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THERMODYNAMICS OF GLYCEROL NITRATION①

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ABSTRACT An entire thermodynamic research of the reaction of glycerol nitration with nitric acid is reviewed, in which the basic equations and data are of great scientific and practical importance, especially for the nitration of the primary and secondary hydroxyl groups.

KEY WORDS thermodynamic, glycerol, nitration.

The reaction of glycerol nitraton by nitric acid, producing glycerol nitrates, is of great scientific and practical importance. Glycerol trinitrate (nitroglycerol) is one of the fundamental components of modern explosives and propellants. Glycerol 1, 3-dinitrate may also find some applications. The reaction is important for development of theoretical basis for hydroxyl compounds nitration, because glycerol is the simplest polyhydric alcohol, which contains primary and secondary hydroxyl groups. Investigation of its nitration allows to elucidate distinctions in equilibrium state of all consecutive-parallel reactions, which describes a transition of glycerol to trinitrate.

By now the Institute of Chemical Physics in Chernogolovka the cycle of works[1~4] devoted to investigation of thermodynamics of this reaction was performed, equilibrium constants, changes of enthalpies and entropies for all stages of the reaction of nitration and thermodynamic properties of intermediate products were determined, the dependence of the equilibrium constants on composition, aqueous acidity and temperature was also defined. These data allow to establish conditions of maximum yield for any nitration product.

In this report the review of these data is presented.

The complex process of glycerol transferring to trinitrate may be presented as a sum of seven consecutive-parallel reactions with the corresponding equilibrium constants:

$$\mathrm{(OOO)} + \mathrm{HNO_3} \rightleftharpoons \mathrm{(NOO)} + \mathrm{H_2O} \qquad K_1 = a_{\mathrm{(NOO)}}a_{\mathrm{H_2O}}/2a_{\mathrm{(OOO)}}a_{\mathrm{HNO_3}} \qquad (1)$$

$$\mathrm{(OOO)} + \mathrm{HNO_3} \rightleftharpoons \mathrm{(ONO)} + \mathrm{H_2O} \qquad K_2 = a_{\mathrm{(NOO)}}a_{\mathrm{H_2O}}/a_{\mathrm{(OOO)}}a_{\mathrm{HNO_3}} \qquad (2)$$

$$\mathrm{(NOO)} + \mathrm{HNO_3} \rightleftharpoons \mathrm{(NON)} + \mathrm{H_2O} \qquad K_3 = a_{\mathrm{(NON)}}a_{\mathrm{H_2O}}/a_{\mathrm{(NOO)}}a_{\mathrm{HNO_3}} \qquad (3)$$

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$$(NOO) + HNO_3 \rightleftharpoons (NNO) + H_2O \qquad K_4 = a_{(NNO)}a_{H_2O}/a_{(NOO)}a_{HNO_3} \qquad (4)$$

$$(ONO) + HNO_3 \rightleftharpoons (NNO) + H_2O \qquad K_5 = a_{(NNO)}a_{H_2O}/2a_{(ONO)}a_{HNO_3} \qquad (5)$$

$$(NON) + HNO_3 \rightleftharpoons (NNN) + H_2O \qquad K_6 = a_{(NNN)}a_{H_2O}/a_{(NON)}a_{HNO_3} \qquad (6)$$

$$(NNO) + HNO_3 \rightleftharpoons (NNN) + H_2O \qquad K_7 = a_{(NNN)}a_{H_2O}/a_{(NNO)}a_{HNO_3} \qquad (7)$$

Here (OOO)——glycerol molecule, in which hydroxyl group is marked by symbol O, nitrate group by N.

The experiments of nitrate equilibrium investigation were performed at temperature interval 0~48℃ and concentration of aqueous nitric acid 58~87(wt.)%。

Glycerol, 1,3-dinitrate or trinitrate of glycerol were added separately into acid aqueous. If (OOO) was used as original reagent, the motion to equilibrium occured if the nitration rates were faster than the hydrolysis rates, as forming (NNN), the system went to equilibrium from another side and (NON) was consumed in parallel reactions of nitration up to (NNN) and of hydrolysis to (NOO) at the begining of reaction. The kinetics of reaction for production and their equilibrium concentrations were analysed by integral intensity of C—H—group signal for every compound using proton magnetic resonance (PMR) spectrometer at frequency 294 MHz. The reaching of equilibrium was characterized by constancy of signal intensity and by equilibrium composition independence on way of approaching to equilibrium. Concentrations of HNO_3 and H_2O were calculated according the reactions (1)~(7). The summary nitrate concentration was lower 1 mol/L than that of in equilibrium, so it was believed that concentrations influenced the ratio of a_{H_2O}/a_{HNO_3} to a small extent and the activity data for double system HNO_3-H_2O[5], which were used in calculation.

It is necessary to take into account protonation of alcohols and nitrates in acid aqueous for calculation of nitration equilibrium. Evaluation of protonation degree has been recieved from dependence of chemical shift of CH— and CH_2— groups signals of every component relative to the signal position of CH— group (NNN), which practically is not protonated. In the studied interval of HNO_3 concentrations glycerol and its nitrates are in neutral and once protonated form, basicity of these compounds decreases in the row: (OOO)>(NOO)>(ONO)>(NNO)>(NON)>(NNN) and can be expressed by ionization constant of conjugated acid:

$$RH \rightleftharpoons R + H^+$$

$$K_{RH^+} = a_R\, a_{H^+}/a_{RH^+} \qquad (8)$$

where R ——(OOO), (NOO), (ONO), (NNO), (NON), (NNN).

As the sum of concentrations, protonized and neutral form for all components can be defined from PMR spectra, equilibrium constants K_{exp} calculated from these concentrations differing from truth constants, are connected with them by:

$$\begin{aligned}
K_{1,\mathrm{exp}} &= K_1 \frac{K_{(\mathrm{OOO})^+}(K_{(\mathrm{NOO})^+} + a_{\mathrm{H}^+})}{K_{(\mathrm{NOO})^+}(K_{(\mathrm{OOO})^+} + 2a_{\mathrm{H}^+})} \\
K_{2,\mathrm{exp}} &= K_2 \frac{K_{(\mathrm{OOO})^+}(K_{(\mathrm{ONO})^+} + 2a_{\mathrm{H}^+})}{K_{(\mathrm{ONO})^+}(K_{(\mathrm{OOO})^+} + 2a_{\mathrm{H}^+})} \\
K_{3,\mathrm{exp}} &= K_3 \frac{K_{(\mathrm{NOO})^+}(K_{(\mathrm{NON})^+} + a_{\mathrm{H}^+})}{K_{(\mathrm{NON})^+}(K_{(\mathrm{NOO})^+} + a_{\mathrm{H}^+})} \\
K_{4,\mathrm{exp}} &= K_4 \frac{K_{(\mathrm{NOO})^+}(K_{(\mathrm{NNO})^+} + a_{\mathrm{H}^+})}{K_{(\mathrm{NNO})^+}(K_{(\mathrm{NOO})^+} + a_{\mathrm{H}^+})} \\
K_{5,\mathrm{exp}} &= K_5 \frac{K_{(\mathrm{ONO})^+}(K_{(\mathrm{NNO})^+} + a_{\mathrm{H}^+})}{K_{(\mathrm{NNO})^+}(K_{(\mathrm{ONO})^+} + 2a_{\mathrm{H}^+})} \\
K_{6,\mathrm{exp}} &= K_6 \frac{K_{(\mathrm{NON})^+}(K_{(\mathrm{NNN})^+} + 2a_{\mathrm{H}^+})}{K_{(\mathrm{NNN})^+}(K_{(\mathrm{NON})^+} + a_{\mathrm{H}^+})} \\
K_{7,\mathrm{exp}} &= K_7 \frac{K_{(\mathrm{NNO})^+}(K_{(\mathrm{NNN})^+} + 2a_{\mathrm{H}^+})}{K_{(\mathrm{NNN})^+}(K_{(\mathrm{NNO})^+} + a_{\mathrm{H}^+})}
\end{aligned} \qquad (9)$$

Here $(\mathrm{NOO})^+$ and others are protonized forms of corresponding nitrates.

For each $K_{i,\mathrm{exp}}$ the constants of more basic compounds are in the denominator. To clarify the meaning of $K_{i,\mathrm{exp}}$, the interval of solution acidity can be divided into three regions. If $a_{\mathrm{H}^+} \ll K_{\mathrm{RH}^+}$ in the denominator and all the more in the numerator, a_{H^+} can be neglected, at $K_{i,\mathrm{exp}} = K_i$, protonation is insignificant. If $a_{\mathrm{H}^+} > K_{\mathrm{RH}^+}$ in the numerator and all the more in the denominator, $K_{i,\mathrm{exp}} = K_i K_{\mathrm{R_1H}^+} / K_{\mathrm{R_2H}^+}$, and the relation of ionization constants of initial compounds and nitration product is included in the equation for experimental constant. In intermediate case the magnitude a_{H^+} can be neglected only in the numerator and $K_{\mathrm{R_1H}^+}$ can be neglected in the denominator; it follows that $K_{i,\mathrm{exp}} = K_i K_{\mathrm{R_1H}^+} / a_{\mathrm{H}^+}$, so the constant decreases with increasing acidity. The dependence of $\lg K_{i,\mathrm{exp}}$ on Hammet's acidity function H_0 evaluated by the derivaties of aniline is shown on Fig. 1. The meanings of $K_{1,\mathrm{exp}}, K_{2,\mathrm{exp}}, K_{5,\mathrm{exp}}, K_{6,\mathrm{exp}}, K_{7,\mathrm{exp}}$ are constants, but $K_{3,\mathrm{exp}}, K_{4,\mathrm{exp}}$ and $K_{5,\mathrm{exp}}$ decrease with increasing acidity; it corresponds to the following conditions:

$$K_{(\mathrm{NNN})^+}, K_{(\mathrm{NNO})^+}, K_{(\mathrm{NON})^+} > a_{\mathrm{H}^+} > K_{(\mathrm{ONO})^+}, K_{(\mathrm{NOO})^+}, K_{(\mathrm{OOO})^+}$$

so: $$K_{1,\mathrm{exp}} = K_1 K_{(\mathrm{NNN})^+} / K_{(\mathrm{NOO})^+}; \quad K_{2,\mathrm{exp}} = K_2 2K_{(\mathrm{OOO})^+} / K_{(\mathrm{ONO})^+} \qquad (10)$$

$$K_{3,\mathrm{exp}} = K_3 K_{(\mathrm{NOO})^+} / a_{\mathrm{H}^+}; K_{5,\mathrm{exp}} = K_5 K_{(\mathrm{ONO})^+} / 2a_{\mathrm{H}^+}; K_{6,\mathrm{exp}} = K_6; \ K_{7,\mathrm{exp}} = K_7$$

Only five from seven constants are independent, the equilibrium between (OOO) and (NNN) is defined by one of three multplied constants $K_{1,\mathrm{exp}} K_{3,\mathrm{exp}} K_{6,\mathrm{exp}} = K_{1,\mathrm{exp}} K_{4,\mathrm{exp}} K_{7,\mathrm{exp}} = K_{2,\mathrm{exp}} K_{5,\mathrm{exp}} K_{7,\mathrm{exp}}$. The dependence of $\lg K_{i,\mathrm{exp}}$ on $1/T$ at $H_0 = -4.5$ is shown on Fig. 2. At other acidities the inclinations of straight lines are analogous, because constants are independent of acidity, or change linearly. It is visible that relative magnitude of constants changes greatly with the temperature, so the higher yeild of (NON) than that of (NNN) can be reached as decreasing the temperature. The experimental magnitudes of enthalpy ($\Delta H^0_{i,\mathrm{exp}}$) and entropy ($\Delta S^0_{i,\mathrm{exp}}$) changes in the reactions (1)～(7) were calculated by using dependences described above Table 1. In accordance with (11) the magnitudes of $\Delta H^0_{1,\mathrm{exp}}$ and $\Delta H^0_{2,\mathrm{exp}}$ ($\Delta S^0_{1,\mathrm{exp}}$ and $\Delta S^0_{2,\mathrm{exp}}$) equate to the algebraic sum of true enthalpies (entropies) of nitration and enthalpies (entropies) of dissociation for corresponding conjugated acids; $\Delta H^0_{6,\mathrm{exp}}$ and $\Delta H^0_{7,\mathrm{exp}}$ ($\Delta S^0_{6,\mathrm{exp}}$ and $\Delta S^0_{7,\mathrm{exp}}$) are equal to the true enthalpies (entropies) of nitration and medium acidity and $K_{3,\mathrm{exp}}$, $K_{4,\mathrm{exp}}$, $K_{5,\mathrm{exp}}$ are dependent on the temperature . The magnitudes of $K_{i,\mathrm{exp}}$ can be calculated for any temperature by using data from Table 1.

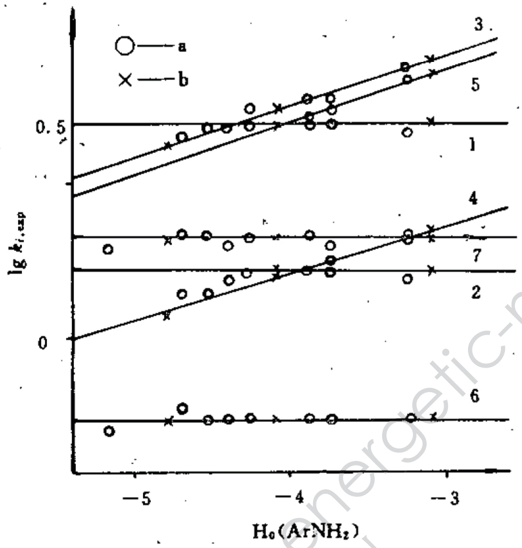

Fig. 1 The dependence of lg$K_{i,\mathrm{exp}}$ on H_0 at 0℃:
a——initial reagent is (OOO);
b——initial reagent is (NNN).
Value of *i* is marked by figures here and on Fig. 2.

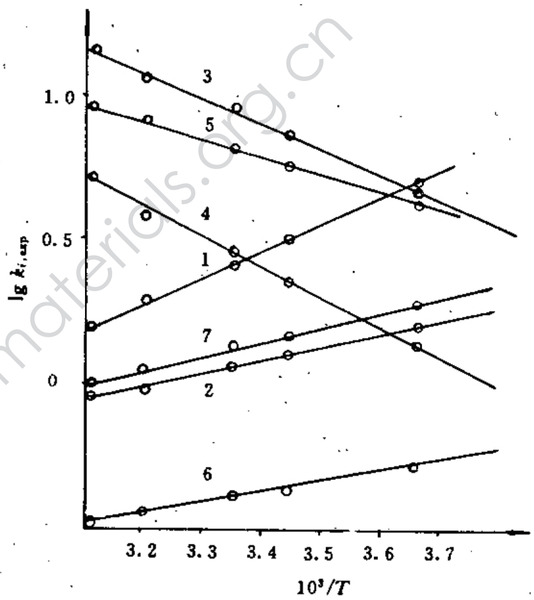

Fig. 2 The dependence of lg$K_{i,\mathrm{exp}}$ on $1/T$ at $H_0 = -4.5$

Table 1 The enthalpy and entropy changes in the reactions of glycerol and its nitrate nitration

kJ/mol

i	1	2	3	4	5	6	7
$-\Delta H^0_{i,\mathrm{exp}}$	17.15±1.26	8.79±0.84	15.90±1.26	20.08±1.26	11.72±0.84	6.28±0.84	10.46±1.26
$\Delta S^0_{i,\mathrm{exp}}$	−49.79±1.26	28.45±0.84	71.96±1.26	76.57±1.26	55.22±0.84	28.87±0.84	33.47±0.84
$-\Delta H^0_i$	18.83±2.09	10.46±2.51	12.13±1.67	7.11±2.51	15.48±2.92	5.44±1.26	10.46±1.26

Nitration heat for (OOO), (NOO) and (NON) in excess of 100% HNO_3, heat of mixing (NNN) with HNO_3 and heat of 100% HNO_3 diluted by water were determined at massive oscillating calorimeter KY−1000[6] with microcalorimetric cell. The sole product of glycerol nitration by 100% HNO_3 is (NNN) as defined by PMR spectra. Change of enthalpies in reactions (11) and (12) was calculated from received heats:

$$(OOO)(l)+3HNO_3(l)=(NNN)(l)+3H_2O(l) \quad -\Delta H^0_{11}=36.40\pm1.67\ \mathrm{kJ/mol} \quad (11)$$

$$(NOO)(l)+2HNO_3(l)=(NNN)(l)+2H_2O(l) \quad -\Delta H^0_{12}=15.57\pm1.26\ \mathrm{kJ/mol} \quad (12)$$

and from the combination of equations (11),(12) and (6), we can calculate the changes of enthalpies in reactions (1) and (3): $\Delta H^0_1=\Delta H^0_{11}-\Delta H^0_{12}$, $\Delta H_3=\Delta H_{12}-\Delta H_6$. Other changes of nitration enthalpies were calculated by combination of experimental enthalpies of the reaction, received from equilibrium constants, supposing the equality of heats of dissociation for conjugated acids $(NOO)^+$ and $(ONO)^+$: $\Delta H^0_2=\Delta H^0_1-(\Delta H^0_{1,\mathrm{exp}}-\Delta H^0_{2,\mathrm{exp}})$; $\Delta H^0_4=\Delta H^0_3+\Delta H^0_6-\Delta H^0_7$; $\Delta H^0_5=\Delta H^0_1+\Delta H^0_4-\Delta H^0_2$. All received values are presented in Table 2, the errors are expressed by 95% confidence interval.

Table 2　The standard enthalpies of nitrate formation

kJ/mol

Compound	(NOO)	(ONO)	(NON)	(NNO)	(NNN)
$-\Delta H^0_f$	576.97±2.51	567.77±3.77	477.39±2.09 476.56 ±2.09	472.37±2.09	369.87±2.09

The magnitude of $-\Delta H^0_{f(NNN)l}=369.87\pm2.09$ kJ/mol was calculated from ΔH_8 and literature data for standard enthalpies of formation (OOO), H_2O and HNO_3 and it coincides with the most reliable literature magnitude 371.12±1.67 kJ/mol, also the standard formation enthalpies of all partly substituted glycerol nitration were received. These data are presented in Table 2. For the scheme of calculating ΔH^0_f, contributing the energies of neighborhood functional groups were examined as follow: $E_{1,2(NO,OH)}=6.69$, $E_{1,3(NO,OH}=0$, $E_{1,3(OH,OH)}=2.09$ kJ/mol, in the last case NO_3—group is connected to secondary carbon atom. The magnitude of $-\Delta H^0_{f(NNO)l}=471.96$ kJ/mol was calculated on the basis of these contributions and it was equal to the experimental value. Analyses of received data shows that ΔH_f is essentially more at substitution of primary hydroxyls, thanthat of secondary ones and all these magnitudes are lower than enthalpies of nitration for monobasic aliphatic alcohols. Thus thermodynamic parameters, describing all stages of glycerol nitration, have been determined.

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