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SHORT COMMUNICATIONS

The Influence of the Structure of Aliphatic Amine on Its Catalytic Activity in the Oxidation of Anthrone in Dimethyl Sulfoxide

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Abstract—The catalytic activity of several aliphatic amines in the liquid-phase oxidation of anthrone by molecular oxygen in dimethyl sulfoxide was studied. The kinetic data obtained were compared with the results of quantum-chemical calculations. The catalytic activity of aliphatic amines in the reaction under consideration was directly proportional to an increase in the absolute value of the heat of formation of the corresponding ammonium cation.

Keywords: catalytic activity, anthrone oxidation, aliphatic amine structure.

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INTRODUCTION

Amines of various nature exhibit catalytic activity in several reactions, in particular, they catalyze the liquid-phase oxidation of aromatic ketones by molecular oxygen in aprotic solvents [1]. Interrelation between the structure and activity of amines was considered in [2–4], where the influence of the structure was related to such factors as the influence of substituents (the induction and steric effects and the effect of conjugation), the solvation of amines and their protonated forms, and the influence of the geometry of electronic orbitals (the hybrid state responsible for the properties of the lone pair of electrons on nitrogen).

The purpose of this work was to study the catalytic activity of amines depending on their structure and determine the amine electronic structure characteristics that allow their catalytic activity to be predicted. The object of study was the reaction of anthrone oxidation by molecular oxygen in dimethyl sulfoxide (DMSO). The kinetics of this reaction was studied in [1]. We used aliphatic amines with different chain lengths (3-methylbutylamine, butylamine, ethylamine, 2-methylpropylamine, *t*-butylamine, dodecylamine, diethylamine, triethylamine, and trimethylamine) as catalysts.

EXPERIMENTAL

The kinetics of the reaction was monitored by volumetric measurements of oxygen absorption, the reaction was performed under kinetic conditions. Constant oxygen pressure (760 torr) and temperature (307 K) were maintained in experiments. The initial concentration of anthrone was 0.05 mol/l in all experiments. Anthrone is not oxidized in DMSO without the addition of amines under the specified conditions, equally as amines without anthrone. In presence of ammonia or aliphatic amines, the reaction has a high rate. The kinetic curves have the form of curves with saturation; that is, in certain time, that absorption of oxygen by the solution stops. Such curve shape is explained by the complete consumption of the substrate undergoing oxidation.

The kinetic curves are described by the first-order kinetic equation

$$[O_2]_t = [O_2]_\infty(1 - \exp(-k_{\text{eff}}t)),$$

with a correlation coefficient of 0.99. Here, $[O_2]_t$ is the equilibrium concentration of oxygen absorbed at the given time moment, mol/l; $[O_2]_\infty$ is the equilibrium concentration of oxygen that would be absorbed if the reaction continued infinitely long, mol/l; k_{eff} is the effective rate constant, s^{-1}; and t is time, s.

Proton NMR studies were performed on a BRUKER Avance II instrument (400 MHz). It was found [1] that anthrone transformed into anthraquinone when it was oxidized almost completely (only traces of the side product of the reaction, bianthrone, were present [5]).

RESULTS AND DISCUSSION

The effective constants (k_{eff}) and other kinetic parameters are listed in Table 1. The ratio between the number of moles of oxygen (N_{O_2}) absorbed by the end of the reaction and the number of moles of the substrate introduced into the reaction was stoichiometric (1 : 1). Typical kinetic curves of the absorption of oxygen in the catalytic oxidation of anthrone are shown in Fig. 1.

Table 1. Stoichiometry of the oxidation of anthrone ($c = 0.05$ mol/l) in DMSO at 760 torr and 307 K in the presence of ethylamine (c_e is the concentration of ethylamine)

$c_e \times 10^2$, mol/l	$[O_2]_\infty \pm 0.001$ mol/l	$(k_{ef} \pm 0.06) \times 10^2$, s^{-1}	$W_0 \times 10^5$, mol/(l s)	N_S/N_{O_2}
0.17	0.05	0.10	5.1	0.98
0.26	0.04	0.12	5.3	1.13
0.5	0.05	0.21	10.5	1.01
0.6	0.05	0.24	11.3	1.05
0.77	0.05	0.38	17.5	1.08
				Mean 1.05 ± 0.05

Table 2. Electronic structure characteristics and the rates of reactions catalyzed by amines

Substance	$-\log W_0$	$-\Delta H$, kcal/mol	$-E_{HOMO}$, eV	E_{LUMO}, eV	$-E_{HOMO}$(ion), eV	E_{LUMO}(ion), eV
Dodecylamine	3.96	117.74	9.67	2.92	11.30	1.34
3-Methylbutylamine	3.94	117.83	9.88	2.95	11.80	1.32
Ethylamine	3.98	118.22	9.90	3.03	12.49	1.38
2-Methylpropylamine	4.04	118.12	9.77	3.03	12.15	1.27
Butylamine	4.09	117.79	9.90	2.95	11.67	1.31
t-Butylamine	4.12	115.25	10.04	2.93	13.03	0.92
Diethylamine	4.42	103.20	9.64	2.62	12.59	0.34
Triethylamine	4.5	98.06	9.32	2.42	12.11	−0.02
Trimethylamine	4.71	95.83	9.61	2.55	13.74	0.31

Note: Calculations were performed using MOPAC-2009(COSMO, in a medium with permittivity 48.9); the kinetic data on the last four compounds were taken from [8].

Important parameters characterizing the reactivity of amine molecules are the energies of the highest occupied (E_{HOMO}) and lowest unoccupied (E_{LUMO}) molecular orbitals. According to Fukui, the properties of frontier orbitals can to a considerable extent determine the character of chemical transformations of a molecule [6]. It was, in particular, shown that the pK_a values of solutions of certain aliphatic amines in glacial acetic acid changed linearly as the energy of the highest occupied molecular orbital changed, but in the opposite direction [7].

The results of quantum-chemical calculations of the heat effects of protonation of amines (ΔH) and the properties of amine frontier orbitals (E_{HOMO} and E_{LUMO}) and the frontier orbitals of their cations (E_{HOMO}(ion) and E_{LUMO}(ion)) and the kinetic data obtained are listed in Table 2. The method for semiempirical calculations of molecules was selected by comparing the results obtained using several semiempirical methods (PM3, PM6, and AM1) with the experimental data [8]. The correlation coefficient for the PM3 method was 0.98, which allowed the heats of formation of amine molecules to be estimated with accuracy within ±1.86 kcal/mol.

For $\log W_0$, the best correlation is observed with the heat effect of protonated amine formation (ΔH) ($r = 0.98$) (Fig. 2) and with E_{LUMO} ($r = 0.91$) of the molecule of the corresponding unprotonated amine in a medium with permittivity equal to that of DMSO. Compared with heat effects and frontier orbital energies calculated in a medium with permittivity 48.9, heat effects and frontier orbital energies calculated in

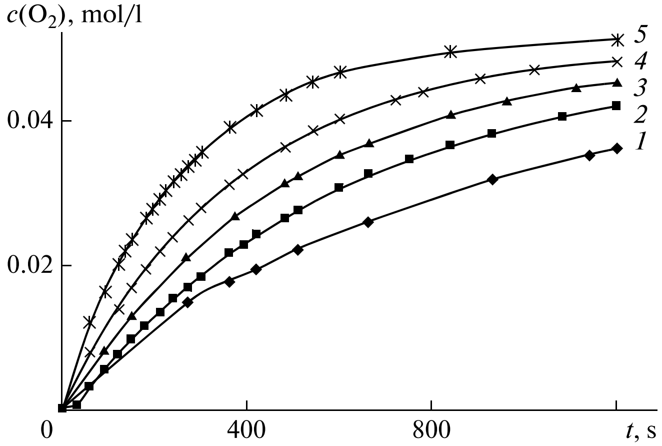

Fig. 1. Kinetic curves of oxygen absorption in the oxidation of anthrone ($c = 0.05$ mol/l) in DMSO at 760 torr and 307 K in the presence of ethylamine; (*1*) 0.0017, (*2*) 0.0026, (*3*) 0.005, (*4*) 0.006, and (*5*) 0.0077 mol/l.

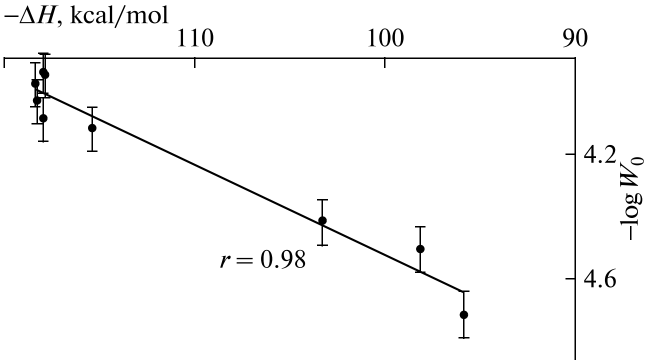

Fig. 2. Correlation between the logarithm of the initial catalytic reaction rate and the heat effect of protonation of the corresponding amine.

the vacuum give correlation coefficients 0.56 and 0.81, respectively.

To summarize, only the ΔH value allows the catalytic activity of amines to be predicted with a high accuracy: the higher the E_{LUMO} value and the higher ΔH in magnitude, the more active is the amine.

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