ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2016, Vol. 90, No. 10, pp. 1921–1924. © Pleiades Publishing, Ltd., 2016.
Original Russian Text © A.N. Kalenchuk, S.E. Bogorodskii, V.I. Bogdan, 2016, published in Zhurnal Fizicheskoi Khimii, 2016, Vol. 90, No. 10, pp. 1447–1451.

CHEMICAL KINETICS AND CATALYSIS

Kinetic and Thermodynamic Parameters of Hydrogen Release during the Heterogeneous Catalytic Dehydrogenation of *cis*- and *trans*-Isomers of Perhydro-*m*-terphenyl

A. N. Kalenchuk[a,b]*, **S. E. Bogorodskii**[c], **and V. I. Bogdan**[a,b]
[a]*Department of Chemistry, Moscow State University, Moscow, 119991 Russia*
[b]*Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia*
[c]*Advanced Laser Technologies Division, Institute of Laser and Information Technologies,*
Russian Academy of Sciences, Troitsk, Moscow oblast, 142092 Russia
**e-mail: akalenchuk@yandex.ru*

Received November 16, 2015

Abstract—Comparative studies on the temperature dependence of the dehydrogenation of *cis*- and *trans*-isomers of perhydro-*m*-terphenyl are performed in a flow catalytic reactor. Rate constants and equilibrium constants of all elementary acts of this reaction are calculated on basis of experimental data using the KINET 0.8 program for the mathematical modeling of the kinetics of complex reactions. The resulting data indicate that perhydro-*m*-terphenyl *cis*- and *trans*-isomers structural differences have no appreciable effect on dehydrogenation.

Keywords: dehydrogenation, perhydro-*m*-terphenyl, catalysis, hydrogen
DOI: 10.1134/S0036024416100162

INTRODUCTION

Catalysis is becoming an important tool for developing new technologies needed in the energy industry and the chemistry of new materials [1, 2]. The search for new types of fuels with acceptable environmental characteristics is a matter of special importance. The introduction of supersonic aircraft once required the development of new fuels that were characterized by high heat capacities and chemical and thermal stabilities, compared to the traditional oil and gas fuels that were used earlier. Such carbon-saturated condensed and/or aromatic compounds as decalin and terphenyl largely meet these requirements [3]. Along with the development of green energy sources based on hydrogen fuel cells, it was shown recently that these compounds can serve as the basis for mobile chemical systems of hydrogen storage that ensure safe and fast feeds of pure hydrogen via reversible hydrogenation-dehydrogenation reactions [4]. It is known that the thermal characteristics of *cis*- and *trans*-isomers of certain cyclic compounds sometimes differ considerably from each other. It has been established (using decalin as an example) that such differences influence the rate of hydrogen release [5].

The aim of this work was to identify the features and patterns of the heterogeneous catalytic dehydrogenation of *cis*- and *trans*-isomers of perhydro-*m*-terphenyl in a flow reactor.

EXPERIMENTAL

For dehydrogenation, we used perhydro-*m*-terphenyl prepared in our laboratory via the hydrogenation of commercial grade *m*-terphenyl (99%, Aldrich). Samples of the investigated solid substrate (40 g) and catalyst (4 g) were loaded into a high-pressure PARR-300 laboratory autoclave, purged with an inert gas, and then pressed and hydrogenated with stirring at 180°C. The hydrogen pressure was 70 atm, and the reaction was conducted until the hydrogen pressure reached a constant value. Reaction products were identified and analyzed on a Crystallux-4000M chromatograph equipped with a ZB-5 capillary column (ZEBRON, United States) and a flame ionization detector, along with a FOCUS DSQ II GC-MS equipped with a TR-5ms capillary column.

It is known that the maximum rate of hydrogen release is reached at high levels of substrate conversion. At the same time, it is better to use lower levels of conversion in order to obtain valid kinetic parameters. Catalysts of different dehydrogenation activity were used for the sake of comparison: no. 1 was 3 wt % Pt/C; no. 2 was 1 wt % Pt/C; and no. 3 was 1 wt % Pt/C*. All catalysts were prepared using aqueous solutions of H_2PtCl_6 by impregnating carbon supports followed by reduction with hydrogen (except for catalyst no. 3) at 320°C in a 30 mL/min flow of hydrogen for 2 h [6].

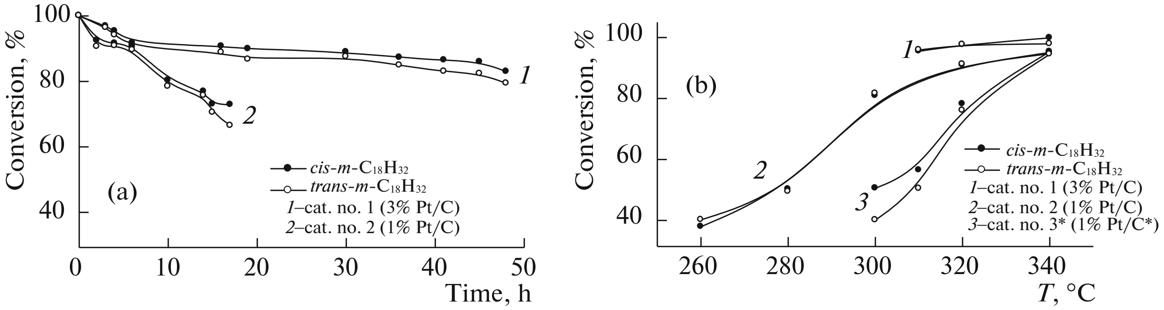


Fig. 1. (a) Time and (b) temperature dependences of *cis*- and *trans*-perhydro-*m*-terphenyl conversions upon dehydrogenation for catalysts nos. 1–3 ($V_L = 1$ h^{-1}, $P = 1$ atm).

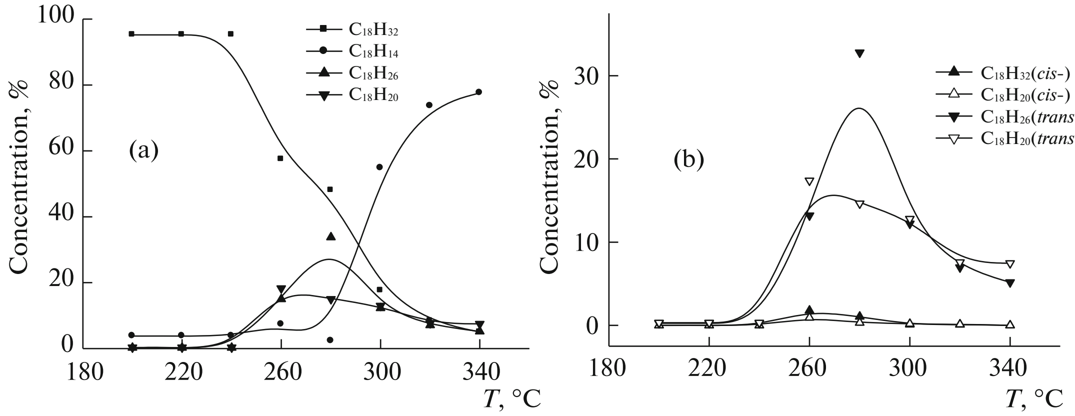


Fig. 2. Temperature dependences of the concentration of the initial perhydro-*m*-terphenyl and the products of its dehydrogenation for 1 wt % of Pt/C ($V_L = 1$ h^{-1}, $P = 1$ atm): (a) total for both isomers; (b) allowing for *cis*- and *trans*-isomers.

Dehydrogenation was performed in a flow reactor at 260–340°C; the linear flow rate of the substrate was 6 mL/h [7]. Volumetric flow rate V_L [cm^3 h^{-1} (cm^3 K$_t$)$^{-1}$] of the substrate was calculated as the ratio of the linear flow rate of the substrate in its liquid state at 20°C to the catalyst volume and was estimated at 1 h^{-1}.

Hydrogenation and dehydrogenation conversions (K) were calculated using the equation $K = (c^0 - c)/c^0 \times 100\%$, where c^0 and c are the initial and final concentrations of the transformed substrate, respectively.

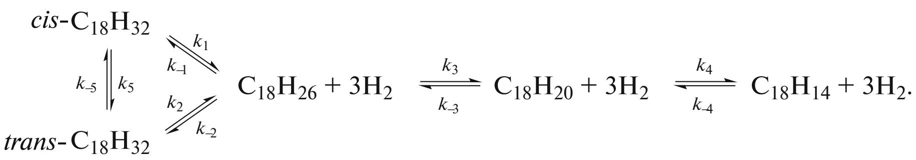
Selectivity (S) was calculated using the equation $S(i) = \sum c(i)/\sum c(k) \times 100\%$, where $\sum c(i)$ is the sum of the concentration of part of the products and $\sum c(k)$ is the sum of the concentrations of all products, respectively.

RESULTS AND DISCUSSION

The hydrogenation of *m*-terphenyl yielded a substrate consisting of two perhydro-*m*-terphenyl isomers (I, 17.3% of isomer; II, 78.0% of isomer), 3.8% of the initial *m*-terphenyl, and 0.9% of partially hydrogenated *m*-terphenyl compounds. It is known [8] that the *trans*-isomer of perhydro-*m*-terphenyl has a more rigid structure and its melting temperature T_m is 62°C, while the melting temperature of more flexible *cis*-isomer is 20–25°C. We identified isomers (I) and (II) as the *cis*- (I) and *trans*- (II) isomers of perhydro-*m*-terphenyl because the melting temperature of the resulting substrate was 55–56°C. The time and temperature dependences of conversion alterations of the *cis*- and *tran*s-isomers upon the dehydrogenation of perhydro-*m*-terphenyl are presented in Fig. 1. It can be seen in Fig. 1 that the temperature dependences of the *cis*- and *trans*-perhydro-*m*-terphenyl conversions were virtually identical if catalyst no. 1 (3 wt % of Pt/C) was used. Some differences between the curves for *cis*- and *trans*-isomers can be seen if the catalysts containing 1 wt % Pt/C were used.

The temperature dependences of the concentration of the initial perhydro-*m*-terphenyl and the products of its dehydrogenation on catalyst no. 2 are presented in Fig. 2.

Analysis of the product yield of perhydro-*m*-terphenyl dehydrogenation shows that the formation of final *m*-terphenyl predominated at temperatures higher than 300°C. At the same time, the content of partially hydrogenated *trans*-isomer compounds is greatly superior to the content of *cis*-isomer derivatives in the total volume over the given range of temperatures. The rate constants of all elementary acts of this reaction were determined from the obtained experimental data using the KINET 0.8 mathematical modeling program. This program optimizes the values of the constants up to the best agreement between calculated and experimental kinetic curves. Using the experimental data presented above, the optimized scheme of perhydro-*m*-terphenyl dehydrogenation takes the form



Dehydrogenation proceeds with the simultaneous and mutual transformations of *cis*- and *trans*-isomers of perhydro-*m*-terphenyl and the formation of the final *m*-terphenyl ($C_{18}H_{14}$) and the products of partial hydrogenation, which contain one unsaturated six-membered ring ($C_{18}H_{26}$, dicyclohexylbenzene and 1-cyclohexyl-3-phenylcyclohexane) or two unsaturated rings ($C_{18}H_{20}$, 1,3-diphenylcyclohexane and 3-cyclohexylbiphenyl).

It is known that differential equation systems describing the kinetics of chemical reactions have analytical solutions in the simplest cases. We therefore used a simplified model of perhydro-*m*-terphenyl dehydrogenation (A) first. All elementary acts of the reaction were reduced to three: mutual isomerization of the *cis*- and *trans*- perhydro-*m*-terphenyl (I, *cis*-$C_{18}H_{32} \leftrightarrow$ *trans*-$C_{18}H_{32}$); 1,3-dehydrogenation of the *cis*-isomer (II, *cis*-$C_{18}H_{32} \leftrightarrow \sum(C_{18}H_{26-14} + C_nH_m + H_2)$); and the dehydrogenation of the *trans*-isomer (III, *trans*-$C_{18}H_{32} \leftrightarrow \sum(C_{18}H_{26-14} + C_nH_m + H_2)$). The *cis*- and *trans*-isomers of perhydro-*m*-terphenyl were considered separately as substrates, and the sums of all products ($C_{18}H_{26}$, $C_{18}H_{20}$, and $C_{18}H_{14}$) and co-products (C_nH_m) of dehydrogenation were (along with hydrogen, expressed in g/(L h)) considered products of the reaction. This model allowed us to assess most accurately the effect *cis*-*trans*-isomerization had on dehydrogenation.

Equilibrium constants were calculated from the determined rate constants of the elementary acts of the reaction. The equilibrium constants of the mutual isomerization of *cis*- and *trans*-isomers on catalyst no. 2 at 260°C were estimated at $K_{\mathrm{I}} = 7.90$ and $K_{-\mathrm{I}} = 0.013$. The equilibrium constants of the dehydrogenation of *cis*- and *trans*-isomers were $K_{\mathrm{II}} = 293.07$ and $K_{\mathrm{III}} = 252.61$, respectively. The values of all equilibria constants grew as the temperature was raised to $T = 300$°C, and were $K_{\mathrm{I}} = 11.39$, $K_{\mathrm{II}} = 1014.52$, and $K_{\mathrm{III}} = 492.46$, respectively. They remained virtually the same as the temperature was raised further. The calculated equilibrium constants of the transformation of *cis*-perhydro-*m*-terphenyl into *trans*-isomer attained lower values on the inactive catalyst at 300°C and were $K_{\mathrm{I}} = 1.93$ and $K_{-\mathrm{I}} = 0.52$, respectively; $K_{\mathrm{I}} = 9.38$ and $K_{-\mathrm{I}} = 0.11$ when $T = 320$°C. At the same time, $K_{\mathrm{II}}/K_{\mathrm{III}} \sim 2$ at both temperatures.

Simplified dehydrogenation model (A) considered above was subsequently complicated by adding experimental data for other products obtained from the reaction. In enhanced model (B), we considered reaction acts I, *cis*-$C_{18}H_{32} \leftrightarrow$ *trans*-$C_{18}H_{32}$); II, *cis*-$C_{18}H_{32} \leftrightarrow \sum($*cis*-$C_{18}H_{26} + H_2)$; III, *trans*-$C_{18}H_{32} \leftrightarrow \sum($*trans*-$C_{18}H_{26} + H_2)$; IV, *cis*-$C_{18}H_{26} \leftrightarrow \sum(C_{18}H_{20-14} + C_nH_m + H_2)$; and V, *trans*-$C_{18}H_{26} \leftrightarrow \sum(C_{18}H_{20-14} + C_nH_m + H_2)$, with allowance in particular for the formation of two isomers of a partial hydrogenation product ($C_{18}H_{26}$). The comparative range of equilibrium constants calculated using this model for catalyst no. 3 at $T = 300$°C was $K_{\mathrm{I}} = 1.69 < K_{\mathrm{II}} = 17.15 < K_{\mathrm{III}} = 25.34 \ll K_{\mathrm{V}} = 230.17 \ll K_{\mathrm{IV}} = 523.31$. The order of the constants obtained for catalyst no. 2 was the same. A slight increase in equilibrium constant K_{I} was observed on both nos. 2 and 3 as the temperature rose. At the same time, ratio $K_{\mathrm{IV}}/K_{\mathrm{V}}$ grew significantly, reaching its maximum at $T = 320$°C. K_{II} tended toward zero as the temperature rose and K_{III} fell, reaching its maximum at $T = 310$°C.

Model (C) includes all products of the reaction according to the optimized scheme of perhydro-*m*-terphenyl dehydrogenation given above and can be written as I, *cis*-$C_{18}H_{32} \leftrightarrow$ *trans*-$C_{18}H_{32}$; II, *cis*-$C_{18}H_{32} \leftrightarrow \sum($*cis*-$C_{18}H_{26} + H_2)$; III, *trans*-$C_{18}H_{32} \leftrightarrow \sum($*trans*-$C_{18}H_{26} + H_2)$; IV, *cis*-$C_{18}H_{26} \leftrightarrow \sum(C_{18}H_{20} + H_2)$; V, *trans*-$C_{18}H_{26} \leftrightarrow \sum(C_{18}H_{20} + H_2)$; and VI, $C_{18}H_{20} \leftrightarrow \sum(C_{18}H_{14} + C_nH_m + H_2)$. The comparative range of the equilibrium constants calculated using this model at $T = 260$°C for catalyst no. 2 was $K_{\mathrm{I}} = 2.13 < K_{\mathrm{II}} = 19.22 < K_{\mathrm{VI}} = 31.32 < K_{\mathrm{III}} = 35.95 < K_{\mathrm{V}} = 58.62 \ll K_{\mathrm{IV}} = 229.38$. This range changes somewhat as the temperature rises to $T =$

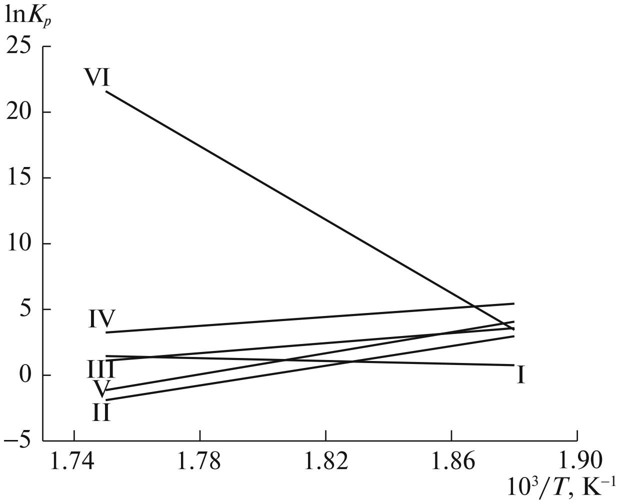


Fig. 3. Perhydro-*m*-terphenyl dehydrogenation equilibrium constants $K_{\rm I}$, $K_{\rm II}$, $K_{\rm III}$, $K_{\rm IV}$, $K_{\rm V}$, and $K_{\rm VI}$, calculated using the KINET program.

300°C: $K_{\rm II} = 0.15 \le K_{\rm V} = 0.32 < K_{\rm III} = 299 < K_{\rm I} = 427 < K_{\rm IV} = 25.45 \ll K_{\rm VI} = 2.39 \times 10^7$. The position of the calculated equilibrium constants is almost the same for the constants obtained for catalyst no. 3.

A comparison of the kinetic parameters of perhydro-*m*-terphenyl dehydrogenation calculated with experimental data using the KINET modeling program, which allows us to model complex reactions, showed that there was a correlation between the data obtained using different reaction models. The temperature dependences of the equilibrium constants for every elementary act of the dehydrogenation process were therefore calculated on basis of the enhanced model (Fig. 3).

In practice, the reaction's activation energy is estimated from the tangent to the slope of the $\ln K_p$–$1/T$ curve. Our data show that there are virtualy no differences between the $\ln K_p$–$1/T$ curves for the transformations of the *cis*-isomer (II and IV) and *trans*-isomer of perhydro-*m*-terphenyl (III and V). This could be evidence of the limited influence of the structural differences between *cis*- and *trans*-perhydro-*m*-terphenyl on the dehydrogenation reaction. We may therefore conclude that the dehydrogenation of perhydro-*m*-terphenyl differs substantially from that of decalin.

CONCLUSIONS

The dehydrogenation of perhydro-*m*-terphenyl allows us to obtain high levels of conversion in a flow reactor. The rate of dehydrogenation for the more active *cis*-isomer is higher than that for the *trans*-isomer over the considered range of temperatures. However, we found no significant differences between the effects the *cis*- and *trans*-isomery of perhydro-*m*-terphenyl have on dehydrogenation. The equilibrium shifts toward the transformation of *trans*-perhydro-*m*-terphenyl into *cis*-isomer at lower temperatures.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Education and Science, contract no. RFMEFI61314X0012.

REFERENCES

1. A. L. Tarasov, L. M. Kustov, V. I. Isaeva, et al., Kinet. Catal. **52**, 273 (2011).
2. A. L. Tarasov, O. A. Kirichenko, N. N. Tolkachev, I. V. Mishin, A. N. Kalenchuk, V. I. Bogdan, and L. M. Kustov, Russ. J. Phys. Chem. A **84**, 1122 (2010).
3. M. H. Gollis, L. I. Belenyessy, B. J. Gudzinowicz, et al., J. Chem. Eng. Data **7**, 311 (1962).
4. J. S. Sung, K. Y. Choo, T. H. Kim, et al., Int. J. Hydrogen Energy **33**, 2721 (2008).
5. Bo Wang, D. W. Goodman, and G. F. Froment, J. Catal. **253**, 229 (2008).
6. A. N. Kalenchuk, V. I. Bogdan, and L. M. Kustov, Catal. Ind. **7**, 60 (2015).
7. A. N. Kalenchuk, V. I. Bogdan, and L. M. Kustov, Russ. J. Phys. Chem. A **89**, 16 (2015).
8. W. Brugel, E. Kuss, P. Pollmann, et al., J. Mol. Struct. **1**, 61 (1967).

Translated by P. Vlasov