NITRATION EQUILIBRIUM IN THE MESO-ERYTHRITOL-AQUEOUS NITRIC ACID SYSTEM

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Twelve equilibrium constants have been measured from 16 for sequential-parallel reactions in meso-erythritol nitration to the fully nitrated compound in aqueous HNO_3 . Free-energy changes during nitration of the aliphatic polyatomic alcohols, glycerol and meso-erythritol, are highest when diprimary dinitrates (NOON) and (NON) are produced.

Previously we have measured equilibrium constants and ΔH and ΔS for glycerol nitration in aqueous HNO₃ [1-3]. The aim of the present work was to measure equilibrium constants for nitration in the system meso-erythritol-aqueous HNO₃, to analyze their dependence on acidity of the medium H₀(ArNH₂) and the structure of the compound being nitrated, and to study the effect of two secondary hydroxyl groups on the equilibrium state for nitration of this diprimary disecondary tetraol compared with the previously studied glycerol.

EXPERIMENTAL

Experiments were carried out in aqueous solutions over a range of HNO_3 concentrations from 62.85 to 80.42 mass % at 20°C; initial solutions were prepared to produce an equilibrium set of products by dissolving separately meso-erythritol and its 1,4- and 2,3-dinitrates in HNO_3 solutions to give concentrations of 0.15, 0.25, and 0.15 mole/liter respectively. The HNO_3 solutions were prepared by diluting 100% HNO_3 produced according to [4]. Meso-erythritol and its 1,4- and 2,3-dinitrates were synthesized from cis-butene-2-diol-1,4 according to Scheme 1 (see following page) [5-8].

Meso-erythritol (mp 120°C) was recrystallized from MeOH [5], its 1,4-dinitrate (mp 91-91.5°C) from dichloroethane [7], and the 2,3-dinitrate (mp 129.5-130°C) from H₂O [8].

A PMR spectrometer with an operating frequency of 294 MHz, designed and assembled in this Institute, was used to record spectra of the reaction mixtures (Fig. 1), which represent a superposition of the spectra of reactants and products at equilibrium. The concentration of each substance involved in the equilibrium was determined from integral intensities of the CH-group signals, taking into account that the spectra observed correspond to neutral (unprotonated) forms averaged by rapid chemical exchange. Spectra were assigned on the basis of spectra obtained during the study of glycerol nitrates [9].

The equilibrium system is described by the sum of 16 sequential a parallel reactions, of which nine are independent:

 $0000 + HNO_3 \approx NO00 + H_2 0 \quad K_1 = a_{NO00} a_{H_20} / 2a_{OO00} a_{HNO_3}$ (1)

 $0000 + HNO_3 \neq 0N00 + H_20 \quad K_2 = a_{0N00} a_{H_20} / 2a_{0000} a_{HNO_3}$ (2)

 $N000 + HNO_{3} \rightleftharpoons NONO + H_{2}O K_{3} = a_{NONO} a_{H_{2}O} / a_{NOOO} a_{HNO_{3}}$ (3)

$$N000 + HNO_{3} \rightleftharpoons NN00 + H_{2}O K_{4} = a_{NN00}a_{H_{2}O}/a_{N000}a_{HN0_{3}}$$
(4)

 $N000 + HNO_{3} \approx N00N + H_{2}O K_{5} = 2a_{N00N}a_{H_{2}O}/a_{N000}a_{HNO_{6}}$ (5)

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Fig. 1. PMR SPECTRUM (294 MHz) of the equilibrium reaction mixture during nitration of meso-erythritol in 80.42 mass % aqueous HNO₃ solution. The upper diagram shows the position of CH and CH₂ signals for the entire series of compounds observed.

$ONOO + HNO_3 \rightleftharpoons NNOO + H_2O K_6 = a_{NNOO} a_{H_3O} / a_{ONOO} a_{HNO_3}$	(6)
$ONOO + HNO_3 \rightleftharpoons ONNO + H_2O K_7 = 2a_{ONNO}a_{H_2O}/a_{ONOO}a_{HNO_3}$	(7)
$0NOO + HNO_3 \rightleftharpoons NONO + H_2O K_8 \approx a_{NONO}a_{H_2O}/a_{ONOO}a_{HNO_3}$	(8)
$NNOO + HNO_3 \rightleftharpoons NNNO + H_2O K_9 = a_{NNNO}a_{H_2O}/a_{NNOO}a_{HNO_3}$	(9)
$NNOO + HNO_3 \rightleftharpoons NNON + H_2O K_{10} = a_{NNON}a_{H_{2O}}/a_{NNOO}a_{HNO_3}$	(10)
NONO + HNO ₃ \rightleftharpoons NNNO + H ₂ O $K_{11} = a_{NNNO}a_{\mathbf{H}_{2}O}/a_{NONO}a_{\mathbf{H}NO_{3}}$	(11)
$\text{NONO} + \text{HNO}_3 \neq \text{NNON} + \text{H}_2 \text{O} K_{12} = a_{\text{NNON}} a_{\text{H}_3 \text{O}} / a_{\text{NONO}} a_{\text{HNO}_3}$	(12)
$ONNO + HNO_3 \rightleftharpoons NNNO + H_2O K_{13} \approx a_{NNNO} a_{H_2O} / 2a_{ONNO} a_{HNO_3}$. (13)
$NOON + HNO_3 \rightleftharpoons NNON + H_2O K_{14} = a_{NNON} a_{H_2O}/2a_{NOON} a_{HNO_3}$	(14)
$\text{NNON} + \text{HNO}_3 \rightleftharpoons \text{NNNN} + \text{H}_2 \text{O} \ K_{15} = 2a_{\text{NNNN}}a_{\text{H}_2\text{O}}/a_{\text{NNON}}a_{\text{HNO}_3}$	(15)
$\text{NNNO} + \text{HNO}_{s} \rightleftharpoons \text{NNNN} + \text{H}_{2}\text{O} K_{16} = 2a_{\text{NNNN}}a_{\text{H}_{2}\text{O}}/a_{\text{NNNO}}a_{\text{HNO}_{s}}$	(16)

where 0000 is an erythritol molecule in which the hydroxyl groups are represented by the symbol 0 and the nitrate groups in nitrates are represented by the symbol N. Doubled activities in the constants are due to the fact that there are two symmetrical positions where reaction occurs.

True equilibrium constants for nitration (K_i) differ from the experimental constants (K_i, exp) (Table 1) because the latter are calculated from experimental values of the concentrations of neutral and protonated forms of the original compounds and the nitration products. Depending on the relative acidity of the nitrating medium and basic properties of the reactants, they occur either in a neutral or protonated form; the concentration of the latter is inversely proportional to the dissociation constant of the conjugate acid of the reactant and increases with increase in acidity of the medium. To sum up, the K_i , exp may be equal to the true constants when the reactants occur in the neutral form, or are equal to the true constants when both the compound being nitrated and the nitration product are predominantly in the protonated form, or are equal to the true constant of the conjugate acid of the ratio of the dissociation constants multiplied by the ratio of the true constants multiplied form, or are equal to the true constant of the compound being nitrated and the nitration product are predominantly in the protonated form, or are equal to the true constant of the conjugate acid of the ratio of the dissociation constants multiplied by the ratio of the true constants multiplied by the ratio protonated acid of the nitration product are predominantly in the protonated form, or are equal to the true constants multiplied by the conjugate acid of the compound being nitrated and the nitration product are predominantly in the protonated form, or are equal to the true constants multiplied by the conjugate acid of the constants multiplied by the conjugate acid of the nitration product are predominantly in the protonated form, or are equal to the true constants multiplied by the conjugate acid of the compound being nitrated and the nitration product are predominantly in the protonated form, or are equal to the true constants multiplied by the conjugate acid of the compound being nitrated acid of the compound being

TABLE 1

^K i,exp	HNO ₃ , mass %							
	62,85 *	65,2 +	67,25 +	70,14 *	73,16 \$	76,84‡	76,84 *	80,42 *
$K_1 \\ K_3$	15,2	15,1 0,761	15,3 0,680	15,2 0,607	15,1	15,3	15,2	15,1
K ₄ K ₅ K ₉ K ₁₀ K ₁₁ K ₁₂	9,72	1,82 8,94 0,415 4,45 1,03 9,93	1,63 8,00 0,416 4,46 1,01 9,94	1,46 7,13 0,415 4,44 1,0 9,93	1,256,130,4154,45	1,06 5,20 0,416 4,47	$1,06 \\ 5,20 \\ 0,415 \\ 4,44$	0,893 4,37 0,415 4,46
K ₁₃ K ₁₄ K ₁₅ K ₁₆	0,81	0,82	0,81	0,83	$0,82 \\ 0,149 \\ 1,44$	1,83 0,81 0,147 1,45	1,82 0,82 0,148 1,46	1,83 0,81 0,148 1,44

*Initial 0000. †Initial ONNO. ‡Initial NOON.

to the activity of solvated protons, if the compound being nitrated is protonated and the nitration product is neutral. A detailed description of monitoring the attainment of equilibrium in the system and the basis for the calculation of the experimental equilibrium constants have been published [2, 3].

The sensitivity of the apparatus did not permit detection of ONOO in the equilibrium mixure at any of the HNO₃ concentrations used. The value of K_2 , exp for glycerol nitration [2] may be taken as an upper estimate for K_2 , exp, and on that basis lower estimates were determined for K_6 , exp, K_7 , exp, and K_8 , exp using the equations K_1 , exp K_3 , exp = K_2 , exp K_8 , exp, K_1 , exp K_4 , exp = K_2 , exp K_6 , exp, and K_2 , exp K_7 , exp K_{13} , exp = K_1 , exp K_3 , exp K_{11} , exp. The relative variance in concentration of OOOO derivatives is 0.5% and in activity of HNO₃ and H₂O 0.7% the cumulative variance experimental equilibrium constants for reactions (1), (3-5), and (9-16) is 1.25%.

RESULTS AND DISCUSSION

Glycerol and meso-erythyritol are adjacent members of the series of polyatomic alcohols with a homologous difference of HC(OH). The main properties of glycerol and its nitrates have been studied in detail [9]. Using the results of that study it is considered that in the concentration range of HNO₃ in the present investigation meso-erythritol and its mononitrates occur mainly in a form protonated at one of the oxygen atoms, the trinitrates and tetranitrate in a neutral form, and in the dinitrate solutions the amount of protonated form is lower than that of the neutral form. Taking into account the acid dissociation constants of the conjugate acids of 0000 and its nitrates by analogy with [2] the experimental equilibrium constants for nitration are equal to K_1 , $exp = 4K_1K_{\alpha}/3K_{\beta}$; K_2 , $exp = 4K_2K_{\alpha}/3K_{\beta}$;

$$K_{3,\exp} = 3K_3K_\beta/a_{\rm H^+}...;$$

 $K_{8,\exp} = 3K_8K_\beta/a_{\rm H^+}; K_{9,\exp} = K_{9}...; K_{16,\exp} = K_{16}.$

where K_{α} is the acid dissociation for 0000 and 0000 and K_{β} for N000, N000, N000, 0000, 0000, and 0000.

For 0000 and its nitrates the acid dissociation constants of the conjugate acids depend slightly on the protonation site [9]; we have also assumed that this property is retained for 0000 derivatives. The experimental equilibrium constants for reactions (9)-(16) do not depend on the acidity of the medium (Fig. 2) and are qual to the true equilibrium constants; $K_{1, exp}$ also does not depend on the acidity of the medium but differs from the true value by a factor of $4K_{\alpha}/3K_{\beta}$; log $K_{3, exp}$, log $K_{4, exp}$, and log $K_{5, exp}$ decrease linearly



Fig. 2. Dependence of log $K_{i, exp}$ on $H_0(ArNH_2)$ at 20°C: (1') initial 0000, (2') ONNO, (3') NOON; the numbers on the lines denote values of i.

Fig. 3. Free energy changes (ΔG_i^0) in nitration reactions of 0000 and 000 [2]: full line represents identical equilibria in 000 and 0000, broken line represents additional equilibria in 0000.

with decrease in $H_0(ArNH_2)$ with the same tangent of slope equal to 0.33. This agreement of the tangents of slope corresponds to equality of the products K_3 , $expK_{11}$, $exp = K_4$, $expK_9$, expand K_5 , $expK_{14}$, $exp = K_3$, $expK_{12}$, exp, where K_9 , exp, K_{11} , exp, K_{12} , exp, and K_{14} , exp are independent of the acidity function which mean that changes in K_3 , exp, K_4 , exp, and K_5 , expmust be proportional to the acidity function of the medium $H_0(ArNH_2)$.

Standard Gibbs free energy changes ($\Delta G_1^{\circ} = RT \ln K_1, exp$) for nitration of glycerol and mesoerythritol are compared in Fig. 3 to reveal common features for the nitration equilibria of aliphatic polyatomic alcohols. Values of $K_{1,exp}$ for $H_0(ArNH_2) = -4.5$ are shown and the zero level is taken as the sum of the standard energies of formation of the alcohol and HNO₃. The highest ΔG_1° occurs on passing from the alcohol to the dinitrate substituted at the primary hydroxyl groups, the change being 0.68 kcal/mole higher for meso-erythritol. In both alcohols subsequent additional nitration of the intermediate dinitrate at secondary hydroxyl groups to the fully nitrated compound occurs with an increase in free energy. The sign of the ΔG_{14}° and ΔG_{15}° changes may be associated with a negative ΔS in reactions (14) and (15) by analogy with the glycerol derivatives [3]. In comparison with glycerol, nitration of meso-erythritol has five additional equilibria for nitration at secondary hydroxyl groups: reactions (3), (7), (9), (11), and (15), four of which, excluding (7), proceed with increased or constant standard Gibbs free energy.

As in the case of glycerol, $-\Delta G_i^0$ for nitration at both primary and secondary hydroxyl groups decreases on the whole with increase in the degree of substitution in the compounds being nitrated. For primary hydroxyls $-\Delta G_i^0$ decreases in the series QOOO, QNOO, NONQ, ONOQ, NOOQ, NNOQ, ONNQ, QNNN and for secondary hydroxyls ONQO, OQOO, NQOO, NQOO, NQON, NOQO, NNQO, NNQON (the wavy line indicates the position where nitration occurs).

Distortions in these series occur for $-\Delta G_i^0$ in the production of NONO from mononitrates and the conversion of NONO into trinitrates, where $-\Delta G_i^0$ for the conversion is higher than $-\Delta G_i^0$ for the production of NONO.

A common feature of the nitration of polyatomic aliphatic alcohols is the substantial value of $-\Delta G_1^0$ during introduction of a second nitrate group at a primary hydroxyl position in the original 2-mononitrate compared with $-\Delta G_2^0$ for production of the latter from the alcohol. In the case of meso-erythritol nitration it was found that this feature is also retained during introduction of a nitrate group at the second secondary hydroxyl position.

Comparison of $-\Delta G_i^0$ for introduction of nitrate groups at primary and secondary hydroxyl positions in 0000 and its nitrates with identical structure and degree of nitration shows that, as in the case of glycerol, $-\Delta G_i^0$ is higher during introduction of nitrate groups at primary hydroxyls, the maximum difference being between Q000 and OQ00 and the minimum between ONOQ and ONQ0.

In the mononitrate group $-\Delta G_1^{0}$ for formation of NOOO is 1.54 kcal/mole higher than $-\Delta G_2^{0}$ for formation of ONOO from meso-erythritol, and among the corresponding values for dinitrate production $-(\Delta G_1^{0} + \Delta G_5^{0})$ for NOON is 1.8 and 1.0 kcal/mole higher than $-(\Delta G_2^{0} + \Delta G_7^{0})$ for ONNO and $-(\Delta G_2^{0} + \Delta G_6^{0})$ for NNOO respectively. Such a difference in standard energies of nitration to NOON, ONNO, and NNOO explains the result of the reaction described previously of selective (incomplete) nitration of meso-erythritol at the two primary hydroxyl groups with production of meso-erythritol diprimary dinitrate [6]. Among the meso-erythritol trinitrates $-(\Delta G_1^{0} + \Delta G_5^{0} + \Delta G_{14}^{0})$ for NNON production is 1.34 kcal/mole higher than $-(\Delta G_2^{0} + \Delta G_7^{0} + \Delta G_{13}^{0})$ for NNNO production. The standard Gibbs free energy changes for production of fully nitrated glycerol and meso-erythritol are not high and the nitrating activity $(a_{\rm HNO_3}/a_{\rm H_2O})$ in the nitrating mixtures is also not high, so that the equilibrium is shifted to the side of incompletely nitrated compounds. To produce the completely nitrated compounds with a yield close to 100% it is necessary to use nitrating systems with a high $a_{\rm HNO_3}/a_{\rm H_2O}$ ratio (HNO₃ solutions with a concentration close to 100 mass %).

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