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Quantum-Chemical Study of Thermodynamics of Ethylene Carbonate Reactions with Methanol

A. Ya. Samuilov[a], A. R. Valeev[a], F. B. Balabanova[a], Ya. D. Samuilov[a], and A. I. Konovalov[b]

[a] *Kazan National Research Technological University, ul. K. Marksa 68, Kazan, Tatarstan, 420015 Russia*
e-mail: ysamuilov@yandex.ru

[b] *Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center,*
Russian Academy of Sciences, Kazan, Tatarstan, Russia

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Abstract—Thermodynamic parameters of the major and side reactions in the course of dimethyl carbonate formation from ethylene carbonate and methanol have been determined by means of the B3LYP/6-311++G(df,p) quantum-chemical method. Enthalpy and entropy of the reactions have increased with enhanced association of the alcohols. Temperature dependences of the equilibrium constants have been determined. Technological conditions of dimethyl carbonate production via ethylene carbonate methanolysis have been elaborated.

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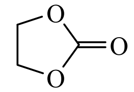
The transesterification of ethylene carbonate with methanol is the major route to dimethyl carbonate production [1–3]. Dimethyl carbonate is a low-toxic compound that is easily environmentally decomposed and thus is widely used as a “green” solvent [4] and high-octane fuel additive [5, 6]. It is an intermediate product in the phosgene-free synthesis of polycarbonates [7, 8], isocyanates [9, 10] (starting compounds for polyurethanes manufacture), and is widely used in organic synthesis [11–14].

Ethylene carbonate transesterification conditions depend on the thermodynamic characteristics of the process. A few attempts to estimate the parameters of ethylene carbonate interaction with methanol have been reported [15–18]. In the mentioned papers the process has been treated as a single stage; and the alcohol molecules have been assumed as present only in the monomer form. However, alcohols are highly associated liquids; in particular, liquid methanol consists mainly of linear dimers and trimers [19, 20]. Kinetic and thermodynamic parameter of the reactions involving alcohol associates and its monomeric form are significantly different [21, 22]. Thus, we studied thermodynamic characteristics of ethylene carbonate methanolysis taking into account that the process was multi-staged and the linear associates of alcohols were involved. The following set of transformation was considered [Eqs. (1)–(3)].



$$+ \ (CH_3OH)_n \rightleftarrows CH_3OCOOCH_2CH_2OH + (CH_3OH)_{n-1} \qquad (1)$$

I **IIa–IIc** **III**

$$\mathbf{III} + \mathbf{IIa–IIc} \rightleftarrows \underset{\mathbf{IV}}{CH_3OCOOCH_3} + (CH_3OH)_{n-1} + \underset{\mathbf{Va}}{HOCH_2CH_2OH} \qquad (2)$$

$$\mathbf{IV} + (HOCH_2CH_2OH)_n \longrightarrow \mathbf{III} + (HOCH_2CH_2OH)_{n-1} + CH_3OH \qquad (3)$$

n = 1 (**IIa, Va**), 2 (**IIb, Vb**), 3 (**IIc**).

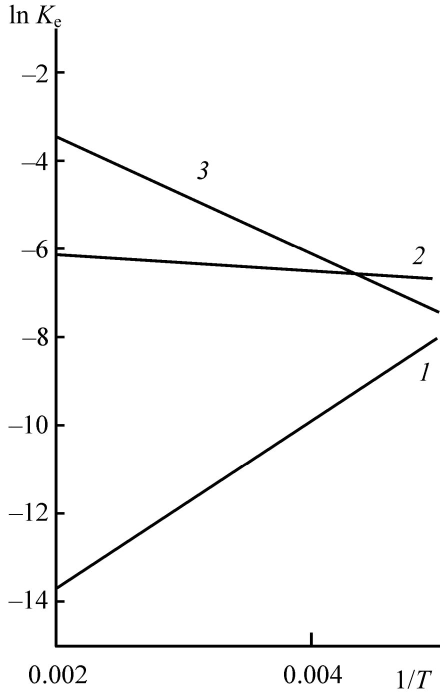


Fig. 1. Logarithm of equilibrium constant (ln K_e) of the reaction (1) as a function of reciprocal temperature (1/*T*) in the cases of compounds **IIa–IIc** (*1–3*, respectively).

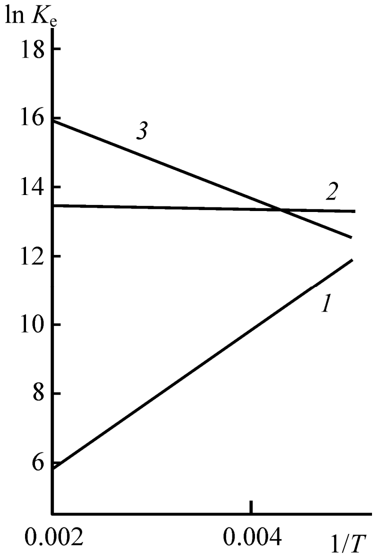


Fig. 2. Logarithm of equilibrium constant (lnK_p) of the reaction (2) as a function of reciprocal temperature (1/*T*) in the cases of compounds **IIa–IIc** (*1–3*, respectively).

Stage (1) consisted of reversible formation of methyl(2-hydroxyethyl)carbonate **III** in the primary reaction. Formation of **III** in the course of carbonate **I** methanolysis was experimentally proved in [18]. Reaction (2) led to the target product, carbonate **IV**. Reaction (3) was a side one, leading to a decrease in the target product yield; it was the reversible interaction of **IV** and glycol **Va** with the formation of carbonate **III**.

Thermodynamic parameters of the reactions (1)–(3) as obtained with the B3LYP/6-311++G(df,p) method using the GAUSSIAN 03 software package [23] are given in the table.

From the presented data, the degree of association of methanol **II** and glycol **V** influenced greatly the thermodynamics of the discussed reactions. In all cases the same trend was observed: with increasing degree of association of alcohols **II** and **V** the reaction enthalpies increased. Thus, from the energy point of view the equilibrium of reactions (1)–(3) should be shifted to initial compounds with enhanced alcohols association. However, alcohols association increased the reactions (1)–(3) reaction entropies as well, this should shift the equilibria (1)–(3) towards the products.

Entropy effects are more pronounced at elevated temperatures. Figures 1–3 demonstrate the Arrhenius plots of the equilibrium constants in the range of 250–500 K. The equilibrium constants were calculated from the tabulated data.

Figure 1 illustrates the temperature dependence of the equilibrium constant of reaction (1). In the cases of methanol associates **IIa–IIc** the significantly different

Enthalpy (ΔH_r) and entropy (ΔS_r) of reactions (1)–(3) in gaseous phase

Reaction	ΔH_r, kJ mol^{-1}	ΔS_r, J mol^{-1} K^{-1}
I + **IIa**	–15.6	–145.2
I + **IIb**	1.6	–47.7
I + **IIc**	10.6	–8.7
III + **IIa**	–16.8	14.6
III + **IIb**	0.4	112.2
III + **IIc**	9.4	151.2
IV + **Va**	16.8	–14.6
IV + **Vb**	31.3	97.3

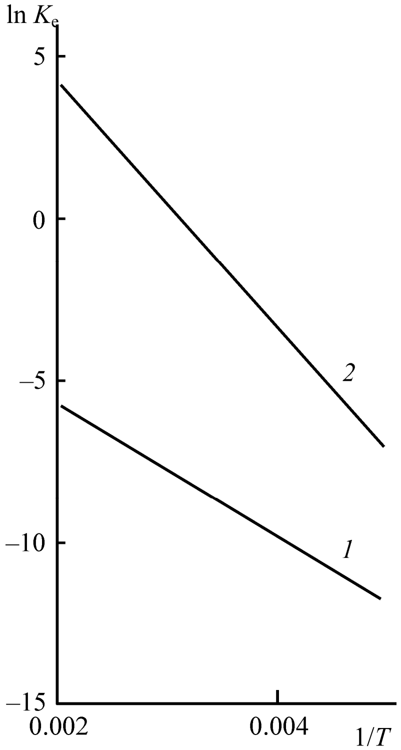


Fig. 3. Logarithm of equilibrium constant (ln K_e) of the reaction (3) as a function of reciprocal temperature (1/*T*) in the cases of compounds **Va** and **Vb** (*1* and *2*, respectively).

behavior was observed. Equilibrium constant of the reaction involving methanol monomer **IIa** increased with decreasing temperature. In the reaction with methanol dimer **IIb** the equilibrium constant was relatively independent of temperature. Finally, the equilibrium constant of the reaction with methanol trimer **IIc** increased with increasing temperature. Note that for the reaction (1), notwithstanding the reacting associate type the equilibrium constants were generally low.

In the case of the reaction (2) similar trends in the temperature dependences of the equilibrium constants were observed (Fig. 2). In contrast to reaction (1) the equilibrium constants of reaction (2) were generally high; reaction (2) was practically irreversible.

Reactions (1) and (2) both led to the target product **IV**. From the presented data it is clear that to maximize the yield of **IV** the conditions should be such that the equilibrium (1) is rapidly established. Then, the highest possible concentration of intermediate **III** will be maintained in the reaction medium, and thus the rate of production of **IV** will be increased.

Figure 3 shows the temperature dependence of equilibrium constant of reaction (3) that leads to loss of the target product. In the case of monomeric glycol **Va** the equilibrium constant increased with temperature, however over the whole range of temperature the equilibrium was shifted towards the initial compounds. Thus, from thermodynamic considerations that reaction may be neglected. In the case of the reaction with dimeric glycol **Vb** the equilibrium constant as well was increased with temperature. Being relatively high it can lead to significant loss of the target product, and thus technology of the production of **IV** should include the means to continuously remove glycol **V** from the reaction mixture.

The presented data demonstrated that in the reactions involving alcohols the thermodynamic parameters can be significantly different depending on the type of reacting associate; even temperature dependence of the equilibrium constant can be qualitatively different.

Thermodynamic analysis of the interaction of ethylene carbonate with methanol revealed that its first stage was characterized by quite low equilibrium constant, whereas the second stage was almost irreversible. In the industry, a suitable catalyst should be used allowing instant establishing of the equilibrium (1).

Ethylene carbonate methanolysis leads to reversible formation of dimethyl carbonate and ethylene glycol. The equilibrium constant of the reaction of dimethyl carbonate with monomeric ethylene glycol were quite low, and this process could not decrease the target product yield. However, the interaction of dimethyl carbonate with dimeric ethylene glycol was characterized by much higher equilibrium constants, and this process could not be neglected. Thus, to obtain the target product with the highest yield, the reaction should be performed under conditions of continuous removal of ethylene glycol from the reaction mixture, for instance, by distillation.

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