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CHEMICAL KINETICS AND CATALYSIS

Anthrone Complexation with Aliphatic Amines in an Aprotic Medium

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Abstract—Aromatic ketone (anthrone) complexation with aliphatic amines is studied by UV–Vis, ^{1}H, ^{1}H–^{1}H COSY NMR spectroscopy. It is found that the catalytic activity of aliphatic amine is observed in the reaction of anthrone oxidation by molecular oxygen in aprotic media due to the formation of intermolecular complexes consisting of two anthrone molecules and one aliphatic amine molecule.

Keywords: oxidation, catalysis, mechanism, anthrone, molecular complex, addition product to carbonyl group.

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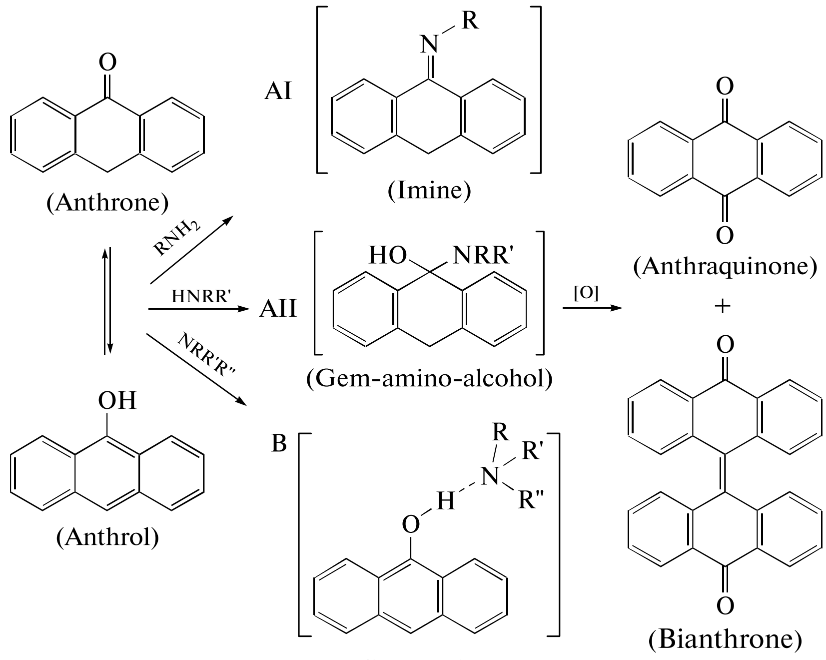
INTRODUCTION

Basic catalysis (particularly amine catalysis) is actively used to promote oxidation by molecular oxygen [1]. In [2], we studied in detail the kinetic features (the effect of reagent concentrations, oxygen pressure, and solvent nature) on aromatic ketone (anthrone) oxidation by molecular oxygen, catalyzed by amines in polar aprotic media. Based on our results, we proposed a mechanism for the process [2]. In this work, we consider in more detail one of its stages, i.e., complexation.

The catalytic effect of amines in such processes can manifest itself in two ways: one is the formation of amine adducts from a substrate carbonyl group (Scheme 1, A) [3]; the other is the formation of molecular complexes between the substrate and amine (Scheme 1, B) [4].



Scheme 1.

In this work, we studied the reaction of anthrone oxidation by molecular oxygen, resulting in the formation of anthraquinone and small amounts (1–3%) of bianthrone in aprotic media (dimethyl sulfoxide

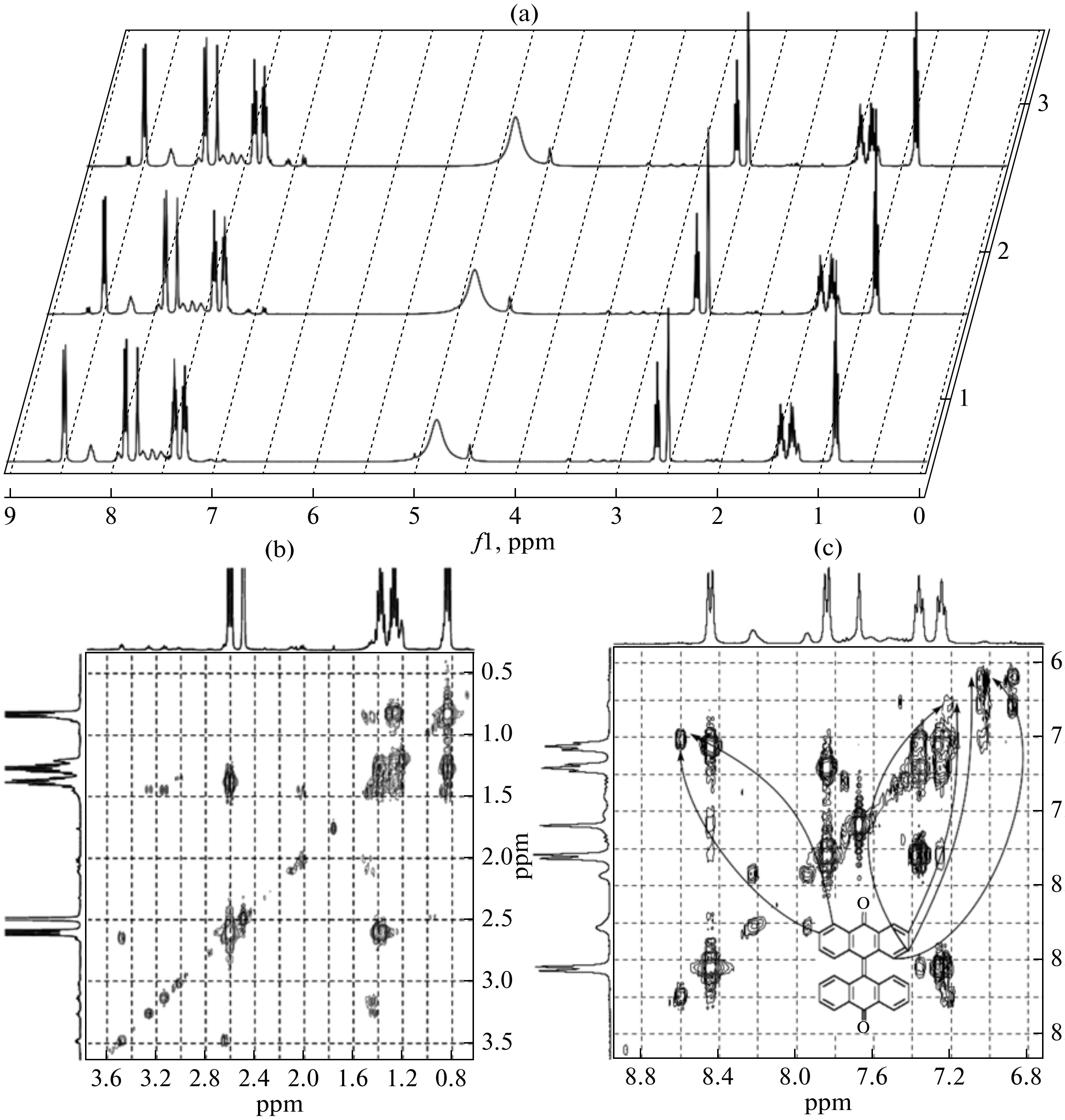


Fig. 1. NMR spectra of anthrone in the presence of *n*-butylamine in DMSO-d_6; (a) ^{1}H NMR spectra of anthrone in the presence of *n*-butylamine; DMSO-d_6, 400 MHz: *1*, immediately after mixing; *2* and *3*, in 15 and 30 min after mixing of reagents; (b, c) ^{1}H–^{1}H COSY spectra of anthrone solution in DMSO-d_6 in the presence of *n*-butylamine (400 MHz) in the regions of (b) aliphatic protons and (c) aromatic protons.

(DMSO), acetonitrile). The mechanism of anthrone activation by aliphatic amines (*n*-butylamine, diethylamine, and triethylamine) was studied in greatest detail via one-dimensional (^{1}H) and two-dimensional (^{1}H–^{1}H COSY) NMR and UV-Vis spectroscopy.

EXPERIMENTAL

Anthrone (Aldrich, 97%), acetonitrile (Merck, ≥99.5%), and DMSO-d_6 (Aldrich, ≥99%) were used without additional purification. *n*-Butylamine, diethylamine, and triethylamine were purified by distillation at atmospheric pressure. The purity was assessed by the refractive index agreement with reference data. NMR spectra were recorded using a BRUKER Avance II 400 spectrometer (400 MHz); spectra in the ultraviolet and visible regions were recorded using a Genesys 10 S UV-Vis (Thermo Electron Corp.) spectrophotometer. All experiments were performed at 25°C.

RESULTS AND DISCUSSION

Note that adducts can form with anthrone only primary and secondary amines, yielding imines (Scheme 1, A I) in the former case, and gem-amino-alcohols (II) in the second case (Scheme 1, A II). The existence of catalytic activity of tertiary amines [5] allows the con-

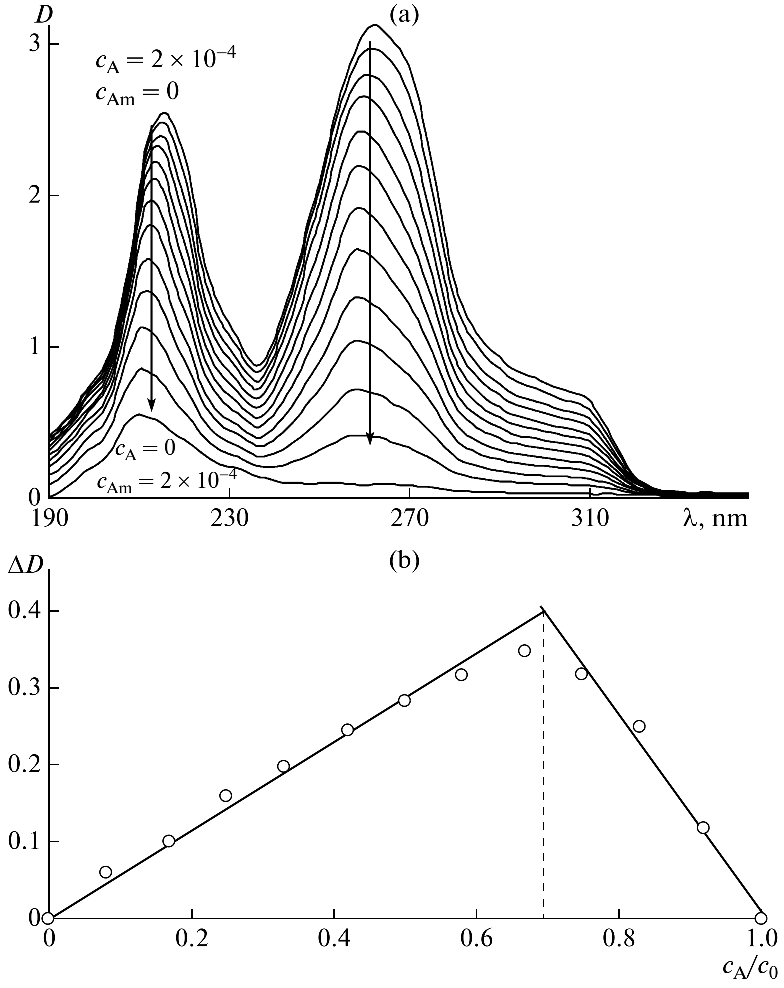


Fig. 2. Determination of the anthrone–amine complex stoichiometry via UV–Vis: (a) absorption spectra of the isomolar series of anthrone–triethylamine (2×10^{-4} mol/L) in acetonitrile at 298 K; (b) dependence of the optical density of the complex on the solution's composition (acetonitrile; 254 nm) at 298 K.

clusion that with anthrone, catalysis of the anthrone oxidation reaction cannot occur due only to adduct formation (AI, AII).

In series ^{1}H of NMR spectra of solutions of mixtures of both primary (Fig. 1a) and secondary amines with anthrone in DMSO-d_6, the signals at 6.8 (doublet), 7.05 (multiplet), 7.25 (a multiplet partially overlapped by the anthrol signal), and 8.55 ppm (doublet) increased in the region of aromatic protons over time. The presence of the corresponding cross peaks in ^{1}H–^{1}H COSY spectra (Figs. 1b and 1c) gives grounds to assert that these signals are associated with the same compound. Based on our analysis of the multiplicity and total peak intensity, this substance can be identified either as one of the by-products of anthrone (bianthrone) oxidation or as an amine adduct. However, the presence of the same signals in the spectra of anthrone solution in the presence of triethylamine, which cannot form adduct (AI, AII), and the lack of such signals, which could be attributed to aliphatic protons of a similar structure (see Figs. 1b and 1c) in the range of 0.50–4.00 ppm, allows the conclusion that they belong only to bianthrone. The unresolved signals at 8.21, 7.94, 7.61, 7.52 ppm, and the signal at 4.46 ppm in the spectra of Fig. 1 correspond to anthrone; the doublets at 8.44 and 7.84 ppm, the singlet at 7.68 ppm, and the triplets at 7.37 and 7.25 ppm are due to anthrol. None of the impurities existing in the region of aliphatic protons (in cases of both *n*-butylamine and diethylamine) cannot be attributed to protons of an adduct aliphatic fragment, as it is impossible to separate an appropriate set of cross peaks in ^{1}H–^{1}H COSY spectra (Fig. 1b).

Since no signals that could be attributed to adducts of primary and secondary amines formed by anthrone carbonyl groups were detected, we may conclude with a high degree of probability that the catalytic effect of amines is associated only with the formation of anthrone–amine molecular complexes. We detected anthrone–triethylamine complexes in a nonpolar medium (cyclohexane) using UV–Vis spectroscopy in [6]. In this work, we studied complexation in a polar solvent (acetonitrile). The complex's composition was determined using the standard procedure, i.e., by analyzing the isomolar series spectra by the Job method (the total concentration of complex components in solution is held constant while their ratio is varied; Fig. 2a) [7]. The method assumes that the solution contains two components (anthrone and amine) with molar concentrations c_A and c_{Am}, respectively, which form the A_mAm_n complex by the reaction

$$mA + nAm = A_mAm_n. \quad (1)$$

The dependence of the complex's content on the solution's composition has its maximum at a component ratio corresponding to stoichiometric coefficients in the complexation equation (Fig. 2b). The measure of the complex content in the solution is the optical density at the wavelength corresponding to the absorption band of the complex compound. Deconvolution of the measured spectra was performed to determine the maximum of the complex absorption band [8], and the spectra with a constant anthrone concentration and a gradually increasing amine concentration were recorded. Analysis of the results made it possible to determine the wavelength (~254 nm) corresponding to one of the absorption maxima of the formed complex. Since both components of the system under study absorb at the same wavelength, the measure of the complex content is the difference ΔD between the observed optical density and the one calculated from the extinction coefficients and component concentrations,

$$\Delta D = D_{obs} - (\varepsilon_A c_A + \varepsilon_{Am} c_{Am}), \quad (2)$$

where ΔD is the optical density of the complex, D_{obs} is the observed optical density, ε_A and ε_{Am} are the extinction coefficients of anthrone and amine, respectively.

Our data (table and Fig. 2) suggest that a complex consisting of two anthrone molecules and one amine molecule is formed in acetonitrile. These data are in good agreement with the earlier results on the anthrone oxidation kinetics catalyzed by amines: it was found that the reaction orders for anthrone and amine were 1 and 0.5, respectively, indicating the involvement of the anthrone–amine (2 : 1) complex in the proposed process mechanism [2]. Estimating the stability of this complex is an independent, rather complicated problem that will be solved in further studies.

The catalytic effect of aliphatic amines in the reaction of liquid-phase anthrone oxidation in polar aprotic media is thus associated with the formation of intermolecular complexes in ratio 2 : 1, rather than with adducts formed from carbonyl groups. Substratum activation is most likely achieved by facilitating the formation of the enol form (anthrol) in an aprotic polar medium and the subsequent detachment of protons from the anthrol molecule.

Isomolar anthrone--amine series at $\lambda = 254$ nm

$c_A \times 10^3$	$c_{Am} \times 10^3$	x_A	ΔD
0.200	0	1	0
0.184	0.016	0.92	0.12
0.166	0.034	0.83	0.25
0.150	0.050	0.75	0.32
0.134	0.066	0.67	0.35
0.116	0.084	0.58	0.32
0.100	0.100	0.5	0.28
0.084	0.116	0.42	0.25
0.066	0.134	0.33	0.20
0.050	0.150	0.25	0.16
0.034	0.166	0.17	0.10
0.016	0.184	0.08	0.06
0	0.200	0	0

Note: c_A and c_{Am} are the anthrone and amine concentrations, respectively, mol/L; x_A is the molar fraction of anthrone.

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