Equilibrium constants of nitration of alcohols and thermal stability of their nitrates

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The data on equilibrium constants of the nitration of polyhydric alcohols and cellulose were examined and generalized. Changes in values of the equilibrium constants and Gibbs's energy of nitration related to the position of the nitrated hydroxyl group in the molecule and the existence of the adjacent hydroxyl and nitrate groups were established. An empirical method for calculating rates of thermal decomposition of different nitrate groups using experimental equilibrium constants of nitration was suggested.

Key words: alcohols, nitration; equilibrium constants; nitrates, rate of thermal decomposition.

The nitration of alcohols, including polyhydric alcohols, is a reversible reaction. At the same time, reactions of *C*-nitration are almost irreversible. Several works[1-8] on determination of the equilibrium constants of nitration (K_e) of several polyhydric alcohols and cellulose are available. The nitration of glycerol has been studied in most detail.[2-4] For this reaction, the temperature dependences of K_e of all consequent stages of nitration and the corresponding values of changes in Gibb's energies, enthalpy, and entropy (ΔG, ΔH, ΔS) were obtained. For other alcohols, the K_e values were determined only at 20—25 °C. In this work, based on our results and published data, we discuss a correlation between K_e and the structure of nitrated molecules and their stability.

Results and Discussion

The K_e values of the alcohol nitration in the HNO_3—H_2O system, which are determined by the correlation $K_e = a_{RONO_2}a_{H_2O}/(a_{ROH}a_{HNO_3})$, and the values of $\Delta G_H = -RT \cdot \ln K_e$ are presented in Table 1.

The state of neat components was chosen as standard, the ratio of activity coefficients of alcohol and nitrate was taken to be equal to unity, and the values of a_{H_2O} and a_{HNO_3} were determined from the vapor pressures of the components. The K_e values for monoalkyl nitrates were calculated from the standard thermodynamic data, and the other values were obtained experimentally. In all cases, except cellulose, the K_e value was determined in the homogeneous liquid phase from the data on the amounts of alcohol and nitrate in the equilibrium mixture. These data were obtained mainly by the ^{1}H NMR method for both direct nitration of alcohols and hydrolysis of nitrates. The protonations of ROH and $RONO_2$ were taken into account in the calculation. Examination of the data obtained allows one to establish the following regularities in changes in K_e depending on the structure of the molecule of the nitrated compound:

1. The greatest value of K_e is observed for the methanol nitration. When the carbon chain grows, K_e decreases. The insertion of more complex substituents decreases K_e to a greater extent. The sharp decrease in the yield of nitrate in solutions of HNO_3 with concentration lower than 60% is related to the alcohol oxidation, whose relative contribution increases as the acid is diluted.

2. The equilibrium constants of nitration to the hydroxyl group at the secondary carbon atoms are 3—10 times lower than K_e for the primary hydroxyl groups in the single-type compounds. The analysis of kinetic data showed that this difference is mainly determined by the difference between rates of nitration at the primary and secondary hydroxyl groups, and the rate of the reverse reaction (hydrolysis) slightly depends on the number and position of nitrate groups.[9]

3. In polyhydric alcohols, the existence of the nitrate group at the primary C atom increases K_e by 2—3 times, as a rule, for the nitration of the secondary hydroxyl group at the adjacent atom (or at the next one) compared to K_e for this hydroxyl group in the initial alcohol.

4. When the third and four (in mesoerythrite) nitrate groups are introduced, the K_e values decrease successively. This decrease is especially substantial for the nitration at the secondary OH group when the adjacent hydroxyl groups are replaced by the ONO_2 groups.

5. For nitration of the latter hydroxyl groups in polyhydric alcohols, $K_e < 1$, and high degrees of the

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Table 1. K_e and ΔG values for nitration of alcohols and nitrates and estimation values of rate constants of decomposition of nitrates (k) at 140 °C

Compound (temperature)	Structure	K_e	$-\Delta G$ /kcal mol^{-1}	k /s^{-1}
Glycerol and	OOO˙	2.6	0.56	0.7
its nitrates	O˙ON	9.6	1.32	0.33
1,2,3-OOO	ONO˙	7.4	1.16	0.4
(25 °C[2])	NO˙N	0.4	−0.5	2.2
	OO˙O	1.15	0.08	1.2
	OO˙N	3.0	0.64	0.65
	NNO˙	1.3	0.16	1.1
Mesoerythrite and	O˙OOO	15	1.6	0.25
its nitrates	NO˙OO	1.3	0.16	1.1
1,2,3,4-OOOO	NNO˙O	0.4	−0.5	2.2
(20 °C[5])	NO˙NO	1.0	0.01	1.3
	O˙NNO	1.8	0.35	0.9
	NNO˙N	0.15	−1.1	4.1
	NOO˙O	0.7	−0.22	1.6
	NOOO˙	6.8	1.1	0.4
	NNOO˙	4.5	0.9	0.5
	NONO˙	9.9	1.3	0.33
	NO˙ON	0.8	−0.12	1.5
	NNNO˙	1.5	0.22	1.0
Cellulose and	OOO˙	7.0	1.15	0.4
its nitrates	OO˙N	0.1	−1.3	5.1
2,3,6-OOO	O˙NN	0.3	−0.8	2.9
(20 °C[8])	O˙ON	0.2	−0.9	3.4
	NO˙N	0.15	−1.1	3.8
Levoglucosan and	NO˙O	0.5	−0.4	2.0
its nitrates	NOO˙	0.6	−0.3	1.7
2,3,4-OOO	NNO˙	0.25	−0.8	3.0
(20 °C[7])	O˙NN	0.2	−0.9	3.4
	O˙NO	0.2	−0.9	2.0
	ONO˙	0.7	−0.2	1.6
	NO˙N	0.25	−0.8	3.0
Carboxy-		δ-OH*		
cellulose	type 1**	0.09	−1.4	5.5
(20 °C[6])	type 2**	0.1	−1.35	5.1
		α,β-OH		
	type 1**	$5 \cdot 10^{-4}$	−4.5	125
	type 2**	$2 \cdot 10^{-4}$	−5	215
Monohydric	MeOH	$1 \cdot 10^{5}$	6.7	$1 \cdot 10^{-3}$
alcohols (25 °C[1],	PrOH	$9 \cdot 10^{3}$	5.3	$6 \cdot 10^{-3}$
calculation)	EtOH	$2.8 \cdot 10^{-4}$	6.0	$3 \cdot 10^{-3}$

Note. O is hydroxyl, *N* is nitrate group, "˙" is the position in which a new nitrate group was introduced or from which it was eliminated due to thermal decomposition.

* δ-OH are hydroxyls in the δ-position with respect to the lactone group of carboxycellulose. ** 1st type, the terminal residue of the unit of the carboxycellulose oligomer contains four C atoms, two of which enter the composition of the carboxyl groups; 2nd type, the terminal residue of the unit contains six C atoms, two of which also enter the composition of the carboxyl groups.

nitration of these groups are achieved only when the a_{HNO_3}/a_{H_2O} ratio in the nitrating mixture is great.

6. The nitration of cellulose in the HNO_3-H_2O system occurs in the heterogeneous system. The K_e value is approximate, since the activity of the ONO_2 groups are changed for their average molar fractions. However, since the a_{RONO_2}/a_{ROH} ratio enters the K_e value, this replacement is acceptable. The K_e value for the primary hydroxyl at the C(6) atom of cellulose is close to the K_e value for the primary hydroxyl groups in glycerol molecules and mesoerythritol, but the K_e value of the nitration of the secondary hydroxyls at the C(2) and C(3) atoms is noticeably lower, and the effect of the adjacent nitrate group is almost absent. At the same time, in levoglucosan, in which nitration proceeds homogeneously and all of the three hydroxyls are located at the adjacent secondary C atoms, the K_e value is somewhat higher for the introduction of the second nitrate group, and for the third group, it is close to the corresponding K_e values in cellulose.

7. The OH groups at the α- and β-positions relative to the carboxyl group of carboxycellulose have the lowest K_e values. The increase in ΔG in this reaction is 4.5—5.0 kcal mol^{-1}, and hence, high degrees of nitration are achieved only when a solution of N_2O_5 in HNO_3 is used as the nitrating mixture.

At the present time, it is established that the initial rate of thermal decomposition of nitroesters is determined by the rate of cleavage of the $O-NO_2$ bond. A significant feature of the thermal decomposition of nitroesters is strong autoacceleration, which is the reason for the considerable scatter of different (presented by different authors) experimental values of the rate constants of the initial stages, their activation energies, and energies of the $O-NO_2$ bond.[10–12] Therefore, empirical methods for estimating the initial rates of the process are of interest.

We observed (Fig. 1) that for the studied reactions of decomposition of the secondary and primary nitrate groups in nitrocellulose (**1**),[13–14] in 1,4- and 2,3-butyleneglycol dinitrates (**2**)[10] and of two secondary nitrate groups in nitrocellulose (**3**),[13] the $\log(k_i/k_j) = \gamma \cdot \log(K_{e,j}/K_{e,i})$ dependence approximately holds, where k_i and k_j are the rate constants of decomposition of the ith and jth nitro groups at the temperature (140 °C) at which the secondary reaction of the nitroester hydrolysis can be neglected;[13] and $K_{e,i}$ and $K_{e,j}$ are the equilibrium constants of their formation in the nitration at 20—25 °C, $\gamma \approx 0.6$.

Using this empirical dependence and data in Table 1, we can estimate the ratio of rate constants of decomposition for different nitrate groups and, if the absolute value of at least one rate constant is known, we can estimate the absolute values of the others. The overall rate of the nitroester decomposition is equal to the sum of the rates of decomposition of each of the nitrate groups entering the molecule. These estimations were performed for the compounds presented in Table 1, and the rates of their decomposition at 140 °C were determined. One of the most reliable values, the rate constant of thermal decomposition of nitrocellulose,[13] was used as the starting value in these calculations. The calculated

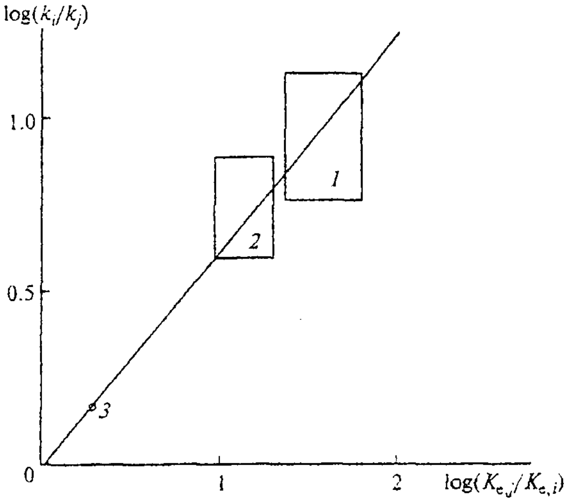

Fig. 1. Dependence of log(k_i/k_j) on log($K_{e,j}/k_{e,i}$). The lower and upper sides of rectangles correspond to the minimum and maximum ratios of the rate constants of decomposition of the secondary and primary nitrate groups of nitrocellulose[13] (*1*) and in butyleneglycol dinitrates[10] (*2*); the left and right sides correspond to the minimum and maximum ratios of the equilibrium constants of nitration to the primary and secondary hydroxyl groups (*1*) and hydroxyl groups in mesoerythritol and its nitrates (*2*); secondary nitrate groups in nitrocellulose[13] (*3*).

values of constants agree with the experimental values for nitroglycerol, but those for glycerol 1,3-dinitrate and mononitrates differ from the experimental data.[11] The divergence may be related to experimental errors in the determination of both equilibrium constants and rate constants. The further justification and refinement of the approach proposed requires more polynitrates to be experimentally studied.

References

1. Yu. I. Rubtsov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 27 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 19 (Engl. Transl.)].
2. A. I. Kazakov, G. V. Lagodzinskaya, L. P. Andrienko, N. G. Yunda, A. M. Korolev, Yu. I. Rubtsov, G. B. Manelis, and L. T. Eremenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1723 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 1560 (Engl. Transl.)].
3. A. I. Kazakov, E. P. Kirpichev, G. V. Lagodzinskaya, L. P. Andrienko, N. G. Yunda, A. M. Korolev, Yu. I. Rubtsov, G. B. Manelis, and L. T. Eremenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1729 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 1565 (Engl. Transl.)].
4. N. G. Yunda, G. V. Lagodzinskaya, A. I. Kazakov, A. M. Korolev, Yu. I. Rubtsov, G. B. Manelis, and L. T. Eremenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 381 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 325 (Engl. Transl.)].
5. A. I. Kazakov, G. V. Lagodzinskaya, N. G. Yunda, L. P. Andrienko, A. M. Korolev, Yu. I. Rubtsov, G. B. Manelis, and L. T. Eremenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 2248 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 1966 (Engl. Transl.)].
6. A. I. Kazakov, G. V. Lagodzinskaya, M. V. Loginova, Yu. I. Rubtsov, V. A. Koleno, Z. Sh. Sharshenalieva, G. B. Manelis, and L. T. Eremenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 2254 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 1972 (Engl. Transl.)].
7. M. V. Loginova, A. I. Kazakov, G. V. Lagodzinskaya, and A. M. Korolev, in *Khimiya i reaktsionnaya sposobnost' tsellyulozy i ee proizvodnykh* [*Chemistry and Reactivity of Cellulose and Its Derivatives*], Cholpon-Ata, 1991, 147 (in Russian).
8. A. A. Chicherov, A. V. Kuznetsov, Yu. M. Kargin, V. V. Klochkov, G. N. Marchenko, and G. G. Garifzyanov, *Vysokomol. Soedin.*, 1990, **32**, 502 [*Polym. Sci. USSR*, 1990, **32** (Engl. Transl.)].
9. A. I. Kazakov, Yu. I. Rubtsov, G. V. Lagodzinskaya, E. P. Kirpichev, and G. B. Manelis, in *Khimiya i reaktsionnaya sposobnost' tsellyulozy i ee proizvodnykh* [*Chemistry and Reactivity of Cellulose and Its Derivatives*], Cholpon-Ata, 1991, 142 (in Russian).
10. A. G. Afanas'ev, B. A. Lur'e, and B. S. Svetlov, in *Teoriya vzryvchatykh veshchestv* [*Theory of Explosives*], Vysshaya Shkola, Moscow, 1967, 63 (in Russian).
11. Ch. E. Waring and G. Krastins, *J. Phys. Chem.*, 1970, 999.
12. B. A. Lur'e and B. S. Svetlov, in *Khimiya i reaktsionnaya sposobnost' tsellyulozy i ee proizvodnykh* [*Chemistry and Reactivity of Cellulose and Its Derivatives*], Cholpon-Ata, 1991, 184 (in Russian).
13. E. A. Panina, V. A. Rafeev, T. V. Sorokina, Yu. I. Rubtsov, and N. V. Chukanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1273 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 1143 (Engl. Transl.)].

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