

EFFECT OF AROMATIC AMINES ON THE ACTIVITY OF COBALT BROMIDE OXIDATION CATALYSTS*

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Aniline and its derivatives except for diphenylamine positively affect the cobalt bromide-catalysed oxidation of alkylated aromatic hydrocarbons in acetic acid as solvent. This activity depends on reaction conditions, concentration, donor-acceptor properties of substituents, and particularly on steric relations. The oxidation is retarded by diphenylamine and accelerated by benzylaniline. At temperatures below 100°C, *o*-aminobenzoic acid and *p*-nitroaniline are almost indifferent and affect the activity of the catalyst to a low extent only. The activation effect manifests itself at higher temperatures. When the molar ratio of the aniline derivative to cobalt becomes higher than 2 : 1, the catalytic activity and selectivity decreases.

Most of the aromatic amines and their derivatives belong to efficient antioxidants of organic compounds¹. The inhibitory effect is also shown by combinations of amines with metals or salts of metals. By a suitable choice of the metal and the amine very efficient inhibitors of the oxidative aging of hydrocarbons can be prepared^{2,3}.

In addition to steric factors, the change of the metal reactivity due to the presence of nitrogen compounds also depends on ligands coordinated with the metal ion. Depending on the character of ligands bound to the metal, the addition of aromatic amines need not manifest itself in inhibition but on the contrary, in a very efficient and selective promotion of the oxidation reaction. As it will be shown below, this effect highly depends on functional groups attached to the aromatic amine ring system as well as on their steric relations.

EXPERIMENTAL

Aniline, *N,N*-diethylaniline, and *o*-anisidine were purified by distillation. *o*-Aminobenzoic acid, *N*-phenyl-*o*-aminobenzoic acid, and *p*-toluidine were purified by crystallisation. *N*-Benzylaniline was prepared from aniline and benzyl chloride⁴. *N*-Benzyl-*o*-aminobenzoic acid was prepared analogously. 2,2'-Azobis(2-methylpropionitrile) (AIBN) was purified by two recrystallisations from ether. Tetralin and mesitylene were shaken with conc. sulfuric acid, washed with

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water, dried, and distilled under diminished pressure in an inert atmosphere. The other chemicals were of the Analytical Grade and were used without any additional purification. The oxidation procedure and analysis of the oxidation mixture were the same as reported in an earlier paper³.

RESULTS

In order to examine the antioxidant activity of aromatic amines in the presence of acetic acid as solvent and in the absence of metal catalysts, the AIBN-initiated oxidation of tetralin was investigated. As it may be seen from Table I, diphenylamine, N,N-diethylaniline, and N-phenyl-*o*-aminoanthranilic acid exhibit also in polar media the properties of inhibitors of radical reactions and differ solely in the extent of the effect, particularly with respect to the reaction rate and the induction period. The other aniline derivatives shown in Table I are almost inactive as inhibitors (at 70°C).

In the presence of cobalt bromide catalysts, the influence of aromatic amines becomes more complex and different in most cases. Figures 1, 2, and 3 show the effect of aniline derivatives substituted on the ring or on the nitrogen atom on the cobaltous bromide catalysed oxidation of mesitylene in acetic acid. It may be seen that small changes in the structure and steric arrangement of the nitrogen compound result in considerably different effects on the oxidation. There are affected oxidation rates, induction periods, and also (as it may be inferred from Table II) the reaction times and yields of trimesic acid. Under a given ratio of the cobalt atom to the bromine

TABLE I
Inhibitory Effect of Amines on the AIBN-Initiated Oxidation of Tetralin at 70°C

Amine	Relative rate in oxidation	
	tetralin ^a	1·83M tetralin in acetic acid ^b
—	1·0	1·0
Acetanilide	—	1·0
N,N-Diethylaniline	0·71	0·2
<i>p</i> -Nitroaniline	—	1·0
Diphenylamine	0·07	0·08
<i>o</i> -Aminobenzoic acid	0·94	1·0
N-Phenyl- <i>o</i> -aminobenzoic acid	0·25	0·54

^a 0·10M-AIBN, $2·0 \cdot 10^{-2}$ M-amine; $r_{\text{tetralin}}^0 = 3·78 \cdot 10^{-5} \text{ mol l}^{-1} \text{ s}^{-1}$. ^b 0·05M-AIBN, $2·75 \cdot 10^{-2}$ M-amine.

atom, the activity of the catalyst not only depends on the character and structure of the nitrogen compound but also on the molar ratio of the nitrogen compound to the cobalt atom (Figs 4 – 6).

DISCUSSION

In the cobalt bromide catalysed oxidation of alkylated aromatic hydrocarbons in acetic acid as solvent, the aromatic amines mostly act as oxidation promoters

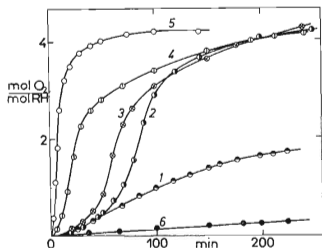


FIG. 1

Effect of N-Substituted Aniline Derivatives on the Oxidation of 1,2-Mesitylene in Acetic Acid at 140°C and 11 atm Catalysed by $1.82 \cdot 10^{-2} \text{M-CoBr}_2 \cdot 6 \text{H}_2\text{O}$

Molar ratio cobalt/amine 1 : 2. 1 No amine, 2 N-benzylaniline, 3 aniline, 4 benzylamine, 5 N,N-diethylaniline, 6 diphenylamine.

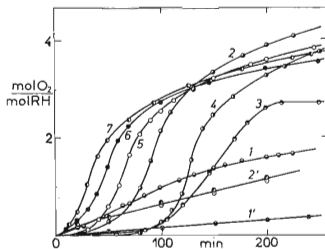


FIG. 2

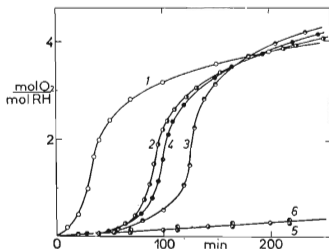
Effect of Ring-Substituents on the Activity of Aniline

Conditions: 140°C, 11 atm, 1.23M mesitylene, $1.82 \cdot 10^{-2} \text{M-CoBr}_2 \cdot 6 \text{H}_2\text{O}$, cobalt : aniline 1 : 2; 1 no amine 1' no amine but at 100°C, 2 *p*-phenylenediamine, 2' *p*-nitroaniline but at 100°C, 3 *o*-phenylenediamine, 4 *o*-anisidine, 5 *p*-toluidine, 6 *o*-nitroaniline, 7 *p*-nitroaniline.

FIG. 3

Effect of N-Substituted Aminobenzoic Acids on the Oxidation of Mesitylene

For conditions see Fig. 2; 1 *p*-aminobenzoic acid, 2 N-benzyl-*o*-aminobenzoic acid, 3 N-phenyl-*o*-aminobenzoic acid, 4 *o*-aminobenzoic acid, 5 *p*-aminobenzoic acid but at 100°C, 6 in the absence of *o*-aminobenzoic acid at 100°C.



while the inhibitory effect is limited to special cases only depending on the structure of the amine.

The catalytic activity of cobaltous bromide is considerably affected by N-alkyl and N-aryl derivatives of aniline. Furthermore, the activity can be increased or decreased depending on the steric relations of the nitrogen compound which affect the probability of the mutual interaction between the amine and the central metal. It may be seen from Fig. 1, that replacement of two hydrogen atoms in the amino group of aniline by ethyl groups results in a manyfold increase of the catalytical activity manifesting itself in a substantial increase of the oxidation rate. Substitution of the amino group in aniline by one phenyl or one benzyl group results in quite different effects. Whereas the presence of diphenylamine almost completely inhibits the oxidation, N-benzylaniline acts similarly to aniline and accelerates the oxidation.

TABLE II

Dependence of the Yield of Trimesic Acid on the Presence of Aromatic Amines in Oxidation of Mesitylene in Acetic Acid

Experimental conditions: 140°C; 11 atm; 1.23M mesitylene; $1.82 \cdot 10^{-2}$ M-CoBr₂ · 6 H₂O; cobalt/aromatic amine 1 : 2.

Aromatic amine	Reaction time min	Yield of acids, mol%	
		5-methyliso- phthalic	trimesic
No amine	210 ^a	8.4	1.2
No amine ^b	310 ^a	0.0	—
Aniline	280	5.1	78.8
Benzylamine	240	4.2	80.4
N,N-Diethylaniline	140	6.2	80.6
Diphenylamine	240	—	—
N-Benzylaniline	300	7.4	70.2
<i>p</i> -Toluidine	330	5.9	77.4
<i>o</i> -Anisidine	380	4.4	78.5
<i>o</i> -Nitroaniline	375	16.2	50.1
<i>p</i> -Nitroaniline	365	15.5	51.6
<i>p</i> -Nitroaniline ^b	300 ^a	2.9	0.0
<i>p</i> -Phenylenediamine	300 ^a	8.6	72.6
<i>o</i> -Phenylenediamine	220	37.1	2.9
<i>o</i> -Aminobenzoic acid	310	4.3	77.8
<i>o</i> -Aminobenzoic acid ^b	310 ^a	0.0	—
<i>p</i> -Aminobenzoic acid	300	4.9	77.6
N-Phenyl- <i>o</i> -aminobenzoic acid	315	4.4	76.7
N-Benzyl- <i>o</i> -aminobenzoic acid	320	3.9	72.8

^a The oxidation continued; ^b reaction temperature 100°C.

The inhibitory activity of diphenylamine (in contrast to the effect of other N-substituted anilines) might be ascribed to a kinetically significant steric hindrance in the cobalt–nitrogen bond formation, or, diphenylamine could exhibit in the reaction medium an independent activity, as an inhibitor of radical reactions. This idea is supported by results of conductivity measurements and by spectra. Thus for example the reaction of cobaltous bromide with diphenylamine was not accompanied by changes in conductivity that are usual with other nitrogen compounds. In spectral measurements in the visible region, the absorption of the cobaltous bromide band at 14650 cm^{-1} was decreased by the presence of a twofold concentration of diphenylamine by about 10% only; this decrease is very low when compared with that due to the presence of other amines⁵.

The inhibitory effect of diphenylamine which is probably due to the hindrance in the formation of the cobalt–nitrogen bond, may be circumvented by lengthening the distance between the two benzene nuclei by one methylene group. The greater accessibility of the nitrogen atom in N-benzylaniline for the bond formation with cobalt results in a manyfold increase of the oxidation rate and in improved yields of trimesic acid. These steric effects assert themselves to a lesser extent in the series aniline, benzylamine, and N-benzylaniline.

The ring-substituted aniline derivatives also exhibit in most cases a high promotive effect (Fig. 2). With some amines such as *o*-anisidine, long induction periods result in considerably long reaction times but notwithstanding (as it may be seen from Table II), the yields of aromatic acids are similar to those obtained in the presence of aniline.

Substitution of aniline by nitro groups results in longer reaction times and a decreased selectivity of the reaction. The amino derivatives of aniline capable of producing chelate structures with metals such as *o*-phenylenediamine, are not suitable as activators of cobalt bromide catalysts; after a certain period of time, the oxidation is spontaneously interrupted in their presence. A different behaviour may be observed in the case of *o*-aminobenzoic acid and its N-substituted derivatives that also belong to strong chelate-forming compounds (Fig. 3). Only the nitrogen atom of compounds of this type should be involved in the complex formation in order to keep the cobalt–bromine atom bond of the catalyst intact. The carboxylic group does not play any important role in the complex formation but only affects the steric and electron properties of the nitrogen atom (Table I). It is of interest to compare the effect of *o*-aminobenzoic acid with that of *p*-aminobenzoic acid which cannot form chelates. When some differences are omitted in the initial stage of the oxidation process that are probably due to the steric effect of the carboxylic groups in the *ortho* position or to a potential formation of a weak chelate, the same yields of trimesic acid are obtained in the presence of both *o*- and *p*-aminobenzoic acids. Small differences are also observed in activation effects of *o*-aminobenzoic acid and its N-phenyl and

N-benzyl derivatives. Nevertheless, in the cobalt bromide catalysed oxidation of mesitylene in acetic acid, diphenylamine is inhibitor and N-phenyl-*o*-aminobenzoic acid is an efficient promotor in spite of the identical bonding of the nitrogen atom.

As mentioned above, the activation effect of the present aromatic amines is highly influenced by steric factors. Of a lesser importance are the properties of the electron-donor nitrogen atom affected by electron-releasing and electron-withdrawing substituents. Thus, no correlation was found between the basicity of nitrogen compounds and their activation effects in the oxidation of mesitylene. Furthermore, despite some differences in pK_a constant values of amines that can be expected in acetic acid in water, the differences in activation effects of amines are very high^{6,7}. No linear dependence was observed between stability constants of complexes of co-

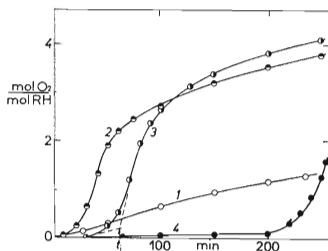


FIG. 4

Dependence of the Catalytic Activity on the Concentration of N,N-Diethylaniline

Conditions: 140°C, 11 atm, 1.23M mesitylene, $1.82 \cdot 10^{-2}$ M cobalt, $9.1 \cdot 10^{-3}$ M bromide (a mixture of CoBr_2 and $(\text{CH}_3\text{COO})_2 \cdot \text{Co}$), the ratio of N,N-diethylaniline to Co: 1 zero, 2 1 : 1, 3 2 : 1, 4 3 : 1.

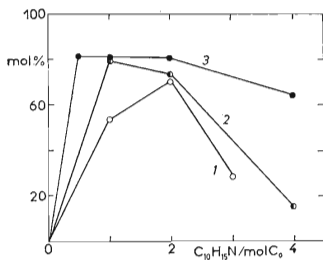


FIG. 5

Dependence of the "Induction Period" t_i on the N,N-Diethylaniline/Cobalt Ratio for the Co/Br ratios, 1 1 : 0.5, 2 1 : 1, 3 1 : 2, For the experimental conditions see Fig. 4.

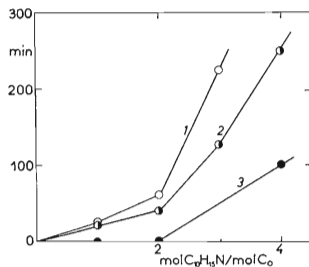


FIG. 6

Dependence of the Yield of Trimesic Acid on the N,N-Diethylaniline/Cobalt Ratio for Various Co/Br Ratios (Fig. 5)

baltous chloride with aniline and its derivatives in acetone and their Hammett constants⁸. The change of the reaction entropy which accompanies the formation of the metal-ligand bond, is influenced by steric factors in the molecule of the amine. As it may be inferred from thermodynamical and spectral data, this contribution is rather high in the case of *ortho* substituted and N-substituted derivatives of aniline⁹⁻¹¹.

The nitro and carboxylic derivatives of aniline readily produce intermolecular or intramolecular structures. In acetic acid, such derivatives exhibit a very low conductivity⁵ and cannot be titrated with cobaltous bromide even at 90°C. In acetic acid at 70°C in the absence of metals, these derivatives do not inhibit the oxidation (Table I). As it may be seen from Figs 2 and 3, the cobalt bromide catalysed oxidation of mesitylene is not affected at 100°C by these derivatives. At temperatures above 100°C, the hydrogen bonds are loosened in acetic acid as solvent and a complex with cobalt is formed. As a consequence, the catalytic activity considerably increases and the yields of trimesic acid are higher (Table II).

In general, the ring-substitution of aniline by methyl, methoxyl, carboxyl, amino or nitro groups has a negative effect on the activity of the cobalt bromide catalysts.

In the evaluation of the oxidation rate, selectivity, and yields of aromatic acids at a constant ratio of the cobalt atom to the bromine atom, also the effect of the ratio of the nitrogen compound to cobalt must be taken into account. In the case of the highly active N,N-diethylaniline, higher ratios than 1 : 1 with respect to cobalt result in a rapid increase of the „induction period” t_i (Fig. 4). The t_i is defined as the time necessary for acquirement of the maximum rate. The growth of the t_i value is exponential and the faster, the lower is the concentration of the bromine atom in the system (Fig. 5). The yield of trimesic acid rapidly increases with an increasing concentration of the amine up to a maximum and then decreases. The position of the maximum depends on concentration of the bromine atom in the whole system since with lower concentrations it is shifted to higher ratios of the amine to cobalt (Fig. 6).

Dependence of the catalytic activity on the ratio of the main components of the complex, Co : Br : amine, is in connection with the formation of active cobalt bromide complexes. In accordance with the hitherto published papers, a decrease of the concentration of the bromo atom results in a decreased activity of the catalyst and a decreased rate of the oxidation process. By coordination with suitable nitrogen compounds, this decrease of the activity of the catalyst can be compensated or, more frequently, increased to a manyfold extent. The increase occurs in the case of optimum concentrations of amines. In excess of amines, the activity decreases due to transformations of cobalt bromide complexes by reactions similar to those discussed in the preceding paper. In these cases, when the aromatic amine in the absence of cobaltous bromide acts in acetic acid as inhibitor of radical reactions, it is no more bound into complexes when present in a high concentration in the system, and, in addition

to transformations of complexes and effect on their equilibrium concentration, the action of the amine in the solution is independent, *i.e.*, increases the t_i value.

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