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Thermodynamic Parameters of the Thermal Decomposition of Dimethyl Toluylenedicarbamates to Toluylene Diisocyanates

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Abstract—By B3LYP/6-311++G(df,p) quantum-chemical method complete thermodynamic characteristics (enthalpies, entropies, total Gibbs energies, equilibrium constants) were evaluated for separate stages of the thermal decomposition of dimethyl toluylene-2,4- and dimethyl toluylene-2,6-dicarbamates with the formation of 2,4- and 2,6-diisocyanates and methanol. The temperature ranges providing the equilibrium yield of 2,4- and 2,6-toluylene diisocyanates equal to 95–99% were estimated. Principal possibility of obtaining practically pure 2,4- and 2,6-toluylene diisocyanates while decomposing the mixture of dimethyl toluylene-2,4- and -2,6-dicarbamates due to the regulation of temperature of the process was shown.

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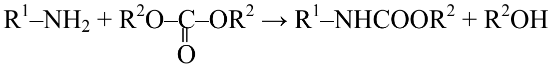
Thermal decomposition of carbamates proceeds according to the equation

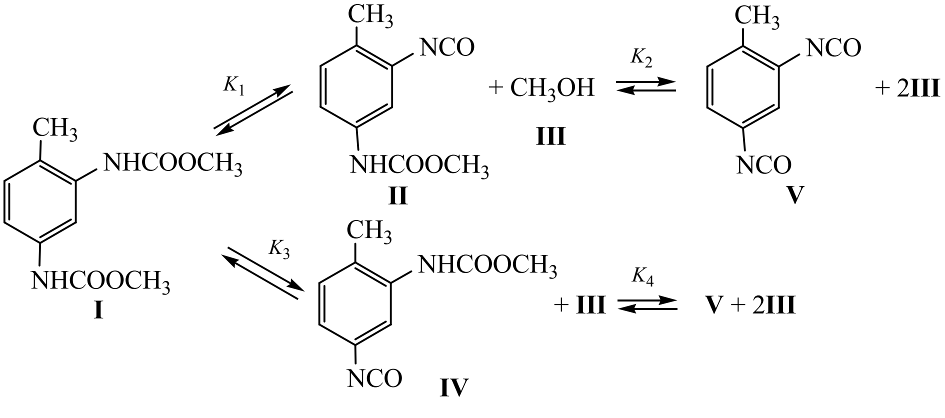


$$R^1\text{–}NH_2 + R^2O\text{–}\underset{\displaystyle O}{\underset{\|}{C}}\text{–}OR^2 \rightarrow R^1\text{–}NHCOOR^2 + R^2OH$$

It is a promising ecologically safe method of obtaining isocyanates [1–3]. In its turn the synthesis of carbamates is carried out by the reaction of primary amines with dialkyl carbonates, mainly with dimethyl carbonate [4–6].

The above-presented transformations form the basis of the phosgene-free method of synthesis of isocyanates corresponding to all demands of the "green chemistry" [7].

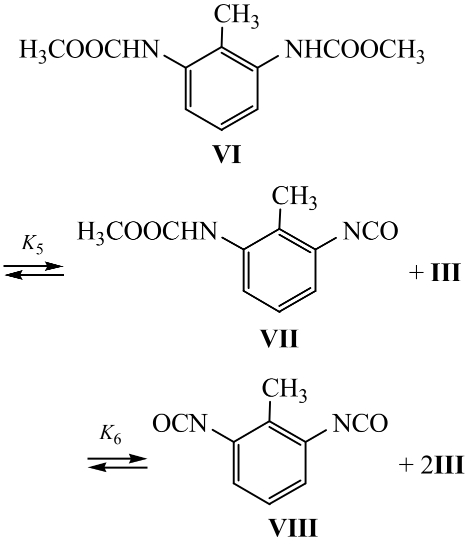
2,4- and 2,5-Toluylene diisocyanates are among the most widespread industrial isocyanates which find wide application in the polyurethane industry [8]. By the reaction of 2,4- and 2,6-toluylenediamines with dimethyl carbonate the corresponding carbamates may be prepared in a sufficiently high yield [4, 6, 7]. A reasonsble approach to the development of conditions of their cleavage to isocyanates and methanol requires the knowledge of thermodynamic parameters of these reactions. Nowadays are no published data on the thermodynamics of the process. We report here on the



quantum-chemical evaluation of thermodynamic parameters of decomposition of dimethyltoluylene-2,4- and dimethyltoluylene-2,6-dicarbamates with the formation of 2,4- and 2,6-toluylene diisocyanates and methanol.

Thermal decomposition of dimethyltoluylene-2,4-dicarbamate may proceed gradually according to two alternative pathways.

The decomposition of dimethyltoluylene-2,6-dicarbamate proceeds according to the following equation.



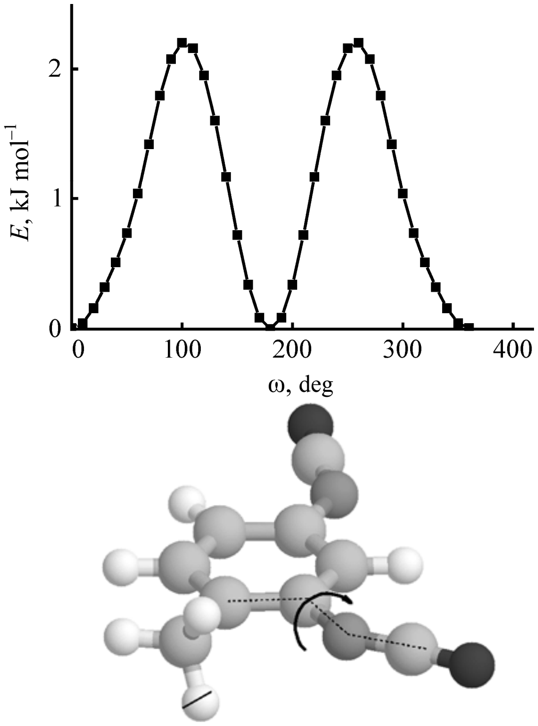


Fig. 1. Dependence of potential energy (E) of 2,4-toluylene diisocyanate **V** on the rotation angle (ω) of o-isocyanate group.

The step-by-step character of decomposition of dicarbamates **I, VI** requires a thermodynamic characterization of each separate stage.

The preliminary optimization of geometry of the compounds under investigation was carried out by semiempirical PM3 method. Substances considered in the calculations may exist in different conformations. For the evaluation of the global energy minimum the evaluation of the rotation barriers between the conformers was carried out.

The search for the optimal dihedral angles corresponding to the global minimum in the compounds containing two groups capable of the internal rotation (carbamates **I, VI**; diisocyanates **V, VIII**; carbamatoisocyanates **II, IV, VII**) was carried out as follows. After the rotation of one group by 10° another group was exposed to gradual rotation with the 10° step from 0 to 360°. From the analysis of the obtained data the conformers with the lowest energy were chosen. In the Figs. 1, 2 examples of variations in energy of conformers depending on the rotation angle are presented.

The established structures of most stable conformers were optimized further by the density functional method PBE/L11 using the package of applied programs "PRIRODA 6" [9, 10]. These structures

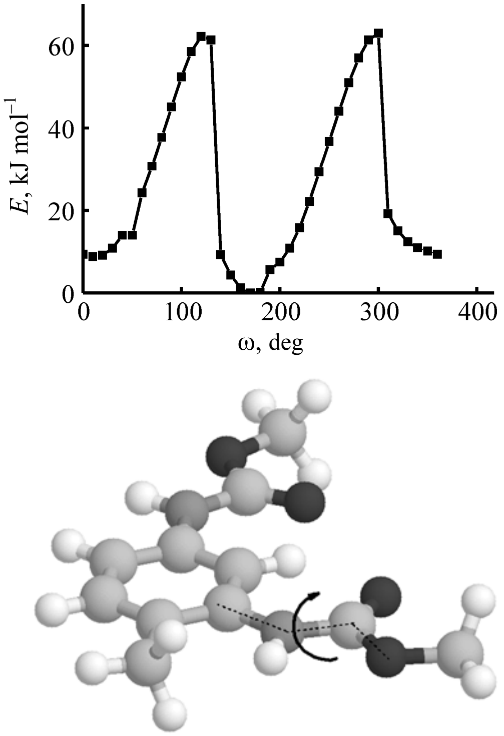


Fig. 2. Dependence of potential energy (E) of biscarbamate **I** on the rotation angle (ω) of o-methylcarbamate group.

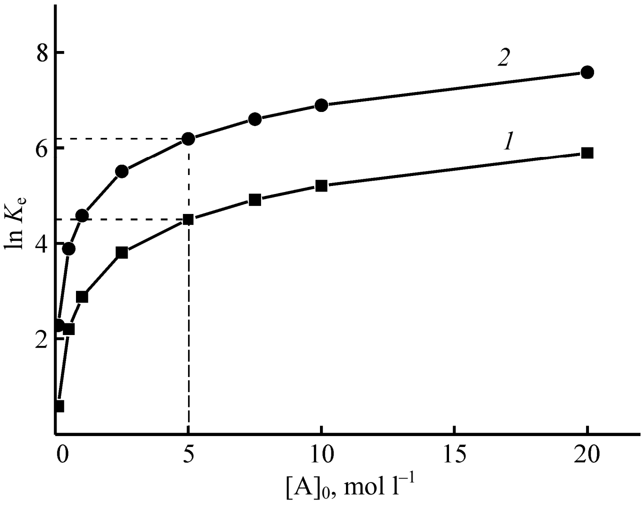


Fig. 3. Dependence of logarithms of equilibrium constants [ln (K_e)] of model reaction A ↔ B + C on the initial concentration of compound A ($[A_o]$). Curve *1* corresponds to the equilibrium yield of the reaction products 95%, curve *2*, to the yield 99%.

were optimized further by the hybride B3LYP/6-311+++G(df,p) method using the "GAUSSIAN 0.3" software [11, 12]. This sequence of optimization of the structures of compounds despite of its seeming complexity leads to a significant economy in the calculation time. Main time was consumed by the B3LYP method calculations where the extended basis was used. It strongly depended on the accuracy of the starting structure of a compound.

Enthalpies and entropies of the reactions were calculated as the difference of enthalpies and entropies of the formation of the reaction products and reagents.

Enthalpies (ΔH_e, kJ mol^{-1}), total (ΔS_{total}), translation (ΔS_{trans}), rotation (ΔS_{rot}), and vibration (ΔS_{vib}) entropies (J K^{-1} mol^{-1}) of the reactions of decomposition of dicarbamates **I, IV**, to isocyanates **V, VIII** and methanol **III** at 298 K in the gas phase

Reaction	ΔH_p	ΔS_{total}	ΔS_{trans}	ΔS_{rot}	ΔS_{vib}
I→II+III	64.6	179.0	150.0	76.0	–47.0
I→IV+III	68.0	174.0	150.0	76.0	–52.0
II→V+III	77.1	175.8	149.8	75.8	–49.8
IV→V+III	73.7	179.8	149.8	75.8	–45.8
I→V+2III	141.7	354.4	300.1	151.7	–97.4
VI→VII+III	27.4	164.0	150.3	76.3	–62.6
VII→VIII+III	61.7	189.7	149.9	75.0	–35.2
VI→VIII+2III	89.1	353.7	300.2	151.3	–97.8

Enthalpies and entropies of the reactions under consideration are presented in the table. Total entropies of the reactions (ΔS_{total}) were calculated as the sum of the translation (ΔS_{trans}), the rotation (ΔS_{rot}), and of the vibration (ΔS_{vib}) entropies:

$$\Delta S_{total} = \Delta S_{trans} + \Delta S_{rot} + \Delta S_{vib}.$$

It follows from the presented data that all the transformations under consideration are endothermic. In all cases the first stages of decomposition of bis-carbamates **I, VI** with the formation of isocyanatocarbamates **II, IV, VII** are characterized by lower values of reaction enthalpies as compared to the enthalpies of the second stages, that is, the formation of diisocyanates **V, VIII** from compounds **II, IV, VII.**

All the reactions under study are characterized by large positive values of entropies. In the course of transformations the degree of freedom of the translation and the rotation movement increases. According to that the processes under investigation are characterized by positive values of the translation and the rotation entropies (see the table). Vibration entropies of the reactions are characterized by negative values. But their contribution in the values of the general entropies of interaction is surpassed by the contribution of the translation and rotation entropies.

The presented data permit the calculation of standard values of free Gibbs energies of the reactions to be done. From these values the equilibrium constants of transformation can be calculated. In chemical technology it is expedient to achieve the yields of the products varying in the range 95–99%. With the purpose of evaluation the equilibrium constants providing the above-mentioned yields in the model reaction A $\rightleftarrows$ B + C we have calculated their values depending on the initial concentration of compound A (Fig. 3)

If pure bis-carbamates are subjected to the thermal decomposition, their initial concentrations would not exceed 5 M. It follows from Fig. 4 that the yield of the products of model reaction located in the range 95-99% at a given concentration is provided by the equilibrium constants in the range 90–490. If the initial concentration is lower than 5 M which is possible at the decomposition of bis-carbamates in solution, the above-mentioned values of yields may be achieved at lower values of equilibrium constants (Fig. 4). The obtained limiting values of rate constants permit the evaluation of the temperature range where the above-mentioned values of equilibrium constants of decomposition of bis-carbamates **I, VI** are achieved.

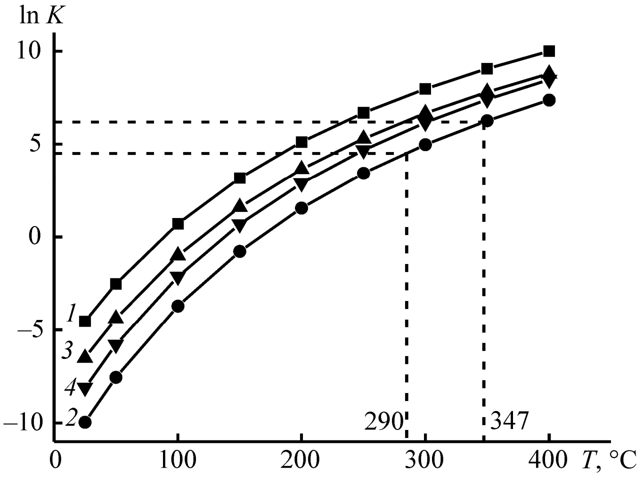


Fig. 4. Dependence of logarithms of equilibrium constants (ln *K*) on temperature (*T*) for the elementary stages of decomposition of bis-carbamate **I** to diisocyanate **V** and methanol **III**. (*1*) ln k_1, (*2*) ln k_2, (*3*) ln k_3, and (*4*) ln k_4.

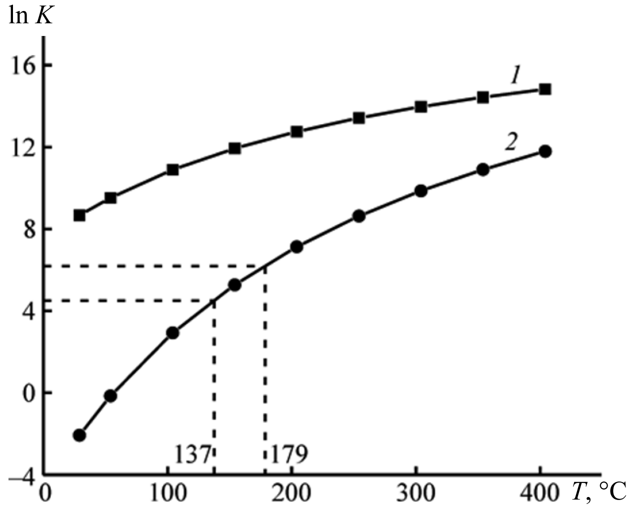


Fig. 5. Dependence of logarithms of equilibrium constants (ln *K*] on temperature (*T*) for the elementary stages of decomposition of bis-carbamate **VI** to diisocyanate **VIII** and methanol **III**. (*1*) ln k_5 and (*2*) ln k_6.

In Figs. 4, 5 temperature dependences of equilibrium constants of transformations under consideration calculated from the data listed in the table are shown.

From the comparison of data presented in the Figs. 4 and 5, the equilibrium constants of decomposition of bis-carbamate **VI** in both stages are significantly higher than those of compound **I**. The first stage of decomposition of bis-carbamate **VI** is characterized by especially large values of equilibrium constants. These findings agree with the published data. For example, Kelly et al. [13] mention that diisocyanates isolated in the course of decomposition of polyurethanes obtained from the mixture of 80% of diisocyanate **V** and 20% of compound **VIII** contain 75–98% of compound **VIII**. Hermandez-Sanchez et al.[14] by an example of the reaction between diisocyanate **VIII** and diethylene glycol showed that complete consumption of isocyanate groups in this transformation was achieved only in the presence of excess ethylene glycol.

It follows from Figs. 4 and 5 that the second stages of the reactions of carbamates **I, IV**, that is, the decomposition of isocyanatocarbamates **II, IV, VII** to diisocyanates **V, VIII**, are less thermodynamically favorable. Therofore the temperature conditions of decomposition must be chosen by attaining the necessary equilibrium constants in these most thermodynamically unfavorable stages. For the decomposition of bis-carbamate **I** thermodynamically most unfavorable stage is the transformation of isocyanatocarbamate **II** to diisocyanate **V** and methanol. In Fig. 4 dashed lines parallel to the x axis are drown. Lower line corresponds to the equilibrium constant equal to 90 while the upper one, to the constant equal to 490. From the crossing points of these lines with the curve describing temperature dependence of equilibrium constant K_2 the lines perpendicular to x axis are drown. Their crossing with this axis permits evaluating thee temperature range (290–347°C) providing the equilibrium decomposition of isocyanatocarbamate **II** with the yield of diisocyanate **V** 95–99%. These data agree with the reported experimental data on the thermal decomposition of bis-carbamate **II** to diisocyanate **V** [1, 15].

The temperature range of decomposition of bis-carbamate **VI** (Fig. 5) providing the equilibrium yield of isocyanate **VIII** equal to 95–99% was evaluated analogously. It is significantly lower (137–179°C). Hence, if a mixture of bis-carbamates **I, VI** is subjected to thermal decomposition, varying the temperature of the process permits to obtain separately practically pure diisocyanates **V** and **VIII**.

Hence, by quantum-chemical B3LYP/6-311++G(df,p) method the complete step-by-step thermodynamic characteristics of the processes of decomposition of dimethyl toluylene-2,4- and dimethyl toluylene-2,6-dicarbamates with the formation of 2,4- and 2,6-toluylene diisocyanates and methanol was estimated. Temperature ranges providing the equilibrium yields of 2,4- and 2,6-toluylendiisocyanates equal to 95–99% were found. The principal possibility of obtaining practically pure 2,4- and 2,6-toluylene diisocyanates by the decomposition of a mixture of dimethyl toluylene-2,4- and dimethyl toluylene-2,6-dicarbamates by regulation of temperature of the process was shown.

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