Synergistic effect for bimetallic Ru—Tc catalysts of cyclohexane dehydrogenation

G. N. Pirogova, N. N. Rimar', and G. E. Kalinina*

*Institute of Physical Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 117915 Moscow, Russian Federation.
Fax: +7 (095) 952 7514*

Catalytic properties of the Ru—Tc/support (γ-Al_2O_3, Y_2O_3, and SiO_2) systems in the dehydrogenation of cyclohexane have been studied. The catalytic activity of the bimetallic catalysts depends on the nature of the support. A nonadditive increase in the catalytic activity of the bimetallic catalysts in comparison with monometallic samples was established. The value of the synergistic effect depends on the ratio between the amounts of the supported metals and the nature of the support. By using the diffuse reflectance spectra in UV- and visible regions and hydrogen chemisorption techniques, the modifying influence of the ionic metal species on the catalytic properties was shown.

Key words: dehydrogenation, bimetallic catalysts, cyclohexane, diffuse reflectance spectra; synergistic effect.

Catalytic systems based on supported metals of the platinum group with the additives of transition metals are widely used in petrochemistry and oil processing. The modifying effect of various metals, the state of the supported metals, and the mechanism of their interaction have been studied.[1—4] Upon doping supported platinum metals (Pt, Pd, Rh) with technetium, a synergistic effect has been observed.[5—7] This work continues the study of this phenomenon by the example of the Ru—Tc/support system in the cyclohexane dehydrogenation.

Experimental

The catalysts were prepared by impregnation of supports with solutions of NH_4TcO_4 and $RuOHCl_3$ (or ruthenate). The ruthenium samples were synthesized according to procedures described previously.[8] The Na or K ruthenates were obtained by fusion of ruthenium metal with an alkali in an oxidative medium. To obtain ruthenium oxychloride, the ruthenate was transformed to hydroxide $Ru(OH)_4$, which forms $RuOHCl_3$ after dissolution in a dilute hydrochloric acid.

In addition to the conventional supports, γ-Al_2O_3 (S_{sp} = 189 $m^2 g^{-1}$) and SiO_2 (KSK-2, S_{sp} = 195 $m^2 g^{-1}$), the Y_2O_3 support (S_{sp} = 1.5 $m^2 g^{-1}$) was also used. We applied Y_2O_3 previously in the synthesis of the supported technetium catalysts and obtained it by the decomposition of a hydroxide precipitated from a nitrate. The supports were used in the form of granules with a size of 1.5—2.0 mm. The supports impregnated with a corresponding solution were dried at 80 °C in air, reduced by hydrogen at 300 °C for 1 h and then at 300, 500, or 700 °C for 6 h.

The content of technetium in the catalysts was determined radiometrically and that of ruthenium was determined spectrophotometrically. The amounts of the supported metals varied from 0.05 to 1.00 %.

The catalytic activity of the samples obtained was studied on a microcatalytic setup in a pulse regime at atmospheric pressure. For each experiment, 0.5 g (1 cm^3) of the catalyst was taken. The reaction products were analyzed by GLC on a Biochrom-1 chromatograph (flame-ionization detector, helium as the carrier gas). Glass capillary columns with PEG-40M were used for the separation of hydrocarbons at 90 °C.

Hydrogen chemisorption was studied on a volumetric adsorption setup. The samples were trained for 16 h at 10^{-6} Torr.

The diffuse reflectance spectra in UV and visible regions were recorded on a Specord M-40 spectrophotometer.

The specific surface area of the samples was estimated with the low-tempetature adsorption of krypton according to the BET method.

Results and Discussion

Similarly to other catalysts,[9] the activity of ruthenium contacts depends on the nature of the starting compound. The samples of Ru/Al_2O_3 prepared with the use of ruthenium oxychloride (**1**), sodium ruthenate (**2**), and potassium ruthenate (**3**), exhibited different activity. For example, the yield of benzene at 500 °C for **1**, **2**, and **3** was equal to 15, 2, and 18 %, respectively. Most likely, the differences in the activity are due to the variation in the content of ruthenium species in different valent states. In the subsequent experiments, the ruthenium catalysts prepared from ruthenium oxychloride were studied.

The supported monometallic Ru catalysts and monometallic Tc catalysts exhibited comparatively low activity in the cyclohexane dehydrogenation (Table 1). The main reaction products are benzene and hydrogen; a

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1959—1963, August, 1996.

1066-5285/96/4508-1857 \$15.00

Table 1. Characterization of the catalysts

Catalyst	S_{sp} /m^2 g^{-1}	T_{det} /°C	Conversion (%)	Yields of the reaction products (%)			Selectivity for benzene (%)
				C_1—C_5	C_6H_6	Toluene	
0.1 % Ru/SiO_2	193	460	11.1	—	11.1	—	100.0
		500	27.3	1.7	25.5	—	93.4
		540	41.7	3.7	35.5	2.3	85.2
0.1 % Ru— —0.1 % Tc/SiO_2	208	460	27.1	—	27.1	—	100.0
		500	42.8	2.1	37.9	2.7	88.6
		550	66.6	8.9	54.6	2.9	82.0
0.1 % Ru/Al_2O_3	51	440	4.4	—	4.4	—	100.0
		520	9.9	2.6	5.9	1.3	59.2
		580	41.9	13.8	24.3	3.7	57.9
0.1 % Ru— —0.1 % Tc/Al_2O_3	67	440	7.3	—	7.3	—	100.0
		540	52.8	5.1	40.0	7.6	75.8
		580	83.0	14.4	61.0	7.5	73.5
0.2 % Ru/Y_2O_3	12	400	9.6	—	9.6	—	100.0
		460	20.5	1.2	19.3	—	93.9
		520	58.2	2.9	53.5	1.7	92.0
0.2 % Ru— —0.2 % Tc/Y_2O_3	10	400	42.0	—	42.0	—	100.0
		460	69.9	—	69.9	—	100.0
		520	83.8	—	83.8	—	100.0

small amount of light hydrocarbons and toluene forms above 400 °C. It is seen that the nature of the support affects the activity of both mono- and bimetallic catalysts. The Y_2O_3-based systems are the most active. The catalysts can be arranged in the following sequence with respect to the benzene yield: Ru—Tc/Y_2O_3 > Ru—Tc/Al_2O_3 > Ru—Tc/SiO_2. In these experiments, a nonadditive increase in the activity of bimetallic catalysts as compared to the monometallic samples is observed, *i.e.*, a so-called synergistic effect takes place. Figure 1 presents as an example the data on the benzene yield over the mono- and bimetallic catalysts supported on Y_2O_3. The results of the experiments with Y_2O_3 on which dehydrogenation occurs at higher temperature is shown for comparison. The temperature of the reaction start lowers significantly in parallel with an increase in the activity of the bimetallic catalysts.

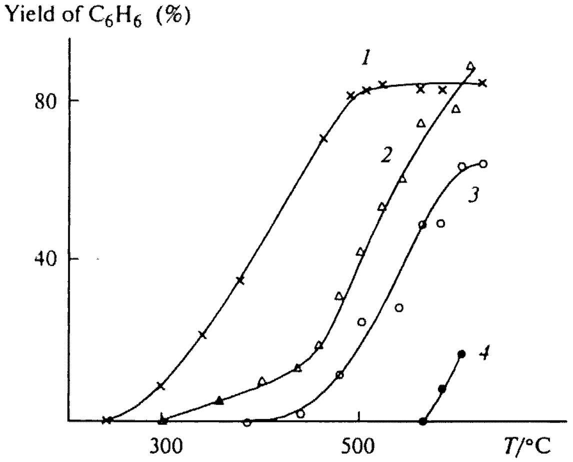

Fig. 1. Yield of benzene upon cyclohexane dehydrogenation on the catalysts: Ru (0.2 %)—Tc (0.2 %)/Y_2O_3 (*1*); Ru (0.2 %)/Y_2O_3 (*2*); Tc (0.2 %)/Y_2O_3 (*3*); Y_2O_3 (*4*).

When SiO_2 and Y_2O_3 are used as the supports, the selectivity for benzene changes slightly upon the introduction of the second metal, unlike the bimetallic catalysts supported on γ-Al_2O_3 (see Table 1). Thus, the nature of the support affects not only the overall activity but also the selectivity.

The synergistic effect is most pronounced for the low-percentage samples. Figure 2 shows that the highest benzene yield is observed at the weight ratio Tc/Ru = 1:1 on the γ-Al_2O_3 and Y_2O_3 supports and at the 3:2 ratio in the case of SiO_2. The effects observed are not connected with the specific surface area, because the S_{sp} values of the mono- and bimetallic systems are close (see Table 1).

Substantial differences between the mono- and bimetallic catalysts are found in the study of the hydrogen chemisorption. Figure 3 shows that the shape of the curves of chemisorption on the mono- and bimetallic samples is substantially different. The chemisorption on the bimetallic low-percentage catalysts is substantially lower than that on the monometallic catalysts on which hydrogen spillover seems to take place. With a rise in the metal concentration, the chemisorption on the bimetallic samples increases and then becomes constant. The chemisorption on the monometallic samples drops with a rise in the metal concentration and becomes lower than that on the bimetallic contacts.

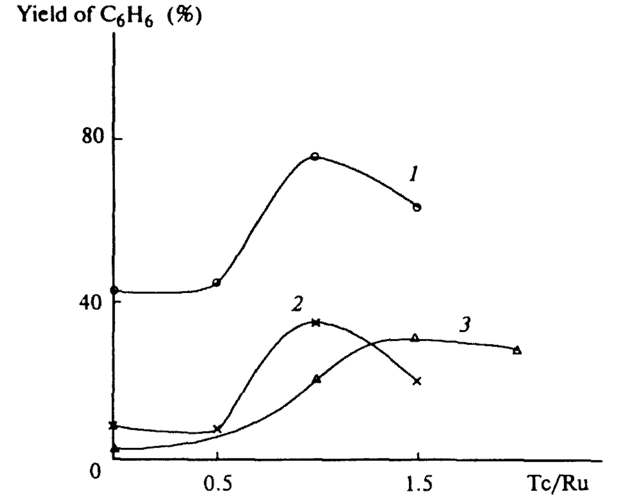

Fig. 2. Dependence of benzene yield on the Tc/Ru ratio for cyclohexane dehydrogenation over the Ru—Tc catalysts at 500 °C: Y_2O_3 support (*1*); Al_2O_3 support (*2*); SiO_2 support (*3*) ([Ru] = const = 0.1 %, the Tc content changes).

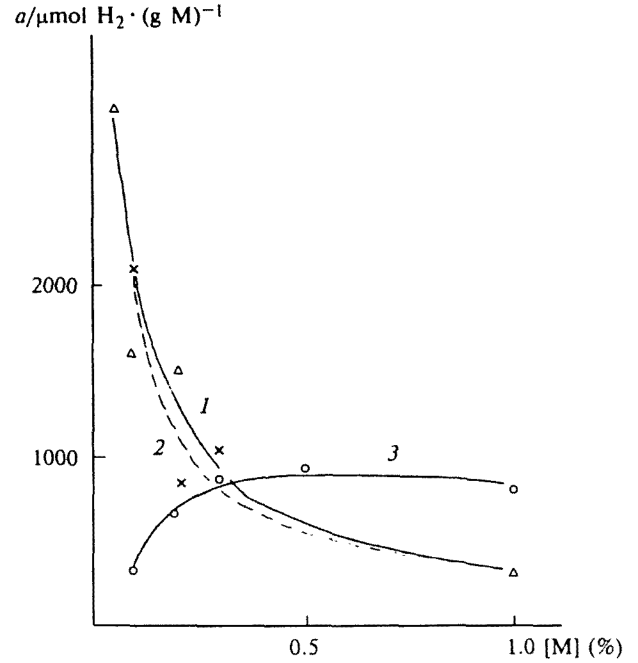

Fig. 3. Dependence of hydrogen chemisorption at p = 2 Torr on the amount of supported metal for the catalysts: Tc/Al_2O_3 (*1*); Ru/Al_2O_3 (*2*); Ru (0.2 %)—Tc/Al_2O_3 (*3*) ([Ru] = const, the Tc content changes).

The catalytic and adsorption data give evidence for different nature of active centers in the mono- and bimetallic catalysts. Similar data has been obtained by other authors. For example, it has been shown[4] that in the $Ir—In/Al_2O_3$ bimetallic catalysts new adsorption centers arise.

Additional data on the surface state is obtained with the use of diffuse reflectance spectra (Fig. 4). The starting solution of ruthenium oxychloride is characterized by three bands at 367, 384, and 470 nm (curve *1*). This spectrum indicates the presence of Ru^{3+} along with Ru^{4+} in a starting solution, because the bands at 367 and 384 nm seem to be due to the Ru^{3+} with electron configuration t_2.[5,8] When ruthenium oxychloride is supported on Al_2O_3, the spectrum changes substantially (curve *2*). The appearance of new bands, a shift of the bands, and the change in their intensity indicate the distortion of the coordination of the supported ions, the change in the content of various ruthenium ionic species. The appearance of the peak at 574 nm seems to be caused by an increase in the fraction of Ru^{4+} (a distorted octahedron) due to oxidation by air oxygen.[10] The formation of the sufficiently stable compound, $Ru(OH)_4$, which does not decompose even at 700 °C [8] is possible. On the other hand, the appearance of a green color upon drying the granules of the impregnated support gives evidence for the presence of the mixture of the ruthenium di- and trichlorides on the surface.[8] The peaks at 245 and 355 nm confirm the existence of Ru^{3+} on the surface and the peak at 400 nm is typical of the octahedrally coordinated Ru^{2+} ion (t^6_{2g} configuration of d-electrons).[11,12] The high intensity of the band at 400 nm seems to be connected with the superimposing of the bands related to Ru^{2+} and Ru^{3+}.

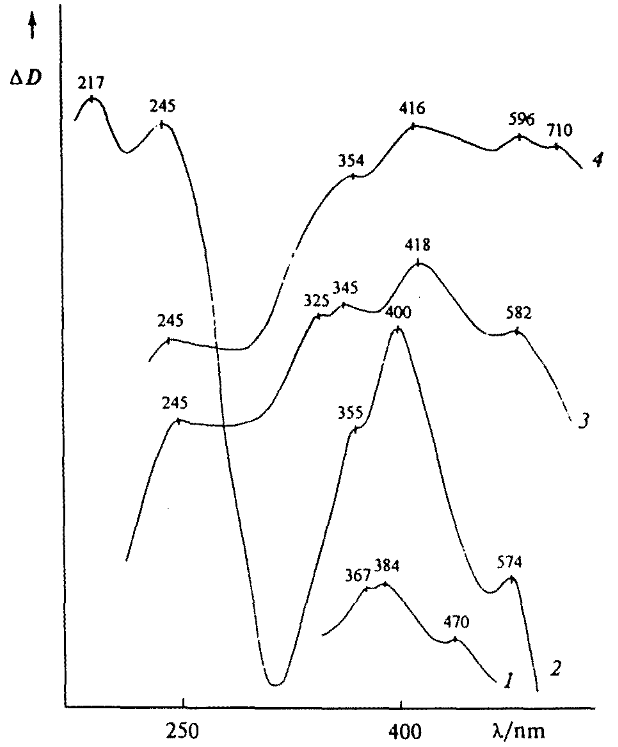

Fig. 4. Diffuse reflectance spectra of the Ru/Al_2O_3 catalysts: *1*, the spectrum of a solution of $Ru(OH)Cl_3$; *2*, that of $Ru(OH)Cl_3/Al_2O_3$; the same after reduction at 300 (*3*) and 700 (*4*) °C.

Let us consider the changes in the spectrum of the monometallic Ru/Al_2O_3 catalyst upon reduction by hydrogen at different temperatures. In the spectrum of the sample treated with H_2 at 300 °C (curve *3*) substantial changes are seen. First, the intensity of the bands decreases sharply to indicate the beginning of reduction and a decrease in the fraction of the Ru ionic species. Secondly, a shift of practically all bands and the appearance of even new band at 325 nm, which can be assighed to Ru^{3+},[13] are observed.

The spectrum of the sample reduced at 500 °C is identical to that of the catalyst reduced at 300 °C. With a further rise in the reduction temperature up to 700 °C, the smoothing of all peaks and total increase in optical density in the visible region are observed, indicating the reduction of Ru to a metal state (curve *4*). The second, less intensive peak typical of Ru^{3+} (λ = 325 nm) disappears, although some amount of the ruthenium ionic species remains on the surface of the reduced catalyst.

These data provide evidence for the strong interaction of the supported ruthenium with the support upon heating. However, in spite of the presence of hydrogen, all ruthenium ionic species (Ru^{2+}, Ru^{3+}, Ru^{4+}) persist. A change in their content and coordination is observed. This is the reason for a significant shift of the bands.

Comparison of the spectra of the NH_4TcO_4 solution (Fig. 5, curve *1*), the Tc/γ-Al_2O_3 catalyst (Fig. 5, curve *3*), and the bimetallic Ru—Tc catalyst (Fig. 5, curves *2* and *4*) shows that the presence of Tc leads to an even more complicated picture. The positions of the bands related to Ru in the spectrum of the unreduced bimetallic catalyst differ from those of the corresponding bands in the spectrum of the monometallic Ru sample. The appearance of the band at 480 nm seems to result from the interaction of the starting solutions, which leads to a change in the degree of the Ru reduction. The presence of the Ru ions affects also the tetrahedrally coordinated TcO_4^- ion in the bimetallic catalyst: the typical bands (247 and 294 nm) in the spectrum of the Ru—Tc sample shift (251 and 312 nm, respectively, curve *2*) due to the interaction with ruthenium. Upon reduction of the bimetallic catalyst, the intensity of all bands and particularly the bands with λ_{max} = 251 and 403 nm decreases. Although the concentration of all ionic species decreases, a total reduction of the supported ruthenium and technetium compounds does not occur.

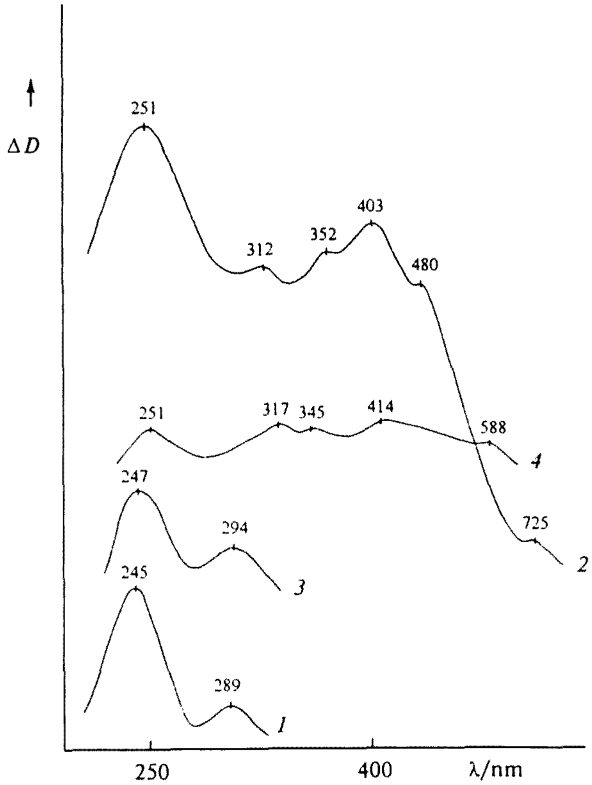

Fig. 5. Diffuse reflectance spectra of the mono- and bimetallic catalysts: *1*, the spectrum of a solution of NH_4TcO_4; *2*, that of $Ru(OH)Cl_3$—NH_4TcO_4/Al_2O_3; *3*, of Tc/Al_2O_3; *4*, of Ru—Tc/Al_2O_3.

The spectral data obtained allow one to conclude that on the surface of the mono- and bimetallic catalysts, ionic species of the metals are present in addition to the metal phases. The appearance of the ionic species is due to the interaction of the supported substances with the support and to one another. The surface species on the mono- and bimetallic samples somewhat differ in their composition. For example, a decrease in the concentration of the Ru ionic species after the introduction of Tc is observed, which can give evidence for the formation of the products of the interaction of two metals, *e.g.*, Ru_xTc_y. Most likely these surface species create additional active centers for adsorption and catalytic reactions.

In conclusion, let us compare the capability for synergism for all M—Tc systems studied by us (M is the element of the platinum group). With this purpose, the so-called coefficient of synergism K_s was calculated:

$$K_s = \frac{\eta_3}{\eta_1 + \eta_2},$$

where η_3 is the yield of the reaction product on the binary sample, η_1 and η_2 are the yields of the product on the monometallic catalysts.[14]

The comparison was carried out for the catalysts with the same metal content (0.05 %). We used the data on the yield of benzene at 300 °C. As seen in Table 2, the coefficient of synergism increases with an increase in the

Table 2. Physicochemical properties of some elements of the platinum group

Element	Atomic number	Coefficient of synergism, K_s	Strength of the M—H bond (rel. units)	Percentage of the d-character of the bond (%)
Ru	44	1.00	70.6	50
Rh	45	3.00	67.7	50
Pd	46	4.00	62.9	46
Pt	78	7.75	62.9	44

atomic number of the platinum group element. The highest capability for synergism was observed for the Pt—Tc system and the lowest one for the Ru—Tc system. Table 2 presents, in addition to the coefficient of synergism, the data on other properties of the elements of the platinum group, which show that the strength of the M—H bond and percentage of the d-character of the metal—metal bond decrease with an increase in the atomic number of the element of the platinum group. The opposite change in the coefficient of synergism, on one hand, and the properties shown, on the other hand, confirms the suggestion about the substantial difference in the chemical composition of the surface species on the mono- and bimetallic catalysts.

References

1. N. E. Kozlov, E. A. Skritsan, M. V. Zaretskii, and G. A. Zhitenko, *Neftekhimiya* [*Petrochemistry*], 1975, **15**, 69 (in Russian).
2. V. D. Stytsenko, O. V. Kovalenko, and A. Ya. Rozovskii, *Kinet. Katal.*, 1991, **32**, 163 [*Kinet. Catal.*, 1991, **32** (Engl. Transl.)].
3. A. A. Vedenyapin, N. G. Giorgadze, I. P. Murina, S. V. Y[illegible]hin, G. O. Chivadze, B. K. Nefedov, and V. M. Akimov, *Izv. AN SSSR, Ser. Khim.*, 1990, 11 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 4 (Engl. Transl.)].
4. A. V. Zaitsev, A. P. Tyupaev, V. Yu. Borovkov, O. D. Sterligov, G. V. Isagulyants, and V. B. Kazanskii, *Izv. AN SSSR, Ser. Khim.*, 1991, 2222 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 1944 (Engl. Transl.)].
5. V. I. Spitsyn, G. N. Pirogova, N. N. Popova, and G. E. Kalinina, *Dokl. AN SSSR*, 1987, **292**, 103 [*Dokl. Chem.*, 1987, **292** (Engl. Transl.)].
6. G. N. Pirogova, N. N. Popova, and G. E. Kalinina, *Izv. AN SSSR, Ser. Khim.*, 1989, 1482 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 1354 (Engl. Transl.)].
7. G. N. Pirogova and N. N. Rimar', *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1563 [*Russ. Chem. Bull., Div. Chem. Sci.*, 1994, **43**, 1475 (Engl. Transl.)].
8. O. E. Zvyagintsev, *Khimiya ruteniya* [*Chemistry of Ruthenium*], Nauka, Moscow, 1965 (in Russian).
9. T. Yoshinari, F. Suganuma, and C. Sera, *J. Jpn. Petrol. Inst.*, 1989, **32**, No. 5, 248.
10. V. M. Ivanov, A. I. Busev, L. V. Popova, and L. I. Bogdanovich, *Zh. Anal. Khim.*, 1969, **24**, 1064 [*J. Anal. Chem. USSR*, 1969, **24** (Engl. Transl.)].
11. F. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience Publ., John Wiley and Sons, New York—London—Sydney, 1965].
12. A. B. Nikol'skii and A. M. Popov, *Zh. Anal. Khim.*, 1977, **32**, 999 [*J. Anal. Chem. USSR*, 1977, **32** (Engl. Transl.)].
13. G. P. Mezharaup, I. S. Kunitskaya, and E. Yu. Yanson, *Zh. Anal. Khim.*, 1986, **41**, 99 [*J. Anal. Chem. USSR*, 1986, **41** (Engl. Transl.)].
14. S. M. Shostakovskii, *Dokl. AN SSSR*, 1988, **302**, 1122 [*Dokl. Chem.*, 1988, **302** (Engl. Transl.)].

Received October 27, 1995;
in revised form December 25, 1995