KINETICS OF PARALLEL DEHYDROGENATION AND DEHYDRATION OF 2-PROPANOL ON OXIDE CATALYSTS*

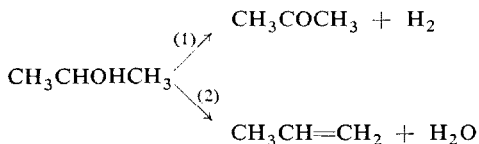J.JAMBOR** and L.BERÁNEK

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague - Suchdol*

Kinetics of parallel dehydrogenation and dehydration of 2-propanol at 350°C on a series of metal oxides whose selectivity changed from prevailing dehydration to prevailing dehydrogenation (ThO_2, TiO_2, La_2O_3, Cr_2O_3, ZrO_2, and MgO) were studied. While the ratio of rate constants of the equations of Langmuir–Hinshelwood type for dehydrogenation and dehydration changes along the series of catalysts by nearly three orders of magnitude, small difference in the ratio of adsorption coefficients of 2-propanol for these two reactions indicated a nonspecific character of its primary interaction with catalyst surface. The effects of products and other substances were also studied and expressed by means of corresponding adsorption coefficients on La_2O_3. Water and acetone exhibited much stronger rate-retarding effect on the reactions which led to their formation than on the other reaction. This indicates that reaction centres for dehydration and dehydrogenation are different, the corresponding product being however weakly adsorbed also on surface sites which do not participate in its formation. Propene and hydrogen were not essentially adsorbed. Selectivity of the decomposition depended on partial pressures of 2-propanol and water and on the conversion of the alcohol.

In previous communications of this series (for survey see[1]) we investigated the kinetics of some consecutive, parallel or parallel-consecutive heterogeneous catalytic reactions in gaseous phase in connection with the study of mutual influencing of single reactions and the analysis of the meaning of the so-called kinetic adsorption coefficients. In all cases studied thus far, single reactions constituting the coupled system were of the same type (*e.g.* hydrogenation reactions[2-4]), so that it could be assumed that single reactions were taking place on surface active sites of the same kind. The aim of this study was to examine the kinetics of a coupled system consisting of reactions of different types. Parallel dehydrogenation and dehydration of 2-propanol on oxide catalysts was chosen as a model system.

$$CH_3CHOHCH_3 \begin{array}{c} \overset{(1)}{\nearrow} CH_3COCH_3 \ + \ H_2 \\ \underset{(2)}{\searrow} CH_3CH{=}CH_2 \ + \ H_2O \end{array}$$

The conversion of 2-propanol leading exclusively either to propene or to acetone has frequently been used as a model reaction in studying the mechanism of dehydration or dehydrogenation and in testing corresponding catalysts. If with some catalysts both reactions proceeded simultaneously, the selectivity, *i.e.* the degree of their relative importance, was mostly discussed in dependence on a variety of factors (*e.g.*[5−11]). A quantitative study of the kinetics of systems where both reactions proceeded as parallel reactions has attracted little attention. The kinetics was interpreted by means of either Frost[12] or Balandin equations (*e.g.*[7,13−16]). Langmuir–Hinshelwood equations were used by Ross and coworkers[17] to analyse kinetic data on decomposition of 2-propanol on some oxide catalysts. In the above mentioned studies the mutual influencing of both reactions have not been expressed in rate equations, although Ross and coworkers did determine the simultaneous effect of the product (both water, and acetone) on both reactions[17,18].

The aim of the kinetic analysis of the reaction of 2-propanol described in this work was to examine on a series of catalysts how the variations in selectivity reflect in changes of the parameters of kinetic equations, *i.e.* whether the varying selectivity of the catalyst will result mainly in changes of rate constants or in changes of adsorption coefficients. The kinetic analysis, including the effect of products and other addends, could also show whether it can provide information about identity or nonidentity of active centers for dehydrogenation and dehydration of the alcohol on oxide catalysts.

EXPERIMENTAL

Compounds used. 2-Propanol was of the *p.a.* purity grade (Lachema, Brno); the content of organic impurities was less than 0·01% mol (by g.l.c.), that of water was 0·04% mol, as determined by Fischer titration. Acetone and pyridine were of the *p.a.* grade (Lachema, Brno), isobutene was *puriss.* (Fluka A. G., Buchs S. G., 99·84% purity). Phenol from cumene, produced in USSR, was purified by vacuum distillation, m.p. 41°C. Nitrogen (for lamps; Technoplyn, Ostrava) was purified by passing over copper on silica at 250°C; the electrolytic hydrogen (Elektrochemische Werke, Bitterfeld, GDR) was purified by passing the gas over a deoxidation palladium catalyst (Chemické závody, Záluži); both gases were dried by a molecular sieve.

Catalysts. Thorium(IV) oxide, chromium(III) oxide, zirconium(IV) oxide, and magnesium oxide were prepared from corresponding *p.a.* nitrates (the zirconium oxide from zirconyl nitrate) by precipitation with ammonia, decantation, washing with distilled water, and drying at 120°C. The catalysts were heated at 650°C for 24 h (magnesium oxide at 1 000°C), rehydrated, dried, and heated at 350°C for 8 h. Their specific surfaces were respectively 8·9, 8·3, 0·84, and 24·7 m^2/g. Titanium(IV) oxide used was commercial titanium white ("White Seal", Moravské chemické závody, Přerov). The oxide was washed with distilled water, dried, and calcinated at 350°C; its specific surface was 8·9 m^2/g. Lanthanum(III) oxide (BDH, 99·99% purity) was used without further purification; its specific surface was 2·8 m^2/g. After determining the region not affected by internal diffusion for all the catalysts, 0·25−0·315 mm particles were used in the present study.

Apparatus and procedure. The glass flow apparatus with reactants in gaseous phase was described earlier[3]. Liquid reactants were fed at a constant rate to an evapourator in which their vapours were mixed with nitrogen or hydrogen (total pressure was atmospheric). The ratio of the liquid to gas feeding rates determined the partial pressure of reactants, the vapours of which passed over a catalyst (0·02−5 g). The catalyst was placed in a glass tubular reactor (16 mm i.d.) which

was provided with a thermocouple well (5 mm e.d.) reaching to the centre of the reactor. The temperature within the catalyst bed was $350 \pm 0.4°C$. Gaseous reaction products were introduced to a six-way valve equipped with the feeding loop from which they were periodically transferred by the carrier gas to a LPCH 2009 chromatograph (Vývojové dílny ČSAV, Prague). The instrument was equipped with a thermal conductivity detector. A mixture of 2-propanol, acetone, propene, water, and nitrogen was separated to individual components on a 3 m-column filled with 7·5% dinonyl sebaccate and 7·5% diglycerol. This column was connected to a 1 m—column filled with 7·5% diglycerol (in both columns Cellite, 30—80 mesh, BDH, was used as a support). The column temperature was 50°C; hydrogen was used as a carrier gas. After steady state had been attained, 3—9 analyses were made in 20 min—intervals. The average value of these analyses was used to calculate conversion at a given pressure. In order to eliminate time changes of the activity which were observed with several catalysts, the conversion in standard experiments at $p_A = 0.5$ atm was determined before commencing the measurement and after completion of each set of measurements of conversion at a given partial pressure of 2-propanol p_A. The conversions determined at various partial pressures were then corrected to the standard activity which was taken as an average of all standard experiments.

Kinetic measurements and treatment of data. Prior to kinetic measurements, the effects of external diffusion and heat transfer were examined and reaction conditions were adjusted such that these effects were negligible. Chromium(III) oxide, which was the most active of all the catalysts, had to be diluted with an inert material in the 1 : 3 ratio before its charging to the reactor. Reaction rate measurements were made with 2-propanol partial pressures from 0·03 atm (with some catalysts from 0·1 atm) to 0·9 atm, the partial pressure being decreased by diluting alcohol vapours with nitrogen or hydrogen (hydrogen did not influence reaction rate). The reaction rates were determined with a maximum error of $\pm 10\%$ rel. from the values of conversions which were measured within 1—5% region. For that case, the expression $r \approx \Delta x / \Delta(W/F)$ could be used as a good approximation. Dehydration conversions were calculated from the amount of propene, and dehydrogenation conversions from the amount of acetone in reaction products. Other side reactions were not observed to take place under conditions of the measurements. Treatment of initial reaction rates of dehydration and dehydrogenation in dependence on partial pressure of the alcohol for six catalysts studied was made by multiple nonlinear regression (the so-called grid search method[19]) on a computer, using the sum of squared deviations of the experimental from calculated reaction rates as a minimalised function.

Effect of products and other substances (phenol, pyridine) was examined by measuring reaction rates on lanthanum(III) oxide with systematic variation of the partial pressure of the compound investigated, which was added to the alcohol. The partial pressure of the alcohol was also changed (0·1—0·9 atm). From these data and from the best rate equations for the reaction of the alcohol alone, the adsorption coefficients of added substances were calculated for different models of their adsorption. Adsorption coefficients were regarded to be an average value of calculations for a set of combinations of partial pressures or were obtained by one-parameter nonlinear regressions.

RESULTS AND DISCUSSION

In the study of kinetics of parallel dehydrogenation and dehydration of 2-propanol we tested 15 oxides of Group II—IV elements, and chromium(III) oxide. Of these oxides, six catalysts were chosen for more detailed study. Their selectivity gradually changed from prevailing dehydration to prevailing dehydrogenation (Table I). In

this work the selectivity is defined as a ratio of dehydrogenation rate to overall reaction rate. Both with the series of 15 oxides, and with the oxides listed in Table I (with a few exceptions) it was observed that prevailing reaction on metal(II) oxides is dehydrogenation, while on metal(IV) oxides it is dehydration. Metal (III) oxides show medium selectivity. A similar effect follows also from the inspection of earlier literature data[20].

While in the studied series of oxides the selectivity was not essentially dependend on partial pressure of the alcohol for thorium(IV), titanium(IV), zirconium(IV), and magnesium oxides, its changes were observed with chromium(III) and lanthanum(III)

TABLE I

Average Values of Experimental Selectivities $\bar{S}$ at 350°C

Catalyst	ThO_2	TiO_2	La_2O_3	Cr_2O_3	ZrO_2	MgO
$\bar{S}$	0·027	0·062	0·27	0·32	0·77	0·97

TABLE II

Effect of Reciprocal Space Velocity of 2-Propanol (W/F_A, min kg mol^{-1}) on Selectivity S at 350°C and $p_A = 0.9$ atm on Lanthanum(III) Oxide

W/F	0·167	0·471	1·54	2·37	4·64
S	0·64	0·60	0·42	0·34	0·28

TABLE III

Basic Types of Rate Equations Used

Denotation	Basic form	Values of exponent s
(I)	$r = kK_A p_A/(1 + K_A p_A)^s$	1—4
(II)	$r = kK_A p_A/[1 + 2(K_A p_A)^{0.5}]^s$	1—4
(III)^a	$r = 2^s k\, K_A p_A/[1 + (1 + 8K_A p_A)^{0.5}]^s$	1—4
(IV)	$r = k(K_A p_A)^{0.5}/[1 + (K_A p_A)^{0.5}]^s$	1—2
(V)	$r = kp_A^n$	—

^{a} The equation of this less common type corresponds to a model which assumes adsorption of the reactant on two centres without dissociation and surface reaction as the rate determining step.

oxides. Fig. 1 shows the experimental dependence for lanthanum(III) oxide. With this catalyst, a significant effect of partial pressure of water was also established (Fig. 2). The fact that water shifts the selectivity of decomposition of the alcohol in favour of dehydrogenation was also reported by other authors[13,21−23]. From dependences of selectivity on partial pressures of 2-propanol and water (*i.e.* the product) it can be concluded that selectivity will depend also on the conversion of the alcohol, and then on apparent contact time. The dependence of the selectivity on reciprocal space velocity has been confirmed by results presented in Table II. As follows from all these examples, selectivity of decomposition of 2-propanol (and likely also of other alcohols) depends strongly on reaction conditions. This may be one of the reasons of great differencies in literature selectivity dáta. Therefore, without knowledge of the detailed kinetics of both parallel reactions, the problem of selectivity of decompositions of alcohols cannot be discussed.

With six catalysts presented in Table I, kinetic analysis was first made by the method of initial reaction rates. By nonlinear regression of experimental data and with the use of 15 rate equations, basic types of which are given in Table III, several statistically significant equations were found for each catalyst which could not be distinguished on the 95% significance level. Apart from the equation of type *V*, they cor-
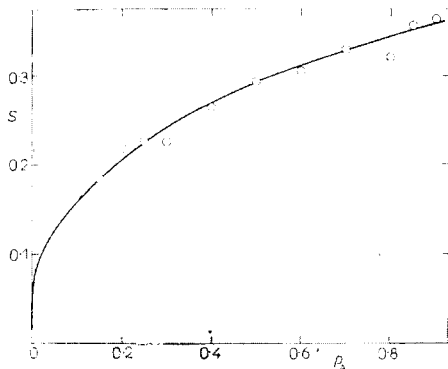
FIG. 1

Dependence of Selectivity S on Initial Partial Pressure of 2-Propanol, p_A [atm], on La_2O_3 at 350°C

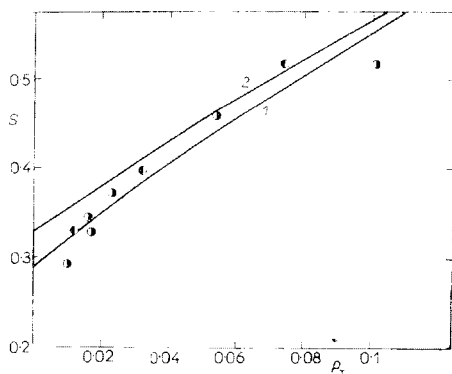   Points are experimental values; the curve was calculated from Eqs (*3*) and (*4*), using the values of constants from Table V.

FIG. 2

Dependence of Selectivity S on Partial Pressure of Water, p_T [atm], Added into the Alcohol Feed

   Catalyst La_2O_3, temperature 350°C. Points are experimental values (◑ for $p_A = 0.5$ atm, ◐ for $p_A = 0.7$ atm) and the curves were calculated from Eqs (*3*) and (*4*), using the values of constants from Table V. *1* $p_A = 0.5$ atm, *2* $p_A = 0.7$ atm.

responded to a model which assumes surface reaction as a rate determining step. Equations of type *II* $(s = 3$, see Eq. $(1))$ and those of type *V* described well both reactions for the greater number of oxides, particularly those whose selectivity did not depend much on the partial pressure of 2-propanol $(ThO_2, ZrO_2, TiO_2,$ and MgO). As equations of type *V* are empirical, Eq. (1) is used in further discussion.

$$r = kK_A p_A/[1 + 2(K_A p_A)^{0.5}]^3 \; . \tag{1}$$

Obtained values of constants of Eq. (1) made it possible to discuss the relation of these parameters to the selectivity. As can be seen from Table IV, the change of selectivity from predominantly dehydrating (ThO_2, TiO_2) to dehydrogenating (ZrO_2, MgO) oxides reflects above all in the change of the ratio of rate constants (by nearly three orders of magnitude), while the ratio of adsorption coefficients lies within $0.5 - 1.6$.

The question about identity or nonidentity of active centers for dehydrogenation and dehydration cannot be convincingly answered on the basis of these data for the above four catalysts. Adsorption coefficients of 2-propanol for these two reactions do not differ such as to unambiguously indicate differences in the type of adsorption, and then also in the kind of active centers. Kinetics observed with lanthanum (III) and chromium(III) oxides were somewhat different, and, along with dependencies of selectivity on partial pressures (Figs 1 and 2), they indicated that on these catalysts both reactions may take place on surface sites of different kind. With the aim of examining further this question we studied the reaction on lanthanum(III) oxide in more detail. While the kinetics of dehydration on this catalyst could be described also by Eq. (1) (however, with substantially different values of the constants), the dehydrogenation could be better described by the equation of type *II* with the exponent $s = 2$ (Eq.(2)).

$$r = kK_A p_A/[1 + 2(K_A p_A)^{0.5}]^2 \; . \tag{2}$$

We further studied the effect of individual reaction products on both reactions with the use of lanthanum(III) oxide. We found that hydrogen did not affect either de-

TABLE IV

Ratios of Rate Constants and of Adsorption Coefficients of 2-Propanol for Its Dehydrogenation (Index 1) and Dehydration (Index 2) at 350°C (Eq. (1))

Catalyst	ThO_2	TiO_2	ZrO_2	MgO
k_1/k_2	0·035	0·062	3·2	25
$K_{A,1}/K_{A,2}$	0·46	1·4	1·6	1·55

hydrogenation or dehydration. The alkene behaved similarly. These results agree with those obtained[17,18] with manganese(II) and beryllium(II) oxides, and as far as hydrogen is concerned, also with data reported for chromium(III) oxide[16]. The influences of the alkene and hydrogen were however established with some rare earth metal oxides[14,15,21,22,24,25] and with titanium(IV) oxide[13].

The effects of water (T) and acetone (R) which were observed on lanthanum(III) oxide for both reactions were expressed by the values of adsorption coefficients. By using these values, the rates of dehydrogenation, r_1, and dehydration, r_2, of 2-propanol on this oxide, inclusive products effects, can be expressed by Eqs (3) and (4) (for the values of constants see Table V).

$$r_1 = k_1 K_{A,1} p_A / [1 + 2(K_{A,1} p_A)^{0.5} + K_{R,1} p_R + K_{T,1} p_T]^2 , \tag{3}$$

$$r_2 = k_2 K_{A,2} p_A / [1 + 2(K_{A,2} p_A)^{0.5} + K_{R,2} p_R + K_{T,2} p_T]^3 . \tag{4}$$

As it is seen from Table V, the adsorption coefficient of acetone, determined from its effect on dehydrogenation, is about five times as great as the coefficient determined from the effect of this substance on dehydration. The adsorption coefficient of water for dehydration is about ten times greater, compared to that for dehydrogenation. The product (both acetone and water) inhibits then stronger the reaction by which it is formed than the other reaction. The effects of acetone and water on parallel dehydrogenation and dehydration of 2-propanol on some metal oxides were observed also by other authors[13-15,21,22,24,25]. However, the simultaneous effect of each of these substances in both reactions was determined only by Ross and cowork-

TABLE V

Constants[a] of Kinetic Equations (3) and (4) and Adsorption Coefficients of Added Substances on Lanthanum(III) Oxide at 350°C

Reaction	k_j	$K_{A,j}$	$K_{R,j}$	$K_{T,j}$	$K_{Ph,j}$[b]	$K_{Py,j}$[c]
Dehydrogenation Eq. (3)	4·6	15·4	236	5·5	19 300	2·6 (7·3)
Dehydration Eq. (4)	103	44	46	54	58 200	1·2 (3·9)

[a] Dimensions: $k_j [10^{-2} \text{ mol min}^{-1} \text{ kg}^{-1}]$; $K_{i,j} [\text{atm}^{-1}]$. [b] Adsorption coefficients of phenol were determined by assuming its nondissociative adsorption on two centres; this assumption agreed better with experimental data than the assumption about its adsorption on one centre. [c] With pyridine, both assumptions were equally valid (the value in parentheses correspond to two-centre adsorption).

ers[17,18]. Their results qualitatively agree with those obtained in the present work. The finding that in dehydrogenation on several oxides acetone has substantially greater adsorption coefficients than hydrogen, and in dehydrogenation it is water which has greater adsorption coefficients[13-16,21,22,24,25] than olefin is also in harmony with our results. As to the effect of the other compounds added, pyridine and phenol, expected markedly different effects of these substances on dehydrogenation and on dehydration were not confirmed (compare their adsorption coefficients in Table V). On the other hand, considerable difference in the behaviour of both compounds does exist: phenol inhibits very strongly both reactions, whereas pyridine exerts only very small effect. This difference can obviously be related to chemical properties of catalytically active surface of lanthanum(III) oxide and to the reaction mechanism determined by these properties.

The difference between rate equations (3) and (4) for dehydrogenation and dehydration on lanthanum(III) oxide as well as different effects of products (acetone, and particularly water) on both reactions show that active centres for both reactions differ from one another. From the different form of Eqs (3) and (4) it can also be deduced how the selectivity of decomposition of 2-propanol will depend on the initial partial pressure of the alcohol and on partial pressures of products. The agreement between experimental selectivities and those calculated from Eqs (3) and (4) (Figs 1 and 2) demonstrates that these equations can be used to describe and discuss selectivity dependences. The calculated limit value of selectivity in Fig. 1 for $p_A \rightarrow 0$ is 0·016 and strongly increases with increasing partial pressure of the alcohol.

The results of this work therefore indicate, at least for lanthanum(III) oxide, that dehydrogenation and dehydration of 2-propanol proceed on different sites of the catalyst. Nevertheless, comparable values of adsorption coefficients of the alcohol for these two reactions on most of the catalysts studied, and particularly the essential independence of its ratio on the selectivity of catalysts (Table IV) show that primary interaction of the alcohol is rather nonspecific; it might take place on surface sites which are not identical with reaction centers participating in further transformation of adsorbed alcohol. This primary interaction could be of physical character[1]; physical character of the adsorption of reaction components is at least partially indicated also by the fact that gaseous components (hydrogen, alkene) do not influence the reaction, whilst higher boiling substances (acetone, water) do. This assumption could explain why the product retards both the reaction by which it is formed, and the reaction which does not lead to its formation. The difference in these effects in both reactions may be due to the fact that adsorption of the product takes place both on reaction centres on which it is formed (i.e. product formation reaction is slowed down), and, nonspecifically, on centres participating in primary adsorption of the alcohol (i.e. both reactions are retarded).

LIST OF SYMBOLS

F flow rate
k rate constant
K_i adsorption coefficient of the substance i
n exponent in the power-law type equation (V)
p_i partial pressure of the substance i
r reaction rate
s exponent in the denominator of rate equations
$S = r_1/(r_1 + r_2)$ selectivity
$\bar{S}$ average value of the selectivity for the studied region of 2-propanol partial pressures
x conversion
W catalyst weight

Indices

Substances: A 2-propanol, R acetone, T water, Ph phenol, and Py pyridine.
Reactions: 1 dehydrogenation and 2 dehydration.

REFERENCES

1. Beránek L.: Advan. Catalysis *24*, 1 (1975).
2. Hančil V., Beránek L.: Chem. Eng. Sci. *25*, 1121 (1970).
3. Šimoník J., Beránek L.: This Journal *37*, 353 (1972).
4. Vejrosta J., Kleňha V., Beránek L.: This Journal *37*, 1097 (1972).
5. Eucken A.: Naturwissenschaften *36*, 48 (1949).
6. Krylov O. V.: *Kataliz Nemetallami*, p. 99. Chimija, Leningrad 1967; *Catalysis by Nonmetals*, p. 115. Academic Press, New York 1970.
7. Tolstopjatova A. A. in the book: *Redkozemelnyje Elementy* (D. I. Rjabčikov, Ed.), p. 113. Izd. Akad. Nauk SSSR, Moscow 1963.
8. Balandin A. A., Tolstopjatova A. A. *Proc. 3rd Intern. Congr. Catalysis, Amsterdam 1964*, p. 533. North-Holland Publ., Amsterdam 1965.
9. Tolstopjatova A. A.: Problemy Kinetiki i Kataliza *11*, 36 (1966).
10. Swaminathan R., Kuriacose J. C.: J. Res. Inst. Catalysis, Hokkaido Univ. *15*, 172 (1967).
11. Balandin A. A., Tolstopjatova A. A., Ferapontov V. A.: Dokl. Akad. Nauk SSSR *103*, 611 (1955).
12. Pašek J., Jošt F., Petrů F.: Chem. listy *52*, 405 (1958).
13. Tolstopjatova A. A., Konenko I. R., Balandin A. A.: Izv. Akad. Nauk SSSR, Otd. Chim. Nauk *1961*, 38.
14. Balandin A. A., Konenko I. R., Tolstopjatova A. A.: Kinetika, Kataliz 2, 900 (1961).
15. Tolstopjatova A. A., Balandin A. A., Ch'i-Ch'-uan Yu.: Ž. Fiz. Chim. *37*, 2220 (1963).
16. Tolstopjatova A. A., Balandin A. A., Karpejskaja E. I.: Izv. Akad. Nauk SSSR, Otd. Chim. Nauk *1958*, 1184.
17. McCaffrey E. F., Micka T. A., Ross R. A.: J. Phys. Chem. *76*, 3372 (1972).
18. Klissurski D. G., McCaffrey E. F., Ross R. A.: Can. J. Chem. *49*, 3778 (1971).
19. Hančil V., Mitschka P., Beránek L.: J. Catal. *13*, 435 (1969).
20. Mars P. in the book *The Mechanism of Heterogeneous Catalysis* (J. H. de Boer, Ed.), p. 49. Elsevier, Amsterdam 1960.
21. Balandin A. A., Bi-Hsiang P'ing., Tolstopjatova A. A.: Izv. Akad. Nauk SSSR, Otd. Chim. Nauk *1962*, 1330.

22. Tolstopjatova A. A., Bi-Hsiang P'ing, Balandin A. A.: Izv. Akad. Nauk SSSR, Otd. Chim. Nauk *1962*, 1322.
23. Pandao S. N., Kuriacose J. C., Sastri M. V. C.: Indian J. Technol. *1*, 102 (1963).
24. Tolstopjatova A. A., Balandin A. A., Ch'-i-Ch'uan Yu.: Izv. Akad. Nauk SSSR, Ser. Chim. *1964*, 3.
25. Balandin A. A., Tolstopjatova A. A., Ch'-i-Ch'uan Yu.: Izv. Akad. Nauk SSSR, Ser. Chim. *1964*, 262.

Translated by J. Hetflejš.