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Interaction of 2,2,6,6-tetramethylpiperidine-1-oxyl chlorite with alcohols

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The kinetics of the oxidation of a series of alcohols (*viz.*, ethanol, propan-2-ol, butan-1-ol, butan-2-ol, heptan-4-ol, decan-2-ol, propan-1,3-diol, butan-2,3-diol, cyclohexanol, benzyl alcohol, and borneol) with the oxoammonium salt 2,2,6,6-tetramethylpiperidine-1-oxyl chlorite in acetonitrile was studied by spectrophotometry. The products of oxidation of primary alcohols are the corresponding aldehydes and carboxylic acids, and the products of oxidation of secondary alcohols are ketones. The reaction rate is described by the second order equation. The rate constants and activation parameters were determined. The rate constant as a function of the alcohol nature is described by the one-parameter Taft equation.

Key words: oxoammonium salt, 2,2,6,6-tetramethylpiperidine-1-oxyl chlorite, alcohols, rate constant.

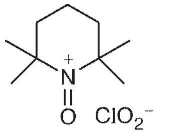
The interaction of ClO_2 with stable nitroxyl radicals occurs through a charge transfer complex, which further transforms to an oxoammonium salt.[1,2] Oxoammonium salts are known[3,4] to be the efficient oxidation agents and active intermediates in the oxidation of organic substances catalyzed by nitroxyl radicals.[5,6] The interaction of alcohols with the oxoammonium salts proceeds rapidly, and the oxidation products are the corresponding carbonyl compounds.[7] However, the data on kinetic features of the alcohol oxidation with oxoammonium salts have not been documented.

In this work, the kinetics of oxidation of a series of alcohols with 2,2,6,6-tetramethylpiperidine-1-oxyl chlorite (**1**) was studied in acetonitrile at 10—60 °C.

Experimental

Oxoammonium salt **1** was prepared by mixing solutions of chlorine dioxide and nitroxyl radical 2,2,6,6-tetramethylpiperidine-1-oxyl (**2**). A solution of oxyl **2** in anhydrous benzene (0.3 *M,* 5 mL, molar ratio ClO_2 : **2** = 1 : 1) was added to a solution of ClO_2 in benzene (1.0 mol L^{-1}, 15 mL). The beaker was kept in dark at ~20 °C for 12—20 h. The orange-red precipitate was filtered under argon flow, washed with pentane, and dried in a vacuum (7 Torr). The yield of oxoammonium salt **1** based on the nitroxyl radical was 98%. Found (%): C, 49.8; H, 8.4; Cl, 14.4; N, 6.0; O, 21.4. Calculated (%): C, 50.5; H, 8.5; Cl, 14.9; N, 5.9; O, 20.2. The intense absorption band at 1624 cm^{-1}, which is absent in the spectra of reactants and is typical of the $>^{+}N=O$ group of the oxoammonium salts[8] is present in the IR spectrum of the product; the absorption band with the maximum at λ = 450 nm (molar absorptivity ε = 200±5 L mol^{-1} cm^{-1}) is present in the visible region.

Chlorine dioxide was synthesized by a known method.[9] A procedure of the radical preparation was described earlier.[10,11] The alcohols (*viz*., ethanol (**3**), propan-2-ol (**4**), butan-1-ol (**5**), butan-2-ol (**6**), heptan-4-ol (**7**), decan-2-ol (**8**), propan-1,3-diol (**9**), butan-2,3-diol (**10**), cyclohexanol (**11**), benzyl alcohol (**12**), and borneol (**13**)), as well as acetonitrile and benzene were purified according to known procedures.[12,13]



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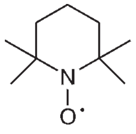

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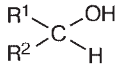

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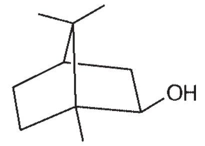

13

	R^1	R^2		R^1	R^2
3	Me	H	**8**	*n*-C_8H_{17}	Me
4	Me	Me	**9**	$CH_2(OH)—CH_2$	H
5	Pr^n	H	**10**	Me—CH(OH)	Me
6	Et	Me	**11**	*cyclo*-C_8H_{10}	
7	Pr^n	Pr^n	**12**	$PhCH_2$	H

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The kinetics of alcohol oxidation was studied spectrophotometrically by the consumption of oxoammonium salt **1** at λ_{max} = 450 nm on a Specord M-40 instrument (Carl Zeiss, Jena). A solution of an alcohol in acetonitrile was placed in a quartz cell, and acetonitrile was placed into a reference cell. The cells were kept at constant temperature (10—60 °C) in the spectrophotometer compartment. Then, the required amount of the solution of **1** in acetonitrile was added and changes in the absorbance of **1** were monitored. The initial concentrations of **1** and **3—13** were varied within the limits $(2.5—5.0) \cdot 10^{-3}$ and $(0.95—10.40) \cdot 10^{-2}$ mol L^{-1}, respectively.

The alcohols and oxidation products were analyzed by GLC on a Chrom-5 instrument (column 3.5 m×3 mm, 5% SE-30 on Chromaton) and by ^1H NMR on a Bruker AM-300 instrument (300 MHz, $CDCl_3$ as solvent, Me_4Si as standard). Benzene was used as the standard for the quantitative determination of the products.

Results and Discussion

Reaction products. The composition of the products of reaction between salt **1** and alcohols was determined at the equimolar ratios of the oxoammonium salt **1** and alcohols. When **1** reacts with primary alcohols **3**, **5**, **9**, and **12**, mixtures of the corresponding aldehydes and carboxylic acids with the most amount of aldehydes is formed (Table 1). Aldehydes are likely formed at the initial stages and then are oxidized to the corresponding carboxylic acids. Under similar conditions, ketones are formed from secondary alcohols **4**, **6—8**, **10**, **11**, and **13** in high yields. Methanol, ethylene glycol, and menthol are not oxidized under the experimental conditions.

Table 1. Yields of the products of oxidation of alcohols **3—13** with oxoammonium salt **1** at 20 °C

Alcohol	Product	Yield* (%)
3	Acetic acid	32
	Acetaldehyde	50
4	Acetone	93
5	Butyric acid	20
	Butyraldehyde	65
6	Butan-2-one	95
7	Heptan-4-one	96
8	Decan-2-one	90
9	3-Hydroxypropanoic acid	29
	3-Hydroxypropanal	65
10	3-Hydroxybutane-2-one	83
11	Cyclohexanone	97
12	Benzoic acid	70
	Benzaldehyde	12
13	Camphor	97

* Calculated per consumed oxoammonium salt **1**.

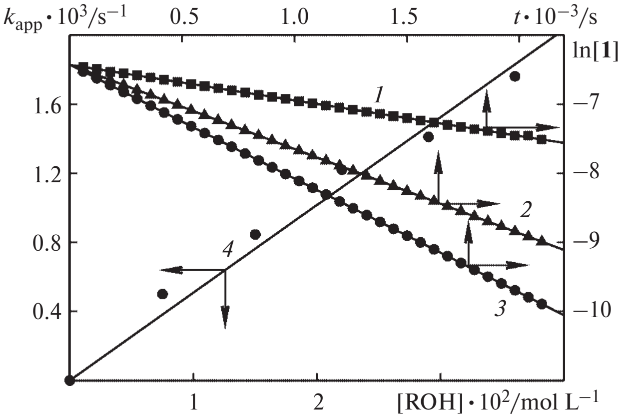


Fig. 1. Semilogarithmic anamorphoses of consumption of oxoammonium salt **1** ($1.6 \cdot 10^{-3}$ mol L^{-1}) in the reaction with butan-2-ol at $[ROH]_0 = 7.3 \cdot 10^{-3}$ (*1*), $2.2 \cdot 10^{-2}$ (*2*), $3.6 \cdot 10^{-2}$ mol L^{-1} (*3*) and dependence of the apparent rate constant on the alcohol concentration (*4*); 20 °C, MeCN.

Reaction kinetics. The reaction kinetics was studied at the initial concentrations ratio $[\mathbf{1}]_0 \ll [ROH]_0$. For all the compounds, the kinetic curves with a high correlation coefficient (*r* = 0.950—0.999) are described by the first order equation (Fig. 1). The apparent first-order rate constants k_{app} were calculated from semilogarithmic anamorphoses and were shown to be independent of the concentration of **1**. It is known[14,15] that alcohols are prone to self-association, which can affect considerably their reactivity. The effect of the alcohol association was not found under the experimental conditions. The plot of k_{app} *vs.* $[ROH]_0$ is linear (see Fig. 1), indicating the first order with respect to the alcohol concentration; the kinetic equation has the form

$$d[\mathbf{1}]/dt = k[\mathbf{1}][ROH].$$

The temperature dependences of the rate constants were measured for all the alcohols, and the activation parameters were determined (Table 2). It can be seen in Table 2 that an increase in the activation energy is accompanied by an increase in the preexponential factor (compensation effect).

$$E_a = (2.06 \pm 1.6) + (2.83 \pm 0.13)\ln A \ (r = 0.980)$$

The activation enthalpy increases with the activation entropy (Fig. 2).

$$\Delta H^{\neq} = (85.6 \pm 5) + (0.34 \pm 0.02)\Delta S^{\neq} \ (r = 0.980)$$

The compensation effect likely implies a common reaction mechanism for the above series of alcohols.

Effect of the alcohol structure on the reaction rate constant. The reactivity of alcohols at 10 °C changes as follows (see Table 2): **10** < **9** < **3** < **7** < **8** < **6** < **13** < **5** < < **4** < **11** < **12**.

Table 2. Activation parameters for the reaction[a] of alcohols **3—13** with oxoammonium salt **1**

Alcohol	$k^b \cdot 10^2$ /L mol^{-1} s^{-1}	lnA^b	$E_a{}^b$	$\Delta H^{\neq b}$	$\Delta G^{\neq b}$	$\Delta S^{\neq b}$ /J mol^{-1} K^{-1}	σ*[19]
			kJ mol^{-1}				
3	1.67	11.46	36.6	34.3	78.8	−157.4	−0.14
4	3.31	13.60	40.0	37.6	77.2	−139.6	−0.20
5	2.71	7.15	25.3	22.9	77.6	−193.2	−0.20
6	2.33	13.76	41.2	38.8	78.0	−138.3	−0.15
7	1.81	14.10	42.6	40.2	78.6	−135.5	−0.35
8	2.07	16.15	47.1	44.7	78.3	−118.5	−0.15
9	1.17	19.43	56.2	53.8	79.7	−91.2	0.00
10	0.40	18.65	56.8	54.4	82.1	−97.7	0.15
11	14.22	9.19	26.2	23.8	73.7	−176.3	−0.26
12	37.31	6.03	16.5	14.1	71.5	−202.6	0.16
13	2.55	17.89	50.7	48.3	77.8	−104.0	−0.16

[a] Solvent, MeCN; 10 °C.

[b] Error of measurments was at most 15%.

Examination of our findings using the one-parameter Taft equation[16]

$$\ln(k/k_0) = \rho^*\sigma^*$$

showed that the second-order rate constants for the oxidation of alcohols with the salt **1** decrease with an increase in the substituent inductive constants σ* (Fig. 3) (compounds **7**, **11**, and **12** were eliminated from the correlation). A negative sign of $\rho^* = -5.4$ in the correlations gives evidence that a partial positive charge arises on the reaction center in the transition state and the introduction of electron-acceptor substituents in the alcohol molecule retards its oxidation. A high absolute ρ* value indicates a high charge separation in the transition state and a strong polarity of the transition state. The absolute ρ* value increases with the temperature decrease from 30 to 10 °C (Table 3). This is likely due to an increase in the polarity of the transition state. The substituent effect on the reactivity of alcohols enhances with the temperature decrease.

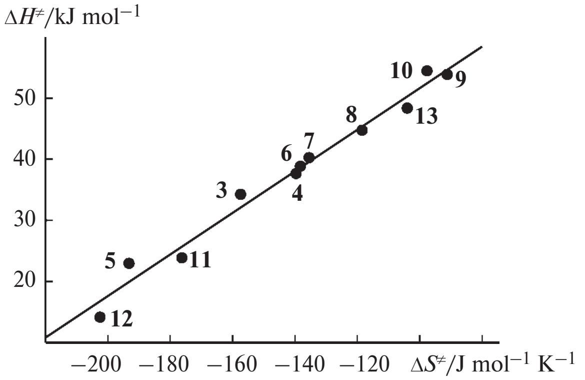


Fig. 2. Plot of $\Delta H^{\neq}$ *vs.* $\Delta S^{\neq}$ for the reaction of salt **1** with alcohols **3—13** at 10 °C, solvent is MeCN.

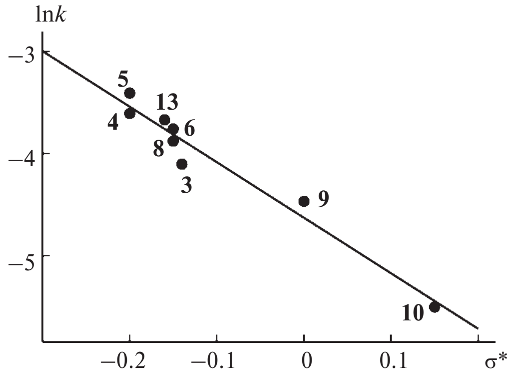


Fig. 3. Logarithm of the rate constant of the oxidation of alcohols with oxoammonium salt **1** as a function of the inductive constant of substituents in the alcohol molecule (σ*) at 10 °C (compounds **7**, **11**, and **12** were eliminated from the correlation).

Reaction mechanism. Examination of the literature data[17] showed that the mechanism of oxidation with oxoammonium salts is unclear so far. Both radical and polar oxidation mechanisms have been proposed.[3,7,18]

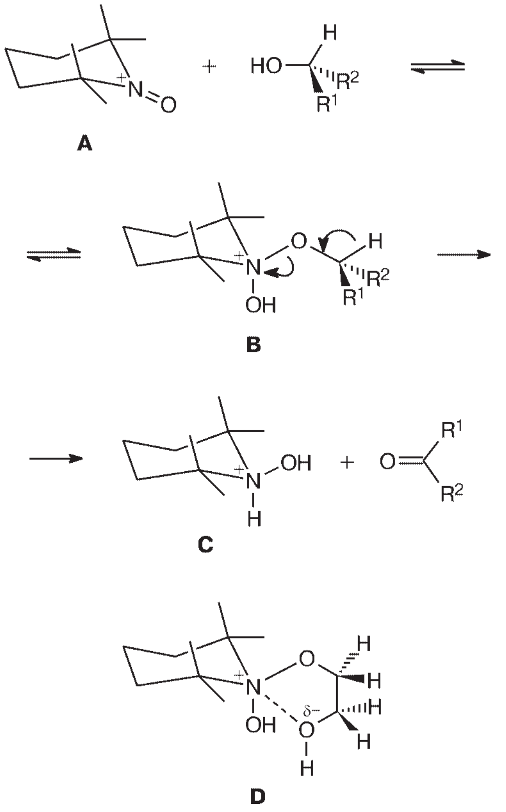
In our opinion, the mechanism proposed in Ref. 17 is most preferable (Scheme 1), since it allows one to realize why ethylene glycol is not oxidized under the experimental conditions. This fact can be explained by

Table 3. Temperature dependence of ρ*

T/°C	ρ*	*r*
10	−5.4±0.5	0.96
20	−4.5±0.7	0.92
30	−3.6±1.0	0.86

the formation of the intermediate complex (**D**) between the molecules of alcohol and oxoammonium salt due to the interaction of the O atom of the adjacent OH group in ethylene glycol with a positively charged N atom in the $>^{+}N=O$ group of the oxoammonium salt, decreasing the positive charge on the N atom and the reactivity of oxoammonium salt.

Scheme 1



In addition, the above mechanism suggests the formation of highly polar transition state, and the ρ* value calculated by us according to the Taft equation confirms this assumption. Hence, the findings of this work do not contradict the reaction mechanism proposed earlier.[17]

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