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Mechanism of Formation of Tetrahydrofuran in the Catalytic Hydrogenation of Dialkyl Succinates

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Abstract—The kinetics of formation of tetrahydrofuran from dibutyl succinate were studied. The mechanism of catalytic hydrogenation of dialkyl succinates was found to involve consecutive formation of γ-butyrolactone, butane-1,4-diol, and tetrahydrofuran. Parameters of kinetic equations that properly describe the system of concurrent and consecutive reactions were determined.

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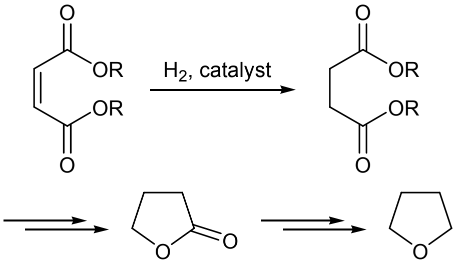
Tetrahydrofuran is widely used as solvent in organic synthesis, membrane technologies [1], processing of natural and synthetic resins, and liquefaction of bituminous coal [2]. Polymerization of tetrahydrofuran or its copolymerization with alkylene oxides and diols gives oligomeric polyalkylene ether glycols which are then converted into polyurethanes and thermoplastic polyesters [3–5].

Several procedures for the preparation of tetrahydrofuran have been reported: from furfural through furan [6], from maleic anhydride obtained from benzene or by oxidation of butane [7], from butadiene via oxidation [8] or acetoxylation [9], and from butane-1,4-diol via dehydration [10]. In the past decade, the synthesis of tetrahydrofuran by hydrogenation of maleic acid esters has attracted increased attention in many countries [11–15]. However, the mechanism of this process was not studied. Kanetaka et al. [16] and Loktev et al. [7] described the mechanism of catalytic hydrogenation of maleic anhydride, which involved intermediate formation of γ-butyrolactone. It may be presumed that tetrahydrofuran is formed in a similar way in the hydrogenation of maleic acid esters (Scheme 1), though the reactivity of a linear dialkyl maleate could differ considerably from the reactivity of cyclic maleic anhydride.

Scheme 1.



The first step is hydrogenation of the double bond activated due to conjugation with electron-withdrawing ester carbonyl groups. This step is fast, and it does not affect the kinetics of the overall process [16]. Therefore, the goal of the present work was to examine in detail the kinetics of the formation of tetrahydrofuran from dibutyl succinate (**I**) and determine the mechanism of this process. Dibutyl succinate was selected as substrate, taking into account that butyl alcohol liberated during the hydrogenation process can readily be separated from tetrahydrofuran and dehydrated for further recycling.

Catalytic hydrogenation of dibutyl succinate (**I**) was carried out in a rocking high-pressure reactor in the temperature range from 180 to 260°C under a hydrogen pressure of 8–14 MPa over nickel–cobalt catalyst which showed a high efficiency in analogous processes [18]. We found that the reaction rate does not depend on the grain size of the catalyst in the range from 0.4 to 2 mm and on the rate of stirring within 180–480 rpm, i.e., the reaction occurs in the kinetic region under these conditions.

Initially we examined the kinetics of hydrogenation of γ-butyrolactone (**II**). Figure 1 shows that lactone **II** is rapidly consumed in the initial period of time and that the reaction slows down when 50% conversion is

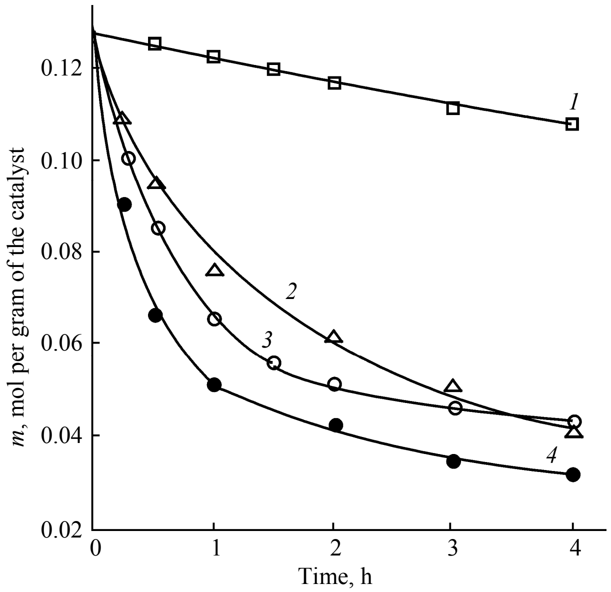


Fig. 1. Kinetic curves for the consumption of γ-butyrolactone (**II**) in the hydrogenation process: (*1*) 180°C, 10 MPa; (*2*) 220°C, 10 MPa; (*3*) 240°C, 10 MPa; (*4*) 240°C, 14 MPa. Points correspond to the experimental data, and the calculated dependences are shown with solid curves.

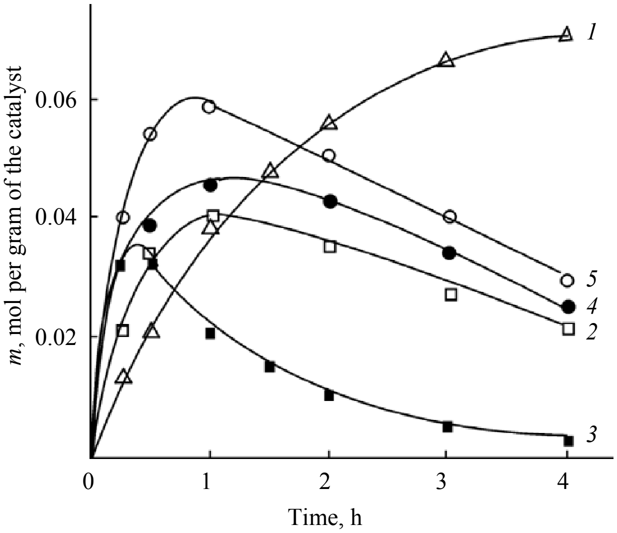


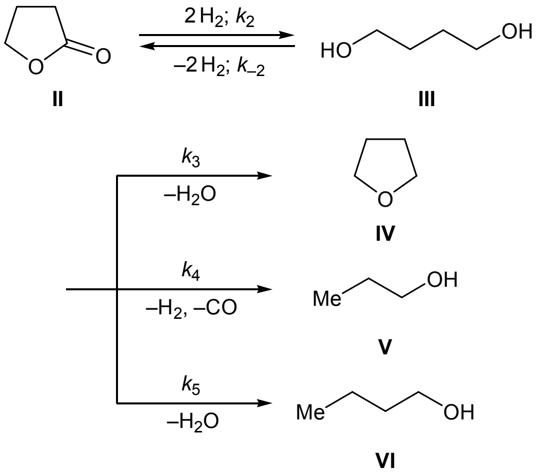
Fig. 2. Variation of the concentration of butane-1,3-diol (**III**) in the hydrogenation of γ-butyrolactone (**II**): (*1*) 220°C, 10 MPa; (*2*) 240°C, 8 MPa; (*3*) 260°C, 10 MPa; (*4*) – 240°C, 10 MPa; (*5*) – 240°C, 14 MPa. Points correspond to the experimental data, and the calculated dependences are shown with solid curves.

attained. By special experiments with addition of final and possible intermediate products to the reaction mixture we found that the following factors are responsible for the observed pattern. The first factor is strong adsorption of water liberated during the process on the catalyst surface, which hampers adsorption of initial lactone **II**, and the second factor is reversibility of the formation of butane-1,4-diol (**III**). Variation of the concentration of intermediate **III** is described by characteristic kinetic curves for accumulation and subsequent consumption after a maximum (Fig. 2). The maximal concentration of **III** is attained in a shorter time at higher temperature.

The kinetic curves for accumulation of the final product, tetrahydrofuran (**IV**), are *S*-shaped (Fig. 3). Analogous curves were found for accumulation of by-products, propan-1-ol and butan-1-ol, which were identified by GLC. Depending on the conditions, they were formed in up to 15 and 5% yield, respectively.

Thus the kinetic relations holding in the hydrogenation of γ-butyrolactone are typical of consecutive–concurrent processes [19], where the major product and by-products are formed from intermediate diol **III** according to Scheme 2.

Scheme 2.



This scheme may be described by a kinetic model consisting of a system of differential equations (1) for the formation of the main and intermediate products and by-products with account taken of reversibility of the γ-butyrolactone (**II**) hydrogenation step and concurrent adsorption.

$$\begin{cases} -\partial m_{\mathrm{II}}/\partial\tau = k_2 m_{\mathrm{II}} p/(m_{\mathrm{II}} + \beta m_{\mathrm{water}}) - k_{-2} m_{\mathrm{III}} p^{-1} \\ \partial m_{\mathrm{III}}/\partial\tau = k_2 m_{\mathrm{II}} p/(m_{\mathrm{II}} + \beta m_{\mathrm{water}}) \\ \quad - (k_{-2} p^{-1} + k_3 + k_4 p^{-1} + k_5) m_{\mathrm{III}} \\ \partial m_{\mathrm{IV}}/\partial\tau = k_3 m_{\mathrm{III}} \\ \partial m_{\mathrm{V}}/\partial\tau = k_4 m_{\mathrm{III}} p^{-1} \\ \partial m_{\mathrm{VI}}/\partial\tau = k_5 m_{\mathrm{III}} \end{cases} \tag{1}$$

Here, m_i is the number of moles of *i*th component per gram of the catalyst, p is the hydrogen pressure, β is the ratio of the adsorption coefficients of water and γ-butyrolactone, and τ is the reaction time (h).

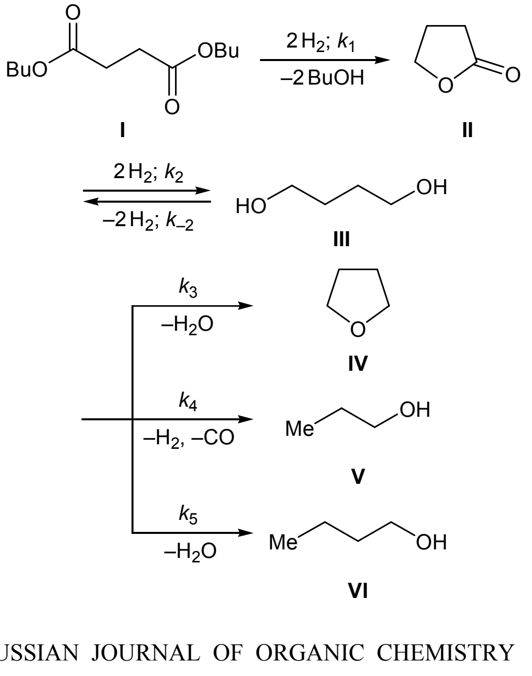
Equation system (1) was processed to solve the reverse kinetic problem [19]: rate constants for all steps of the process (Scheme 2) were determined at different temperatures, and the corresponding energies of activation and pre-exponential factors were calculated (see table). The calculated kinetic dependences plotted in Figs. 1–3 as solid curves were very consistent with the experimental data (dots).

Measurement of the rate of hydrogenation of ester **I** in the temperature range from 220 to 260°C at a pressure of 8–14 MPa showed that its consumption can be described by first-order equation with respect to **I** and hydrogen:

$$-\partial m_{\mathrm{I}}/\partial\tau = k_1 m_{\mathrm{I}} p. \qquad (2)$$

The parameters of the Arrhenius equation calculated by Eq. (2) from the kinetic curves are also given in table. The hydrogenation of ester **I** was characterized by the same kinetic relations as those found for the hydrogenation of lactone **II**. In this case, lactone **II** is considered to be intermediate product. The kinetic curves for its formation and subsequent consumption come from the origin and pass through a maximum. On the other hand, accumulation of diol **III** in the initial part is described by an *S*-shaped curve, which is also typical of products of its subsequent transformations, targeted tetrahydrofuran and propan-1-ol (byproduct). Butan-1-ol is formed even in the first step of hydrogenation of **I**; therefore, the corresponding kinetic curves have no initial inflection. The observed kinetic relations largely correspond to the mechanism of hydrogenation of ester **I**, shown in Scheme 3, though successive closure, opening, and repeated closure of furan ring may seem surprising at first glance.

Scheme 3.



Energies of activation E_i and pre-exponential factors k_i° of elementary steps in the catalytic hydrogenation of dibutyl succinate (**I**)

k_i	E_i, kJ/mol	k_i°
k_1	104	2.51×10^8 h^{-1} g^{-1} MPa^{-1}
k_2	109	1.84×10^9 mol h^{-1} g^{-1} MPa^{-1}
k_{-2}	138	1.37×10^{14} h^{-1} g^{-1} MPa^{-1}
k_3	142	8.3×10^{13} h^{-1} g^{-1}
k_4	163	2.61×10^{16} h^{-1} g^{-1} MPa^{-1}
k_5	157	2.86×10^{14} h^{-1} g^{-1}

Strictly speaking, a similar kinetic pattern may be observed if lactone **II** is not an intermediate product

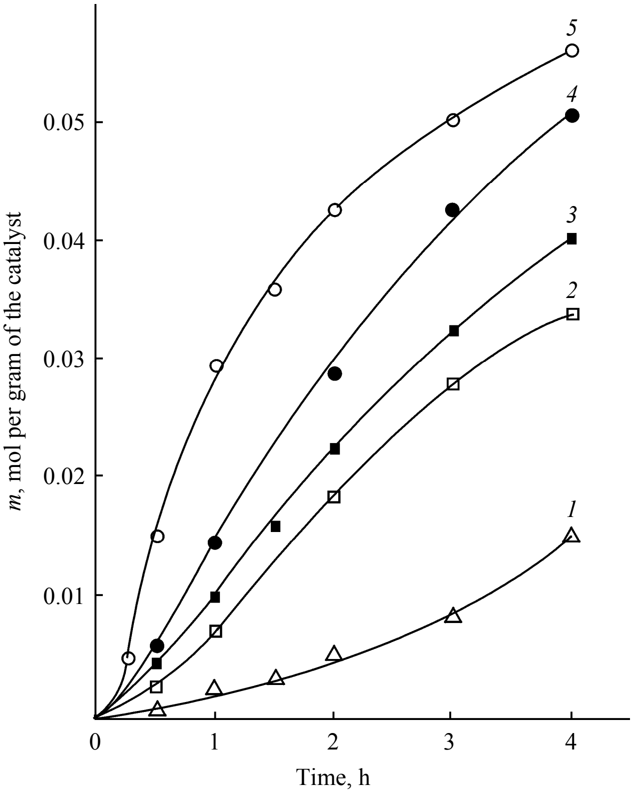
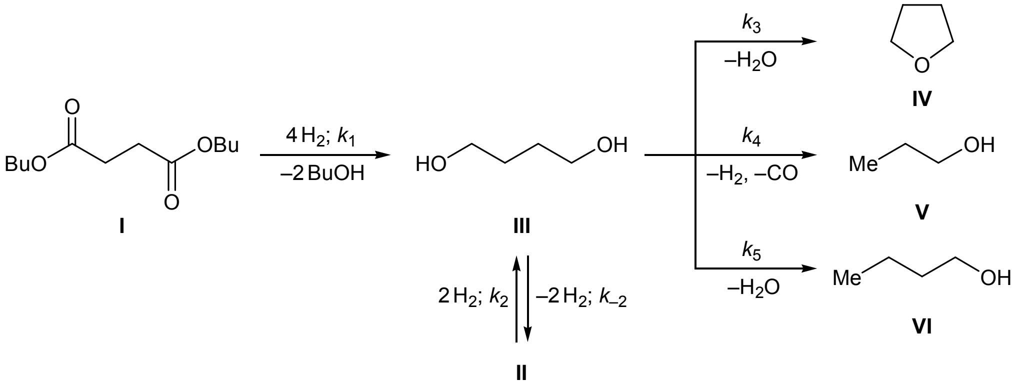


Fig. 3. Kinetic curves for accumulation of tetrahydrofuran (**IV**) in the hydrogenation of γ-butyrolactone (**II**): (*1*) 220°C, 10 MPa; (*2*) 240°C, 8 MPa; (*3*) 240°C, 10 MPa; (*4*) – 240°C, 14 MPa; (*5*) – 260°C, 10 MPa. Points correspond to the experimental data, and the calculated dependences are shown with solid curves.

Scheme 4.



formed along the main reaction path but exists in equilibrium with diol **III** (see above) which gives rise to tetrahydrofuran (**IV**) and alcohols **V** and **VI** as by-products, in keeping with Scheme 4.

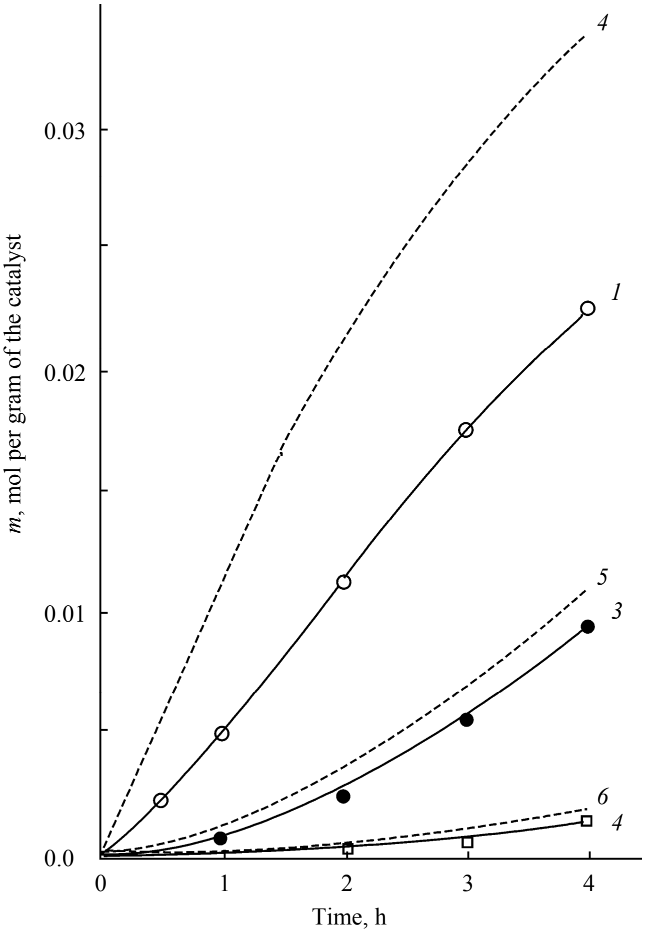


Fig. 4. Kinetic dependences for accumulation of tetrahydrofuran (**IV**) in the hydrogenation of dibutyl succinate (**I**), calculated according to (*1–3*, solid curves) Scheme 3 and (*4–6*, dotted curves) Scheme 4 for the temperatures (*1*, *4*) 260, (*2*, *5*) 240, and (*3*, *6*) 220°C at a hydrogen pressure of 10 MPa. Points correspond to the experimental data.

Our experimental data allowed us to make a rigorously substantiated choice between the above alternative schemes. For this purpose, kinetic models corresponding to Schemes 3 and 4 were constructed. By substituting the rate constants and Arrhenius parameters (already determined as described above; see table) into the obtained equation systems we solved the direct kinetic problem [19], i.e., drew kinetic dependences describing variation of the amount (in moles per gram of catalyst) of γ-butyrolactone (**II**), butane-1,4-diol (**III**), tetrahydrofuran (**IV**), propan-1-ol (**V**), and butanol (**VI**) versus time. The dependences derived on the basis of Scheme 3 were very consistent with the experimental kinetic data for compounds **II**–**VI**, whereas those calculated for Scheme 4 revealed considerable differences from the experimental data. Figure 4 shows a typical example of such correlation for the formation of tetrahydrofuran at different temperatures. These results exclude the possibility for formation of butane-1,4-diol (**III**) directly from ester **I** and unambiguously indicate that the process follows Scheme 3.

Thus detailed kinetic study on the catalytic hydrogenation of dibutyl succinate allowed us to determine the mechanism of formation of tetrahydrofuran from dialkyl succinates, which includes successive formation of γ-butyrolactone and butane-1,4-diol as intermediates. The proposed kinetic model ensures highly accurate prediction of the product composition (±1.3–2.4%) and optimization of the reaction conditions.

EXPERIMENTAL

The initial compounds and hydrogenation products were analyzed by GLC on a Tsvet-500 chromatograph equipped with a thermal conductivity detector and a 2000×3-mm column packed with 12% of PFMS-4 (polyphenylmethylsiloxane) on Polikhrom-1; carrier gas helium; oven temperature programming from 75 to 225°C; 1,4-dioxane was used as internal standard.

Succinic anhydride, γ-butyrolactone, butane-1,4-diol, propan-1-ol, and butan-1-ol were preliminarily distilled. Dibutyl succinate (**I**) was synthesized according to the procedure described in [20] and was purified by rectification. The catalyst contained 15% of Ni, 10% of Co, 3.5% of Fe, and 5% of Al_2O_3 on hydrothermally treated silica gel; it was prepared by impregnation of silica gel with a solution containing nitrates of the corresponding metals, followed by drying, calcination, and reduction in a stream of hydrogen at 400°C. The catalyst was then purged with nitrogen, passivated with air, and ground to a required grain size.

The kinetic measurements were performed in a rocking 60-ml stainless steel high-pressure reactor under continuous stirring while controlling pressure and temperature. Before charging into the reactor, the catalyst was depassivated in a glass reactor at 300°C in a stream of hydrogen. To prevent contact with air, the catalyst was covered with the initial compound while transferring it into the reactor; 0.75–1.5 g of the catalyst and 16–22 g of the substrate were used. Samples were withdrawn from the reaction mixture at definite time intervals, and their composition was determined by GLC.

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REFERENCES

1. Schuhmacher, E., Soldi, V., and Nunes, P.A.T., *J. Membr. Sci.*, 2001, vol. 184, p. 187.
2. Joseph, J.T., *Fuel*, 1991, vol. 70, p. 139.
3. Kahn, A.P., Gastinger, R.G., and Cai, G., US Patent no. 5210283; *Ref. Zh., Khim.*, 1994, no. 19N85P.
4. Kussi, S., *Lubric. Eng.*, 1991, vol. 47, p. 926; *Ref. Zh., Khim.*, 1992, no. 9P127.
5. Kodama, T., Fukuzono, T., and Furubeppu, S., US Patent no. 7217783, 2007; *Ref. Zh., Khim.*, 2008, no. 19S339P.
6. Wambach, L., Irgang, M., and Fischer, M., FRG Patent no. 3632255, 1988; *Chem. Abstr.*, 1988, vol. 109, no. 24520.
7. O' Sullivan, D., *Chem. Eng. News*, 1992, vol. 70, p. 6.
8. Abreimova, M.A., Bobyleva, L.I., Kryukov, S.I., Srednev, S.S., Moskvichev, Yu.A., Karpov, O.P., and Surovtsev, A.A., *Abstracts of Papers, V konferentsiya po intensifikatsii neftekhimicheskikh protsessov "Neftekhimiya-99"* (Vth Conf. on Intensification of Petrochemical Processes "Petrochemistry 99"), Nizhnekamsk: Nizhnekamskneftekhim, 1999, vol. 2, p. 26.
9. Onoda, T., *J. Synth. Org. Chem. Jpn.*, 2000, vol. 58, p. 399; *Ref. Zh., Khim.*, 2002, no. 19N142.
10. Hunter, S.E., Ehrenberger, C.E., and Savage, P.E., *J. Org. Chem.*, 2006, vol. 71, p. 6229.
11. Wood, M.A., Willett, P., Wild, R., and Colley, S.W., EU Patent Appl. no. 1108702, 2001; *Chem. Abstr.*, 2001, vol. 135, no. 47921.
12. Chaudhari, R.V. and Vaidya, S.H., Indian Patent no. 185714, 2001; *Chem. Abstr.*, 2005, vol. 142, no. 219138.
13. Borchert, H., Schlitter, S., Hesse, M., Stein, F., Fischer, R.-H., Rahn, R.-T., Week, A., and Roesch, M., FRG Patent no. 10061558, 2002; *Chem. Abstr.*, 2002, vol. 137, no. 34773.
14. Chaudhari, R.V., Jaganathan, R., Chaudhari, S.T., and Rode, Ch.V., US Patent no. 7037877, 2006; *Chem. Abstr.*, 2006, vol. 144, no. 412350.
15. Guo, R., Qiao, M., Zhu, Y., Fan, K., Zhang, X., Zhao, Z., and He, M., Chinese Patent no. 1857771, 2006; *Chem. Abstr.*, 2006, vol. 145, no. 478628.
16. Kanetaka, J., Kiryu, S., Asano, T., and Masamune, S., *Bull. Jpn. Petrol. Inst.*, 1970, p. 89.
17. Loktev, S.M., Dyshlis, V.D., and Rozovskii, F.Ya., *Kinet. Katal.*, 1979, vol. 20, p. 686.
18. Shevchenko, V.S., Timofeev, A.F., Tereshchenko, G.F., Chistyakova, G.A., and Tereshchuk, L.S., USSR Inventor's Certificate no. 763341, 1978; *Byull. Izobret.*, 1980, no. 34.
19. Emanuel', N.M. and Knorre, D.G., *Kurs khimicheskoi kinetiki* (Lectures on Chemical Kinetics), Moscow: Vysshaya shkola, 1984.
20. Couteau, W., Dungelhoeff, M.-L., Hendrickx, A., and Verbeest, R., UK Patent no. 1464263, 1976; *Ref. Zh., Khim.*, 1977, no. 19N22.