

LIQUID PHASE OXIDATION OF MESITYLENE TO 3,5-DIMETHYLBENZALDEHYDE

Gabriela VALEHRACHOVÁ, Milan HRONEC and Václav VESELY

Faculty of Chemical Technology, Slovak Institute of Technology, 812 37 Bratislava

Received October 30th, 1985

Liquid phase oxidation of mesitylene to 3,5-dimethylbenzaldehyde has been studied in the presence of cobalt bromide catalysts activated with triethanolamine or pyridine. The selectivity for the aldehyde is affected by the presence of the amine, by solvent, and only little by concentration of the catalyst and its components. The lower value of rate constant of the subsequent oxidation of the aldehyde, $k_2 = (7.66 \pm 0.39) \cdot 10^{-5} \text{ s}^{-1}$, as compared with that of the oxidation of mesitylene, $k_1 = (1.66 \pm 0.13) \cdot 10^{-4} \text{ s}^{-1}$ at 60°C, indicates an important role of the cooxidation reactions in the process of oxidation of mesitylene, which affects the reaction selectivity.

Methyl substituted aromatic compounds are oxidized to the corresponding carboxylic acids at enhanced temperatures in the presence of transition metals. The reaction proceeds *via* aldehydic intermediates which are formed in amounts of 5 to 40% depending on the conditions of the oxidation, catalyst and hydrocarbon type. As many of the substituted aldehydes are important intermediates in production of perfumes, pharmaceuticals, or insecticides, the possibility of their preparation has been studied by oxidation of the corresponding toluene derivatives. So, *e.g.*, in the presence of strong acids (trifluoroacetic, H_2SO_4), toluene is oxidized by stoichiometric amounts of Mn(III) or Co(III) acetates in acetic acid at room temperature to give benzaldehyde in a yield of 71% (ref.¹). Ce(IV) trifluoroacetate also represents an efficient oxidizing agent². In these cases the oxidizing agent is a metal in higher valence state, and the reaction proceeds by the electron-transfer mechanism.

The most frequently studied, however, are the catalyzed oxidations with participation of transition metals which can additionally be activated by bromides. Such catalysts give high selectivity for aldehydes in the oxidations of various alkyltoluenes³⁻⁶ and especially alkoxy- and aryloxytoluenes⁷⁻¹⁰. The reaction is carried out usually in acetic acid as solvent at 60–170°C, the necessary catalyst concentrations being high (0.1 to 0.4 mol *per* mol of substrate). The selectivity varies from 50 to 78% at the conversion of 40 to 70%. Formation of large amounts of aldehydes as the intermediate was also observed with the oxidation of mesitylene (1,3,5-trimethylbenzene) in acetic acid, however, in the presence of only catalytic amounts (which is important) of cobalt bromide coordinated with triethanolamine¹¹.

In the present work the oxidation of mesitylene has been studied in more detail with special respect to comparison of the factors affecting the selectivity increase for formation of 3,5-dimethylbenzaldehyde. Cobalt bromide catalyst complexes with nitrogen ligands, triethanolamine, and pyridine were used as the catalysts.

EXPERIMENTAL

Reagents. Mesitylene (98.9%), chlorobenzene, and the aliphatic monocarboxylic acids were purified by distillation or crystallization. 3,5-Dimethylbenzaldehyde and 3,5-dimethylbenzoic acid were prepared¹² by oxidation of mesitylene with MnO_2 and purified by vacuum distillation and crystallization, respectively. The other reagents were of analytical purity and were used without purification.

Catalysts. The complexes CoBr_2Py_2 , $\text{CoBr}_2\text{TEA}_2$, and $\text{CoCl}_2\cdot\text{TEA}_2$, where Py and TEA mean pyridine and triethanolamine, respectively, were prepared by mixing the cobalt dihalide with excess (10–20%) of the nitrogen compound in butanol¹³. After filtration, washing with butanol, and drying in vacuum they were used as the oxidation catalysts. The other metal catalysts were commercial products.

The oxidation procedure. The oxidations were carried out in a 100 cm^3 glass reactor equipped with a reflux condenser preventing the liquid to escape from the system into which oxygen was introduced at a rate of $3.75\text{ cm}^3\text{ s}^{-1}$. The liquid reaction mixture (45 cm^3) containing 5 cm^3 chlorobenzene (internal standard) and 5 cm^3 mesitylene along with the catalyst was heated to the reaction temperature (usually 75°C) in the atmosphere of nitrogen and was intensively stirred (42 s^{-1}) during the reaction with oxygen. At definite time intervals samples of the reaction mixture were withdrawn for analysis (injection syringe). The selectivity determined from the distribution of products is expressed as percentual amount of the 3,5-benzaldehyde formed *per* the amount of the mesitylene converted.

Analysis. The content of bromide anions in the samples of the reaction mixture was determined by potentiometric titration with AgNO_3 solution using a silver and a calomel electrodes. The conversion of mesitylene, formation of 3,5-dimethylbenzaldehyde and the corresponding acid were determined by gas chromatography after esterification of the sample with diazomethane. The chlorobenzene present in the reaction mixture served as the internal standard. The glass columns $1.8\text{ m} \times 3\text{ mm}$ were packed with 10% neopentyl glycol succinate on Chromosorb WNAW DMCS (0.125–0.160 mm) impregnated with 1% H_3PO_4 . The temperature interval used was $80\text{--}210^\circ\text{C}$, the temperature gradient being 5°C min^{-1} .

RESULTS AND DISCUSSION

The oxidation of mesitylene was studied in acetic acid and other aliphatic acids. The cobalt bromide complexes with pyridine or triethanolamine ligands or salts of cobalt and bromide in the presence of amines were used in catalytic amounts as catalysts. Fig. 1 shows the effect of triethanolamine on distribution of the oxidation products from mesitylene with catalysis by cobalt bromide in acetic acid. The presence of certain concentrations of triethanolamine increases the selectivity of formation of 3,5-dimethylbenzaldehyde (Fig. 2), but – as experimental measurements showed

– higher concentrations of triethanolamine prolong the reaction time. A similar dependence was also found in the presence of pyridine. The effects of concentrations of bromine, hydrocarbon, and overall concentration of the cobalt bromide catalyst on the selectivity of the oxidation catalyzed with $\text{CoBr}_2\text{TEA}_2$ or CoBr_2Py_2 complexes are not distinct, the reaction rate only being affected.

The activity and selectivity of the complex catalyst $\text{CoBr}_2\text{TEA}_2$ are affected by the type of the solvent used (Fig. 3). Investigation of the effect of $\text{C}_2 - \text{C}_6$ aliphatic acids

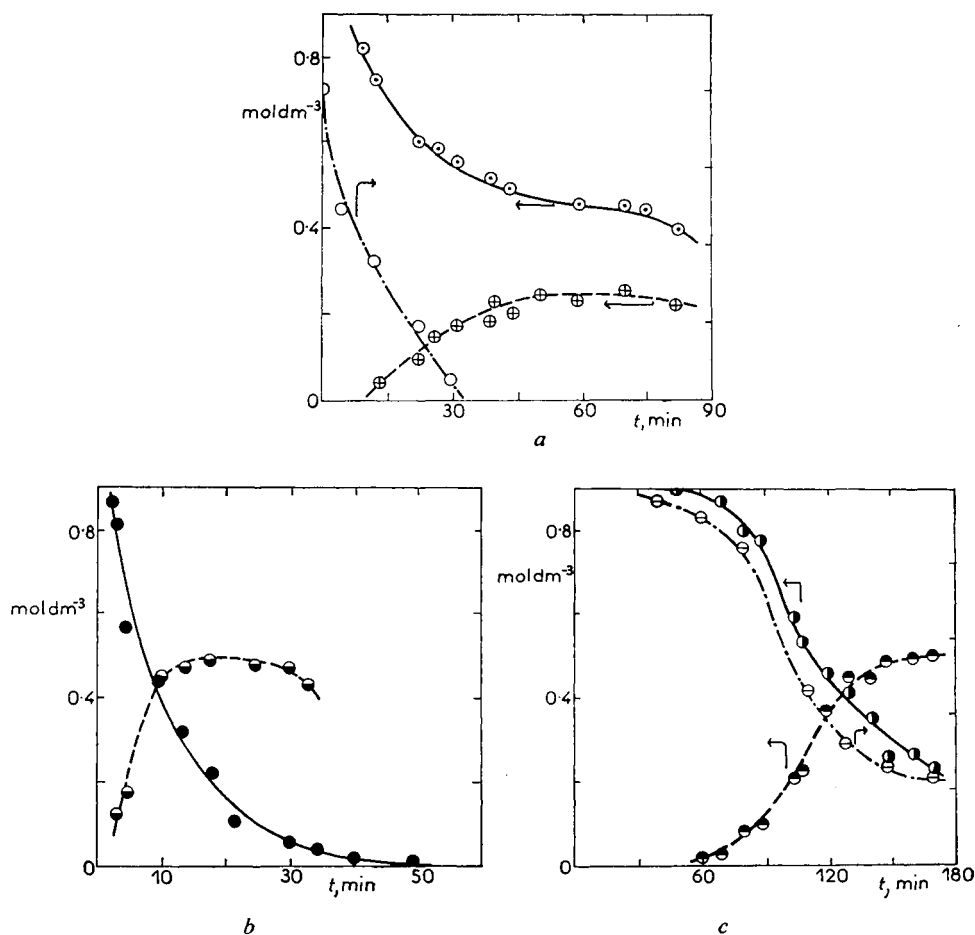


FIG. 1

Distribution of products of oxidation of mesitylene in acetic acid. *a* $0.03 \text{ mol dm}^{-3} \text{CoBr}_2 \cdot 6 \text{H}_2\text{O}$, \odot mesitylene, \oplus 3,5-dimethylbenzaldehyde, \circ Br^- ; *b* $0.03 \text{ mol dm}^{-3} \text{CoBr}_2 \cdot 6 \text{H}_2\text{O} + 0.03 \text{ mol} \cdot \text{dm}^{-3}$ triethanolamine, \bullet mesitylene, \ominus 3,5-dimethylbenzaldehyde; *c* $0.03 \text{ mol} \cdot \text{dm}^{-3} \text{CoBr}_2\text{TEA}_2 + 0.06 \text{ mol dm}^{-3}$ triethanolamine, \bullet mesitylene, \ominus 3,5-dimethylbenzaldehyde, \ominus Br^-

on the oxidation showed that increasing chain of the aliphatic acid and/or dilution of acetic acid with chlorobenzene resulted in decreased oxidation rate and decreased selectivity of formation of 3,5-dimethylbenzaldehyde. A synergic effect of manganese and cerium on selectivity of the $\text{CoBr}_2\text{TEA}_2$ catalyst was observed at the molar ratio of the metals 4 : 1 (Fig. 4). The activity and selectivity of the CoBr_2 catalyst itself are positively affected also by the presence of alkali metal bromides (Fig. 5). The oxidation of mesitylene to the corresponding aldehyde and monocarboxylic acid proceeds *via* several consecutive irreversible reactions. As the 3,5-dimethylbenzaldehyde is formed with high selectivity in the oxidation process, the kinetic interpretation of experimental data presumed the validity of the following scheme:

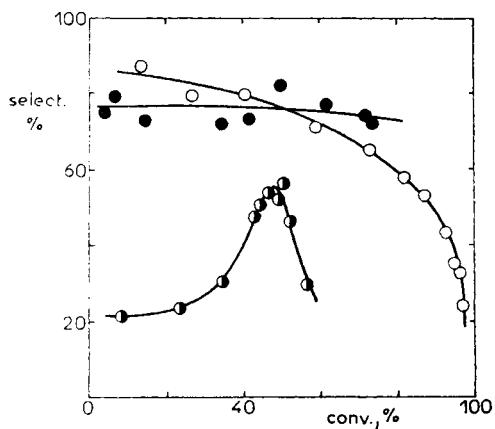
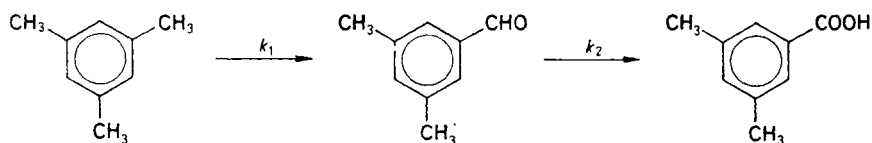


FIG. 2
Effect of triethanolamine concentration on the selectivity of formation of 3,5-dimethylbenzaldehyde. ● $0.03 \text{ mol dm}^{-3} \text{ CoBr}_2 \cdot 6 \text{ H}_2\text{O}$, ○ $0.03 \text{ mol dm}^{-3} \text{ CoBr}_2 \cdot 6 \text{ H}_2\text{O} + 0.03 \text{ mol dm}^{-3} \text{ TEA}$, ● $0.03 \text{ mol dm}^{-3} \text{ CoBr}_2\text{TEA}_2 + 0.06 \text{ mol dm}^{-3} \text{ TEA}$

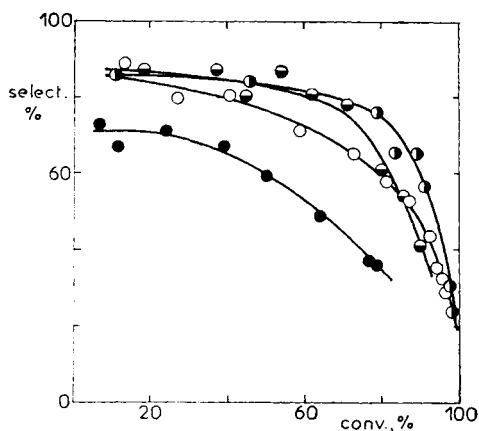


FIG. 3
Effect of solvent on the selectivity of formation of 3,5-dimethylbenzaldehyde at various values of mesitylene conversion. Catalyst: $0.03 \text{ mol dm}^{-3} \text{ CoBr}_2\text{TEA}_2$. Solvent: ○ 35 cm^3 acetic acid + 5 cm^3 chlorobenzene; ● 35 cm^3 0.1 mol dm^{-3} trichloroacetic acid solution in acetic acid + 5 cm^3 chlorobenzene; ● 10 cm^3 acetic acid + 30 cm^3 chlorobenzene; ● 35 cm^3 valeric acid + 5 cm^3 chlorobenzene

Both the reaction steps can be described as the 1st order reactions, which is indicated by the agreement between experimental and calculated data in Fig. 6. At the temperature of 60°C the rate constants of these reactions are $k_1 = (1.66 \pm 0.13) \cdot 10^{-4} \text{ s}^{-1}$ and $k_2 = (7.66 \pm 0.39) \cdot 10^{-5} \text{ s}^{-1}$. The activation energies of the two reactions are $100 \pm 11 \text{ kJ mol}^{-1}$ and $73 \pm 9 \text{ kJ mol}^{-1}$, respectively, in the temperature interval of 60–80°C. The values of the rate constants calculated for the two reactions indicate that in the system studied the rate of the subsequent oxidation of 3,5-dimethylbenzaldehyde is lower than that of the oxidation of mesitylene. As the oxidation rate of 3,5-dimethylbenzaldehyde is very high in the absence of the hydrocarbon and is rapidly decreased in the presence of even low concentrations of mesitylene¹¹, it is obvious that cooxidation reactions between the hydrocarbon oxidized and the aromatic aldehyde formed play an important role in the process of the oxidation investigated.¹⁴

The experimental measurements showed that the selectivity of formation of 3,5-dimethylbenzaldehyde in the presence of cobalt bromide catalysts is affected by nitrogen bases but depends only slightly on the overall concentration of the catalyst

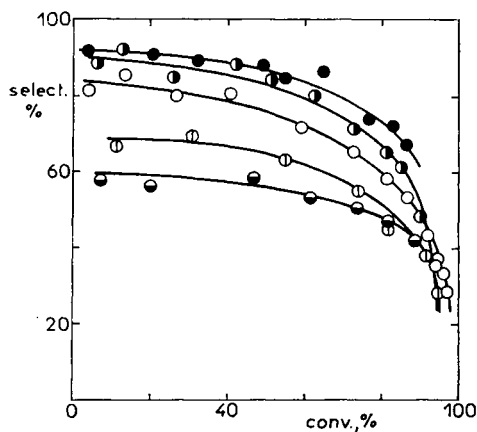


FIG. 4

Effect of metal co-catalysts ($0.006 \text{ mol} \cdot \text{dm}^{-3}$) on the selectivity of the $\text{Co}(\text{OAc})_2 \cdot 4 \text{ H}_2\text{O}$ ($0.024 \text{ mol dm}^{-3}$) catalyst activated with 0.06 mol dm^{-3} triethanolammonium bromide. ● $\text{Ce}_2(\text{CO}_3)_3 \cdot 5 \text{ H}_2\text{O}$, ● $\text{Mn}(\text{OAc})_2 \cdot 4 \text{ H}_2\text{O}$, ◐ Mo naphthenate, ◑ $\text{Ni}(\text{acac})_2$, ◒ $\text{CoBr}_2\text{TEA}_2$ complex (0.03 mol dm^{-3}) as the only catalyst. The symbols OAc and acac denote the acetate and acetylacetonate ligands, respectively

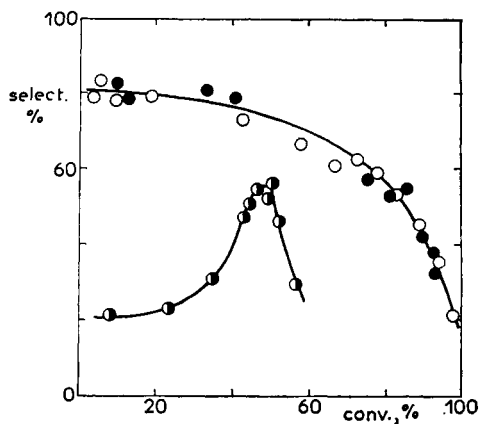


FIG. 5

Effect of Li and Na salts on the selectivity of mesitylene oxidation. ● $0.03 \text{ mol dm}^{-3} \text{ CoBr}_2 \cdot 6 \text{ H}_2\text{O}$, ○ $0.03 \text{ mol dm}^{-3} \text{ Co}(\text{OAc})_2 \cdot 4 \text{ H}_2\text{O} + 0.06 \text{ mol dm}^{-3} \text{ NaBr}$, ● $0.03 \text{ mol} \cdot \text{dm}^{-3} \text{ CoBr}_2 \cdot 6 \text{ H}_2\text{O} + 0.03 \text{ mol dm}^{-3} \text{ LiOAc}$

and of some of its components. The formation of aldehyde, however, depends substantially on the type of the hydrocarbon oxidized^{8,15}. At the experimental conditions given, toluene, xylenes, and some other methyl substituted aromates are oxidized with lower selectivity than that of the mesitylene oxidation. Therefore, it seems very likely that the selectivity of formation of the aldehyde is determined predominantly by the retardation effect of the hydrocarbon on the oxidation of the respective aromatic aldehyde. Hence the experimentally found effects of temperature, solvent, and synergism of metal mixtures on the selectivity of the oxidation reaction can be ascribed also to their effects on the rate of cooxidation reactions between the aromatic aldehyde and the hydrocarbon being oxidized.

It is well known that the process of oxidations of alkylaromatic hydrocarbons in acetic acid involves transient formation of peroxy radicals which prefer the reaction with metal ions (Eq. (A)) to the reaction with a hydrocarbon^{16,17}.

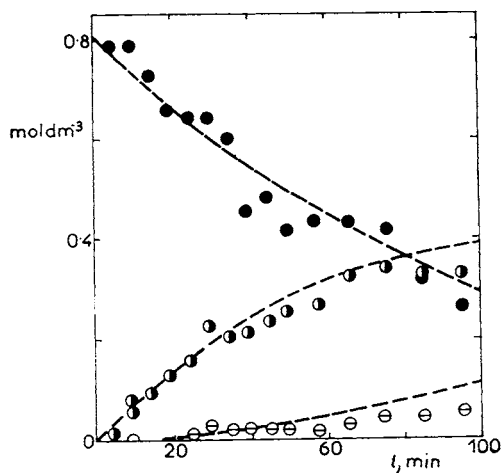
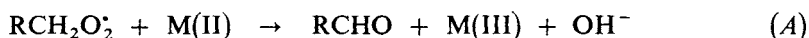


FIG. 6

Product distribution from the oxidation of mesitylene catalyzed with 0.03 mol dm^{-3} $\text{CoBr}_2 \cdot \text{TEA}_2$. ● mesitylene, ● 3,5-dimethylbenzaldehyde, ○ 3,5-dimethylbenzoic acid; the dashed lines have been calculated (see the text)

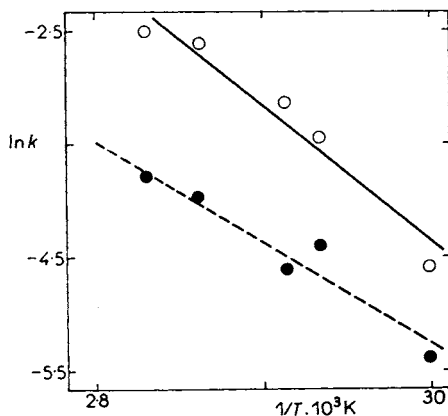


FIG. 7

The Arrhenius dependence for the oxidation of mesitylene ○ and 3,5-dimethylbenzaldehyde ● in the presence of 0.03 mol dm^{-3} $\text{CoBr}_2 \cdot \text{TEA}_2$

The reaction *A* gives the aldehyde as the main product. In the oxidations of alkylaromatic hydrocarbons catalyzed with cobalt and bromide ions, the reaction rates are always substantially higher than those in the absence of bromides, this fact being due presumably to higher reactivity of the cobalt bromide complexes with peroxy radicals¹⁷.



In a system containing bromide ions, the attained concentration of the intermediate aldehydes is higher, too^{18,19}. As the bromide ions are converted into inactive forms of organic bromides during the reaction course, the reaction *C* is replaced by the reaction *B*, and due to that — presumably — the formation of aldehydes is decreased, too. In Fig. 1 it can be seen, however, that the conversion of bromide ion into the inactive forms is slowed down in the presence of nitrogen compounds. Thereby the reaction system retains a higher concentration of active cobalt bromide complexes all the time, and the course of the aldehyde-forming reaction *C* is supported. Moreover, it can also be presumed that the cobalt complexes with nitrogen ligands are more reactive in the reaction with peroxy radicals, which is similar to the reaction *C*.

From the results obtained it can be concluded that the selectivity of formation of 3,5-dimethylbenzaldehyde by the oxidation of mesitylene catalyzed with cobalt bromide complexes with nitrogen ligands is determined predominantly by the co-oxidation reaction between the aldehyde formed and the hydrocarbon being oxidized and, furthermore, by the propagation reaction between the intermediate peroxy radical and metal complex.

REFERENCES

1. Hanotier J., Hanotier-Brideux M., De Raditzky P.: *J. Chem. Soc., Perkin Trans. 2*, 1973, 381.
2. Marrocco M., Brilmyer G.: *J. Org. Chem.* 48, 1487 (1983).
3. Lloyd E.: U.S. 4208352; *Chem. Abstr.* 93, 167 929 (1980).
4. Massie S. N.: U.S. 3732314; *Chem. Abstr.* 79, 18391 (1973).
5. Imamura J., Kazuhiro K.: *Jpn.* 79157534; *Chem. Abstr.* 92, 215 066 (1980).
6. Chalk A. J., Magennis S. A., Newman W. E. in the book: *Fundamental Research in Homogeneous Catalysis* (M. Tsutsui, Ed.), Vol. 3, p. 445. Plenum, New York 1979.
7. Matsuda T., Shirafuji T., Murata T.: *Jpn.* 7959243; *Chem. Abstr.* 91, 192 993 (1979).
8. Imamura J.: *Yoki Gosei Kagaku Kyokaishi* 37, 667 (1979); *Chem. Abstr.* 92, 6158 (1980).
9. Shimizu S., Kizawa K., Yoshimoto T., Imamura J.: *Jpn. Petrol. Inst.* 27, 7 (1982).
10. Kuckertz H., Schaeffer G.: *Ger. Offen.* 310129194; *Chem. Abstr.* 98, 160 425 (1983).
11. Hronec M., Veselý V.: *This Journal* 40, 2165 (1975).
12. Bawn C., Jolley J.: *Proc. R. Soc.* 273 A, 297 (1956).
13. Gill N. S., Nyholm R. S.: *J. Inorg. Nucl. Chem.* 18, 88 (1961).
14. Novak A. M., Kucher R. V., Opeida I. A.: *Dokl. Akad. Nauk Ukr. SSR*, 1977 Ser. B 995.
15. Ivanov A. M., Chervnskii K. A., Mikhaylovskaya T. N., Pluznikov B. V., Galabickii B. V., Ivanova L. A., Pavlyuk G. V.: *Neftekhimiya* 18, 680 (1978).

16. Ravens D. A. S.: *Trans. Faraday Soc.* *55*, 1768 (1959).
17. Kamiya Y.: *J. Catal.* *33*, 480 (1974).
18. Sakota K., Kamiya Y., Ohta N.: *Bull. Chem. Soc. Jpn.* *41*, 641 (1968).
19. Borgaonkar H. V., Raverkar S. R., Chandalla S. B.: *Ind. Eng. Chem., Prod. Res. Develop.* *23*, 455 (1984).

Translated by J. Panchartek.