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Comment on "Kinetics of Catalyzed Liquid Phase Oxidation of *p*-Nitrotoluene by Air in Basic Medium"

To the Editor:

In the recent issue of *Organic Process Research and Development* (**1999**, *3*, (2), 109−113) was published the paper of S. B. Chandalia and S. Mukhopadhyay "Kinetics of Catalyzed Liquid-Phase Oxidation of *p*-Nitrotoluene by Air in Basic Medium".

The attentive study of this paper raises a number of questions.

1. Authors used as the catalysts $CoBr_2$ and $CoCl_2$. It is known that these compounds in a strongly basic medium undergo the reaction $CoX_2 + 2OH^- = Co(OH)_2\downarrow + 2\ X^-$, forming the precipitates of cobaltous hydroxide. In this connection it is interesting to know how the homogeneity of the reaction mixture was secured.

2. The observed low activation energy of 4.5 kcal/mol (the usual activation energy for the homogeneous reactions is about 16−18 kcal/mol) serves as indirect evidence of the presence of diffusion-limited processes caused by the formation of the solid phase. This is also confirmed by the higher product yields in the presence of the cobalt phthalocyanine. The latter catalyst in strongly alkaline media is truly homogeneous (see ref 1)[1] whereas the former ones are, in fact, heterogeneous.

3. The dependence of the initial rate on the catalyst loading (Figure 6 in the cited article) although it is linear, does not go through zero. It shows that the noncatalyzed reaction is possible or that the dependence is actually nonlinear.

(In response to the response, the following has been added by the author:) A few final notes if that is allowable. Don't know why a completely justifiable curiosity is called an oddity, but less with that.

Beside the mass transfer resistance there exists such a thing as the pore diffusion resistance that cannot be eliminated by the intensive stirring or the high flow rate. As shown in p 390 of Levenspiel's "Chemical Reaction Engineering"; J. Wiley & Sons: New York, 1999, activation energy in the presence of pore diffusion resistance is described by the equation: $E_{obs} = (E_{true} + E_{diff})/2$. And just this effect can be the reason for the low observed activation energy. Moreover, if the activation energy is small, it does not mean that the reaction is slow. Thus, the very fast reaction: $F_2 + HI \rightarrow F\bullet + HF + I\bullet$ has the activation energy of 5 kcal/mol. On the other hand, oxidation of *o*-xylene by oxygen (a comparatively slow reaction) has the activation energy of 31 kcal/mol (Emmanuel, N.; Knorre, D. *Kurs khimicheskoi kinetiki* [*Chemical Kinetics*]; Vysshaya Shkola: Moscow, 1994. It is a pity that these simple truths are forgotten. However, we do not think that a further debate is needed.

Tatiana Bukharkina

Department of Carbon Materials, Mendeleev University of Chemical Technology of Russia, 9 Miusskaya sq., Moscow, 125047, Russia. E-mail: htum@muctr.edu.ru.

Felix Sirovski*

N. D. Zelinsky Institute of Organic Chemistry, 47 Leninsky pr., 117913, Moscow, Russia. E-mail: sirovski@gol.ru.

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[1] Hoffman, M. R.; Lim, B. C. Environ. Sci. Technol., **1979,** *13*, 1406−1414.

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