Activity of basic catalysts in oxidation of 2-ethyl-5,6,7,8-tetrahydro-9,10-anthrahydroquinone

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Abstract

Oxidation of 2-ethyl-5,6,7,8-tetrahydro-9,10-anthrahydroquinone (ETHAHQ) by oxygen in a stirred reactor was studied. It was found that substances of basic character (organic amines, basic heterogeneous catalysts) could successfully catalyze this oxidation. Linear dependence of the oxidation rate on the basic compounds concentration was determined. This reaction can be also utilized for measuring the relative basicity of substances (catalysts) in organic solvents.
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1. Introduction

In general, physical and physicochemical methods are used for the prediction of catalyst activity. Their disadvantage is the requirement of a special modification of samples, observation of a catalyst under extraordinary conditions (e.g. very low pressure), difficult interpretation of results for real systems, necessity of combination of both, respectively. Furthermore, these methods often fail to characterize catalytic activity during reactions in liquid phase, i.e. the solvent can significantly affect the catalyst activity. For these reasons, chemical methods appear to be suitable and experimentally easy for the catalyst characterization.

Several test reactions are described for the determination of activity of heterogeneous basic catalysts: decomposition of isopropylalcohol [1–3], decomposition of 2-methyl-but-3-yn-2-ol [4], decomposition

of butane-1-ol [5]. These reactions are designed for a gas phase.

For testing of the catalyst activity in a liquid phase retroaldolization of 4-hydroxy-4-methylpentane-2-on [1] to acetone or aldolic condensation or isomerization of isophorone [6] were used. Knoevenagel condensation for both heterogeneous and homogeneous catalysts was described by Corma et al. [7,8]. They studied reactions of benzaldehyde with methylenic compounds of different acidities such as ethyl cyanoacetate (pK_a 9.0), ethyl acetoacetate (pK_a 10.7), ethyl malonate (pK_a 13.2) and ethyl bromoacetate (pK_a 16.5) without solvent. During reaction in liquid phase, however, solvents are often used whose effect on the course of a catalyzed reaction is negligible and hardly predicable. Therefore, the similarity between the conditions of the test reactions and the conditions of the intended catalyst use facilitates the data transferability to the real systems.

One of the characteristic properties generally known about amines is the ability of a basic behavior, which can be applied to a homogeneous catalysis.

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Nevertheless, no single opinion has yet been agreed on the chemism of amine basicity. The literature [9–12] provides several options how to test the basicity. However, the results differ depending on whether the basicity is measured in aqueous or organic environment, in gaseous phase, respectively.

Riddick et al. [9] emphasizes that the measured basic strength changes in dependence to the solvent used. There is no suitable measurement, which would express by an explicit physical quantity (as, e.g. conductance, boiling and solidification points, etc.). The ionization constants applied for comparison of basicities differ with every solvent and have to be individually determined in each solvent.

For determination of basicity in non-aqueous environments, methods were developed that measure basicity of a hydrogen bond between a base and an organic donor of the hydrogen bond (HB-donor). Therefore, the value of pK_{HB} represents the extent of basicity. Taft delineated the basic method [10] and

increase the electron density depends on the character of the solvent used. On the other hand, the experimental data show [12] that the changes of the basic force in dependence to the solvent used are surprising and unpredictable.

This finding inevitably leads to a proclamation that the basicity of substances is not a generally applicable property, but markedly depends on the measurement method used. The data applicability is always limited by their mode of acquirement. Basicity measured in various solvents is possible to apply only in arrangements with similar properties. It is apparent that the basicity of substances can not be generally predicated and the relative values are necessary to be acquired experimentally.

The aim of this work is the measurement of activity of basic substances (catalysts) in liquid phase. The Eq. (1) depicts the test reaction. This reaction is the basis for the production of hydrogen peroxide, which on industrial scale, proceeds without any catalyst action.

$$(1)$$
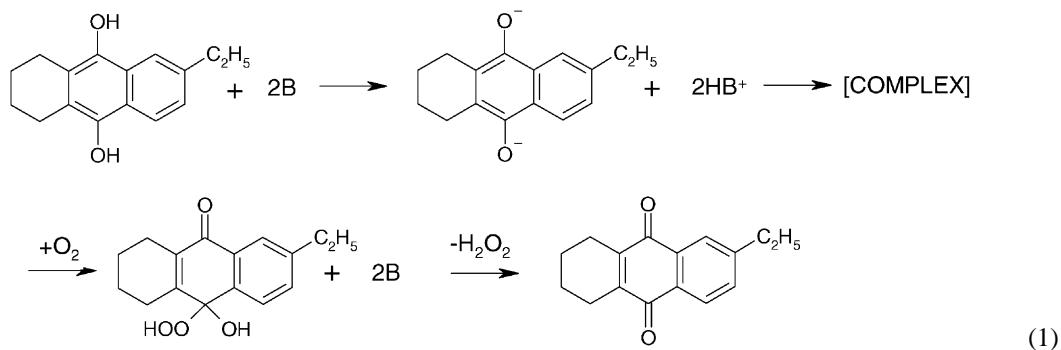
defined pK_{HB} as $\log(K_f)$ for a mixture of a base and a reference HB-donor. However, if the basicity is tested in other solvents, the results of this measurement differ from the basicities determined in CCl_4. Not only the change of a solvent brings about a change in the absolute value of the basic force, but also the changes in the relative values occur within an identical amine sequence.

Reyes and Scott [11] explain these changes of amines' basicity in various solvents by the formation of a specific hydrogen bond. The solvent's hydrogen atoms and amine eventually start interacting. The authors assume that an increase of basicity is the result of a growth of electron density occurring around the basic center (nitrogen atom of amine). This ability to

2. Experimental

2.1. Materials and reagents

The precursor of the substrate was a solution of 2-ethyl-5,6,7,8-tetrahydro-9,10-anthraquinone (ETHAQ) with concentration of $0.3\,mol\,l^{-1}$. The mixture of 2-ethylhexane-1-ol (30%) and xylene (70%) was used as the solvent. The substrate was prepared by hydrogenation of ETHAQ at the temperature of $60\,°C$ carried out to its 50% conversion. Two percent Pd/Al_2O_3, SiO_2 was used as the hydrogenation catalyst. Its concentration in the reaction mixture was $0.2\,wt.\%$. Thorough separation of the catalyst from

the substrate was achieved using gravity sedimentation and careful pipetting of the hydrogenated solution from its surface.

Amines, MgO and Lewatite MP 500 were tested during the work. Lewatite is the trademark for a macro-porous anion exchanger from Bayer Co. containing quaternary ammonium groups of type I anchored on 3D-net polystyrene. Solid catalysts were first pulverized and sieved to two fractions of <0.04 and <0.1 mm. Different fractions were prepared as to prove the elimination of pore diffusion.

2.2. Apparatus and measurement procedure

The apparatus [13] consisted of a glass stirred reactor and a gasometer burette of a volume of 100 ml calibrated to 0.2 ml. The gasometer burette served as an oxygen reservoir. The reactor as well as the burette was equipped with a tempered mantle.

The reaction (1) was carried out under atmospheric pressure. The stirring was procured by a Teflon-covered stirring element, propelled by a magnetic stirrer. The frequency was kept at $2600 \, \text{min}^{-1}$, which secured an ultimate aeration of the liquid reaction mixture. The accomplishment of the kinetic region was always verified. Five milliliters of the substrate was pipetted from a stock solution to the oxidation reactor. Prior to initiation of the oxidation reaction, the tested catalyst was added to the reactor, whose concentration ranged within the interval of 0.02–$250 \, \text{g} \, \text{l}^{-1}_{\text{(l)-phase}}$. After the catalyst was added, the air atmosphere contained in the reactor was exchanged by nitrogen and stirring initiated. After half an hour of stirring, a complete homogenization of the substrate and the catalyst was achieved. After homogenization of the reaction mixture, the nitrogen atmosphere was exchanged by oxygen. Oxidation was initiated by stirring. The time dependence of the oxygen consumption was recorded during the measurement. Immeasurable consumption of oxygen lasting already 15 min indicated the end of oxidation.

The stability of triethylamine under the reaction conditions of the discussed experiments was followed chromatographically. No significant concentration decrease of this simply oxidisable amine was observed during the reaction. Otherwise the possible amine transformation in the oxidation process must be reflected in kinetic variations of the catalyzed and noncatalysed reactions.

2.3. Evaluation of experimental data

The activity of catalysts can be compared to values of the oxidation rate constants of 2-ethyl-5,6,7,8-tetrahydro-9,10-anthrahydroquinone (ETHAHQ). Under a constant partial oxygen pressure, the oxidation course can be described by a simple exponential rate Eq. (2), where $r \, (\text{g} \, \text{l}^{-1} \, \text{s}^{-1})$ is the reaction rate, $c \, (\text{g} \, \text{l}^{-1})$ concentration of ETHAHQ, a the reaction order and k $(\text{g}^{1-a} \, \text{l}^{a-1} \, \text{s}^{-1})$ the oxidation reaction rate.

$$r = kc^a \tag{2}$$

Experimentally, it was found that the reaction order related to hydroquinone is $a = 0.6$. This value has been achieved regardless of whether oxidation was catalyzed or proceeded in the catalyst absence.

The relative rate constant was calculated from the values measured under identical reaction conditions for the substrate with catalyst and without the catalyst (Eq. (3)).

$$k_{\text{rel.}} = \frac{k_{\text{cat.}}}{k_{\text{no-cat.}}} \tag{3}$$

3. Results and discussion

3.1. Methods of measurement of ETHAHQ oxidation rate

Oxidation of ETHAHQ proceeds with a sufficient reaction rate, quantitatively even in the absence of a catalyst already under laboratory temperature. The oxidation rate-determining step is the hydrogen abstraction from hydroxylic group of hydroquinone, during which basic substances take a catalytic action.

With catalysts of a high relative activity, it is necessary to verify that the reaction proceeds in the kinetic region. For the measurement with very basic catalysts, it is advantageous to decrease the reaction temperature or decrease the substrate concentration. This way, it is possible to eliminate the effect of the external diffusion and achieve reliability in the acquired results. Fig. 1 implies that the dependence of the rate constant on the concentration of $(\text{Et})_2\text{-NH}$ and $(n\text{-Bu})(\text{Me})_2\text{-N}$
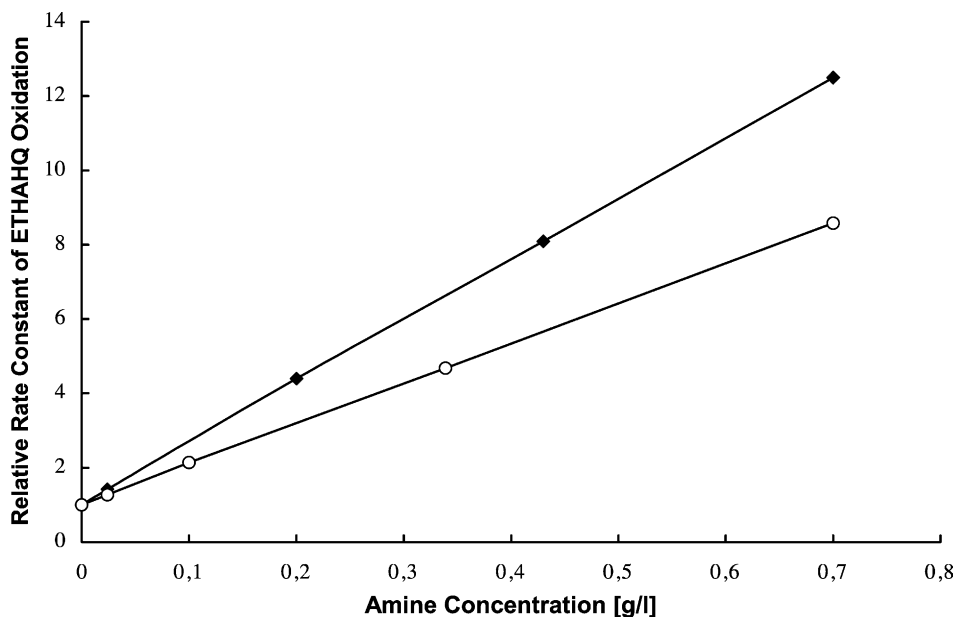
Fig. 1. Dependence of relative rate constant of ETHAHQ oxidation on concentration of $(n\text{-Bu})(\text{Me})_2\text{-N}$ (○) and $(\text{Et})_2\text{-NH}$ (◆). Substrate concentration: $0.3 \, \text{mol}/l_{\text{(l)-phase}}$; temperature: $0\,^\circ\text{C}$.

in the reaction mixture is linear in the entire measured interval.

Since the oxidation rate is of a positive order related to the substrate, decreasing its concentration can decrease the reaction rate. This fact was used during the activity tests of the basic Lewatite and MgO. A high concentration of these heterogeneous catalysts would decrease the aeration efficiency in the reaction mixture.
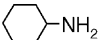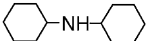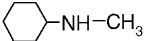
Fig. 2 transparently shows that the dependence of the rate constants on the concentration of solid catalysts is not as steep as in the catalysis of amines (Fig. 1) or during catalysis by aqueous solution of NaOH [14]. The linear dependence in the Fig. 2 offers an opportunity to utilize ETHAHQ oxidation for the determination of the relative activity of the basic catalysts. In the case of the catalysts A and B, it can be expressed, e.g. by the ratio $(k_{\text{cat.A}} - k_{\text{no-cat.}})/(k_{\text{cat.B}} - k_{\text{no-cat.}})$, in which the rate constants $k_{\text{cat.}}$ are measured at an identical catalyst concentration.

3.2. Effect of amines on ETHAHQ oxidation rate

The properties of amines are generally dependent on the degree of nitrogen substitution and the type of

a substituent. The effect of the number of alkyls on ETHAHQ oxidation rate was monitored using ethylamine, diethylamine and triethylamine. Table 1 shows the acquired oxidation rate constants. In the studied system, the ratio of activities of three ethylamines was

Table 1
Effect of amine substitution on ETHAHQ oxidation rate constant by oxygen

Amine	ETHAHQ oxidation rate constant $(g_{\text{ETHAHQ}}^{0,4} \, l_{\text{(l)-phase}}^{-1(0,4)} \, s)$	Relative oxidation rate constant
–	0.026	1.00
Et-NH$_2$	0.084	3.23
(Et)$_2$-NH	0.235	9.04
(Et)$_3$-N	0.218	8.39
⬡-NH$_2$	0.207	7.99
⬡-NH-⬡	0.148	5.71
⬡-NH-CH$_3$	0.222	8.55
(Ph)$_2$-NH	0.027	1.06
(n-Bu)$_2$-NH	0.256	9.84
(sec-Bu)$_2$-NH	0.124	4.77
(n-Bu)(Me)$_2$-N	0.077	2.96

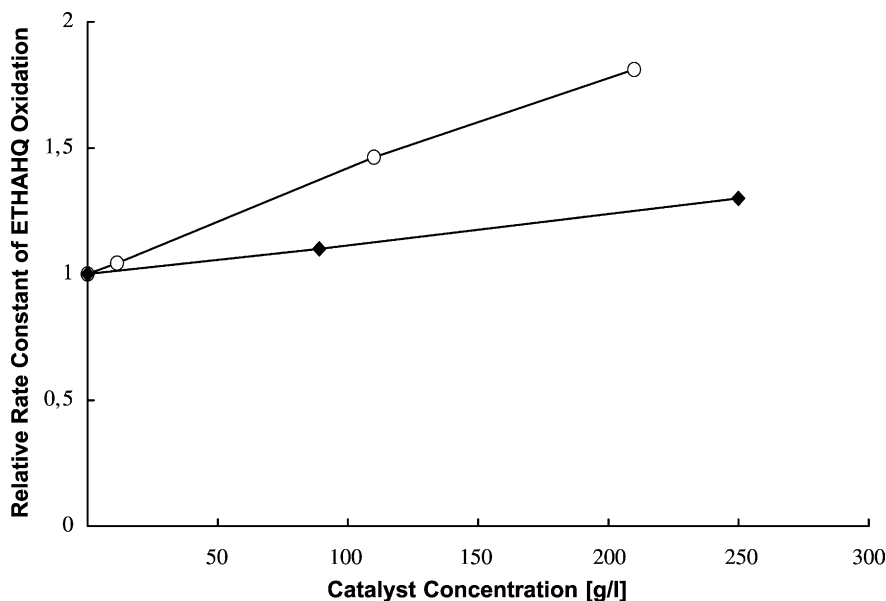Temperature: $30\,^\circ\text{C}$; amine concentration: $0.24 \, \text{g}/l_{\text{(l)-phase}}$.

Fig. 2. Dependence of relative rate constant of ETHAHQ oxidation on concentration of MgO (◆) and Lewatite (○). Substrate concentration: 0.075 mol/l$_{(l)\text{-phase}}$; temperature: 30 °C.

Et-NH$_2$:(Et)$_2$-NH:(Et)$_3$-N = 1.0:3.6:3.3. This result for ethylamines corresponds [15] not so well to pK_b ratios = 1.0:1.0:0.9.

The significant effect of alkyl in primary amines is apparent from the comparison of the effect of cyclohexylamine and ethylamine on the relative basicity (the ratio was 3.1).

Having compared the substrate oxidation rate in the presence of dicyclohexylamine and diphenylamine, a markedly different activity of these substances is also apparent, which is in correspondence with the theory on basicity of aromatic and aliphatic amines. The similar result was obtained at basicity comparison of pyridine and piperidine [7].

Having compared the relative activities of six secondary amines, it is apparent that a steric effect is predominant in their case. The example is the replacement of *n*-butylic alkyls with *sec*-butylic. In the presence of di-(1-butyl)amine, the rate constant of ETHAHQ oxidation is twice higher than of di-(2-butyl)amine.

A significant steric effect is also apparent from the comparison of basicity of cyclohexylamine and dicyclohexylamine, where the rate constant decreases with the number of alkyls. If methyl represents the alkyl of a low bulkiness integrated in a secondary amine, the positive induction effect of the second alkyl is more significant than the steric hindrance. This is clearly visible from an increase of the oxidation rate during transition from dicyclohexylamine to cyclohexyl-*N*-methylamine.

4. Conclusion

It was proved that the ETHAHQ oxidation rate is linearly increasing with an increasing concentration of basic substances. These substances affect the studied reaction as catalysts and this reaction can be used for the determination of their relative basicity. The described method suitable for the basicity testing offers an opportunity of a great choice of individual solvents (alcohols, esters, aromates, etc.) and their mixtures. Its primal advantage is the outstanding sensitivity to homogeneous catalysts, which enables the basicity testing already in catalytic amounts. The applicability of this method is limited by the solubility of a substrate, a homogeneous catalyst, respectively, in the selected solvent.

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