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Effect of Solvent and Catalyst on the Liquid-phase Oxidation of *p*-Tolualdehyde

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The liquid-phase oxidation of *p*-tolualdehyde was studied at 20 °C and atmospheric pressure in a glass reaction apparatus. The total rate of oxidation was found to depend on the solvent; decreasing in the order: ethyl acetate > ethyl methyl keton > chlorobenzene ~ benzene > acetic acid > ethanol > acetonitrile. After an initiation period, the reaction was found to be about 1st order with respect to *p*-tolualdehyde in ethyl acetate solution.

Transition metal salts in solution may accelerate or retard the reaction. Thus, with a metal salt concentration of 10^{-3} mol/l in ethyl acetate solution the aldehyde oxidation rate decreased in the following order: V ~ Fe > Co > Mn > Ni ~ Cu > uncatalyzed > Ti > Mo > tetrabutylammonium bromide > Cr. Ni-acetylacetonate at higher concentrations than about 5×10^{-3} mol/l completely inhibited the reaction. The selectivity to peracid after 3 h of reaction decreased in the following order: uncatalyzed > Ni > Fe > Cu > Ti > Mo > Co > Cr > V ~ Mn with a salt concentration of 10^{-3} mol/l.

Liquid phase oxidation of aldehydes is of considerable interest for production of peracids and acids.[1,2] Although the literature shows a large number of papers on oxidation of aldehydes,[3] especially benzaldehyde,[4–14] little but patents has been published about the oxidation of *p*-tolualdehyde.[15]

The autoxidation of aldehydes follows a radical mechanism.[16] The reaction may be thermally or or photo-chemically initiated, the thermal initiation is dominating at higher temperatures, while the photo-chemical initiation may be dominating at lower temperatures.[3,14a] Different types of initiators may also be added.[17] Some transition metal salts are known to accelerate the oxidation of aldehydes.[3,17] The overall kinetics of the autoxidation of aldehydes seems to depend on the nature of the aldehyde and the solvent and on the experimental conditions.[8,10,14,17]

The main purpose of the present work was to investigate the effect of the solvent and the effect of some transition metal salts on the oxidation of *p*-tolualdehyde in the liquid phase.

EXPERIMENTAL

Reagents. p-Tolualdehyde "pure" from Koch-Light Laboratories Ltd. was distilled in an atmosphere of nitrogen at 90 Torr pressure and 135–136 °C. Most of the solvents used were of *p.a.* quality from Merck. *Chlorobenzene* "zur Synthese" from Merck was distilled. *Potassium iodide p.a.* and *titrisol* 0.1 N of *sodium hydroxide, sodium thiosulfate* and *hydrochloric acid* were from Merck. *Chromium(III)* and *iron(II) acetylacetonates* of "pure" quality from Koch-Light Laboratories. *Acetylacetonates* of *cobalt(II), copper(II), molybdenyl, nickel(II), titanyl,* and *vanadium(IV) oxide* were all "zur Synthese" from Merck. *Manganese(II) acetate p.a.* from Merck. *Tetrabutylammonium bromide "purum"* from Fluka AG. *Oxygen* and *nitrogen* were of high purity.

Apparatus. The oxidation reactions were carried out in a glass apparatus made by Otto Fritz GmbH, Western Germany. The apparatus is shown in Fig. 1. The reactor A (volume 50 ml) has a temperature control jacket B. The gas burette C is surrounded by a temperature control jacket D. The mercury levelling vessel E is connected to the burette through a PVC tube. The reactor is equipped with a magnetic stirrer F, and a 6 V, 35 W lamp K. The reactor is shielded from other light sources by aluminium foil L on the outside. The tube connection G is for the vacuum line and/or

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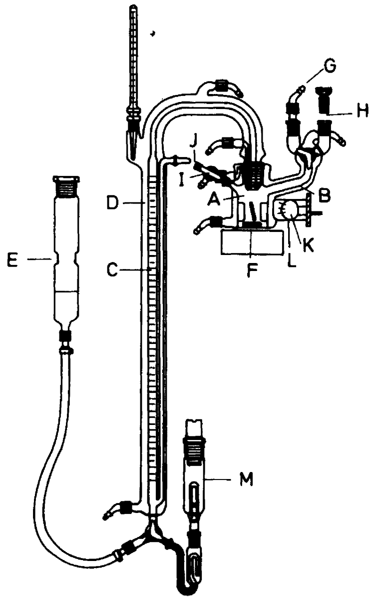


Fig. 1. Apparatus for liquid phase oxidation.

the (oxygen/nitrogen) gas line. Liquid may be filled into the reactor through the inlet H. Injections or samples may be taken through the nipple I which is closed by a silicon rubber septum J. The reaction system may be closed by stopcocks. With no mercury in the burette, gases may be brought to flow through the burette and the gas absorption tube M.

Procedure. The temperature of the reaction apparatus was kept constant at 20 °C by circulating water from a thermostat bath. The reactor and the burette were filled with oxygen, and 30 ml of solvent or catalyst solution was transferred to the reactor. The desired amount of *p*-tolualdehyde was injected into the reactor, and the magnetic stirrer and the lamp were switched on. The consumed volume of oxygen was measured as a function of time at a constant pressure of 1 atm.

Liquid and gas samples for analysis were in most cases taken at the end of an experiment. Principally, accumulated carbon dioxide in the system may then be determined by absorption, but gas chromatographic analysis was generally preferred.

In some experiments liquid samples (2 x 2 ml each time) were taken during the oxidation. The initial liquid volume in the reactor was then 48 ml, and oxygen was fed continuously from the line to the reactor. Oxygen consumption in these cases was consequently not measured.

The liquid samples were analyzed for total acid by titration with standard sodium hydroxide solution using thymolphthalein as indicator. Peracid was determined iodometrically by titration with standard sodium thiosulfate solution. Unconverted *p*-tolualdehyde and toluene were determined with a Pye Unicam GCD gas chromatograph connected to a Perkin-Elmer PEP-2 integrator system. The gas chromatograph was equipped with thermal conductivity detector, and a 1.5 m x 4 mm glass column packed with 3 % methyl silicon gum (E 30) on Diatomite CQ, 100 – 120 mesh.

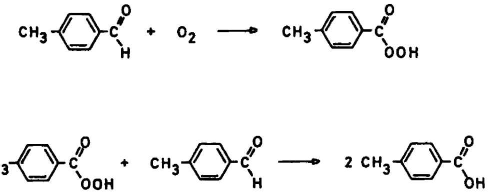
Gas analysis was accomplished with a Varian 90 P gas chromatograph equipped with thermal conductivity detector, and a two column system. One internal column (at 100 °C) 3 m x 6 mm was packed with Porapak Q, 80 – 100 mesh, and another external column (at 20 °C) 3 m x 6 mm was packed with Molecular Sieves 13 X, 80 – 100 mesh.

RESULTS AND DISCUSSION

Preliminary results showed that the rate of oxidation of *p*-tolualdehyde was dependent on light. Therefore it was important for the present investigation to have a fixed light source. In a dark reactor at 20 °C there was no measurable reaction within 3 h. even with some of the catalysts. Light is known to have a strong effect on the autoxidation of benzaldehyde.[14a,16a,18]

Light of wavelength > 300 nm is transmitted through the glass from the tungsten lamp. The UV spectrum of *p*-tolualdehyde showed only a small absorption above 300 nm, the main $n \rightarrow \pi^*$ absorption being below.

The oxidation of *p*-tolualdehyde at 20 °C gave primarily the corresponding peracid; the only other main product was *p*-toluic acid which may be formed by the Baeyer-Villiger reaction:[6,19]



The effect of different solvents on the oxidation of *p*-tolualdehyde was measured as shown in Fig. 2. The reaction is seen to be autoaccelerating at the beginning. The maximum rate of reaction is defined as

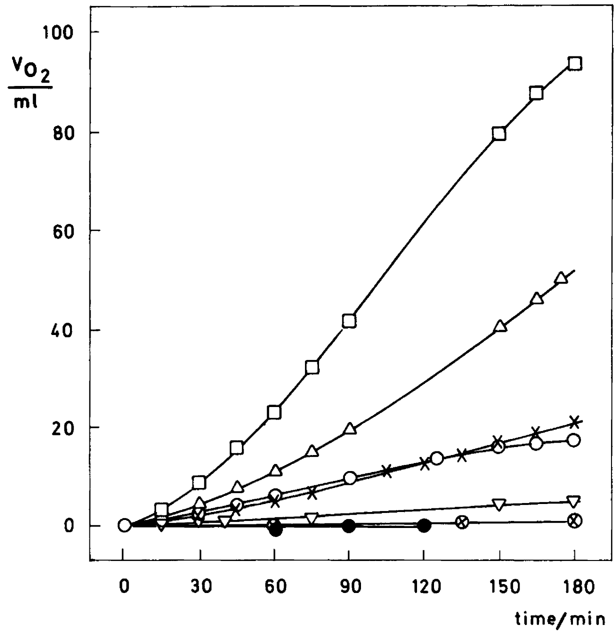


Fig. 2. Volume of oxygen consumed at 20 °C and 1 atm in oxidation of *p*-tolualdehyde with initial concentration 0.53 mol/l in different solvents: □, ethyl acetate; △, ethyl methyl keton; ×, chlorobenzene; ○, benzene; ▽, acetic acid; ⊗, ethanol; ●, acetonitrile. Reactor irradiated with 35 W, 6 V tungsten lamp. Liquid volume 32 ml.

$$r_{\max} = \frac{1}{V_R}\left(\frac{dn_{O_2}}{dt}\right)_{\max}$$

where V_R is the reaction volume, and n_{O_2} is the number of mol of oxygen consumed at time t. An equivalent conversion of oxygen may be defined as

$$\eta_{O_2} = n_{O_2}/C^\circ_{al}V_R$$

where C°_{al} is the initial concentration of aldehyde. Since the reaction volume may be considered constant, the yield of total acid is given by

$$\eta_{ta} = C_{ta}/C^\circ_{al}$$

where C_{ta} is the concentration of total acid. The selectivity for peracid is calculated from

$$\phi_{pa} = C_{pa}/C_{ta}$$

where C_{pa} is the concentration of peracid. The maximum rate of reaction was estimated from the curves in Fig. 2, and the other quantities were determined after a reaction time of 180 min.

The results are shown in Table 1. The rate of oxidation of *p*-tolualdehyde is seen to decrease in the order: ethyl acetate > ethyl methyl keton > chlorobenzene ≥ benzene > acetic acid > ethanol > acetonitrile. The oxidation was obviously inhibited

Table 1. Maximum rate of oxidation of *p*-tolualdehyde, $r_{\max}$, in different solvents. Equivalent conversion of oxygen η_{O_2}, yield of total acid η_{ta}, and selectivity for peracid. ϕ_{pa}, are given after a reaction time of 180 min. Same conditions as in Fig. 2.

Solvent	$\frac{10^5 r_{\max}}{M\ min^{-1}}$	η_{O_2}	η_{ta}	ϕ_{pa}
Ethyl acetate	82	0.23	0.25	0.84
Ethyl methyl keton	56	0.12	0.14	0.73
Chlorobenzene	18	0.05	0.10	0.45
Benzene	17	0.04	0.08	0.45
Acetic acid	5.2	0.01	–	–
Ethanol	1.3	0.002	–	–
Acetonitrile	0	0	–	–

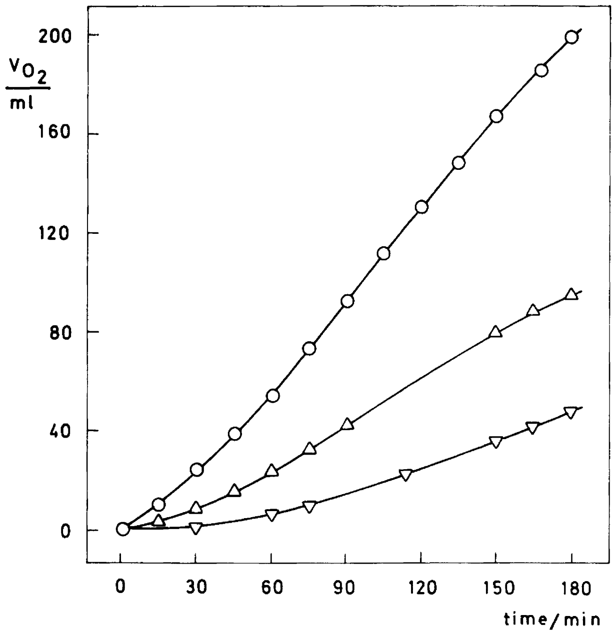


Fig. 3. Volume of oxygen consumed at 20 °C and 1 atm with different concentrations of *p*-tolualdehyde in ethyl acetate solution: ○, 1.00 mol/l; △, 0.53 mol/l: ▽, 0.27 mol/l. Reactor irradiated with 35 W, 6 V tungsten lamp. Liquid volume 32 ml.

in acetonitrile. The selectivity for peracid was highest in ethyl acetate and it seems to be lower in solvents where the oxidation rate is lower.

For oxidation of benzaldehyde in different solvents Dick and Hanna[20] reported the order of decreasing rate in ethyl acetate > chlorobenzene > benzene which is the same as found by us, and the yield of perbenzoic acid decreased in the same order. Their general conclusion that the yield decreases as the polarity decreases does not seem to hold in our case.

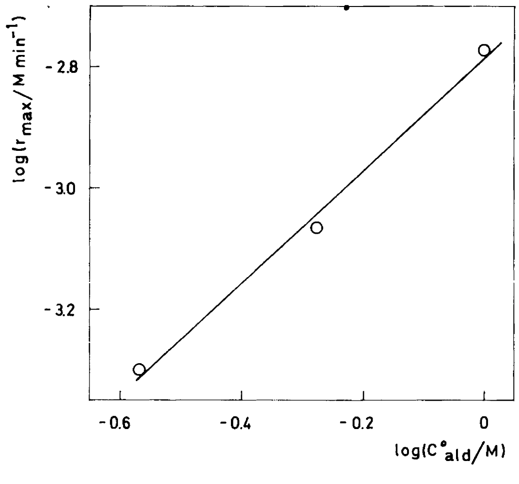


Fig. 4. Plot for determination of reaction order and rate constant.

Under similar conditions, the rate of oxidation of benzaldehyde has been reported to be independent of the oxygen pressure.[5,10,18] Different reaction orders has been reported with respect to the aldehyde concentration.[5,8–10,13,14a,21] The rate of reaction may be expressed by the equation

$$r = kC_{\text{ald}}^n$$

or in the logarithmic form

$$\log r = \log k + n \log C_{\text{ald}}$$

To determine the order of reaction n the oxygen consumption was measured as a function of time for three different concentrations of *p*-tolualdehyde (Fig. 3). Based on these experiments the logarithmic diagram shown in Fig. 4 was drawn. From the slope of the line the reaction order was determined to

$n=0.93$ which is close to first order in the aldehyde concentration as reported by Ingles and Melville[18] for liquid phase photooxidation of benzaldehyde, and by Hendriks *et al.*[14a] for some aromatic aldehydes. From Fig. 4 the pseudo first order rate constant under our experimental conditions (20 °C) was determined to $k=1.6\times10^{-3}\ \text{min}^{-1}$.

Some of the results may be discussed from the free radical chain mechanism of aldehyde oxidation shown below

$$\text{RCHO}+\text{O}_2\xrightarrow{+h\nu}\text{R}\dot{\text{C}}\text{O}+\text{HO}_2\cdot$$

$$\text{R}\dot{\text{C}}\text{O}+\text{O}_2\longrightarrow\text{RCOOO}\cdot$$

$$\text{RCOOO}\cdot+\text{RCHO}\xrightarrow{k_p}\text{RCOOH}+\text{R}\dot{\text{C}}\text{O}$$

$$\left.\begin{array}{ll}\text{R}\dot{\text{C}}+\text{R}\dot{\text{C}}\text{O} & \longrightarrow\\ \text{RCOOO}\cdot+\text{R}\dot{\text{C}}\text{O} & \xrightarrow[k_t]{}\\ \text{RCOOO}\cdot+\text{RCOOO}\cdot & \longrightarrow\end{array}\right\}\text{molecular products}$$

At sufficiently high oxygen pressure the termination takes place by the last reaction.[3,17] Assuming the chains to be long[7,14a,17] the following expression may be derived for the rate of oxygen consumption

$$r=r_p=k_p\sqrt{\frac{r_i}{k_t}}[\text{RCHO}]$$

r_i is the rate of initiation which depends on light. k_p and k_t are rate constants for propagation and termination respectively. If the rate of initiation r_i is independent of the aldehyde concentration, the expression for the total rate of oxidation is seen to be first order in the aldehyde concentration as has been measured.

According to Bäckström and Rüner[7] the photochemical oxidation of benzaldehyde may be regarded initiated mainly by a reaction between an aldehyde molecule in the triplet state and an unexcited molecule

$$\text{RCHO}\xrightarrow{+h\nu}\text{R}\dot{\text{C}}\text{H}\dot{\text{O}}$$

$$\text{R}\dot{\text{C}}\text{H}\dot{\text{O}}+\text{RCHO}\longrightarrow\text{R}\dot{\text{C}}\text{O}+\text{R}\dot{\text{C}}\text{HOH}$$

From such a mechanism, it is difficult to explain an initiation reaction which is independent of the aldehyde concentration unless the rate is limited by the incident light, *i.e.* almost all of the incident light is absorbed by the aldehyde, or light quanta are absorbed by the solvent or by the walls of the reactor and the energy is transferred to the reacting molecules. Only little UV light is, however, absorbed by the aldehyde or the solvent ethyl acetate above 300 nm.

The effect of the solvent on the rate of oxidation cannot alone be explained as a general dielectric solvation.[3] Specific solvation is due to the formation of various types of complexes between the reacting species and the solvent molecules. The low rate of oxidation in the protic solvents acetic acid and ethanol (Table 1) may be attributed to a deactivation of the acylperoxy radicals RCOOO· by forming hydrogen bonds to the solvent molecules. Benzene and chlorobenzene may form weak π-complexes with radicals and thus decrease the oxidation rate. Acetonitrile may either inhibit the formation of radicals or trap them.

The effect of different catalysts on the oxidation of *p*-tolualdehyde was measured in ethyl acetate solution at 20 °C. Soluble acetylacetonates of transition metals were used besides manganese(II) acetate and tetrabutylammonium bromide. Some of these compounds were real catalysts, others were inhibitors. The results are shown in Table 2. With a metal salt concentration of 10^{-3} mol/l the maximum rate of oxidation of *p*-tolualdehyde was found to decrease in the following order: V ~ Fe > Co > Mn > Ni ~ Cu > uncatalyzed > Ti > Mo > tetrabutylammonium bromide > Cr.

Measured converted oxygen per initial mol of aldehyde η_{O_2} may be compared with calculated accumulated oxygen in the total acid product (not shown here). These oxygen values agreed fairly well for the uncatalyzed reaction and with the Ti, Ni, Mo and Cu acetylacetonates, and with tetrabutylammonium bromide, but for the V, Fe, Co, Cr and Mn compounds the disagreement was significant. In these cases less oxygen was found in the acids than gas consumed.

Since the main products are *p*-toluic acid and the peracid the total acid may be used as an approximate measure of the aldehyde converted. This was in many cases confirmed by gas chromatographic analysis of the liquid product.

Gas chromatographic analysis of the liquid product showed that toluene usually was formed in small quantities, possibly by decarboxylation of the acid. The highest yield of toluene was found with the iron catalyst. In this case the yield of toluene was measured to 10 % after 3 h of reaction when the conversion of aldehyde was almost complete

Table 2. Effect of different catalysts on the oxidation of *p*-tolualdehyde in ethyl acetate solution at 20 °C and 1 atm. Conversion, yield and selectivity data are given after a reaction time of 180 min. Symbols as in Table 1. Catalyst concentration 0.0010 mol/l. Initial aldehyde concentration C^{o}_{ald}. Reactor irradiated with 35 W, 6 V tungsten lamp. acac, acetylacetonate; Tbab, tetrabutylammonium bromide.

Catalyst	$\frac{C^{o}_{ald}}{M}$	$\frac{10^3 r_{max}}{M\,min^{-1}}$	η_{O_2}	η_{ta}	ϕ_{pa}
Uncatalyzed	0.53	0.82	0.23	0.25	0.84
Titanyl acac	0.53	0.65	0.23	0.40	0.24
Nickel(II) acac	0.53	2.6	0.56	0.67	0.72
Molybdenyl acac	0.53	0.20	0.03	0.08	0.23
Copper(II) acac	0.53	2.6	0.34	0.44	0.41
Tbab	0.53	0.09	0.02	0.06	0.17
Vanadium(IV) oxide acac	0.27	54	1.05	1.00	0.07
Iron(II) acac	0.27	54	0.95	1.00	0.62
Cobalt(II) acac	0.27	30	1.00	1.00	0.17
Chromium(III) acac	0.27	0.03	0.01	0.06	0.17
Manganese(II) acetate	0.27	8.1	0.74	0.06	0.06

(99 %). The other catalysts gave much less toluene.

As may be expected, carbon oxides were found in the gas phase after the reaction. However, a quantitative relationship between toluene and carbon oxide could not be established. Carbon monoxide was found in much smaller quantities than carbon dioxide.

The last column in Table 2 shows the selectivity for peracid. The highest selectivity for peracid was found for the uncatalyzed reaction, and the selectivity decreased in the order: uncatalyzed > Ni > Fe > Cu > Ti > Mo > Co, Cr, Tbab > V, Mn. This order of selectivity was measured after 3 h of reaction. The order of selectivity may change with the conversion of *p*-tolualdehyde as shown in Fig. 5, where the conversion is represented by the yield of total acid.

Fig. 6 shows the effect of light on the oxidation of *p*-tolualdehyde catalyzed by Ni(II) acetylacetonate. With a dark reactor the oxidation did

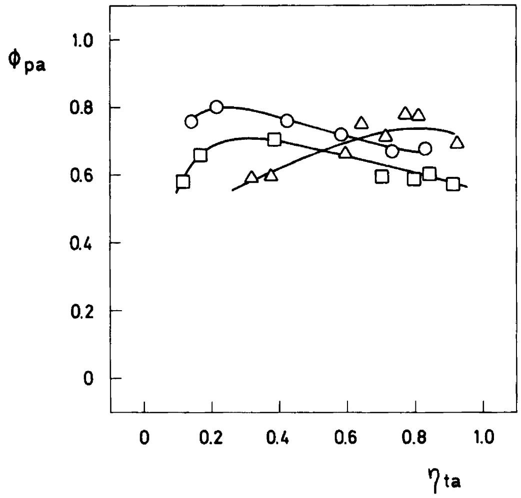


Fig. 5. Selectivity for *p*-toluic peracid ϕ_{pa} as a function of the yield of total acid η_{ta} without and with catalysts. ○, no catalyst; △, Ni acetylacetonate; □, Fe acetylacetonate.

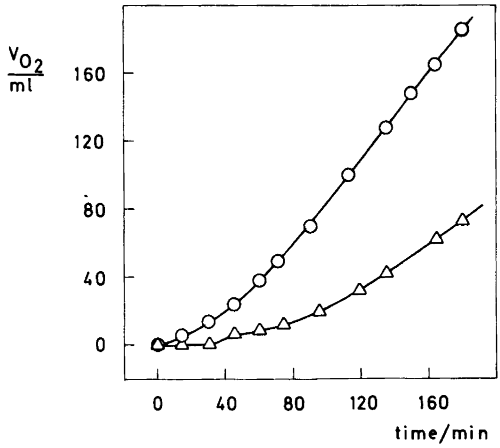


Fig. 6. Effect of light on the oxidation of *p*-tolualdehyde catalyzed by Ni(II) acetylacetonate with concentration 1×10^{-3} mol/l. Temperature 20 °C. ○, Reactor irradiated with 35 W, 6 V tungsten lamp; △, Dark reactor, except between 30 and 45 min from zero time when the lamp was on.

Table 3. The effect of Ni(II) acetylacetonate concentration C_{kat} on the maximum rate of oxidation of *p*-tolualdehyde $r_{\max}$. Initial aldehyde concentration 0.53 mol/l. Temperature 20 °C. Irridiated reactor.

C_{kat}, M	$r_{\max}$, M min^{-1}
1.0×10^{-5}	1.4×10^{-3}
1.0×10^{-4}	1.8×10^{-3}
4.6×10^{-4}	1.9×10^{-3}
1.0×10^{-3}	2.6×10^{-3}
5.0×10^{-3}	0
1.0×10^{-2}	0

not start within 30 min. Then, the lamp was switched on and the reaction started immediately. After 15 min of irradiation the lamp was switched off. The reaction then continued at a lower rate than in the irradiated reactor. This example shows that light is important both for the initiation and the rate of reaction even when a catalyst is present.

The concentration of Ni(II) acetylacetonate was varied and the effect on the rate of oxidation of *p*-tolualdehyde is shown in Table 3. A 100 times increase in the Ni concentration from 10^{-5} to 10^{-3} mol/l gave only a slight increase in the maximum rate. Similar zero order kinetics in catalyst concentration is reported by Marta *et al.*[9,11c] for the oxidation of benzaldehyde catalyzed by Co acetate at a higher concentration. With a concentration of Ni of 5×10^{-3} mol/l or higher we found that the reaction was completely inhibited. An inhibition effect of Mn acetate at higher concentrations has been reported by Golubev *et al.*[15] in the oxidation of *p*-tolualdehyde.

During catalysis with the transition metal compounds a change in the color of the solution could in many cases be observed. This indicates a change in the valence state of the metal ion. These types of catalysts participate directly in the generation of free radicals from the aldehyde and the peracid formed.[3,17]

$$\mathrm{M}^{(n+1)+} + \mathrm{RCHO} \rightarrow \mathrm{M}^{n+} + \mathrm{H}^{+} + \mathrm{RCO}\cdot$$

$$\mathrm{M}^{(n+1)+} + \mathrm{RCOOOH} \rightarrow \mathrm{M}^{n+} + \mathrm{H}^{+} + \mathrm{RCOOO}\cdot$$

$$\mathrm{M}^{n+} + \mathrm{RCOOOH} \rightarrow \mathrm{M}^{(n+1)+} + \mathrm{OH}^{-} + \mathrm{RCOO}\cdot$$

The last of these reactions leads to the formation of acid and may thus be responsible for the low selectivity for *p*-toluic peracid which has been observed with some of the catalysts.

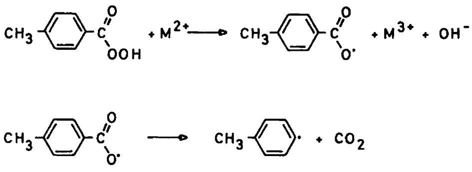
Strong preference for one of the valence states of a transition metal ion may inhibit the oxidation of the aldehyde. Such an effect has been reported for Co(II) acetate in the oxidation of benzaldehyde.[9,11b,22] The conversion of a metal ion from a lower to a higher valence state can also take place by a reaction with an acyl peroxide radical

$$\mathrm{M}^{2+} + \mathrm{RCOOO}\cdot \rightarrow \mathrm{M}^{3+} + \mathrm{RCOOO}^{-}$$

This reaction may inhibit the oxidation by breaking chains.[22]

The relatively strong inhibiting effect of tetrabutylammonium bromide on the oxidation of *p*-tolualdehyde was unexpected since a catalytic effect of onium salts has been reported in the oxidation of hydrocarbons.[23] The inhibiton may depend on a complex formation of the reacting species with the ion pairs of tetrabutylammonium bromide.

The formation of carbon dioxide which was observed with some of the catalysts may be explained by the reactions



The tolyl radical may pick up a hydrogen atom from *p*-tolualdehyde and form toluene or it may react with oxygen and subsequently form *p*-cresol. The latter is known as an oxidation inhibitor, and it may even at very low concentrations explain the inhibition of the oxidation reaction found with some of the catalysts at higher aldehyde conversion.[15]

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