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RESEARCH

THERMODYNAMIC ANALYSIS OF REACTIONS FOR THE SYNTHESIS OF PETROCHEMICAL PRODUCTS FROM OXYGENATES

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A thermodynamic analysis of the reactions for the conversion of dimethyl ether into valuable products of the gas and oil industry and of propylene, formaldehyde, and 1,3-butadiene in particular was carried out. The temperature dependence of the equilibrium composition in the reaction for the production of 1,3-butadiene from dimethyl ether was determined. Calculation of the temperature dependence of the equilibrium composition in the reaction of propylene with formaldehyde with the formation of 1,3-dioxane, 1,3-butanediol, and 2-buten-1-ol showed that the main product at equilibrium is 2-buten-1-ol.

Keywords: oxygenates, thermodynamics, 1,3-butadiene, propylene, formaldehyde, Prins reaction.

Petrochemists have recently paid special attention to the production of valuable chemical products based on dimethyl ether (DME), which is one of the main products of the Fischer-Tropsch synthesis of oxygenates from syngas.

In [1] the mechanism of the reaction for the synthesis of olefins from methanol and DME at zeolite catalysts is considered, and various mechanisms such as isomerization and synchronous mechanisms for the formation of C–C bonds in the transformation of DME as well as the role of catalysts and temperatures in these reactions are discussed. In [2] kinetic aspects of the synthesis of olefins from methanol and DME at zeolite catalysts were examined.

The dependence of the activity of zeolite MFI in the transformations of DME into hydrocarbons on the spectral and textural characteristics and acidity was studied in [3]. Comparative results obtained during the synthesis of C_{5+} hydrocarbons are presented. It was established that high selectivity in the hydrocarbons of the gasoline fraction is achieved with the use of a catalyst based on a sample of zeolite MFI, for which in the infrared diffuse reflection spectra there are bands characteristic of the acid centers of H_3O^+.

It is interesting to note the results of studies [4], which examine the treatment of DME with associated petroleum gas in a mixture of synthetic hydrocarbons. It was established here that it is possible to obtain hydrocarbons direct from DME in a single-stage process. The presence in the vapor–gas mixture of such components as hydrogen, carbon dioxide, and water ensures high stability of the catalytic system. In [5-11] on the basis of data on the state of the intermediates formed from DME on the surface

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of the heterogeneous catalysts some catalytic reactions with the participation of DME were examined: methylation, ethanol synthesis, partial oxidation with the production of a series of compounds.

In order to complete the results from study of the chemistry for the conversion of DME in addition to solving the problems of catalysis and kinetics it is of course also necessary to study the parameters of the reaction region thermodynamically. However, analysis of published shows the absence of a systematic thermodynamic study of these reactions.

In this work reactions in which the thermodynamic probability results are of both theoretical and practical significance are investigated by the methods of chemical thermodynamics:

– the possibility of replacing ethyl alcohol with DME in the synthesis of 1,3-butadiene;

– thermodynamic analysis of the reaction between propylene and formaldehyde – products of the thermal decomposition of DME.

The employed data bases of the thermodynamic functions and the methods of calculation of the equilibrium concentration were presented in [6].

The thermodynamics of synthesis of DME from synthesis gas by the Fischer-Tropsch method was examined in [6]. We will begin our investigations by considering the thermal conversion of DME, in which the composition of the products is determined by the temperature and pressure. The reactions for synthesis from DME and ethyl alcohol are shown in **Fig. 1**.

The CH_3OCH_3 and CH_3CH_2OH molecules are a brilliant example of the fact that substances that have the same molecular formula but different structure under the same thermodynamic and catalytic conditions differ in their transformation products. Differences in the composition of the products here will depend on the nature of the employed catalyst, while the concentration of the components in the equilibrium composition will be characterized by minimum Gibbs energy for the whole thermodynamic system.

For relatively simple reactions the methods of chemical thermodynamics can be used to estimate their equilibrium composition.

Table 1 shows the temperature dependence of the thermodynamic characteristics for complete transformation in the investigated system.

For comparison **Table 2** shows the values of the enthalpy ΔH and Gibbs energy ΔG at 600 K for the transformation of DME and ethanol. In both cases all the examined reactions and particularly the reaction leading to the production of propylene and 1-butene are favorable. According to the data in Table 2, the ΔH_{600} and ΔG_{600} values are –11.91 and –14.207 kcal/mole lower than in the corresponding transformations of ethyl alcohol. Consequently, to judge from the results of the thermodynamic calculations the transformations of DME must take place more strongly and with greater thermal effect than the transformation of ethyl alcohol.

Table 3 shows the components of the decomposition reaction of DME at temperature 370°C and pressure 40 atm and their initial and equilibrium numbers of moles, and **Fig. 2** shows the temperature dependence of the equilibrium composition at pressures of 1 and 40 atm. As seen from Table 3, the equilibrium state contains significant amounts of acetaldehyde, methane, formaldehyde, and ethylene, which can all be raw materials for further syntheses. According to the data in Fig. 2, the equilibrium composition changes little with increase of pressure from 1 to 40 atm. In both cases, starting at 300°C in the equilibrium composition, the number of moles of formaldehyde and ethylene increases while the acetaldehyde and methane decrease.

Table 4 shows the components for the decomposition of DME at 370°C and 40 atm, and **Fig. 4** shows the temperature

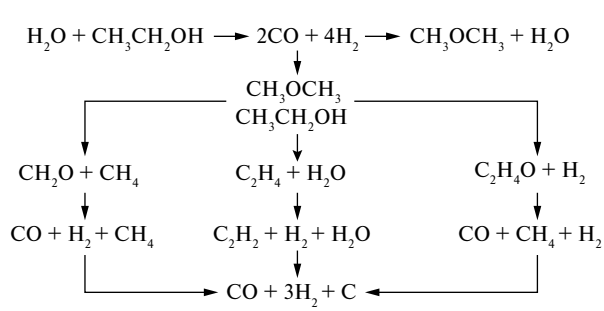

Fig. 1. Scheme of the reactions for thermal transformation of dimethyl ether into various products

Table 1

Temperature		Enthalpy, kcal/mole	Entropy, cal/mole·K	Gibbs energy, kcal/mole	Logarithm of equilibrium constant
K	°C				
		$CH_3–O–CH_3 = C_2H_5OH$			
300	26.8	–12.130	3.362	–13.138	9.572
400	126.8	–12.095	3.456	–13.478	7.364
500	226.8	–12.011	3.643	–13.833	6.047
600	326.8	–11.908	3.832	–14.207	5.175
700	426.8	–11.828	3.956	–14.597	4.558
800	526.8	–11.741	4.072	–14.998	4.098
900	626.8	–11.638	4.193	–15.412	3.743
1000	726.8	–11.517	4.321	–15.837	3.461
		$CH_3–O–CH_3 = CH_4 + CH_2O$ *(formaldehyde)*			
300	26.8	–1.539	32.946	–11.423	8.322
400	126.8	–1.466	33.163	–14.731	8.049
500	226.8	–1.459	33.181	–18.050	7.890
600	326.8	–1.498	33.113	–21.366	7.783
700	426.8	–1.588	32.975	–24.670	7.703
800	526.8	–1.675	32.858	–27.961	7.639
900	626.8	–1.737	32.785	–31.243	7.587
1000	726.8	–1.767	32.752	–34.520	7.545
		$CH_3–O–CH_3 = C_2H_4 + H_2O$			
300	26.8	–1.280	33.619	–11.366	8.281
400	126.8	–1.046	34.295	–14.764	8.067
500	226.8	–0.862	34.708	–18.216	7.963
600	326.8	–0.740	34.934	–21.700	7.905
700	426.8	–0.702	34.994	–25.198	7.868
800	526.8	–0.703	34.992	–28.697	7.840
900	626.8	–0.723	34.969	–32.195	7.819
1000	726.8	–0.750	34.941	–35.691	7.801
		$CH_3–O–CH_3 = C_2H_4O$ *(acetaldehyde)* $+ H_2$			
300	26.8	4.237	30.490	–4.910	3.577
400	126.8	4.647	31.674	–8.022	4.384
500	226.8	5.007	32.478	–11.232	4.910
600	326.8	5.320	33.051	–14.510	5.286
700	426.8	5.580	33.453	–17.837	5.569
800	526.8	5.801	33.748	–21.197	5.791
900	626.8	5.990	33.971	–24.584	5.970
1000	726.8	6.153	34.142	–27.990	6.118
		$CH_3–O–CH_3 = 2/3\ C_3H_6$ *(propene)* $+ H_2O$			
300	26.8	–10.557	23.706	–17.668	12.873
400	126.8	–10.319	24.392	–20.076	10.970
500	226.8	–10.122	24.834	–22.539	9.853
600	326.8	–9.972	25.110	–25.038	9.121
700	426.8	–9.892	25.234	–27.556	8.604
800	526.8	–9.844	25.298	–30.083	8.219
900	626.8	–9.814	25.333	–32.615	7.921
1000	726.8	–9.794	25.355	–35.149	7.682
		$CH_3–O–CH_3 = 0{,}5C_4H_8$ *(1-butene)* $+ H_2O$			
300	26.8	–13.864	17.991	–19.261	14.033
400	126.8	–13.620	18.694	–21.098	11.528
500	226.8	–13.403	19.180	–22.993	10.051
600	326.8	–13.224	19.510	–24.930	9.081
700	426.8	–13.108	19.688	–26.890	8.396
800	526.8	–13.022	19.804	–28.865	7.886
900	626.8	–12.952	19.887	–30.850	7.492
1000	726.8	–12.891	19.951	–32.842	7.178

Table 2

Conversion of DME	Enthalpy, kcal/mole	Gibbs energy, kcal/mole
$CH_3–O–CH_3 = C_2H_5OH$	–11.908	–14.207
$CH_3–O–CH_3 = CH_4 + CH_2O$ (formaldehyde)	–1.498	–21.366
$CH_3–O–CH_3 = C_2H_4 + H_2O$	–0.740	–21.700
$CH_3–O–CH_3 = CH_3CHO$ (acetaldehyde) + H_2	5.320	–14.510
$CH_3–O–CH_3 =2/3\ C_3H_6$ (propene) + H_2O	–9.972	–25.038
$CH_3–O–CH_3 = 0.5C_4H_8$(1-butene) + H_2O	–13.224	–24.930
$C_2H_5OH = C_2H_4 + H_2O$	11.168	–7.493
$C_2H_5OH = CH_3CHO$ (acetaldehyde) + H_2	17.228	–0.303
$C_2H_5OH = CH_4 + CH_2O$ (formaldehyde)	10.410	–7.158
$C_2H_5OH =2/3\ C_3H_6$ (propene) + H_2O	1.936	–10.831

Table 3

Molecule	Original number of moles	Equilibrium number of moles at 370°C and 40 atm
DME	1	$6.2279\cdot10^{-10}$
Ethyl alcohol	0	$5.0399\cdot10^{-5}$
Formaldehyde	0	$2.1953\cdot10^{-3}$
Acetaldehyde	0	0.66119
Methane	0	0.66338
Ethylene	0	$5.9674\cdot10^{-3}$
Hydrogen	0	$1.0011\cdot10^{-5}$
Water	0	0.33656
Total	1	1.6694

dependence of the equilibrium concentration at pressure 1 and 40 atm. As seen, unlike Table 3 and Fig. 2, 1,3-butadiene was added to the number of reaction components. As seen from the data in Table 3 and Fig. 2, in the equilibrium composition 1,3-butadiene begins to appear at a temperature of approximately 100°C and passes through a maximum at 700°C. The temperature at these special points increases with increase of pressure. The qualitative picture of variation in the concentrations of other components is the same as in the case without 1,3-butadiene.

We will examine the thermodynamics of the reaction between propylene and formaldehyde (the Prins reaction).

In the classical version for the conversion of DME formaldehyde 2 is used as the carbonyl component, the 1,3-diols 3 are the main reaction product, and the process is most often described in this form (Fig. 4). At the same time, depending on the reaction

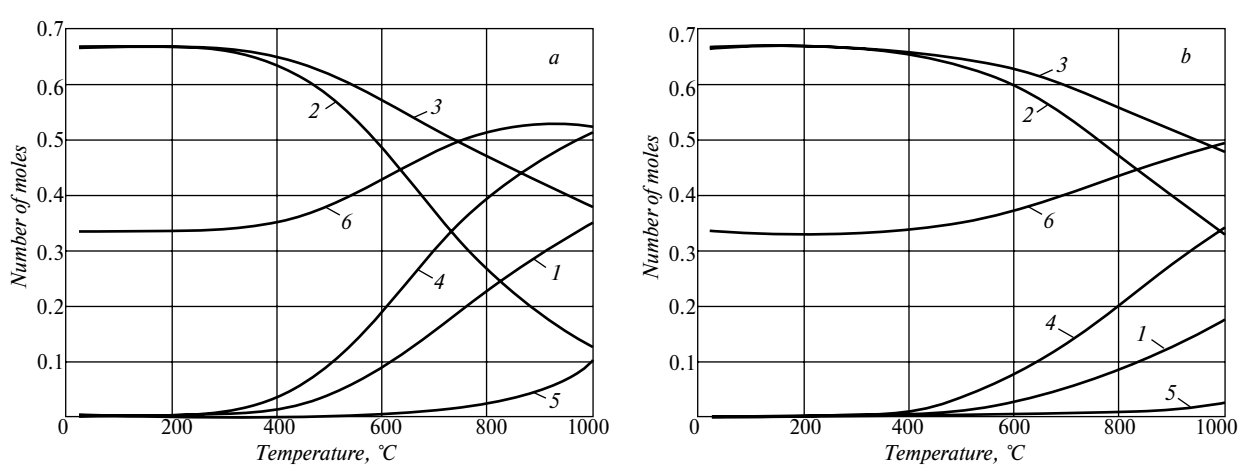

Fig. 2. Temperature dependence of the equilibrium composition in the conversion of dimethyl ether at pressure 1 (a) and 40 atm (b): 1) formaldehyde; 2) acetaldehyde; 3) methane; 4) ethylene; 5) hydrogen; 6) water

Table 4

Molecule	Original number of moles	Equilibrium number of moles at 370°C and 40 atm
DME	1	$5.88 \cdot 10^{-10}$
Ethyl alcohol	0	$4.76 \cdot 10^{-5}$
Formaldehyde	0	$2.2 \cdot 10^{-3}$
Acetaldehyde	0	0.577
Methane	0	0.630
Ethylene	0	$4.55 \cdot 10^{-3}$
Hydrogen	0	$1.09 \cdot 10^{-5}$
Water	0	0.421
1,3-Butadiene	0	0.051
Total	1	1.69

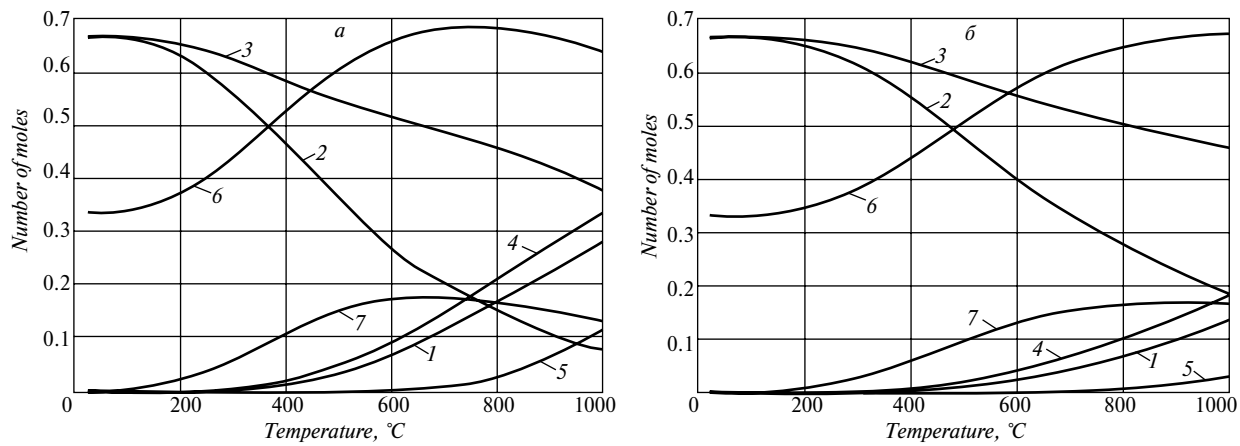

Fig. 3. Temperature dependence of the equilibrium composition in the conversion of dimethyl ether with the formation of 1,3-butadiene at pressure 1 (a) and 40 atm (b): 1) formaldehyde; 2) acetaldehyde; 3) methane; 4) ethylene; 5) hydrogen; 6) water; 7) 1,3-butadiene

conditions, the 1,3-diols 3 can undergo further transformations, the most frequent of which are the formation of cyclic acetals 1,3-dioxanes 5 with an excess of formaldehyde and dehydration with the formation of allyl alcohols 4 [7].

The results from calculations of the thermodynamic functions of the reactions for the formation of the 1,3-butanediol, 1,3-dioxane, propanal, and 2-buten-1-ol are presented in **Table 5**. It is seen that all these reactions are exothermic ($\Delta H = -15 \ldots -77$ kcal/mole), but to judge from the value of the Gibbs energy these reactions can take place at a temperature below 600°C.

It is of interest to consider jointly the thermodynamic characteristics of the components of the reactions for interaction of propylene with formaldehyde (see Fig. 4). The original and equilibrium numbers of moles at 380°C and 40 atm are presented in **Table 6**.

As seen from Table 6, at temperature 380°C and pressure 40 atm 2-buten-1-ol has the largest number of moles in the equi-

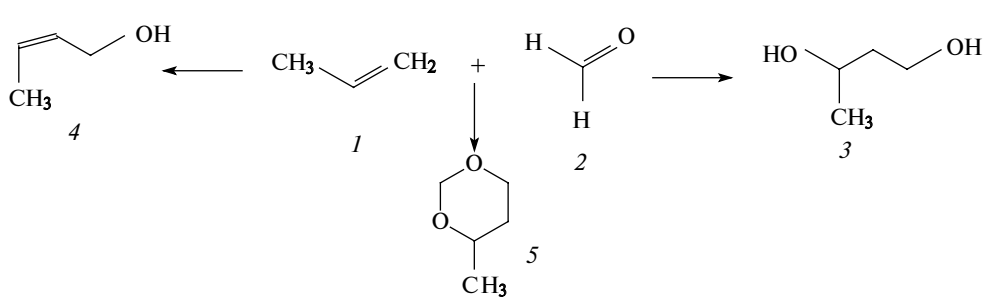

Fig. 4. Transformations in the course of the Prins reaction with the formation of allyl alcohols

Table 5

Temperature		Enthalpy. kcal/mole	Entropy. cal/mole·K	Gibbs energy. kcal/mole	Logarithm of equilibrium constant
K	°C				
$C_3H_6 + 3CH_2O + 1.5H_2 = 1.5C_4H_{10}O_2$ (1.3-butanediol)					
300	26.8	–77.550	–123.722	–40.434	29.458
400	126.8	–77.866	–124.662	–28.001	15.300
500	226.8	–77.877	–124.695	–15.530	6.789
600	326.8	–77.743	–124.453	–3.071	1.119
700	426.8	–77.516	–124.105	9.357	–2.922
800	526.8	–77.212	–123.700	21.748	–5.942
900	626.8	–76.839	–123.261	34.096	–8.280
1000	726.8	–76.411	–122.810	46.400	–10.142
$C_3H_6 + 3CH_2O = 1.5C_4H_8O_2$ (1.3-dioxane)					
300	26.8	–43.104	–112.121	–9.468	6.898
400	126.8	–43.635	–113.690	1.841	–1.006
500	226.8	–43.742	–113.941	13.228	–5.783
600	326.8	–43.612	–113.709	24.613	–8.966
700	426.8	–43.308	–113.244	35.962	–11.229
800	526.8	–42.852	–112.637	47.257	–12.911
900	626.8	–42.253	–111.933	58.486	–14.204
1000	726.8	–41.528	–111.170	69.642	–15.221
$CH_2O + C_2H_4 = C_3H_6O$ (propanal)					
300	26.8	–29.872	–31.906	–20.300	14.790
400	126.8	–29.772	–31.620	–17.124	9.357
500	226.8	–29.640	–31.328	–13.976	6.109
600	326.8	–29.462	–31.004	–10.859	3.956
700	426.8	–29.222	–30.637	–7.777	2.428
800	526.8	–28.911	–30.223	–4.733	1.293
900	626.8	–28.525	–29.769	–1.733	0.421
1000	726.8	–28.065	–29.285	–20.300	–0.267
$C_3H_6 + CH_2O = C_4H_8O$ (2-buten-1-ol)					
300	26.8	–16.128	–33.070	–6.208	4.523
400	126.8	–16.094	–32.976	–2.904	1.587
500	226.8	–16.014	–32.799	0.385	–0.168
600	326.8	–15.918	–32.625	3.656	–1.332
700	426.8	–15.811	–32.459	6.911	–2.158
800	526.8	–15.686	–32.293	10.148	–2.773
900	626.8	–15.544	–32.126	13.369	–3.247
1000	726.8	–15.398	–31.972	16.574	–3.622

librium composition. **Figure 5** shows the temperature dependence of the number of moles in the equilibrium composition of the components from Table 6 at pressure 1 and 40 atm. As seen, with increase of pressure the maximum for the yield of 2-buten-1-ol moves into the region of higher temperatures, and the value of the maximum here remains practically unchanged.

Thus, the following conclusions can be reached from the results of the thermodynamic investigations of the reactions in the transformation of DME:

Table 6

Molecule	Original number of moles	Equilibrium number of moles at 370°C and 40 atm
Propanal	1	0.71991
Formaldehyde	2	1.7199
1,3-Butanediol	0	0
1,3-Dioxane	0	$2.9224 \cdot 10^{-5}$
2-Buten-1-ol	0	0.28007
Total	3	2.7199

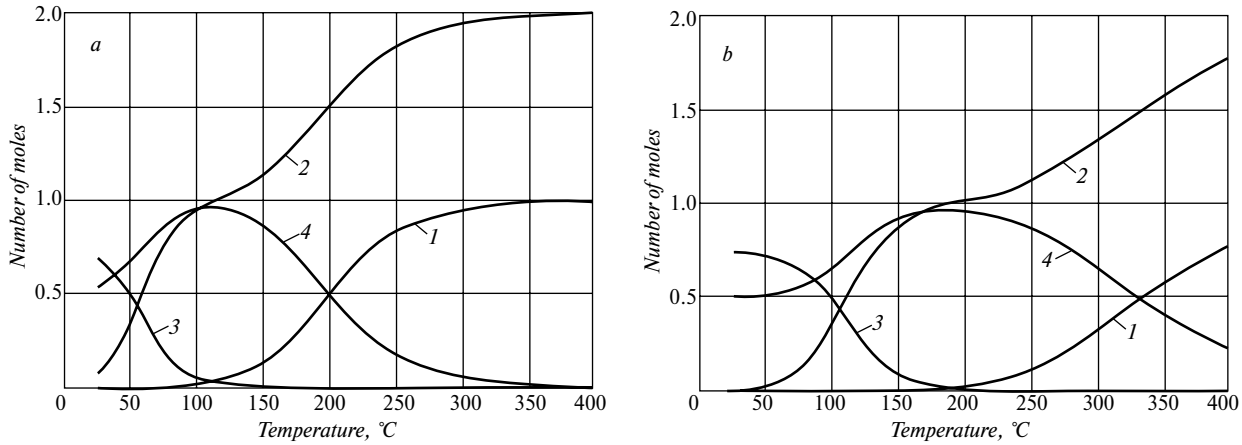

Fig. 5. The temperature dependence of the number of moles of the reaction components in the reaction of propylene and formaldehyde at pressure 1 (a) and 40 atm (b): 1) Propanal; 2) formaldehyde; 3) 1,3-dioxane; 4) 2-buten-1-ol

For the DME conversion reaction, the enthalpy is –11.91, while the Gibbs energy –14.21 kcal/mole is lower than in the corresponding reactions for the conversion of ethyl alcohol, and their probability is therefore higher and has a larger thermal effect;

In the reactions for the synthesis of 1,3-butadiene from the DME transformation products at the equilibrium composition it begins to appear at a temperature of about 100°C and passes through a maximum at 700°C, while the temperature of these special points increases with increasing pressure;

In the transformations of the Prins reaction with the formation of allyl alcohols the main product is 2-buten-1-ol, and with increase of pressure the maximum yield moves into the region of higher temperatures while the number of moles at the maximum remains practically unchanged.

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