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Reaction kinetics and reaction techniques for mediated oxidation of methylarenes to aromatic ketones

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The Mn^{3+}-mediated anodic oxidation of toluene and some substituted toluenes (*p*-chloro-, *p*-xylene-, *p*-nitro-) in 60 wt % H_2SO_4 has been investigated with respect to reaction kinetics and process techniques. The mediators Co^{3+} in 3.5 N HNO_3 and Ce^{4+} in 60 wt % H_2SO_4 are compared with Mn^{3+} in 60 wt % H_2SO_4 for unsubstituted toluene. The mediated oxidation of the toluenes proceeds in three well-distinguished steps: benzyl alcohol, benzaldehyde, benzoic acid. The last step, which destroys the desired product, the aldehyde, is crucial. Therefore, for continuous resaturation of the electrolyte with toluene and for extraction of benzaldehyde, the benzaldehyde content in the emulgated organic phase has to be kept below a critical value. For toluene, *p*-chlorotoluene and xylene Mn^{3+}-mediated oxidation only becomes attractive with process temperatures above 60° C. The conversion of *p*-nitrotoluene to *p*-nitrobenzaldehyde can only be carried out by Co^{3+}. The reactivities of the oxidants declines in the order: $Co^{3+} > Mn^{3+} > Ce^{4+}$. Current efficiencies for the recuperation of all oxidants approaches 100%.

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1. Introduction

Since 1830 [1–3] the mediated anodic oxidation of different toluenes to benzaldehydes has repeatedly been reported (see [4] and citation therein). It was not until 1958, however, that Udupa and co-workers published a paper [5] on the Mn^{3+}-mediated anodic oxidation of toluene to benzaldehyde which contained some limited kinetic information. Ibl and co-workers recently published two papers on the mediated anodic oxidation of *p*-chlorotoluene to *p*-chlorobenzaldehyde [6, 7]. These authors compared different mediator systems (Co^{3+} and Ce^{4+}), and concluded that Co^{3+} in concentrated $HClO_4$ seems to be the most appropriate oxidant for these reactions. They gave some limited information on the operating conditions of the process and were able to communicate a relatively detailed cost estimation without any detailed kinetic data. They found that this type of process is on the fringe of commercial feasibility. According to these authors, highly diluted toluene solutions in kerosene have to be processed in order to overcome difficulties caused by polymerization reactions which were supposed to be of higher reaction order with respect to the substrate. The authors of the present paper intend to report on the basic kinetic data of this type of process. A further paper is intended to deal with the kinetics of polymerization and oligomerization accompanying mediated toluene oxidation and will deal with optimal process strategies. Appropriately tailored reaction techniques provide a two-step oxidation–extraction process.

2. Experimental details

The anodic oxidation of Mn^{2+} was investigated in H_2SO_4 solutions of different composition (20–70 wt %) under well-defined mass-transfer conditions ($k_m = 5 \times 10^{-4} cm\,s^{-1}$) at different temperatures. (For data on Co^{2+}/Co^{3+} and Ce^{3+}/Ce^{4+} oxidation, compare [6, 7 and 8].) Above

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30° C, Co^{3+} is very unstable in 60 wt % H_2SO_4 and, therefore, a concentration of 5×10^{-3} M of three-valent cobalt could never be surmounted on oxidation of 0.1 M solution of Co^{2+}-sulphate (current, 110 mA $\simeq$ 5.5 mA cm^{-2}; volume 500 ml). Therefore, Co^{2+} was oxidized anodically in 3.5 M HNO_3 solutions. Working in perchloric acid solutions, as proposed by Ibl and Robertson [7], was avoided because use of hazardous material such as $HClO_4$ would be absolutely prohibitive in a technical process. Dark green solutions of Co^{3+}-nitrate (3.5×10^{-2} M Co^{3+}) were produced with close to 100% current efficiency and were stable at 25° C for more than 12 h with only little decomposition. The determination of the rate law for the oxidation of toluene by Mn^{3+} and Ce^{4+} in 60 wt % H_2SO_4 demanded the preparation of homogeneous toluene solutions with well-defined toluene concentrations; 60 wt % H_2SO_4 saturated with toluene was diluted for this purpose. Toluene solubilities in 60 wt % H_2SO_4 were determined by exhaustive extraction of toluene from the saturated H_2SO_4 solutions with kerosene and colorimetric determination of toluene in the extracts.

Kinetic measurements at 20, 40 and 60° C were performed by determining the decay of the oxidant concentration in the reaction mixtures. After quenching the reaction of mixing aliquot volumes of the reaction mixture with dilute H_2SO_4 solutions containing an excess of potassium iodide, the liberated iodine was determined with thiosulphate. All kinetic measurements were executed under nitrogen because in contact with air or oxygen the oxidation of toluenes, aromatic alcohols and aldehydes is pronouncedly accelerated. (Thus at 20° C in the presence of air the oxidation rate for toluene doubles.)

Kinetic data for emulsion oxidation were obtained by reacting the different oxidants with toluene, benzyl alcohol and benzaldehyde in 30 vol % emulsions of the organic compounds. For Co^{3+} oxidation it was necessary to dilute the organic substrate with kerosene because the reaction was too fast. Preliminary investigations were performed in order to establish reaction conditions where the mass-transfer of toluene from emulgated toluene into the solution was no longer rate limiting.

3. Results

3.1. *Anodic oxidation of Mn^{2+} to Mn^{3+}*

The anodic oxidation of Mn^{2+} to yield Mn^{3+} species* (Equation 1) can be performed at platinum anodes in the temperature range 20–60° C with high current yields only if the H_2SO_4 concentration is greater than 50 wt % (compare [3]). At lower H_2SO_4 concentration the current yields of Reaction 1 drop below 75%.

$$Mn^{2+} - e \rightarrow Mn^{3+} \tag{1}$$

Fig. 1a depicts a typical current–voltage curve for the oxidation of 5×10^{-2} M Mn^{2+} in 60 wt % H_2SO_4 at a smooth platinum anode (reference: saturated calomel electrode, SCE). The current–voltage curves exhibit a diffusion-limited current plateau. The decay of the oxidation current for 7×10^{-3} M $MnSO_4$ solution in 60 wt % H_2SO_4 oxidized at +1.5 V is shown in Fig. 1b. The solubility of Mn^{3+} species in this electrolyte amounts to 7.5×10^{-3} M at 25° C and approximately 1.5×10^{-2} M at 60° C. Oxidation of $MnSO_4$ solutions of higher concentration results in a slow precipitation of Mn^{3+}-sulphate which may continue for days until the supersaturation of the solution is removed. In 60 wt % H_2SO_4, Mn^{3+} solutions may be kept unchanged for several days if not exposed to bright daylight.

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* Mn^{2+} and Mn^{3+} are forming sulphato-complexes of different and varying composition depending on H_2SO_4 and SO_4^{2-} concentration and temperature [9]. Since the composition of these complexes under different operation conditions are not very well known, they will be called 'Mn^{3+} species'.

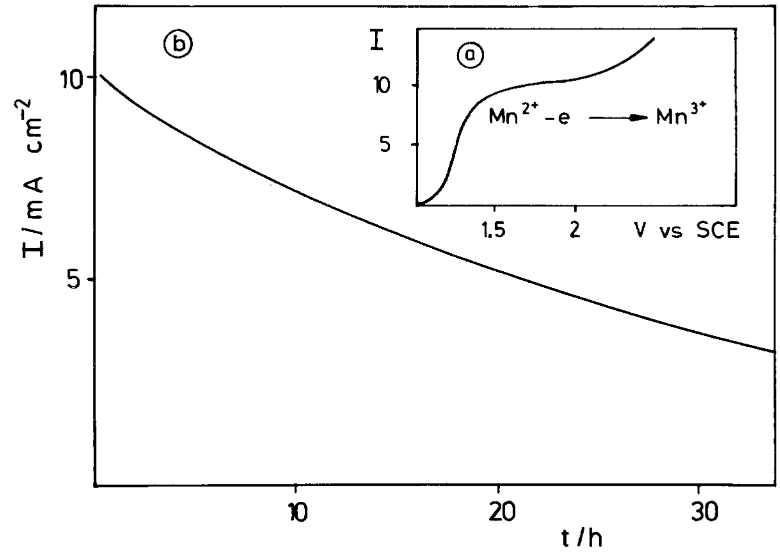

Fig. 1. Diffusion-limited oxidation of Mn^{2+} to Mn^{3+} in 60 wt % H_2SO_4. (a) Current–voltage curve. (b) Oxidation current decay with time, for 7×10^{-3} M $MnSO_4$ oxidized at 1.5 V vs SCE. Current yield, $\eta = 95\%$.

3.2. *Determination of the solubility of toluene in 60 wt % H_2SO_4*

Toluene solubilities were determined in 60 wt % H_2SO_4 at four temperatures. Table 1 shows the solubility data together with the (positive) enthalpy of dissolution of $13 \pm 2\,\mathrm{kJ\,mol^{-1}}$.

3.3. *Kinetics of the homogeneous oxidation of toluene, benzyl alcohol and benzaldehyde by Mn^{3+}*

A systematic investigation of the reaction of Mn^{3+} with dissolved toluene in 60 wt % H_2SO_4 reveals that the reaction proceeds in well-defined separate steps to benzyl alcohol, benzaldehyde and, eventually, to benzoic acid.

$$C_6H_5CH_3 + 2Mn^{3+} + H_2O \xrightarrow{k_1} C_6H_5CH_2OH + 2Mn^{2+} + 2H^+ \qquad (2)$$

$$C_6H_5CH_2OH + 2Mn^{3+} \xrightarrow{k_2} C_6H_5CHO + 2Mn^{2+} + 2H^+ \qquad (3)$$

$$C_6H_5CHO + 2Mn^{3+} + H_2O \xrightarrow{k_3} C_6H_5COOH + 2Mn^{2+} + 2H^+ \qquad (4)$$

Table 1. Toluene solubilities in saturated solution in 60 wt % H_2SO_4

Temperature (° C)	*Saturation concentration (toluene) (M)*
20	1.8×10^{-3}
38	2.4×10^{-3}
58	3.4×10^{-3}
75	5.0×10^{-3}

Dissolution enthalpy, $\Delta H_{\mathrm{diss}} = +(13 \pm 2)\,\mathrm{kJ\,mol^{-1}}$.

Table 2. Rate constants and activation energies for the oxidation of toluene, benzyl alcohol and benzaldehyde by Mn^{3+} *in 60 wt %* H_2SO_4

Substrate and rate constant	*Temperature (° C)*			E
	20	*40*	*60*	*(kJ mol⁻¹)*
Toluene, $k_1 (l\,mol^{-1})$	0.196	0.83	2.0	49 ± 6
Benzyl alcohol, $k_2 (l\,mol^{-1})$	0.005	0.05	0.5	95 ± 5
Benzaldehyde, $k'_3 (s^{-1})$	1.7×10^{-4}	2.8×10^{-4}	8.3×10^{-4}	35 ± 4
Benzaldehyde*, $k_3 (l\,mol^{-1})$	4.2×10^{-4}	6.2×10^{-4}	1.6×10^{-3}	27 ± 3

* Estimated saturation concentrations c_s(benzaldehyde) at temperatures 20, 40 and 60° C are 0.4, 0.45 and 0.5 mol dm^{-3}, respecitvely. $E = 8\,kJ\,mol^{-1}$.

In batch experiments using stoichiometric homogeneous mixtures (Mn^{3+} : toluene = 4 : 1) one observes an initial relatively fast consumption of half of the Mn^{3+} due to Reaction 2 and then a slow consumption of the rest of the Mn^{3+} by the slower Reaction 3. Reactions 2, 3 and 4 are first-order with respect to the organic substrate and the oxidant

$$\frac{dc(Mn^{3+})}{dt} = -k_1 c(Mn^{3+})c(\text{toluene}) = -2\frac{1}{V}\frac{dN(\text{toluene})}{dt} \tag{5}$$

where c is concentration of oxidant, V is volume, t is time and N is number of moles. Reaction 4, the undesired oxidation of benzaldehyde to benzoic acid, was investigated as described above for toluene and by a second technique which used continuous saturation of the sulphuric acid with benzaldehyde, i.e. converting benzaldehyde emulsions.

In emulsions, Mn^{3+} species are consumed according to a pseudo first-order reaction:

$$\begin{aligned} 2\frac{1}{V}\frac{dN(\text{benzaldehyde})}{dt} &= -\frac{dc(Mn^{3+})}{dt} \\ &= -k_3 c_s(\text{benzaldehyde})c(Mn^{3+}) \\ &= -k'_3 c(Mn^{3+}) \end{aligned} \tag{6}$$

where c_s is the saturation concentration. The pseudo first-order rate constant, k'_3, is the product of the benzaldehyde saturation concentration and the second-order rate constant k_3. k'_3 and not k_3 is the rate constant most relevant with respect to process techniques, as the respective rate constant k'_1 (equal to $k_1 c_s$(toluene)) is most relevant with respect to space–time yield. For fully established saturation of the toluene, Equation 5 is changed to Equation 7. Tables 2 and 3 show the rate data for toluene, benzyl alcohol and benzaldehyde oxidation for 20, 40 and 60° C.

$$dc(Mn^{3+})/dt = -k'_1 c(Mn^{3+}) \tag{7}$$

Table 3. Pseudomonomolecular rate constants k'_1 *and* k'_3 *for the oxidation of toluene and benzaldehyde by* Mn^{3+} *in solutions saturated with the respective substrate*

Temperature (° C)	k'_1 *(experimental)* (s^{-1})	$(k'_1 = k_1 c_s(\text{toluene}))$ (s^{-1})	k'_3 (s^{-1})
20	4.3×10^{-4}	(3.5×10^{-4})	1.7×10^{-4}
40	2.5×10^{-3}	(2.0×10^{-3})	2.8×10^{-4}
60	8.0×10^{-3}	(7.8×10^{-3})	7.0×10^{-4}

$E(k'_1) = 62 \pm 5\,kJ\,mol^{-1}$; $E(k'_3) = 35 \pm 4\,kJ\,mol^{-1}$.

Table 4. Pseudomonomolecular rate constants for the conversion of Mn^{3+} with saturated solutions of p*-chlorotoluene, and* p*-methylbenzaldehyde in 60 wt % H_2SO_4*

Substrate and rate constant	*Temperature (° C)*			*Activation energy ($kJ\,mol^{-1}$)*
	20	*40*	*60*	
p-chlorotoluene (emulsion), $k_1'(s^{-1})$	2.5×10^{-4}	8.8×10^{-4}	5.6×10^{-3}	71 ± 2
p-chlorobenzyl alcohol (emulsion), $k_2'(s^{-1})$	2.4×10^{-3}	8.2×10^{-3}	2.8×10^{-2}	50 ± 2
p-chlorobenzaldehyde (emulsion), $k_3'(s^{-1})$	3.4×10^{-5}	8.0×10^{-5}	1.9×10^{-4}	33 ± 3

Table 3 shows the rate constants k_1' and k_3' for toluene and benzaldehyde oxidation by Mn^{3+} and compares experimental k_1' with k_1' as calculated from k_1 and toluene solubilities. Experimentally determined and calculated rate data (k_1') agree satisfactorily. The second-order rate constant (k_1) is highest for toluene oxidation and declines strongly with increasing degree of oxidation over benzyl alcohol (k_2) to benzaldehyde (k_3). Benzoic acid is oxidized even more sluggishly than benzaldehyde. Important with respect to process techniques is the observation that the activation energy for benzyl alcohol oxidation is by far the highest ($\approx 100\,kJ\,mol^{-1}$), whereas for toluene oxidation it amounts to one-half and for benzaldehyde oxidation to only one-third of this value.

3.4. *Oxidation kinetics of substituted toluenes, benzyl alcohols and benzaldehydes*

For the substrates *p*-chlorotoluene, *p*-chlorobenzyl alcohol and *p*-chlorobenzaldehyde; *p*-xylene (*p*-dimethylbenzene), *p*-methylbenzyl alcohol and *p*-methylbenzaldehyde and for *p*-nitrotoluene the kinetic investigation was confined to the determination of the pseudo monomolecular rate constants (k_1' for oxidation of emulsions). This seemed to be sufficient because under technical conditions, emulsions of the respective toluene will be processed and not homogeneous solutions. Tables 4 and 5 show the rate data and activation energies for the *p*-chloro-substituted substrates, respectively.

The oxidation of nitrotoluene emulsions by Mn^{3+} proceeds by two orders of magnitude slower than toluene oxidation. Since this reaction rate is below any value of practical interest, further kinetic investigation was not persued (for Co^{3+}-mediated oxidation compare [11]). Tables 3–5 show that toluene oxidation and benzaldehyde oxidation proceed with comparable rates at room temperture provided they are converted in emulsions. However, the situation improves with increasing temperatures: k_1'/k_3' is 3.4 at 25° C and 7.1 at 60° C.

With the *p*-chloro-substituted and *p*-methyl-substituted compounds, however, the situation is more advantageous: even at 20° C the rate of hydrocarbon oxidation is greater than the rate of aldehyde oxidation by approximately an order of magnitude, and the rate ratio even changes in favour of fast toluene oxidation at higher temperatures. The apparent activation energies for the oxidation of emulsions of the different toluenes are approximately equal ($70\,kJ\,mol^{-1}$) but for benzyl

Table 5. Pseudomonomolecular rate constants for the conversion of Mn^{3+} with saturated solutions of p*-xylene and* p*-methylbenzaldehyde*

Substrate and rate constant	*Temperature (° C)*			*Activation energy ($kJ\,mol^{-1}$)*
	20	*40*	*60*	
p-xylene (emulsion), $k_1'(s^{-1})$	3.0×10^{-3}	1.3×10^{-2}	7.0×10^{-2}	70 ± 2
p-methylbenzaldehyde (emulsion), $k_3'(s^{-1})$	3.2×10^{-4}	1.0×10^{-3}	3.6×10^{-3}	45 ± 4

Table 6. Pseudomonomolecular rate constants k'_1 and k'_3 for oxidation of toluene and benzaldehyde in emulsions of the respective substrate in aqueous 3.5 M HNO_3 solution by Co^{3+}

Temperature (° C)	$k'_1(s^{-1})$	$k'_3(s^{-1})$
20	1.2×10^{-3}	1.5×10^{-4}
40	7.4×10^{-3}	6.0×10^{-4}

$E(k'_1) = 68 \pm 6\,\mathrm{kJ\,mol^{-1}}$; $E(k'_3) = 52 \pm 5\,\mathrm{kJ\,mol^{-1}}$.

alcohol the observed activation energy for k'_2 appears to be extraordinarily high. The activation energy for the oxidation of benzaldehyde is, advantageously, notably lower than for oxidation of the toluenes.

Tables 6 and 7 show the rate data for the oxidation of toluene and benzaldehyde by Co^{3+} and Ce^{4+} (the first oxidant is dissolved in 3.5 M HNO_3, the second in 60 wt % H_2SO_4). Co^{3+} in 3.5 M HNO_3 is the most aggressive oxidant whereas Ce^{4+} in 60 wt % H_2SO_4 reacts slower than Mn^{3+} in the same solvent by nearly one order of magnitude.

3.5. *Demonstration of the role of mass-transfer conditions for toluene conversion in toluene/aqueous emulsions*

Two different mass-transfer conditions were compared. Toluene/water emulsions (10 vol % in the first case, 30 vol % in the second) were stirred at 300 r.p.m. and 600 r.p.m., respectively. The different stirring conditions resulted in a mean droplet diameter of 0.5 and 0.1 mm and a volume-specific mass-transfer surface of 6.67 and $100\,\mathrm{cm^2 cm^{-3}}$, respectively. In both cases the temperature was 60° C in order to keep reaction rates as high as possible.

Fig. 2 depicts for both cases the decay of Mn^{3+} concentration in the stirred solution with initial Mn^{3+} concentrations of 1.5×10^{-2} M, and compares it with the precalculated[†] rate of Mn^{3+}-consumption (broken line). In the first case a pseudo zero-order reaction is observed, which demonstrates that in the first case the volume-specific mass-transfer rate of approximately $6 \times 10^{-4}\,\mathrm{mol\,min^{-1} l^{-1}}$ is rate limiting and is too slow to supply the necessary toluene for continuous saturation of the aqueous solution. In the second case the volume specific mass transfer rate, being higher by more than a factor of ten, achieves almost complete toluene saturation from the very

Table 7. Pseudomonomolecular rate constants k'_1 and k'_3 for oxidation of toluene and benzaldehyde in emulsions of the respective substrate in aqueous 60 wt % H_2SO_4 solution by Ce^{4+}

Temperature (° C)	$k'_1(s^{-1})$	$k'_3(s^{-1})$
20	1.3×10^{-4}	3×10^{-5}*
40	1.7×10^{-4}	6×10^{-5}
60	1.7×10^{-3}	3×10^{-4}
70	6.0×10^{-3}*	6×10^{-4}

* Extrapolated value.
$E(k'_1) = 100 \pm 10\,\mathrm{kJ\,mol^{-1}}$; $E(k'_3) = 70 \pm 3\,\mathrm{kJ\,mol^{-1}}$.

[†] Precalculated with the assumption of fully established distribution equilibrium for toluene distribution between the organic and aqueous phase.

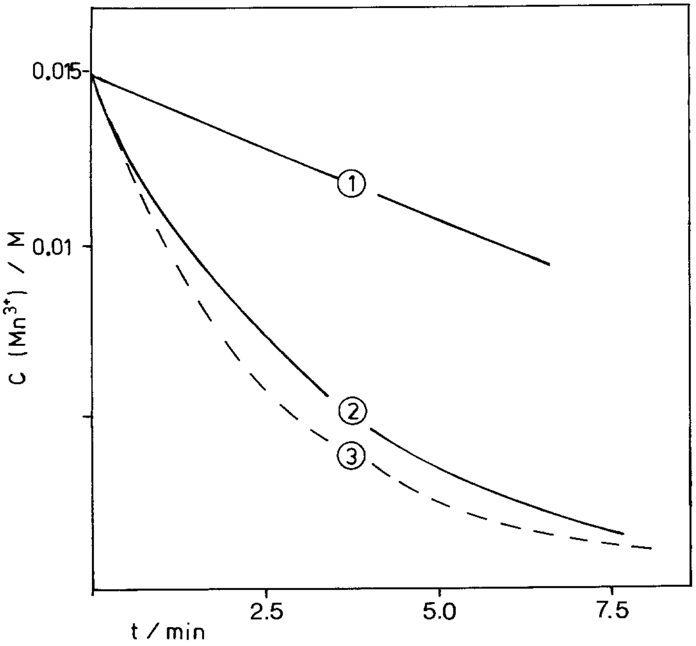

Fig. 2. Mn^{3+} reduction by conversion with toluene (60 wt % toluene H_2SO_4 at 60° C). (1) 10 vol % toluene/water, stirred at 300 r.p.m. Demonstrates mass-transfer control. (2) 30 vol % toluene/water, stirred at 600 r.p.m. Measured with high mass-exchange surface density. (3) Mn^{3+} concentration decay precalculated under assumption of fully established distribution equilibrium for toluene. Calculated using $k_1' = 8 \times 10^{-3} s^{-1}$.

beginning of the experiment and hence first-order decay of Mn^{3+} concentration. This time-independent bulk concentration of toluene results in the rate expression Equation 7.

4. Process model

4.1. *Stages of the process*

Fig. 3a describes a continuously operated process in which toluene is converted to benzaldehyde by mediated anodic oxidation. The process equipment consists of three units: (i) electrolyser, (ii) continuous stirred-tank reactor operated in parallel to the electrolyser, and (iii) separation unit (settler with attached distillation column).

(i) The electrolyser is a divided cell which permits recuperation of the oxidant (Equation 8) and production of hydrogen at the cathode (Equation 9)

$$\text{Red}^{n+} - e \rightarrow \text{Oxidant}^{(n+1)+} \qquad \text{(anode)} \tag{8}$$

$$H^+ + e \rightarrow \tfrac{1}{2}H_2 \qquad \text{(cathode)} \tag{9}$$

(ii) In the stirred-tank reactor an emulsion of toluene is oxidized by, e.g. Mn^{3+}, Equation 10, with a total conversion rate which matches the rate of the anodic Mn^{3+} recuperation

$$C_6H_5CH_3 + 4Mn^{2+} + H_2O \rightarrow C_6H_5CHO + 4H^+ \tag{10}$$

The use of an emulsion of toluene (or dilute toluene solutions in an inert solvent) in 60 wt % H_2SO_4 serves two purposes. First, the well-stirred emulsion is used in order to supply the organic substrate for the homogeneous redox reaction where two extreme cases may be distinguished: (a) mass transfer is fast, so that the equilibrium concentration of toluene is established; (b) the toluene reacts so fast that its concentration in the bulk of the aqueous phase is smaller by more than a factor of ten than its distribution–equilibrium value, so that the rate of mass-transfer governs the volumetric rate of toluene conversion. In this case mass-transfer might even be reaction-enhanced (i.e. for large Hatta numbers). Second, the dispersed toluene phase extracts the product, benzaldehyde, from the aqueous phase,

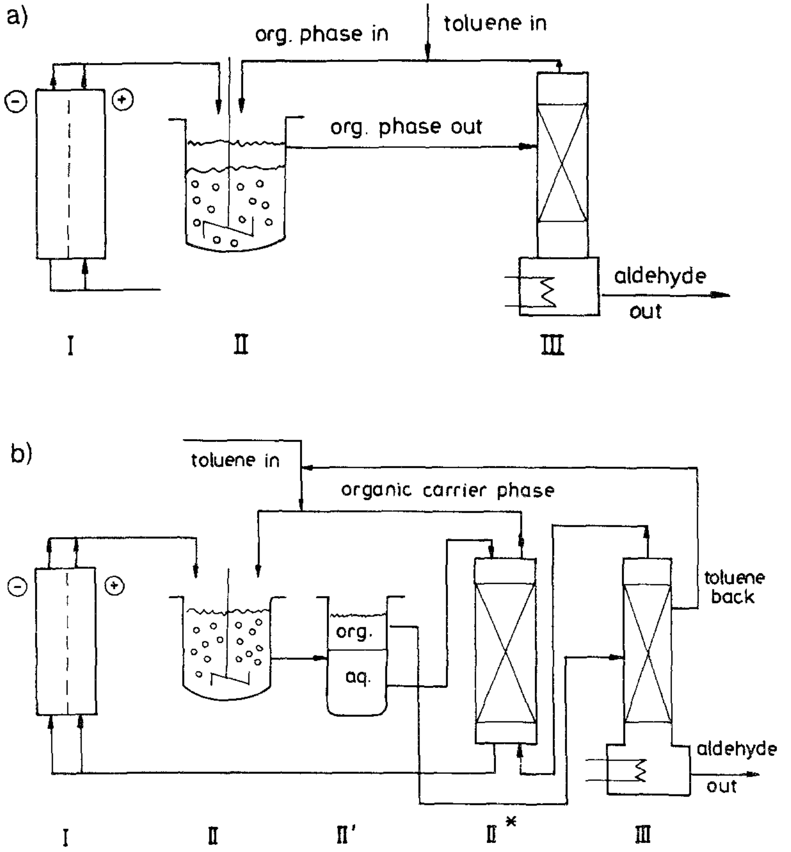

Fig. 3. (a) Simple process model. I, electrolysis cell; II, two-phase STR; III, distillation column. (b) Advanced process model: I, II and III as in Fig. 3a. II', settler; II*, counter-current reactor-extractor.

whereby it becomes protected against further oxidation and its steady state concentration in the aqueous phase is so low that its further oxidation can be kept below a given value. Fig. 4 depicts schematically this sequence of toluene extraction into the aqueous phase, chemical conversion and re-extraction of the aldehyde.

(iii) The separation unit has the purpose of continuously removing the organic phase containing the benzaldehyde produced, together with toluene from the reactor, and to separate the benzaldehyde from the toluene in order to recycle the latter. This is necessary for two reasons: the removal of benzaldehyde together with the products of consecutive and parallel reactions (compare [5, 6]) is necessary to obtain well-defined batch or steady state conditions, and the benzaldehyde concentration must be kept below a critical level in order to prevent its further oxidation.

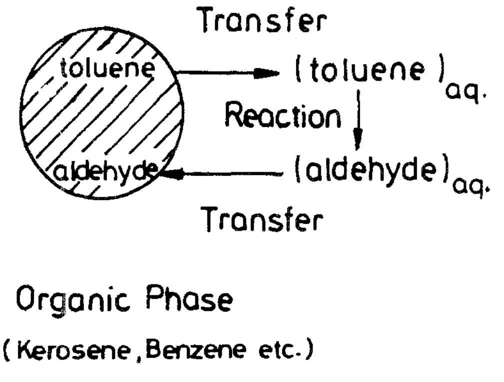

Fig. 4 Schematic presentation of reaction steps for mediated conversion of toluene in two-phase emulsions.

4.2. *Reactor model*

The conventional process design discussed so far and used by Ibl and co-workers (Fig. 3a) is not sufficient. Separation of the dispersed organic phase from the anolyte is also necessary because too high a content of organic matter in the anolyte reduces the O_2 overpotential and hence current efficiencies for the oxidant recuperation [12]. For this reason a second reactor with appropriate (relatively high) residence time, τ_2, has to be added after the first settler in order to convert dissolved benzyl alcohol to benzaldehyde. The latter must then be extracted by an inert organic solvent which does not contain toluene. Such advanced process design is depicted schematically in Fig. 3b.

4.2.1. Characterization of first reactor. The mass balance for the first reactor takes into account differences of mass fluxes at inlet and outlet and the generation and consumption due to chemical reactions, and reads for the polar benzyl alcohol, which is assumed to be extracted into the organic phase only to a negligible extent, as follows:

$$\mathrm{d}c(\mathrm{alcohol})/\mathrm{d}t = -c(\mathrm{alcohol})(1/\tau_1 + \mathrm{k}_2 c(\mathrm{Mn}^{3+})) + \mathrm{k}_1' c(\mathrm{Mn}^{3+}) \tag{11}$$

where τ_1 is the residence time of the first reactor.

The solution (Equation 12) of Equation 11 yields the relaxation time τ_{rel} which characterizes the time-dependence of the benzyl alcohol concentration (Equation 12) upon start-up of the reactor and the eventual steady-state concentration (Equation 13).

$$1 - (c/c^{t=\infty})^{(1)}(\mathrm{alcohol}) = \exp[-(1/\tau_1 + \mathrm{k}_2 c(\mathrm{Mn}^{3+}))t] = \exp(-t/\tau_{\mathrm{rel}}) \tag{12}$$

$$c^{t=\infty} = c_{\text{steady-state}}(\mathrm{alcohol})^{(1)} = \mathrm{k}_1' c(\mathrm{Mn}^{3+})/[\mathrm{k}_2 c(\mathrm{Mn}^{3+})_{\text{steady-state}} + 1/\tau_1] \tag{13}$$

Only steady-state conditions are of practical relevance. Therefore the index 'steady-state' will be omitted in what follows. The limiting cases of very long residence time τ_1^{l} and very short residence time τ_1^{s} can be distinguished.

For very long residence times ($\tau_1^{-1} \ll \mathrm{k}_2 c(\mathrm{Mn}^{3+})$), Equation 13 simplifies to

$$c(\mathrm{alcohol})^{(1)} = \mathrm{k}_1'/\mathrm{k}_2 \tag{14}$$

For very long residence times, τ_1^{l}, the rates of oxidation of toluene and benzyl alcohol are equal

$$\frac{1^{(1)}}{V_{\mathrm{R}}} \frac{\mathrm{d}N(\mathrm{toluene})}{\mathrm{d}t} = \frac{1^{(1)}}{V_{\mathrm{R}}} \frac{\mathrm{d}N(\mathrm{benzyl\ alcohol})}{\mathrm{d}t} \tag{15}$$

where V_{R} is reactor volume.

Since the distribution coefficient for benzyl alcohol may be assumed to be very high, the concentration of benzyl alcohol in the organic phase may be assumed to be negligible. Therefore, equal parts of the current, I, drawn through the electrolysis cell for Mn^{3+} recuperation, are needed to supply the oxidant for hydrocarbon oxidation in the first reactor and for alcohol oxidation in the first and second reactor together. The first two partial currents are

$$I(\mathrm{toluene})^{(1)} = V_{\mathrm{R}}^{(1)} F \mathrm{k}_1 c(\mathrm{Mn}^{3+})^{(1)} c(\mathrm{toluene})^{(1)}(\eta - 1) \tag{16}$$

$$I(\mathrm{alcohol})^{(1)} = [V_{\mathrm{R}}^{(1)} F \mathrm{k}_2 c(\mathrm{Mn}^{3+})^{(1)} c(\mathrm{alcohol})^{(1)} + V_{\mathrm{R}}^{(2)} F \mathrm{k}_2 c(\mathrm{Mn}^{3+})_1^{(2)} c(\mathrm{alcohol})^{(2)}](\eta - 1) \tag{17}$$

$$I(\mathrm{toluene})^{(1)} = I(\mathrm{alcohol})^{(1)+(2)} \tag{18}$$

where F is Faraday's constant and η is the current yield for oxidant recuperation.

For very long residence times, τ_1^{l}, the approximation

$$I(\mathrm{benzaldehyde\ formation})^{(1)} = 2 V_{\mathrm{R}}^{(1)} F \mathrm{k}_1 c(\mathrm{toluene})^{(1)} c(\mathrm{Mn}^{3+})^{(1)}(\eta - 1) \tag{19}$$

is obtained.

In processing emulsions the anolyte is kept saturated with toluene and $k_1 c(\text{toluene})$ may be substituted by k_1'. Equation 19 then becomes

$$I(\text{benzaldehyde formation})^{(1)} = 2V_R^{(1)} F k_1' \, c(\text{Mn}^{3+})^{(1)}(\eta - 1) \tag{20}$$

and the partial current for benzaldehyde oxidation in the first reactor is

$$I(\text{benzaldehyde oxidation})^{(1)} = V_R^{(1)} F k_3 c(\text{benzaldehyde})^{(1)} c(\text{Mn}^{3+})^{(1)}(\eta - 1) \tag{21}$$

For established benzaldehyde distribution equilibrium the aldehyde concentration in the aqueous phase is determined by the steady state aldehyde concentration in the organic phase,

$$c(\text{benzaldehyde})^{(1)} = Kx(\text{benzaldehyde})^{(1)}_{\text{org}} \tag{22}$$

where K is the distribution coefficient $K = (c_{\text{aq}}/x_{\text{org}})$; x_{org} is the mole fraction of the aldehyde in the organic phase; and c_{aq} is its molar concentration in the aqueous phase.

With Equation 22, the partial current for benzaldehyde oxidation is

$$I(\text{benzaldehyde oxidation})^{(1)} = V_R^{(1)} F k_3' c(\text{Mn}^{3+}) x(\text{benzaldehyde})^{(1)}_{\text{org}} \tag{23}$$

where $k_3' = k_3 c(\text{benzaldehyde})_{\text{sat}}$; c_{sat} is the saturation concentration of pure benzaldehyde; and x is the mole fraction.

If benzaldehyde oxidation is negligible in the second reactor, because its concentration in the organic phase in this reactor may be kept much lower than in the first reactor, the partial current for recuperation of the oxidant needed in the second reactor is

$$I(\text{alcohol oxidation})^{(2)} = V_R^{(2)} k_2 c(\text{Mn}^{3+})^{(2)} c(\text{alcohol})^{(2)} \tag{24}$$

In the first reactor, concentration limits for benzaldehyde must be observed in order to achieve acceptable chemical yields for benzaldehyde. The rate of further benzaldehyde oxidation must be kept below a reasonable fraction f (say 5–10%) of the rate of benzaldehyde production, i.e.

$$k_3 c(\text{aldehyde})^{(1)} < f k_1 c(\text{toluene})^{(1)} \tag{25}$$

Equation 25 defines the highest acceptable mole fraction of benzaldehyde x_{max} in the organic phase. For undiluted toluene as the organic phase, one obtains

$$x(\text{aldehyde})^{(1)}_{\text{max}} \leqslant f(k_1'/k_3') \tag{26}$$

For toluene dissolved in an inert organic solvent the limiting mole fraction is

$$x(\text{aldehyde})^{(1)}_{\text{max}} \leqslant f(k_1'/k_3') x(\text{toluene})^{(1)} \tag{27}$$

For different benzaldehydes the critical concentration ratios are collected in Table 8 for Mn^{3+} in 60 wt % H_2SO_4 as oxidant. Table 9 repeats these data for benzaldehyde but adds the minimal residence time which would be necessary to establish 'very long' τ_1^l (i.e. $1/\tau_1 < 1/10k_2 c(\text{Mn}^{3+})$. Table 9 shows the steady state concentration of benzyl alcohol and the ratio $[c/c_0(\text{Mn}^{3+})]$ of unconverted oxidant (c_0 being its inlet concentration) at the outlet of the first reactor. The data demonstrate very clearly that 'very long' residence time is not a meaningful option; neither are the residence times economically acceptable nor is it possible to achieve complete oxidation of the dissolved benzyl alcohol in a second reactor because the oxidant hold-up is already exhausted in the first reactor.

'Very short' residence times, τ_1^s (i.e. $1/\tau_1 > 10k_2 c(\text{Mn}^{3+})$) would not allow maximal benzyl alcohol concentrations in the first reactor (compare Equation 14). Instead, the benzyl alcohol concentration may be approximated by

$$c(\text{alcohol})^{(1)} = k_1' c(\text{Mn}^{3+}) \tau_1^s \tag{28}$$

Table 10 shows, for toluene oxidation by Mn^{3+}, maximally permissible residence times (for the

Table 8. Limiting concentration ratio [x(*aldehyde*/ x(*toluene*)]$_{\max}$ *in the organic phase of the first reactor to be observed in order to prevent losses due to aldehyde oxidation exceeding 5% for very long residence times*

System	*Temperature (° C)*		
	20	*40*	*60*
Toluene/Mn^{3+}	0.1	0.35	0.55
p-chlorotoluene/Mn^{3+}	0.36	0.55	1.4
p-xylene/Mn^{3+}	0.46	0.65	0.97
Toluene/Ce^{4+}	0.021	0.14	0.283
Toluene/Co^{3+}	0.4	0.62	–
Toluene/Mn^{3+}			

Oxidant concentration = 1×10^{-2}M.

option of very short τ_1^s), the benzaldehyde concentration, ratio [$c/c_0(Mn^{3+})$] of non-converted oxidant, and ratio of amount of alcohol which is converted in the first reactor relative to the amount of alcohol to be reacted in the second reactor [$(\dot{N}^{(1)}/\dot{N}^{(2)})$(alcohol)]. The data show that 'very short' residence times seem to be the desirable option because the residence times are acceptable, and there is enough oxidant left at the reactor outlet to allow for an eventual alcohol oxidation after separating the toluene-containing organic phase from the aqueous phase in a 'fast' phase-separator such as a hydrocyclone. Table 10 demonstrates that it would be advantageous to choose an enhanced working temperature, i.e. between 30 and 60° C, because of shorter residence times and because the oxidant concentration of the effluent will be sufficiently high to convert the dissolved benzyl alcohol to benzaldehyde.

4.2.2. Second reactor. The eventual oxidation of benzyl alcohol to benzaldehyde is performed most efficiently, with good space–time yield and high selectivity, in a counter-current extractor with approximate tube-reactor characteristics for the organic and the aqueous phase (Fig. 3b). Again, one obtains the same limiting equation for the second reactor as obtained for the first:

$$f[k_1' + k_2 c(\text{alcohol})]^{(2)} \geqslant k_3' x(\text{aldehyde})^{(2)} \tag{29}$$

4.3. *Process streams and aldehyde extration*

For the first reactor where the alcohol concentration in the aqueous phase and the aldehyde concentration in the organic phase are highest, one obtains by introduction of Equations 13 and 28

Table 9. Limiting concentration ratio in the organic phase of the first reactor, minimal value for 'very long' residence time, stationary benzyl alcohol concentration and degree of conversion, DC(*ox*), *of oxidant for oxidation of toluene by* Mn^{3+}, *60 wt%* H_2SO_4

	Temperature (° C)		
	20	*40*	*60*
[x(aldehyde)/x(toluene)]$_{\max}$	0.1	0.35	0.55
$\tau_{\min}^{(1)}$(s)	2.0×10^5	2.0×10^4	2.0×10^3
$(c/c_0)(Mn^{3+})$	0.01	0.02	0.06
DC(ox)	0.99	0.98	0.94
c(benzyl alcohol) (M)	8.6×10^{-2}	4.6×10^{-2}	1.6×10^{-2}

Table 10. Limiting residence time for option of 'very short' residence time, benzyl alcohol concentration at reactor outlet, relative oxidant concentration, degree of conversion of oxidant and ratio of alcohol conversion in first reactor to alcohol conversion in consecutive reactor for oxidation of toluene by Mn^{3+}. Last two lines: maximal permissible aldehyde mole fraction in organic phase in stirred tank reactor (STR) and the extractor–reactor

	Temperature (° C)		
	20	*40*	*60*
$\tau^{(1)}_{\max}$(s)	2000	200	20
$c(\text{alcohol})^{(1)}$ (M)	8.0×10^{-3}	5.0×10^{-3}	1.6×10^{-3}
$(c/c_0)(\text{Mn}^{3+})^{(1)}$	0.53	0.66	0.86
$DC(\text{Mn}^{3+})^{(1)}$	0.47	0.34	0.14
$(\dot{N}^{(1)}/\dot{N}^{(2)})$ (alcohol)	0.1	0.1	0.1
$x(\text{aldehyde})_{\max}$ (STR)	$0.11\,x(\text{toluene})^{(1)}$	$0.11\,x(\text{toluene})^{(1)}$	$0.11\,x(\text{toluene})^{(1)}$
$x(\text{aldehyde})_{\max}$ (extractor) $= A\,c(\text{alcohol})^{(1)}_{\text{local}}$ (mol^{-1})	$1.5\,c(\text{alcohol})^{(2)}_{\text{local}}$	$8.3\,c(\text{alcohol})^{(3)}_{\text{local}}$	$35\,c(\text{alcohol})^{(4)}_{\text{local}}$

Oxidant concentration $= 2 \times 10^{-2}$ M.

as limiting value for maximal aldehyde concentration:

$$x(\text{aldehyde})^{(1)}_{\max} \leqslant f(\text{k}_1'/\text{k}_3')[1 + \text{k}_2 c(\text{Mn}^{3+})^{(1)}\tau^{s}_{1}] \tag{30}$$

For the second counter-current extracting reactor, after fast oxidation of the homogeneously dissolved toluene, the local concentration limit for the aldehyde changes to

$$x(\text{aldehyde})^{(2)}_{\text{local}} \leqslant f(\text{k}_2/\text{k}_3')c(\text{alcohol})^{(2)}_{\text{local}} \tag{31}$$

The second term of the left-hand side of Equation 30 amounts to only 0.1 for a Mn^{3+} concentration of 10^{-2} M. Thus the limiting values $x(\text{aldehyde})_{\max}$ in Table 9 are only changed by 10% due to consideration of the co-oxidation of benzyl alcohol in the first reactor. Much more serious is the fact that in the extractor, according to Equation 31, only relatively low concentrations of the aldehyde can be allowed for in the organic phase. This condition is accomplished by injecting a pure organic carrier phase into the extractor and using this phase for uptake of the aldehyde in countercurrent extraction. Countercurrent flow of the aqueous and organic phases accounts simultaneously for the highest local alcohol concentration in the aqueous solution and the highest local aldehyde concentrations in the organic phase at the site where the organic phase leaves the column and the aqueous phase coming from the first reactor enters it.

Table 10 presents the factor $A = f(\text{k}_2/\text{k}_3')$ (for $f = 0.05$) for 20, 40 and 60° C. The values of A which limit the concentration of the aldehyde in the organic phase in the extractor increase pronouncedly with increasing temperature. This again underlines the fact that enhanced working temperatures are favourable to practical operation. The organic phase leaving the extractor is then used for the first reactor before being worked up for separation of benzaldehyde and recycled toluene. In the first reactor it possesses the highest local benzaldehyde concentration in the total process. Before entering the first reactor the toluene recycled from the final distillation column and the supply of fresh toluene necessary to account for converted toluene is added to the stream of the organic phase.

5. Conclusion

The most important finding of this investigation is the necessity to keep the benzaldehyde concentrations below a critical value within the organic phase. Optimal performance is obtained by using two reactors. In the first, a two-phase stirred tank is needed to supply toluene to the aqueous phase and to convert it partially to benzyl alcohol. The second reactor is a countercurrent reactor–extractor device needed to convert dissolved benzyl alcohol to benzaldehyde and to extract the benzyldehyde into an inert organic phase not containing toluene. Further, it is shown that due to the activation parameters for the different oxidation steps enhanced working temperatures improve space–time yield and selectivity of the process. Relatively short residence times for the initial stirred tank reactor should be used.

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