respect to the considerable difference between rate constants of the individual steps. The value of rate constants determined from the spectral data have been compared and discussed in terms of the steric hindrance of alkyl groups which co-determines the reactivity of amines in the reactions investigated.

Some technologically important reaction types of curing of modified epoxide mixtures are based on the addition reaction of primary amines to the double bond of acrylate esters. Investigation of this reaction revealed that secondary amino groups can also participate in the reaction under certain conditions[1,2].

The reaction of nucleophilic reagents of the amine type with the double bond of esters of α,β-unsaturated carboxylic acids, especially acrylates (provided that in these systems the reaction rate of the nucleophile with the ester carbonyl group can be neglected as compared with the addition rate at the terminal methylene group) can be represented by the following reaction scheme:

$$R^1{-}NH_2 \; + \; CH_2{=}CH{-}COOR^2 \; \xrightarrow{\; k_1 \;} \; R^1{-}NH{-}CH_2{-}CH_2{-}COOR^2 \quad (A)$$

$$II \qquad\qquad\qquad\qquad\qquad III$$

$$II \; + \; III \; \xrightarrow{\; k_2 \;} \; R^1{-}N(CH_2{-}CH_2{-}COOR^2)_2 \qquad (B)$$

$$IV$$

The effect of structure of the R^1 alkyl group in the starting primary amine molecule represents one of the important factors directly influencing the course of this reaction. With respect to the reaction scheme, the reaction of the acrylate double bond with primary aliphatic and cycloaliphatic amines was followed by means of the NIR spectroscopy. The reaction course was followed with the use of the absorption bands

of the wavenumber $6\,530\,cm^{-1}$ (the first overtone stretching absorption band $2\nu(N\!-\!H)$ of both the primary and secondary amino groups), $4\,950\,cm^{-1}$ (the combination stretching and bending absorption band $\nu + \delta(N\!-\!H)$ of the primary amino group), and $6\,150\,cm^{-1}$ (the first overtone stretching absorption band $2\nu(H\!-\!C\!\!=\!)$ of the terminal methylene group)[3-5].

EXPERIMENTAL

The starting monomers for the kinetic measurements were 1-butyl acrylate and primary aliphatic and cycloaliphatic amines (Janssen Chimica, Belgium). The reaction of primary amino group with the acrylate double bond was carried out without any solvent. Both the components were mixed at the molar ratio of 1 : 1 in a thermostated $0.2\,cm$ quartz cell at $20°C$. At definite time intervals the NIR spectrum was measured by means of a CF 4 NI spectrophotometer (Optica Milano) in the wavenumber range of $8\,000 - 4\,500\,cm^{-1}$. The absorption bands measured were evaluated by means of the base tangent line method. The increase of the secondary amino groups was calculated from the relation

$$A(NH) = A(NH_2 + NH) - A(NH_2)/K(NH_2)\,, \tag{1}$$

where $A(NH_2 + NH)$ means the absorbance of the $6\,530\,cm^{-1}$ band of the primary and secondary amino groups, $A(NH_2)$ is the absorbance of the $4\,950\,cm^{-1}$ band of primary amino groups, $A(NH)$ is the contribution of secondary amino groups to the absorbance of the band at $6\,530\,cm^{-1}$, and $K(NH_2)$ is the absorbance ratio of the absorption bands at $4\,950\,cm^{-1}$ and $6\,530\,cm^{-1}$ (the primary amino groups) which remains constant throughout the reaction.

Ethyl N-tert-butyl-3-aminopropanoate (98%, d^{20} 0·9044, n_D^{20} 1·4204) was prepared[6] by the nucleophilic addition of tert-butylamine to the double bond of ethyl acrylate (Janssen Chimica, Belgium). The NMR spectra of the addition reaction products of amines and acrylates were measured with an FT NMR spectrometer Bruker AM 400 in tubes of 5 mm diameter with $CDCl_3$ as the solvent and tetramethylsilane as the internal standard.

RESULTS AND DISCUSSION

The addition of primary amines to the double bond of acrylates represents a very fast exothermic reaction[2]. In some cases without solvent the addition is practically instantaneous. In these systems the reaction predominantly proceeds contrary to the Markownikoff rule, which was confirmed by identification of the isolated reaction products by means of NMR spectroscopy. Figure 1 presents the ^1H NMR spectrum of the addition reaction product from tert-butylamine and ethyl acrylate, i.e. ethyl N-tert-butyl-3-aminopropanoate. The characteristic system of two triplets belonging to the internal methylene groups in the structure of this compound was found in the ^1H NMR spectra of the reaction products in all the systems studied.

The course of the addition reaction carried out without solvent (see the reaction scheme) was investigated in the reaction system of 1-butylamine and 1-butyl acrylate. The absorbance values of the absorption bands of primary and secondary amino groups and double bonds plotted against time for the case of the addition reaction at

the molar ratio of 1 : 1 are presented in Fig. 2. The equation of bimolecular reaction of overall second order at the stoichiometric ratio of both components was found satisfactory in the calculation of the rate constant[7]. In the whole time range studied, the concentration decrease of primary amino groups and increase of secondary amino groups are analogous to the concentration decrease of double bonds. The IR spectrum of the final reaction mixture contained no absorption bands ascribable to amidic groups. When carrying out this reaction with a double molar concentration of acrylate with respect to the concentration of primary amine (the stoichometric ratio for formation of the reaction product *IV*) an about 54% conversion of the double bonds was reached after 8 h. Applying the mathematic model for calculation of consecutive rate constants of the consecutive competitive reaction by the time ratio method[8] we obtained the value $k_1/k_2 = 55\cdot6$. The high value of this ratio indicates that the step (A) of the reaction scheme can be treated as an isolated reaction.

The addition reaction rate of the double bond of the unsaturated monomer depends especially on the branching of the hydrocarbon chain of the nucleophile molecule. This fact was verified by investigation of the time course of the reactions of selected,
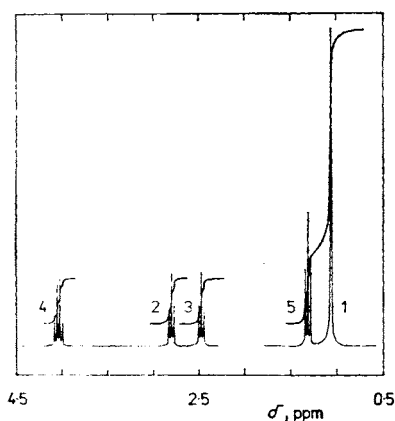

FIG. 1

^{1}H NMR spectrum of ethyl N-tert-butyl-3-
-aminopropanoate

$$\underset{1}{(CH_3)_3}C\underset{2}{NH}\underset{2}{CH_2}\underset{3}{CH_2}\underset{4}{COOCH_2}\underset{5}{CH_3}$$
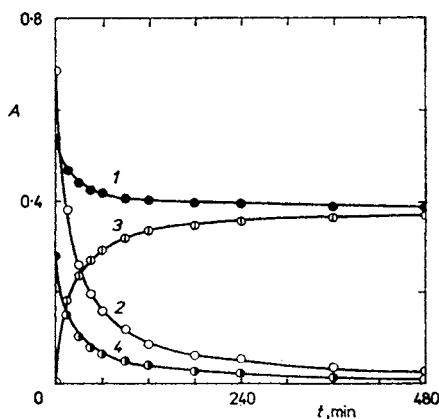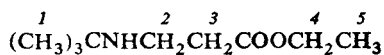
FIG. 2

The addition reaction kinetics of 1-butylamine with 1-butyl acrylate at the molar ratio of 1 : 1; *1* the absorbance of the band of primary and secondary amino groups at $6\,530\ cm^{-1}$, *2* the absorbance of the band of primary amino groups at $4\,950\ cm^{-1}$, *3* the contribution of secondary amino groups to the absorbance of the band at $6\,530\ cm^{-1}$, *4* the absorbance of the band the terminal methylene group at $6\,150\ cm^{-1}$

linear, branched, and cyclic primary amines with 1-butyl acrylate. The effect of alkyl structure in the molecule of primary amine on the addition reaction rate can be seen from the comparison of the k_1 rate constants presented in Table I.

The comparison of the k_1 rate constants of the isolated addition reactions (A) calculated by means of the equation for a bimolecular second-order reaction at the stoichiometric ratio of the starting components leads to the following conclusions:

a) The reaction course is not markedly affected by increasing number of methylene groups (methylene increment) of the molecule of linear aliphatic amines. Increasing $+I$ inductive effect along the hydrocarbon chain slightly increases the rate constant value (in the series 1-butyl, 1-hexyl, and 1-octyl the ratio of the rate constants is $1 : 1\cdot4 : 1\cdot64$).

b) With increasing distance of branching of the hydrocarbon chain from the primary amino group — in a series of isoalkyl structures — the steric hindrance of alkyl group decreases and the addition reaction rate constant increases (the ratio $1 : 3\cdot35 : 6\cdot4$ for isopropyl, isobutyl, and isoamyl).

c) With increasing distance of branching of the hydrocarbon chain from the reaction centre — in a series of tert-alkyl structures — the rate constant values also increase. The steric effect makes itself felt at a greater distance from the primary

TABLE I

The effect of the R^1 alkyl structure in the primary amine molecule on the value of the k_1 rate constant of the addition reaction (A) with 1-butyl acrylate (molar ratio 1 : 1, temperature 20°C, the reaction was carried out without solvent)

R^1	Initial concentration 1 mol^{-1}	$k_1 \cdot 10^6$ $1 \text{ mol}^{-1} \text{ s}^{-1}$	$-\sigma_I \cdot 10^2$	$-\sigma_R \cdot 10^2$	$v \cdot 10$	$-\sigma^* \cdot 10$
Isopropyl	4·376	28·9	6·4	11·0	7·6	1·90
1-Butyl	4·143	214·0	5·8	5·8	6·8	1·30
Isobutyl	4·101	96·9	5·8	5·3	1·25	
Sec-butyl	4·105	21·9	6·6	6·6	10·2	2·10
Tert-butyl	4·038	7·5	7·4	20·8	12·4	3·00
Cyclobutyl	4·387	42·5	—	—	—	—
Isopentyl	3·866	185·0	6·1	8·4	6·8	1·60
Neopentyl	3·853	66·5	6·2	8·8	13·4	1·65
1-Hexyl	3·641	300·0	6·1	8·4	7·3	1·60
3,3-Dimethylbutyl	3·608	163·0	—	—	7·0	—
Cyclohexyl	3·892	13·1	6·5	11·9	8·7	2·00
1-Octyl	3·249	351·0	—	—	6·8	—
Cyclooctyl	3·546	9·0	—	—	—	—

amino group as compared with the branching in the series of isoalkyl structures (1 : 8·87 : 21·7 for tert-butyl, neopentyl, and 3,3-dimethylbutyl).

d) In the series of cycloaliphatic hydrocarbon structures the rate constant value decreases with decreasing ring strain; the effect of increasing valence angle between the methylene groups at α carbon atom approaches — in its character — the steric effect of iso and tert-alkyl hydrocarbon structures in close vicinity of the nucleophilic centre (the decreasing ratio of rate constants 4·7 : 1·46 : 1 with increasing number of methylene groups in the series cyclobutyl, cyclohexyl, and cyclooctyl).

e) Maintaining the molecular mass, we can demonstrate the steric effect of alkyl group in the primary amine on the addition reaction rate with acrylate by the rate constant ratio 1 : 2·9 : 5·7 : 13 : 28·7 in the series tert-, sec-, cyclo-, iso-, and 1-butyl groups.

The k_1 rate constant values experimentally found were correlated with the constants of the extended Taft equation. A robust regression showed that the best results are obtained with the relative error of 4·13% from the four-parameter Taft equation[9] ($\alpha = 606\cdot24$, $\beta = -53\cdot59$, $\psi = 0\cdot39$, $h = 28\cdot10$, $R = 0\cdot998$, $\chi^2 = 0\cdot142$, and $SD = 0\cdot256$). The starting data for the correlations[9-12] are also presented in Table I. The results of the correlation show that the k_1 rate constant of the reaction investigated results from a superposition of inductive, conjugation, and steric effects.

The kinetic studies of steric hindrance of alkyl groups which co-determines the reactivity of amines in the reactions studied are valuable not only for theoretical organic chemistry but also find applications in technological practice. If in a particular application epoxide mixtures have to be used, it is necessary to use more vigorous linear aliphatic amine curing agents in order to obtain rapid curing and high degree of crosslinking. In accordance therewith, the unsaturated monomer is completely incorporated into the macromolecular network.

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