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CHEMICAL KINETICS AND CATALYSIS

Kinetics of Amine Catalysed Oxidation of Anthrone by Oxygen in Aprotic Solvents

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Abstract—Catalytic activity for the series of aliphatic and aromatic amines in liquid-phase oxidation of anthrone with molecular oxygen was studied gas-volumetrically and spectroscopically. It was shown that the studied amines are arranged in the following order of decreasing catalytic activity: $NH_3 > RNH_2 > R^1R^2NH > R^1R^2R^3N > ArNR^2$. A kinetic scheme for the process is proposed.

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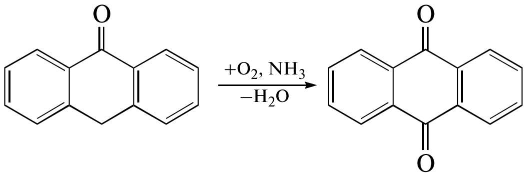
INTRODUCTION

Oxidation of organic compounds occurs selectively and efficiently in the presence of basic catalysts [1]. Anthrone is easily oxidized by an ionic mechanism in the presence of bases and ammonia.



The aim of this work was to investigate the influence of the catalyst structure of amine in the reactions of liquid-phase oxidation of anthrone with molecular oxygen and the influence of media on this process.

EXPERIMENTAL

The reaction kinetics was controlled volumetrically by the absorption of oxygen; the reaction was carried out with kinetic control. The initial concentration of anthrone in all experiments was equal to 0.05 M; $T = 307$ K. PMR investigations were carried out on a Bruker Avance II (400 MHz) apparatus.

Anthrone in DMSO is not oxidized with oxygen without the addition of amine, just as amines do not oxidize in different solvents without anthrone. The reaction proceeds rapidly in the presence of ammonia or aliphatic amines. Kinetic curves appear as saturated curves; after a certain amount of time, the absorption of oxygen by the solution comes to an end. The ratio of the amount of adsorbed oxygen at the end of the reaction to initial amount of substrate is stoichiometric (1 : 1). Anthrone is converted to anthraquinone almost completely (as was shown by PMR spectroscopy, the peaks corresponding to the CH_2 group of ketone at 4.5 ppm and the OH group of enol at 10.25 ppm disappear during the reaction, and the peaks of the aromatic protons of anthraquinone at 7.8 and 8.3 ppm are left); the presence of peaks of anthrone–triethylamine system at 6.8 ppm (3H, *t*) and 7.2 ppm (3H, *t*) indicates the formation of a side product in trace amounts: bianthrone [2]. Typical kinetic curves are presented in the figure.

Kinetic curves with a high correlation coefficient ($R^2 > 0.98$) are described by kinetic equation of the first order

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

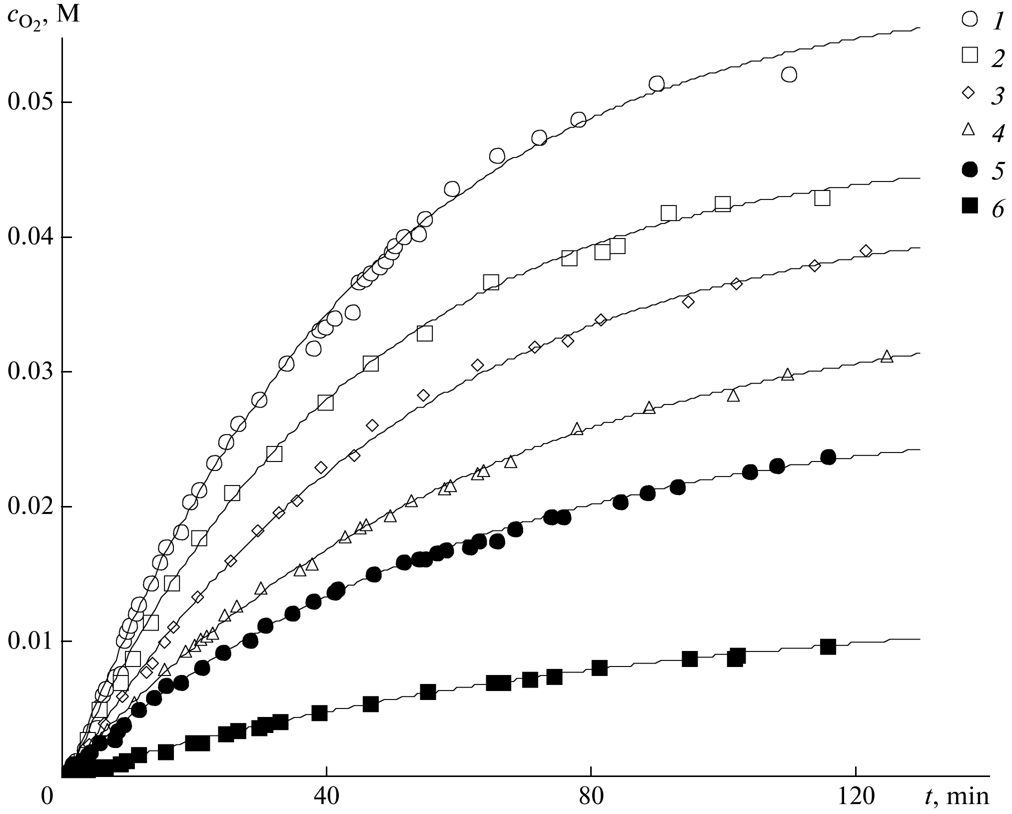
where $[O_2]_t$ is the volume of oxygen absorbed at moment, cm^3; $[O_2]_\infty$ is the volume of oxygen that would be absorbed if the reaction proceeded indefinitely, cm^3; k_{eff} f is the effective rate constant, s^{-1}; and t is time, s.

The values of the effective constants, as well as the other kinetic parameters given in Table 1, were obtained from experimental data using Eq. (1).

The partial rate constants for amine and anthrone were 0.5 and 1, respectively. As can be seen, the greatest catalytic effect is exhibited by the primary amines, while the least effect is exhibited by the tertiary amines.

It is entirely logical to assume that the catalytic effect must depend on the basicity of the catalyst. This tendency is generally observed; there was, however, no strict correlation between the rate of anthrone oxidation and the pK_a of amine (Table 2).

Among the properties of media, the most important factors affecting the kinetics and mechanism of reaction are permittivity (ε), basicity (B), polarity (μ), and the ability to form complexes with molecules of the substrate. A comparison of the initial reaction rates



Kinetic curves of oxygen absorption by anthrone in DMSO in the presence of trimethylamine (molar concentrations are (*1*) 0.0160, (*2*) 0.0080, (*3*) 0.0032, (*4*) 0.0016, (*5*) 0.0008, and (*6*) 0.0002); 307 K, 760 mm Hg.

and the literature data of the properties of the used solvents is given in Table 3.

Anthrone exists in equilibrium with its enol form, the occurrence of which depends on the ability of the solvent to form a complex with the substrate [6].

As can be seen, the change in the initial rate of oxygen absorption does not correlate with the polarity and correlates only weakly with permittivity ($R^2 = 0.73$). The best correlation is with basicity ($R^2 = 0.99$) and the equilibrium part of the enol ($R^2 = 0.97$).

The PMR spectrum of anthrone in DMSO-d_6 δ/ppm is 4.5 (s, $J = 0.02$ Hz, CH_2); in the range 7.4–8.3, there are peaks corresponding to aromatic protons $J = 0.11$, 0.11, 0.11, 0.1, 10.25 (s, $J = 0.04$ Hz, OH). According to the ratio of integral intensities, it was calculated that the equilibrium part of the enol form is 76%. No change was observed in 24 h.

According to the results of our PMR investigations, we may assert that in DMSO and acetonitrile mixtures with ratios of 1 : 1 and 2 : 1, the tautomeric equilibrium of anthrone–anthrol is attained slightly more slowly, and the equilibrium part of the enol form is proportionally less; this correlates with the rate of oxidation.

The influence of the partial pressure of oxygen on the initial rate of anthrone oxidation in the presence of amine is shown in Table 4.

The partial reaction rate constant by oxygen is equal to 1 in both DMSO and DMF.

The use of amines with aromatic rings near the amino group (primary, secondary and tertiary anilines) led to a rapid decline in the anthrone oxidation rate as compared to the use of aliphatic amines as catalysts.

It was shown by the examples of N,N-dimethylaniline, *p*-methylaniline and *p*-dibromaniline (c = 0.001 M) that the rate of anthrone oxidation remains constant and the catalytic effect is less pronounced than in the case of aliphatic amines. The rate of anthrone oxidation in DMF in the presence of N,N-dimethylaniline did not change with the change in the partial pressure of oxygen (from 450 to 760 mm Hg).

RESULTS AND DISCUSSION

The obtained kinetic data (rate constant by anthrone = 1; by oxygen = 1; by amine = 0.5) are in good agreement with the following brutto scheme of oxidation:

$$2A + RN \rightleftharpoons A_2 \cdot NR, \quad k_1, k_{-1}, \qquad (2)$$

$$A_2 \cdot NR \rightleftharpoons A^- + ARN^+, \quad k_2, k_{-2}, \qquad (3)$$

$$A^- + O_2 \longrightarrow AOO^-, \quad k_3, \qquad (4)$$

$$AOO^- + RN^+ \longrightarrow AO + RN + H_2O, \quad k_4, \qquad (5)$$

Table 1. Kinetic data on the liquid-phase oxidation of anthrone in the presence of amines of different concentrations (c)

c, M	$(k_{ef} \pm 0.001) \times 10^2$, s^{-1}	N_s/N_{O_2}	$(W_0 \pm 0.01) \times 10^5$, M/s
t-butylamine			
0.00024	0.028	1.0	1.20
0.0003	0.055	1.0	1.85
0.0006	0.067	0.9	3.31
0.0024	0.141	1.0	4.68
0.0095	0.132	1.0	5.91
Diethylamine			
0.0003	0.039	0.9	1.91
0.0006	0.071	1.0	2.57
0.0018	0.078	1.1	3.39
0.0024	0.097	1.1	4.07
0.0048	0.110	1.1	4.50
0.0095	0.105	1.1	4.95
Trimethylamine			
0.0002	0.003	1.0	0.26
0.0008	0.010	1.0	0.76
0.0016	0.014	1.0	0.99
0.0032	0.024	1.0	1.47
0.0080	0.036	1.0	1.86
0.0160	0.054	0.9	2.25
Triethylamine			
0.0001	0.008	1.0	0.53
0.0018	0.027	1.0	1.27
0.0036	0.056	1.0	1.36
0.0072	0.061	1.0	1.91
0.0090	0.074	1.0	3.25
0.0140	0.080	1.2	4.15

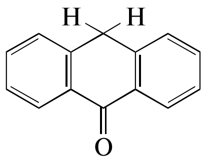
Note: W_0 is the initial rate of oxygen absorption by anthrone solution; N_s/N_{O_2} is the ratio of number of moles of substrate taken and oxygen absorbed at the end of the reaction.

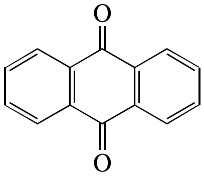
Table 2. Dependence of the rate on the structure of the catalyst

Amine (0.005 M)	$W_0 \times 10^5$, M s^{-1}	T, °C	pK_a [3]
t-butylamine	5.24	34	10.46
Diethylamine	4.49		10.93
Triethylamine	1.80		11.01
Trimethylamine	1.61		9.8
p-Bromaniline	0.45	80	3.91
p-Methylaniline	0.38		5.12
N,N-Dimethylaniline	0.29		5.06

Note: pK_a values are given for the aqueous solutions of corresponding amine

where $A_2 \cdot NR$, ARN^+ is the complex of anthrone with amine, and RN is the amine.


(A)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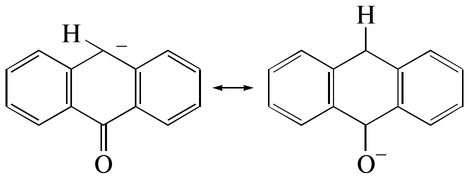
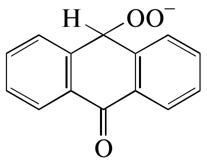

(A^-)


(AOO^-)

The rate of oxygen absorption is described by equation $\frac{dc_{O_2}}{dt} = k_3 c_{O_2} c_{A^-}$. Under the conditions of the experiment, $c_A \gg c_{RN}$; therefore, $c_A \approx c_{A_0}$, $c_{A_2 \cdot N} = c_x$; then, from $c_{RN} = c_{N_0} - c_x$.

Table 3. Initial rates of oxygen absorption by anthrone solution (0.05 M) in the presence of triethylamine (0.0072 M) in different aprotic solvents at 307 K and $p_{O_2} = 760$ mm Hg (x is the equilibrium part of enol)

Solvent	ε_{20} [4]	B, cm^{-1} [5]	μ	x, %	$W_0 \times 10^5$, M/s
DMSO	49	362	3.96	76	1.9
DMF	38	291	3.82	22	1.4
Acetonitrile	36	160	3.92	~0	0.5
Nitrobenzene	35	67	4.22	10	$<10^{-2}$
GMFA	30	–	–	–	$<10^{-2}$
Toluene	2	58	0.36	–	$<10^{-2}$

Table 4. Dependence of initial rates of oxygen absorption by anthrone (0.05 M) in aprotic solvents in the presence of triethylamine (0.0072 M) on the partial pressure of oxygen at 307 K

p_{O_2}, mm Hg	$(W_0 \pm 0.01) \times 10^5$, M/s	
	DMSO	DMF
150	–	0.28
380	0.88	0.60
512	1.21	–
580	1.43	0.93
760	1.93	1.12

If we have $K = k_1/k_{-1}$ and if $c_x \ll c_{N_0}$,

$$c_x = K c_{A_0}^2 c_{N_0}.$$

From Eq. (2),

$$c_{A^-} = \sqrt{c_x} = c_{A_0}(K c_{N_0})^{1/2},$$

$$\frac{dc_{O_2}}{dt} = k_{ef} c_{O_2} c_{A_0} \sqrt{c_{N_0}},$$

where $k_{ef} = k_3\sqrt{K}$.

CONCLUSIONS

Amines of different structure and origin are catalytically active in the reactions of anthrone oxidation in aprotic solvents. Amine behaves as common basic catalyst, facilitating the ionization of anthrone. Amines are arranged in the following order of decreasing catalytic effect: $NH_3 > RNH_2 > R^1R^2NH > R^1R^2R^3N > ArNR^2$.

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