CALCULATION OF THE THERMODYNAMIC PROPERTIES OF THE DIMETHACRYLATE ESTERS OF ALIPHATIC GLYCOLS

S. M. Lomakin, R. M. Aseeva, and G. E. Zaikov

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The thermodynamic stability of substances serves as a measure of their relative thermal stability and combustibility and can be determined with the aid of the enthalpy of formation ($\Delta H_f$) and the Gibbs free energy ($\Delta G_f$). We are aware of attempts at a theoretical approach to calculating the thermodynamics of some unsaturated polyesters [1, 2], which assume the additivity of the functions $S_f^0$, $\Delta H_f^0$, and $\Delta G_f^0$ and are based on data for normal aliphatic hydrocarbons with approximately the same linear carbon chain as in a molecule of an oligoester. With such an approach, the varied state of groups and atoms and the effect of their environment is not considered.

This paper calculates thermodynamic parameters over a broad temperature range (298-1000°K) for a homologous series of dimethacrylate esters of aliphatic glycols (DAG) of the general formula

$$\text{H}_2\text{C} = \text{O} \quad \text{O} \quad \text{CH}_3$$

$$\text{CH}_2 = \text{C} - \text{C} \quad \text{O} - (\text{CH}_2)_n \quad \text{O} - \text{C} \quad \text{C} = \text{CH}_2,$$

where $n$ varies from 2 to 10.

The enthalpy of formation and the Gibbs free energy of the DAG were calculated by a method given in [3, 4] for an ideal gaseous state. The entropy of formation ($S_f^0$) was determined statistically from the IR spectra of the given compounds.

In calculating the enthalpy of formation for the DAG, the group contributions $\Delta H_{f1}$ were summed up for each oligoester at 298°K: $\Delta H_f^{298} = \sum \Delta H_{f1}^{298}$.

The calculation shows that the value of $\Delta H_f^0$ for the DAG in an ideal gas state at 298°K decreases linearly with increasing oligomer molecular weight (Table 1).

The temperature dependence is quite similar for several of the increments encountered most often in organic compounds, whether determined empirically as in [3] or statistically as in [4]. The sum of the respective increments determines the value of $\Delta G_f^0$ without the component $RT \ln \sigma$, where $\sigma$ is the symmetry number and is determined by considering the molecule of a given compound as a rigid rotator without internal rotation. Taking this component into account for the entire homologous oligoester series, we adopted a value of 2 for $\sigma$.

When the number of methylene groups in the glycol is odd, the second-order rotation axis of the molecule goes through the central carbon atom in the glycol and lies in the molecule's plane of symmetry. When it is even, the second-order rotation axis goes through the middle of the $-\text{CH}_2-\text{CH}_2-$ bond in the glycol and is perpendicular to the molecule's plane of symmetry.

The points of intersection of the straight lines $\Delta G_f^0 = f(T)$ (Fig. 1) with the temperature axis, where $\Delta G_f^0 > 0$, correspond to the critical temperatures of the pertinent dimethacrylate esters of aliphatic glycols. For values of $\Delta G_f^0 > 0$ at temperatures above these critical temperatures, the DAG are decomposed and their existence is thermodynamically impossible. The function $\Delta G_f^0 = f(T, n)$, where $n$ is the number of $\text{CH}_2$ groups in the aliphatic glycol, becomes

$$\Delta G_f^0 = [0.19 + 0.02 (n - 2)]T - [159.00 + 4.00 (n - 2)] \text{ kcal/mole}$$

(1)

where $n = 2, 3, 4, \ldots, 10$.

We infer that when $\Delta G_f^0 = 0$ in Eq. (1), we obtain an equation for the critical temperatures for various values of $n$

$$T_{cr} = \frac{(151.00 + 4.00 n)}{(0.15 + 0.02 n)}$$  \hspace{1cm} (2)

Equation (2) is the equation of a hyperbola. The horizontal asymptote is the limiting temperature ($T^*$) below which a stable state is theoretically possible for the dimethacrylate esters of aliphatic glycols with an infinitely long chain (Fig. 2). For the DAG being considered, $T^* = 200{^\circ}K$. Figure 2 also indicates that as the number of CH$_2$ groups increases, i.e., as the DAG molecular weight increases, its thermodynamic stability is significantly reduced. This may be explained by the effect of the entropy factor and the enthalpy of formation on the Gibbs free energy:

$$\Delta G_f^0 = \Delta H_f^0 - T \Delta S_f^0,$$

as the DAG molecular weight increases.

The total entropy of the DAG molecule ($S_{tot}$) can be determined as the sum of the entropy of the molecule's translational motion ($S_{trans}$), the rotational entropy of the entire molecule ($S_{rot}$), the entropy of internal rotation ($S_{int rot}$), and the entropy of vibrational motion [5, 6]:

$$S_{tot} = S_{trans} + S_{rot} + S_{int rot} + S_{vib}.$$  \hspace{1cm} (2.1)

The value of the translational entropy of a molecule for $n = 2$ (Table 2) is calculated by the equation [5, 6]

$$S_{trans}^* = \frac{3}{2}k \ln M + \frac{3}{2} \ln V + \frac{3}{2} \ln k + \frac{3}{2} \ln (2\pi kT)^{1/2}$$

where $M$ is the DAG molecular weight; $V$ is the molar volume; $k$ is the Boltzmann constant; $h$ is the Planck constant; $N$ is Avogadro's number; and $R$ is the universal gas constant.

The rotational entropy in a nonlinear molecule is determined from the equation [5, 6]

$$S_{rot}^* = 1.5R + R \ln \left[ \frac{\pi^{3/2}}{\sigma ow} \left( \frac{8\pi^2 kT}{h^2} \right)^{3/2} (I_x I_y I_z)^{1/2} \right]$$

where $\sigma ow$ is the symmetry number of a rigid polyatomic molecule; $\sigma ow = 2$ for a DAG; $I_x I_y I_z$ is the product of the three principal moments of inertia of a polyatomic nonlinear molecule

$$I_x I_y I_z = \left[ \begin{array}{ccc} A - D - E \\ -D - B - F \\ -E - F - C \end{array} \right] = ABC - AH^2 - CDF - 2DEF - BE^2$$

where

$$A = \sum m_i (y_i^2 + z_i^2) - \frac{1}{M} \left( \sum m_i y_i \right)^2 - \frac{1}{M} \left( \sum m_i z_i \right)^2$$

$$B = \sum m_i (x_i^2 + z_i^2) - \frac{1}{M} \left( \sum m_i x_i \right)^2 - \frac{1}{M} \left( \sum m_i z_i \right)^2$$

$$C = \sum m_i (x_i^2 + y_i^2) - \frac{1}{M} \left( \sum m_i x_i \right)^2 - \frac{1}{M} \left( \sum m_i y_i \right)^2$$

$$D = \sum m_i x_i y_i - \frac{1}{M} \left( \sum m_i x_i \right) \left( \sum m_i y_i \right)$$

$$E = \sum m_i x_i z_i - \frac{1}{M} \left( \sum m_i x_i \right) \left( \sum m_i z_i \right)$$

$$F = \sum m_i y_i z_i - \frac{1}{M} \left( \sum m_i y_i \right) \left( \sum m_i z_i \right)$$

$$M = \sum m_i.$$