ISSN 1070-4272, Russian Journal of Applied Chemistry, 2012, Vol. 85, No. 11, pp. 1676–1680. © Pleiades Publishing, Ltd., 2012.
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ORGANIC SYNTHESIS
AND INDUSTRIAL ORGANIC CHEMISTRY

Reaction of Methyl Acrylate with *N,N*-Dimethylethanolamine in the Presence of a Titanium Alkoxide

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Received July 26, 2012

Abstract—The kinetic features were examined for transesterification of methyl acrylate with *N,N*-dimethylethanolamine in the presence of tetra(*N,N*-dimethylaminoethyl) titanate at different molar ratios of the reactants and at temperatures within 50–80°C, as well as for side reactions of Michael addition at 95–125°C. The major parameters governing the selectivity of the synthesis of *N,N*-dimethylaminoethyl acrylate were determined.

DOI: 10.1134/S1070427212110079

N,N-Dimethylaminoethyl acrylate (DMAEA), the product of transesterification of methyl acrylate with dimethylethanolamine (DMEA), serves as a raw material in synthesis of water-soluble polymers having broad-spectrum applicability (as flocculants, fragrances, and extractants).

The DMAEA synthesis reaction involves an equilibrium process and, consequently, requires withdrawing the resultant methanol from the reaction medium for the equilibrium to be shifted towards the target product.

Commercially, the transesterification reaction is conducted in an ester production apparatus, comprised of a continuously stirred tank reactor coupled with a rectifying column which receives the gas stream to be separated from methanol, at elevated temperatures (100–140°C), atmospheric or reduced pressure (40–80 kPa), in the presence of a homogeneous catalyst and a polymerization inhibitor. The initial methyl acrylate is used in a 2–3-fold molar excess with respect to DMEA [1–3].

As known [4], transesterification of methyl acrylate with DMEA involves, along with the main reaction of DMAEA formation, side Michael reactions (addition of alcohols at the vinyl group). The selectivity of the process is governed primarily by the choice of catalysts, among which neutral catalysts, organotitanium [5, 6] and organotin [1, 3] compounds, have received widespread application. The kinetic features and mechanism of transesterification of methyl acrylate with DMEA in the presence of titanium alkoxides have not yet been examined. Here, we report results that can aid in further optimization of the reactor design and operation.

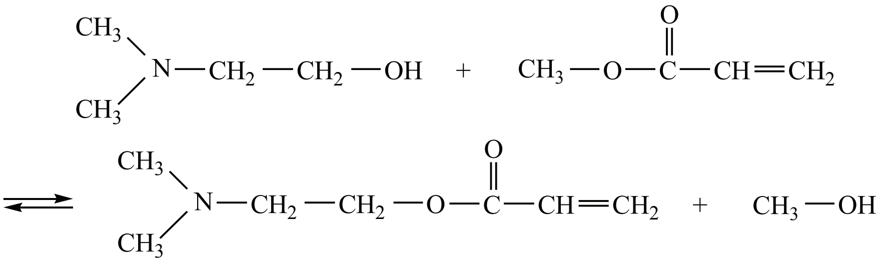
EXPERIMENTAL

We used methyl acrylate [99.7%, TU (Technical Specifications) 2435-003-52470063–2003], DMEA (99.3%, TU 2423-004-78722668–2010), DMAEA (99.9%, Arkema), methanol [99.5%, GOST (State Standard) 6995–77], and titanium tetraisopropylate (99.7%, TU 2423-008-50284764–2006]. The catalyst was prepared by the technique described in [6]. For synthesis of Michael adducts we used the procedure from [7].

The reactions were carried out in a metal reactor equipped with a jacket, a thermometer, a stirrer, and a sampler. Temperature control was achieved via circulation of the coolant (PMS-100 silicone fluid) through the reactor jacket and a LOIP LT-300 thermostatic bath. All the starting chemicals, including the inhibitor (phenothiazine, 0.2%), were introduced into the reactor and heated to the desired temperature; the warm-up period was no longer than 5 min. In the transesterification experiments, the catalyst was introduced into the reaction mixture heated to the desired temperature; prior to analysis, the catalyst was removed from the transesterification samples by precipitation as hydrous titania, and this was followed by filtration of the solution.

Chromatographic analysis was carried out on a Tsvet 800 gas-liquid chromatograph [SE-30 column, 10 m × 0.2 mm, a flame ionization detector, carrier gas (nitrogen) flow rate 200 ml $\mathrm{min^{-1}}$, evaporator and detector temperature 180°C]. The chromatograph temperature programming scheme was as follows: isothermal period 200 s at 60°C; temperature rise rate 20 deg $\mathrm{s^{-1}}$ to 200°C; isothermal period 300 s; temperature rise rate 25 deg $\mathrm{s^{-1}}$ to 240°C; isothermal period 300 s.

Dimethylaminoethyl acrylate is formed by the reaction:



(1)

The kinetic features of the transesterification reaction were examined at different molar excesses of methyl acrylate with respect to DMEA, catalyst concentrations, and temperatures. The reaction rate was monitored by measuring the amount of DMAEA accumulated in the reaction system. Figure 1 presents the kinetic curves of the target reaction.

We found that the reaction rate linearly varies with the catalyst concentration. As shown in [8] for transesterification of methyl benzoate with butanol, the reaction order with respect to the catalyst depends on its concentration, which fact was associated in that study with the tendency to associate, exhibited by titanium alkoxides. At the same time, titanium alkoxides derived from amino alcohols do not form associates [9], which finding agrees well with our data.

As the reaction model we took that based on the outer-sphere transesterification mechanism (see the scheme). This mechanism is described by the formal kinetic equation

$$r_1 = c_{\mathrm{cat}}(k_1 c_{\mathrm{MA}} c_{\mathrm{DMEA}} - k_{-1} c_{\mathrm{MeOH}} c_{\mathrm{DMAEA}}),$$

where c_{cat}, c_{DMAEA}, c_{MA}, c_{MeOH}, and c_{DMEA} are the molar concentrations of the catalyst, DMAEA, methyl acrylate, methanol, and DMEA, respectively, and k_1 and k_{-1}, rate constants of the forward and backward reactions, respectively, $\mathrm{l^2\,mol^{-2}\,h^{-1}}$.

The activation energies of the forward and backward reactions are 76 ± 5 and 46 ± 5 kJ $\mathrm{mol^{-1}}$, respectively. The reaction is endothermic, with the heat effect $\Delta Q = -30$ kJ $\mathrm{mol^{-1}}$.

Along with the main reaction of DMAEA formation,

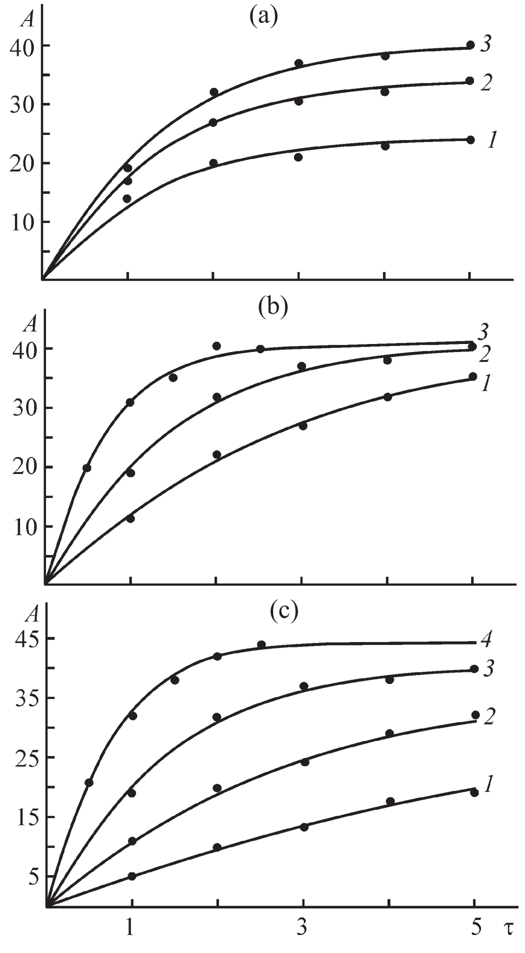
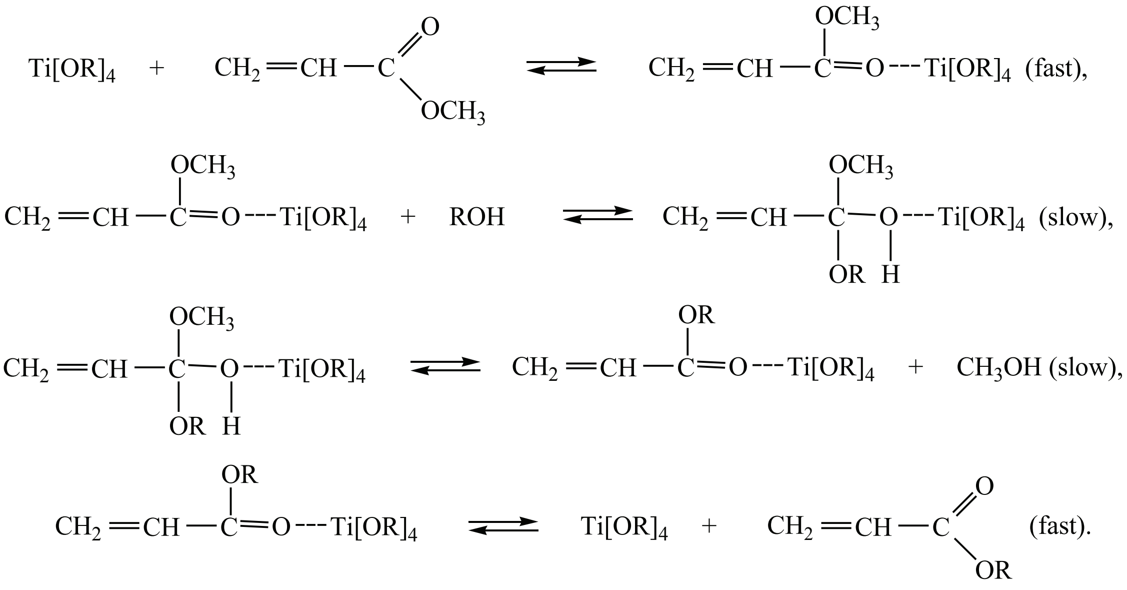
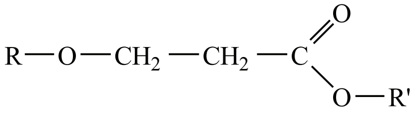


Fig. 1. Kinetic curves of transesterification. (*A*) Yield of DMAEA based on DMEA, %, and (*t*) time, h. (a) Catalyst concentration 0.1 M, temperature 70°C. Methyl acrylate:DMEA molar ratio: (*1*) 1 : 1, (*2*) 2 : 1, and (*3*) 3 : 1. (b) Catalyst concentration 0.1 M, methyl acrylate:DMEA molar ratio 3 : 1. *T*, °C: (*1*) 50, (*2*) 60, (*3*) 70, and (*4*) 80. (c) Methyl acrylate:DMEA molar ratio 3:1, temperature 70°C. Catalyst concentration, M: (*1*) 0.05, (*2*) 0.1, and (*3*) 0.2.

Scheme 1.



side Michael reactions [7] and transesterification reactions proceed, resulting in formation of esters with the general formula

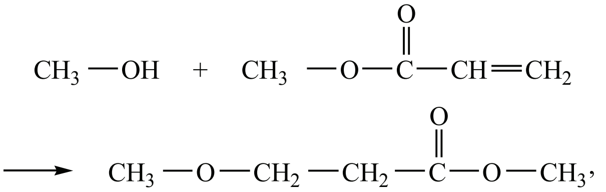


where R=$CH_2CH_2N(CH_3)_2$.

For Michael adducts, see table.

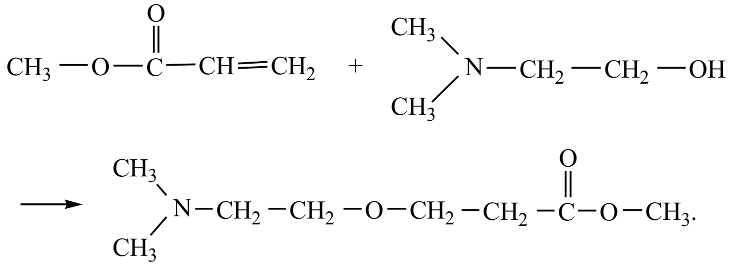
Addition of alcohols at the vinyl group of DMAEA (adducts **II** and **IV**) proceeds to a negligible extent; formation of these compounds in the reaction medium is due to transesterification of adducts **I** and **III** with DMEA.

Adduct **I** is formed by the reaction



$$CH_3-OH + CH_3-O-\overset{O}{\overset{\|}{C}}-CH=CH_2 \longrightarrow CH_3-O-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_3, \quad (2)$$

and adduct **III**, by the reaction



(3)

Michael adducts

Adduct	R	R'
I	CH_3–	CH_3–
II	CH_3–	$(CH_3)_2NCH_2CH_2$–
III	$(CH_3)_2NCH_2CH_2$–	CH_3–
IV	$(CH_3)_2NCH_2CH_2$–	$(CH_3)_2NCH_2CH_2$–

The rate of accumulation of Michael adducts is affected by the basicity of the medium [7]; titanium alkoxides do not give β-alkoxypropionic esters [6].

The kinetic features of the reactions leading to adducts **I** and **III** were examined at different temperatures and molar ratios of the reactants (methanol : methyl acrylate : DMEA for adduct **I** and methyl acrylate : DMEA for adduct **III**). The reaction rate was monitored by measuring the amount of the products accumulated in

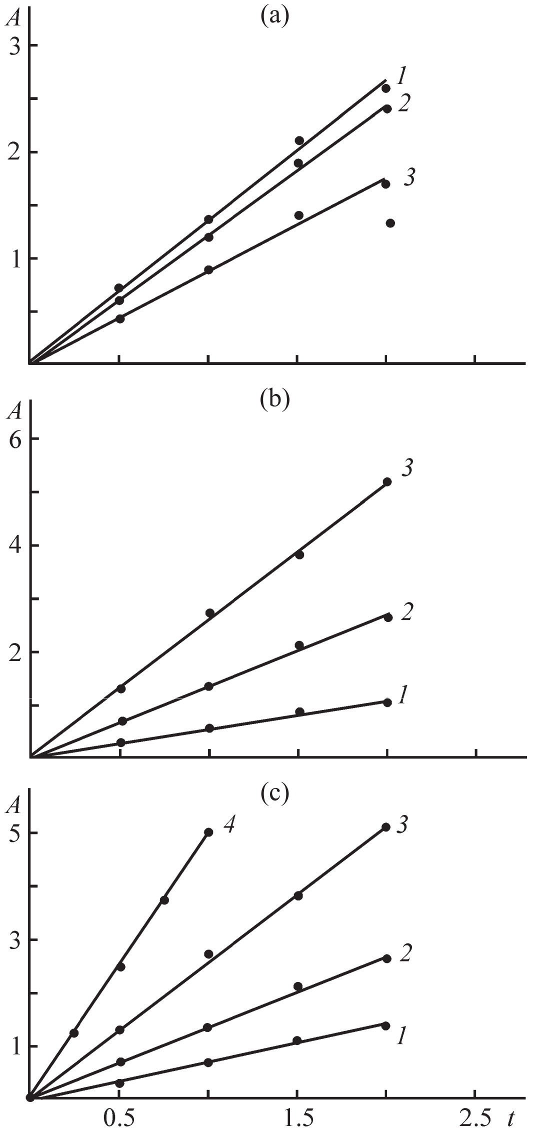


Fig. 2. Kinetic curves of Michael addition reaction for adduct **I**. (*A*) Methanol conversion, %, and (*t*) time, h. (a) DMEA concentration 0.5 M, temperature 105°C. Methanol:methyl acrylate molar ratio: (*1*) 1 : 2, (*2*) 1 : 1, and (*3*) 2 : 1. (b) Methanol:methyl acrylate molar ratio 1:2, temperature 105°C. DMEA concentration, M: (*1*) 0.2, (*2*) 0.5, and (*3*) 1.0. (c) Methanol:methyl acrylate molar ratio 1 : 2, DMEA concentration 0.5 M. *T*, °C: (*1*) 95, (*2*) 105, (*3*) 115, and (*4*) 125.

the reaction system. The examinations were carried out under conditions of pseudo-zero-order kinetics to avoid the interference from consecutive reactions. Figure 2 shows the kinetic curves of formation of adduct **I**, and Fig. 3, those for adduct **III**.

The rate of accumulation of products in the presence of DMAEA is by an order of magnitude lower compared to DMEA because of a low basicity (pK_b at 25°C is 5.4 for DMAEA against 4.52 for DMEA [10, 11]).

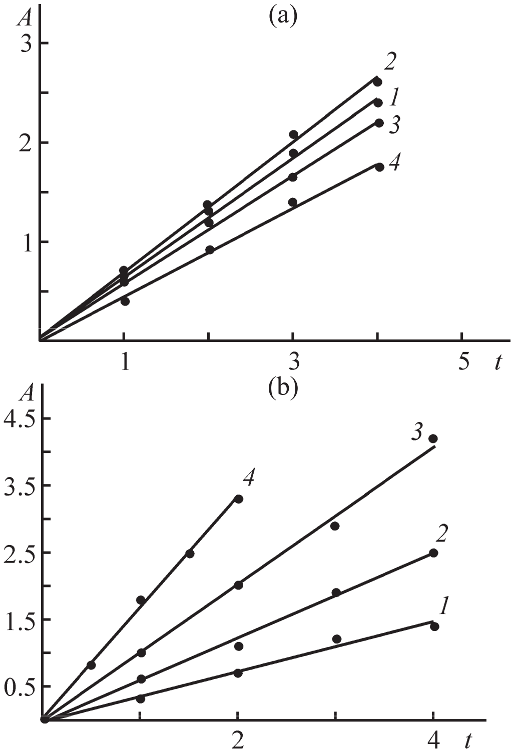


Fig. 3. Kinetic curves of Michael addition reaction for adduct **III**. (*A*) Methanol conversion, %, and (*t*) time, h. (a) Temperature 105°C. Methyl acrylate:DMEA molar ratio: (*1*) 2 : 1, (*2*) 1 : 1, (*3*) 1 : 2, and (*4*) 4 : 1. (b) Methyl acrylate:DMEA molar ratio 2 : 1. *T*, °C: (*1*) 95, (*2*) 105, (*3*) 115, and (*4*) 125.

The kinetics of accumulation of the products is adequately described by the equation

$$r_1 = k_i K_b c_{MA} c_{ROH} = k'_i c_{DMEA} c_{MA} c_{ROH},$$

where k_i is the rate constant of *i*th reaction, and c_{ROH}, c_{MA}, and c_{DMEA}, concentrations of the alcohol, methyl acrylate, and DMEA, respectively.

The activation energies of reactions (2) and (3) are 83 ± 5 and 70 ± 5 kJ mol^{-1}, respectively.

Based on the kinetic features of the target and side reactions examined, we propose the following mathematical model of the process:

$$-\frac{dc_{DMEA}}{dt} = c_{cat}(k_1 c_{MA} c_{DMEA} - k_{-1} c_{MeOH} c_{DMAEA}) + k_3 c_{MA} c^2_{DMEA},$$

Fairly close activation energies of the main and side reactions suggest that the selectivity of transesterification of methyl acrylate with DMEA is weakly affected by temperature variation. Methanol occurring in the reaction medium not only decelerates the DMAEA formation but also leads to accumulation of adduct **I**. Therefore, to enhance the selectivity of the process, methanol needs to be efficiently withdrawn from the reaction system. To reduce the yield of adduct **III**, it is necessary to increase the titanium alkoxide : DMEA molar ratio.

CONCLUSIONS

(1) A kinetic model adequately describing the experimental data was proposed for the reaction of transesterification of methyl acrylate with dimethylethanolamine, catalyzed by tetra(*N,N*-dimethylaminoethyl) titanate. The parameters of the temperature dependence of the rate constants of the forward and backward reactions were calculated. The activation energies were estimated at 76 ± 5 and 46 ± 5 kJ mol^{-1} for the forward and backward reactions, respectively, and the heat effect of the reaction, at -30 kJ mol^{-1}.

(2) The kinetic parameters of the side reactions of addition of alcohols at the vinyl group were determined. It was shown that the rate of formation of Michael adducts depends on the basicity of the medium, as well as on the alcohol and methyl acrylate concentrations.

(3) It was demonstrated that the selectivity of the process will be the higher, the more efficient the withdrawal of methanol and the higher the catalyst:dimethylethanolamine molar ratio.

ACKNOWLEDGMENTS

This study was financially supported by Khimtek Inzhiniring Closed Joint-Stock Company.

REFERENCES

1. EP Patent 0906902.
2. US Patent 6977310.
3. US Patent 7078560.
4. Jiang, P., Zhang, D., Li, Q., and Lu, Y., *Catal. Lett*., 2006, vol. 110, nos. 1–2, pp. 101–106.
5. US Patent Application 2009/0253930 A1.
6. US Patent Application 2004/0171868 A1.
7. Rehberg, C.E., Dixon, M.B., and Fisher, C.H., *J. Am. Chem. Soc*., 1947, vol. 69, no. 12, pp. 2966–2970.
8. Marsi, M., *Inorg. Chem*., 1988, vol. 27, no. 18, pp. 3062–3064.
9. Bharara, P.C., Gupta, V.D., and Mehrotra, R.C., *Z. Anorg. Allg. Chem.,* 1974, vol. 403, no. 3, pp. 337–346.
10. Rowell, P. P. and Chiou, C.Y., *J. Med. Chem.,* 1976, vol. 19, no. 2, pp. 300–303.
11. Kumbhar, A.G., Narasimhan, S.V., and Mathur, P.K., *Anal. Chim. Acta,* 1994, vol. 294, pp. 103–111.