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Humic substances as catalysts in condensation reactions

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Abstract

Humic substances (HS) demonstrate appreciable impact on the rate of the condensation reactions as shown in the example of the reaction between hydrazine and 4-(dimethylamino)-benzaldhyde in an aquatic environment. The catalytic activity of HS has also been demonstrated in Knoevenagel and Claisen–Schmidt reactions for condensation of carbonyl compounds with CH acids. The aquatic fulvic acids are the most active in these reactions. The velocity of the studied reactions also depends on pH, temperature, the concentration and origin of HS used. A possible micellar and acid–base catalysis mechanism in aquatic media has been suggested. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Humic substances; Catalysts; Condensation

1. Introduction

Humic substances (HS) greatly influence soil fertility, and they play a principal role in the turnover of organic carbon (Peuravuori, 1992). HS form the major part of the organic component of soil, peat and natural waters, and they influence groundwater properties and the formation of fossil fuels (Klavins, 1998). HS are known to complex heavy metals and persistent organic xenobiotics (Stewart, 1984). The interaction of HS with xenobiotics may modify the uptake and toxicity of these compounds by aquatic organisms, and affect the fate of pollutants in the environment. Studies of humic matter have a history of more than 200 years, but many of their properties are not yet clear. Only recently has it been suggested that HS in natural environments exist in the form of micelles (Guetzloff and Rice, 1994). One of the humic properties which has been analysed somewhat is their catalytic activity, though HS contain many groups and structures which in similar macromolecules are responsible for their catalytic activity. This question is of special importance because micro-organisms are regarded as the main factor responsible for removal of organic xenobiotica (pesticides, PCB's, PHA's and many other substances), neglecting the role of HS. The catalytic activity of other biomolecules (proteins, nucleic acids) has been widely studied, but there are only a few publications in which catalytic activity of HS has been described (Dunnivant et al., 1992; Klavins, 1993; Moza et al., 1995; Kieber et al., 1999). The study of the catalytic activity of HS may be very important, considering their possible role in the fate of different xenobiotics and high concentrations in natural environments. At the same time, if HS exist as micelles, then they may also possess several structural features (for example, catalytic activity) common to micelles and widely studied for different reactions. Of different reactions, the velocity of which may be influenced by the presence of HS, condensation reactions should be mentioned first, they have been much studied to evaluate the acid–base and micellar catalysis. The aim of the present investigation

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was to study the catalytic activity of HS of different origin in the reactions of condensation. These reactions can be of importance in the fate of environmental pollutants.

2. Materials and Methods

Humic (HA) and fulvic (FA) acids were isolated from soil and peat by extraction with 0.1 M NaOH (Methods of Soil Analysis, 1999), but from water by the Malcom and Thurman method (Thurman and Malcolm, 1981). Concentrations of functional groups in HS were determined by standard methods NaOH (Methods of Soil Analysis, 1999). Commercial humic acid (CHA) was used for comparison (Aldrich). Properties of HS used are summarized in Table 1. UV spectra were obtained on Hitachi 850 spectrometer, but the velocity of the reaction has been studied using spectrometers HACH DR/2000, SF-46.

2.1. Condensation kinetics(4-(dimethylamino)-benzaldehyde with hydrazine)

To the solution (100 ml) of 4-(dimethylamino)-benzaldehyde (5×10^{-4} M, pH 2 adjusted with 6N HCl) in water, either (10 ml, 0.1 M) solution of catalyst (sodium dodecylsulphate or Triton X-100) or changing amounts of humic matter solutions (Figs. 1–4) were added (pH 2). In a quartz cell initial adsorption (A_0) and after addition of 1 ml of hydrazine sulphate (1×10^{-3} M, pH 2) absorption (A_t) of the reaction product (II) (468 nm) as a function of time was measured. After at least 10 half-lives, the absorption was measured for complete reaction (A_∞). Catalysis by buffer only (blank) was measured in the same fashion.

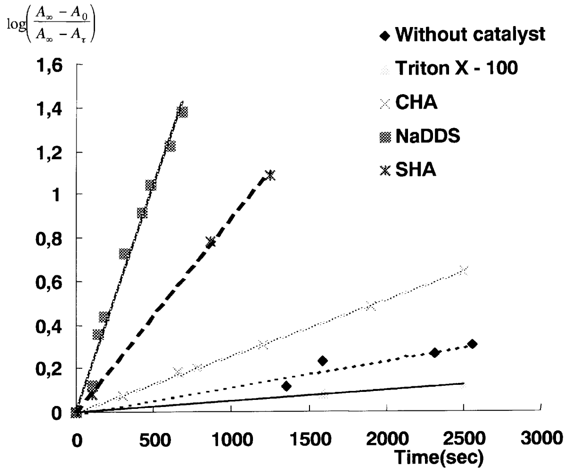


Fig. 1. Condensation of 4-(dimethylamino)-benzaldehyde with hydrazine: without catalyst and in the presence of humic acid and surfactants (◆ – without catalyst; • – catalyst – Triton X-100; × – catalyst commercial humic acid; ∗ – catalyst – soil humic acid; □ – catalyst – sodium dodecylsulphate).

The measured data were treated as first-order kinetics by plotting $(A_\infty - A_0)/(A_\infty - A_t)$ on a log scale vs time on a linear scale. The plots were straight lines for 70% conversion or more. The slope was taken as K_{obsd}.

2.2. Condensation reactions between carbonyl compounds and CH-acids

20 mmol of active methylene or methyl compound were dissolved in 50 ml of solvent (Table 2), containing 100 mg of HS or their $\mathrm{NH_4^+}$ salt, and 20 mmol of carbonyl compound were added. After stirring at heating (Table 2) the solvent had evaporated, and the residue was washed with 0.1 N $\mathrm{NaHCO_3}$, and the obtained product was recrystallized or distilled in vacuo. The yields and properties of substances isolated are summarized in Table 3.

Table 1
Properties of humic substances from water, soil and peat of Latvia

Humic substances		Elemental composition (%)			–COOH (mmol/g)	ArOH (mmol/g)
		C	H	N		
Humic acids						
River Salaca	AHA-S	54.60	3.70	0.93	3.83	2.86
Soil (Sod-podzolic)	SHA	48.89	4.76	3.91	2.45	1.86
Peat (Sece bog)	$\mathrm{P_S}$HA	48.11	5.60	1.95	–	–
Peat (Spigu bog)	$\mathrm{P_{Sp}}$HA	52.47	4.18	2.15	–	–
Peat (Olaine bog)	$\mathrm{P_O}$HA	52.34	4.28	3.86	2.26	1.48
Fulvic acids						
River Salaca	AFA-S	49.68	4.25	0.40	4.32	3.12
River Daugava	AFA-D	51.42	4.48	0.97	5.07	–
Lake Islienas	AFA-I	56.41	3.85	0.87	4.17	1.43

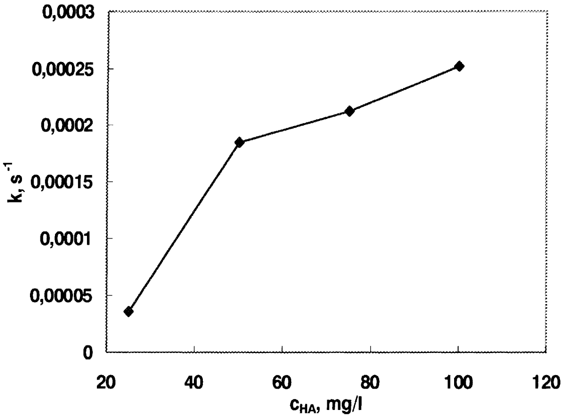


Fig. 2. Dependence of the humic acid (CHA) catalyzed condensation of 4-(dimethyl-amino)-benzaldehyde with hydrazine on pH.

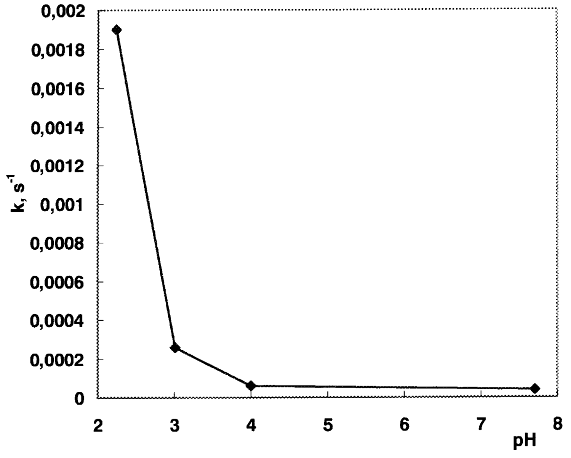


Fig. 3. Dependence of the humic acid (CHA) catalyzed condensation of 4-(dimethyl amino)-benzaldehyde with hydrazine on humic acid concentration.

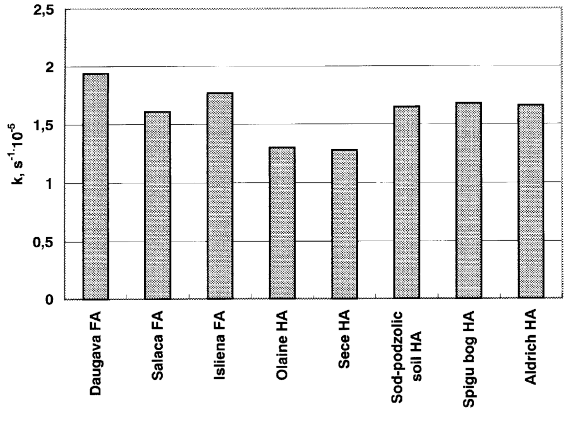


Fig. 4. Catalytic activity of vartious humic acids on condensation of 4-(dimethyl-amino)-benzaldehyde with hydrazine.

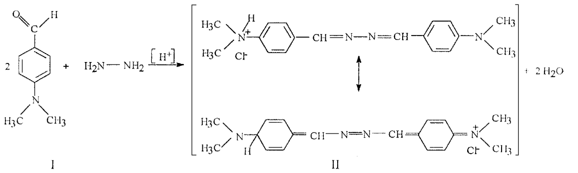
2.3. Condensation kinetics (4-(dimethylamino)-benzaldehyde with nitromethane)

Solution of 4-(dimethylamino)-benzaldehyde (25 ml, 0.2 M), nitromethane (25 ml, 0.25 M) and HS (Fig. 5) was stirred at heating. For 5 h at certain time intervals, 5 ml aliquots were taken off and the sorption of reaction product (4-dimethylamino-ω-nitrostyrene) at 435 nm was determined. The results of the condensation reactions are summarized in the Fig. 5.

3. Results and Discussion

HS were selected for catalytic activity studies to represent the common types of HS and they are comparable with reference samples and commercially available ones. The HS were isolated from soil, peat and water in Latvia and their properties were within the ranges, common for HS (Stevenson, 1982; Orlov, 1990). The dominant structures of HS are benzene and phenolecarboxylic acids (aromatic structural units), and residues of carbohydrates and mono- and dicarboxylic acid (aliphatic structural units) (Klavins et al., 1999). The molecular mass of the studied HS varied from 850 (aquatic fulvic acids) to ~10 000 (peat humic acids) Klavins et al., 1999).

We studied well-known (Roska et al., 1988) reactions of 4-(dimethylamino)-benzaldehyde condensation with hydrazine in the presence and absence of catalyst in aquatic media. The condensation of the 4-(dimethylamino)-benzaldehyde with hydrazine in the excess of the aldehyde goes with the formation of azine (II).



In acidic media, the azine passes into the colored protonated form. Because of the strong reversibility, the reaction was conducted in aqueous organic media in excess of the aldehyde, but as found previously in the presence of anionic surface-active substances, containing acidic groups, practically, a complete shift in the equilibrium toward formation of the azine takes place. The condensation was studied as a pseudo-first-order reaction. Investigations of condensation reaction kinetics (Fig. 1) show that HS act as catalysts. HS (soil humic acids) are poorer catalysts than sodium dodecylsulphate

Table 2
Typical experimental conditions in condensation reactions catalyzed by humic substances and their ammonia salt[a]

Active methylene (methyl) compound	R	Catalyst	Solvent	T (°C)	Time (h)	Product
$NCCH_2COOC_2H_5$	H	AHA-S	DMF	75	20	IIIa
Dimedone	NO_2	SHA	DMF	80	8	IVb
$PhCH_2CN$	H	SHA	Bz	75	15	Vc
Hydantoin	2,4-$(MeO)_2$	SHA—NH_4 salt	MeCN	75	20	VIa
MeCOPh	MeO	SHA—NH_4 salt	Bz	75	25	VIIf
$MeNO_2$	Me_2N	SHA—NH_4 salt	EtOH	65	10	VIId

[a] See general procedure.

Table 3
Properties and yields of condensation products

Product	Yield in presence of catalyst (%)	Yield of uncatalyzed reaction (%)	Melting point (°C) found (from the literature)	^{1}H-NMR(d ppm)
IIIa	58	51	49 (49 [Thurman and Malcolm, 1981])	1.42 (t, 3H), 4.23 (q, 2H), 7.33-7.39 (m, 5H), 8.13 (s, 1H)
IVa	64	28	194 (193 [Thurman and Malcolm, 1981])	–
IVb	38	16	230 (230 [Thurman and Malcolm, 1981])	1.12 (s, 6H), 1.29 (s, 6H), 2.40 (s, 8H), 5.51 (s,1H)
IVc	43	32	143 (144 [Zabicky, 1961])	–
Vc	32	18	95 (95-96 [Thurman and Malcolm, 1981])	3.08 (s, 3H), 5.82 (s, 1H), 6.64 (s, 1H),7.68 (m, 5H)
VIa	43	31	222 (222 [Stevenson, 1982])	–
VIIf	75	43	86 (85-87 [Stewart, 1984])	3.45 (s, 1H), 6.56 (s, 1H), 7.79–8.12 (m, 8H),
VIIIa	83	64	58 (58 [Stevenson, 1982])	–
VIIId	34	21	179 (179 [Stevenson, 1982])	2.25 (s, 6H), 5.06 (s, 1H), 5.45 (s, 1H)

and their catalytic activity differs from each other (if compared with commercial HA). But they are true catalysts, and better than nonionic surfactants and cationic surfactants, thus behaving as substances with acidic functional groups and existing in the form of micelles in aquatic media. The velocity of reactions also depends on the pH (Fig. 3) and the concentration of HS (Fig. 2) and is highest at low pH values.

Increase of HS concentration increased the velocity of the reaction. The velocity of the condensation reaction also depends on the humic matter origin and highest catalytic activity in the studied reaction demonstrates aquatic fulvic acids, but the lowest humic acids were isolated from peat (Fig. 4).

For a more detailed study of the condensation reactions, the Knoevenagel reaction has been selected. In the course of the reaction, an aromatic aldehyde reacts with methylene compounds activated by electron acceptor groups. The facility of the performed reaction is determined by the type and number of

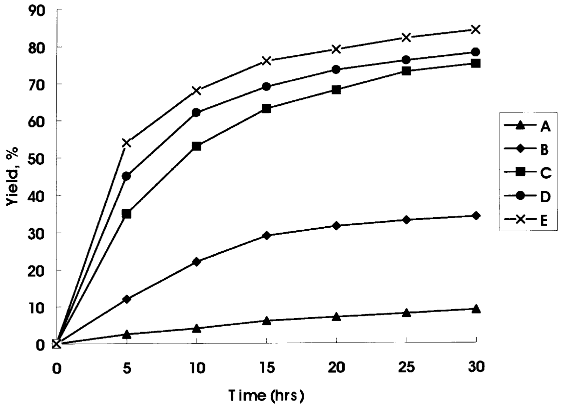
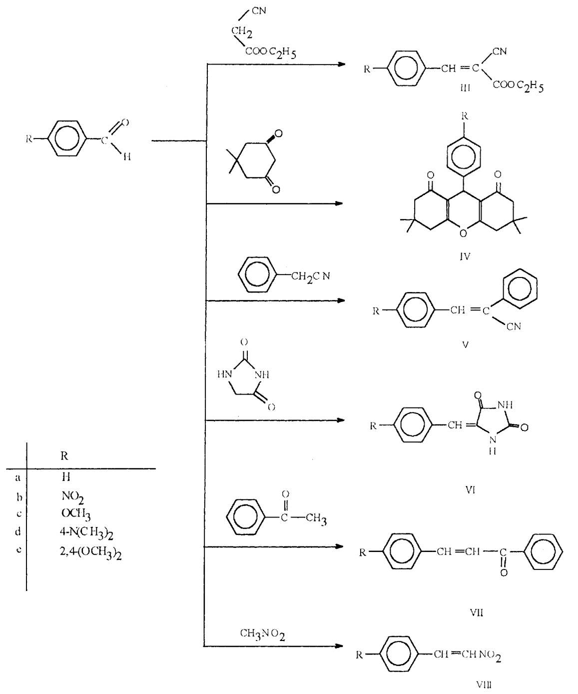


Fig. 5. Condensation of 4-(dimethylamino)-benzaldehyde with nitromethane: uncatalyzed and in presence of humic acid. A – without catalyst, solvent – acetonitrile; B – catalyst – soil humic acid, solvent – acetonitrile; C – catalyst – soil humic acid ammonia salt, solvent – benzene; D – catalyst – soil humic acid ammonia salt, solvent – acetonitrile, E – catalyst – soil humic acid ammonia salt, solvent – ethanol.

substituents in aromatic aldehydes as well as by the type of catalysts required (Jones, 1967), but commonly it is catalyzed by acids. These reactions can be realized in nonaquatic media isolating the condensation products preparatively. HA and FA are able to catalyze the condensation of ethyl cyanoacetate or of cyclic 1,3-diketones with aromatic aldehydes, and the products are formed with comparatively high yields, whereas reaction product yields for condensations between aldehyde and diethyl malonate or benzyl cyanide (requiring stronger acid for ionization of methylene group) are much lower. Condensations of heterocycles are also catalyzed by HS. Thus, benzaldehyde and hydantoin give a preparative yield of 5-benzylidenehydantoine (VIa), the yield being poor in the absence of HS (Table 3).



	R
a	H
b	NO_2
c	OCH_3
d	4-$N(CH_3)_2$
e	2,4-$(OCH_3)_2$

The study of Claisen–Schmidt condensation reaction between aromatic aldehydes and methyl compounds also demonstrates the catalytic activity of HS. In their presence (Table 2), the respective yields of chalcones (VII) and nitrostyrenes (VIII) obtained from the condensation reactions of aromatic aldehydes with acetophenone or nitromethane are higher by 5–15% (Table 3). It should be noted that condensation with nitromethane requires the presence of HS in the form of ammonium salts, whereas HA and potassium or trimethylammonium salts of HA fail to catalyze the condensation.

In the condensation of 4-(dimethylamino)-benzaldehyde with nitromethane, the reaction velocity increases with the increase of the humic acid ammonia salt concentration in the reaction mixture (Fig. 5).

4. Conclusion

The results showed that HS from water, soil and peat exhibit considerable catalytic activity in different condensation reactions and may influence the fate of pollutants in the environment. The rate of condensation reactions depends on the nature and concentration of humic substance, pH and temperature. The maximum catalytic activity is characteristic for aquatic fulvic acids, but the reaction mechanism possibly involves micellar catalysis (in aquatic media) or acid–base catalysis (in nonaquatic media).

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