THEORETICAL STUDY ON THE INFLUENCE OF TEMPERATURE ON THE FREE GIBBS ENERGY OF THE PROCESS OF THE CONVERSION OF PIPERYLENE TO ISOPRENE

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In attempts to increase the efficiency of isoprene synthesis during the dehydrogenation of the C_5 fraction, we considered the basic thermodynamic parameters of the isomerization of piperylene in isoprene.

To study the temperature features of this scheme, we calculated the dependence of the Gibbs energy on temperature:

Table 1. The dependence of the free Gibbs energy ΔG_r^T (kJ/mol) of the conversion of piperylene to isoprene on the temperature (K)

Reagent	Product	T								
		298	323	348	373	398	423	448	473	498
Pip	3-MCB	67.3	59.8	60.1	60.4	60.9	70	70.4	71	61
3-MCB	MCB	-12.2	-12	-11.8	-11.6	-11.5	-11.3	-11	-10.8	-10.6
MCB	Isp	-46.1	-38.8	-39.1	-39.5	-39.8	-40.2	-40.5	-40.9	-41.3
Pip	_Isp_	_9_	_9_	_9.2_	_9.3_	_9.6_	_18.5_	_18.9_	_19.3_	_19.7_

In the same way, we obtained data on the dependence of the entropy of the reaction on temperature: the entropy, in this case, changes discontinuously. Then there is a sharp decrease with increasing temperature from 398 K (125 °C) to 423 K (150 °C).

Table 2. The dependence of the entropy of the reaction ΔS_r^T (J/mol·K^{-1}) on the temperature

Stage	298	323	348	373	398	423	448	473	498
Pip>3MCB	-18.8	-11.6	-12.3	-13	-13.6	-21.7	-22	-22.3	-22.6
3MCB>MCB	-6.1	-6.6	-7.2	-7.6	-8.1	-8.6	-9.1	-9.5	-9.9
MCB>Isp	11.6	12.3	13	13.5	14	14.4	14.9	15.2	15.5
Pip>Isp	-13.3	-5.9	-6.5	-7.1	-7.7	-15.9	-16.2	-16.6	-17

According to the calculated data, the conversion of piperylene to isoprene appears to be a weak endothermic reaction. With increasing reaction temperature, the free Gibbs energy increases nonlinearly. Thus, when the 423 K (150 °C) is reached, the ΔG_r reaction increases by a factor of two. The subsequent increase in temperature slightly increases the free energy of Gibbs. Obviously, the conversion must be carried out at temperatures not higher than 150 °C with removal of the reaction product from the mixture.