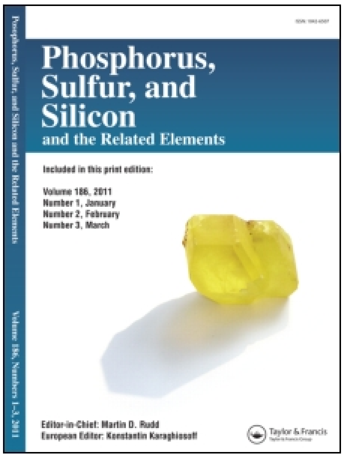

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KINETICS AND INFLUENCE OF MASS TRANSFER ON SELECTIVITY IN THE SULFONATION OF BENZENE WITH SULFUR TRIOXIDE

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Available kinetic data on aromatic sulfonation with SO_3 are critically reviewed. It is concluded that the kinetic reaction rate of the sulfonation of benzene with sulphur trioxide at 25°C is fast compared to the rate of the mass transfer process, moreover it is concluded that the value of the mass transfer coefficient realized in a particular reactor may influence the selectivity of the sulfonation reaction. Experimental results on sulfonation of 30 vol % benzene in 1,2 dichloroethane using three types of gas-liquid reactors which greatly differ in mass transfer characteristics have been summarized. The results show a decrease of the formation of the by-product diphenyl sulfone with increasing liquid side mass transfer coefficient. Especially in a cyclone reactor, by-product formation could be considerably suppressed. Based on the kinetic picture derived, the relationship between sulfone formation and mass transfer coefficient is qualitatively understood.

INTRODUCTION

Aromatic sulfonation is an important process in the surfactant industry. The amount of by-product formation may, among other factors, depend upon the hydrodynamics realized in the reactor. In the particular case of sulfonation of benzene, the formation of the by-product diphenyl sulfone can be substantial. As shown in Table I, selectivity obtained in this process depends upon the manner in which the reaction is carried out. The cause of the large variance in observed selectivity is not yet well understood. This prompted our interest in study of the relationship between by-product formation and the hydrodynamics during reaction. We sulfonated liquid benzene with gaseous sulfur trioxide in three reactor types which greatly differ in mass transfer characteristics. The kinetics of the reactions involved, must be known in order to understand the results of these experiments. However, despite extensive study of sulfonation of aromatics with sulfur trioxide in aprotic solvents,[4,5] the kinetics of sulfonation of (alkyl) benzene are not yet free from speculation.[6]

Homogeneous kinetic experiments on sulfonation of benzene with SO_3, at least in solvents which do not considerably reduce the reactivity of sulfur trioxide, are difficult to conduct. Well controlled, kinetic experiments in heterogeneous systems, in which both mass transfer and reaction occur, have not been reported as yet.

Therefore, a mechanism of benzene sulfonation with SO_3 must be deduced from experimental results with solvents that make the Lewis-acid

TABLE I

Diphenyl sulfone formation in semi-batch sulfonation of benzene with sulfur trioxide. A: drop wise addition of SO_3 to C_6H_6; B: drop wise addition of C_6H_6 to SO_3; C: drop wise simultaneous addition of SO_3 and C_6H_6 to reaction mixture; D: SO_3 vapour passed into liquid benzene; *a "Nomenclature" is added to this contribution; **extrapolated value; ***calculated with the assumption that all SO_3 reacts with benzene, actual values are possibly about 10–15% higher

$\frac{SO_3}{C_6H_6}$	Solvent	T [°C]	Method	$1-\eta^*$ [%]	Reference
0		25	A	25**	Cerfontain[1]
0.12		25	A	30	Cerfontain[1]
0.4		25	A	40	Cerfontain[1]
1.0		25	A	55	Cerfontain[1]
0.5		20–30	A	30***	Gilbert[2]
1.0	SO_2	−8	A	2.9	Leierson[3]
1.0		22–40	B	13.9***	Gilbert[2]
1.0	SO_2	−8	B	1.5	Leierson[3]
1.0	$CHCl_3$	0–15	C	3.1	Leierson[3]
1.0		20–56	D	26*	Gilbert[2]

SO_3 less reactive (Lewis bases) and from kinetic experiments with less reactive aromatics (halobenzenes, aromatics with substituted electron attracting groups which de-activate the aromatic ring: meta directing groups).[7,8]

In this contribution we review critically available kinetic information. Based on the kinetics derived, we will show that for sulfonation with gaseous sulfur trioxide an increase in the mass transfer coefficient in the liquid phase may result in a decrease in by-product formation. The experimental results obtained with the three reactor types mentioned above support this theory. These results will be presented and shortly discussed in this paper while details on the chemical reaction engineering aspects have been extensively described elsewhere.[9–11]

MECHANISTIC MODELS FOR AROMATIC SULFONATION WITH SULFUR TRIOXIDE

Early kinetic investigations on aromatic sulfonation with SO_3 are reported by Hinshelwood and co-workers.[12–14]

Rueggeberg *et al.*[15] sulfonated benzene (B) with sulfur trioxide (A), both solved in sulfur dioxide and suggested:

$$C_6H_6 + SO_3 \longrightarrow C_6H_5SO_3H \qquad (1)$$

$$C_6H_5SO_3H + SO_3 \longrightarrow C_6H_5SO_2OSO_3H \qquad (2)$$

$$C_6H_5SO_2OSO_3H + C_6H_6 \begin{cases} \longrightarrow 2C_6H_5SO_3H \\ \searrow (C_6H_5)_2SO_2 + H_2SO_4 \end{cases} \qquad (3)$$

The assumption of a sulfonic acid, monoanhydride with sulfuric acid ($C_6H_5S_2O_6H$, generally referred to as (benzene)pyrosulfonic acid) as an intermediate allowed them to explain an observed decrease in sulfone formation after adding small amounts of acetic acid to the sulfonating mixture by

$$C_6H_5S_2O_6H + CH_3COOH \longrightarrow C_6H_5SO_3H + CH_3CO_2SO_3H \qquad (4)$$

$$CH_3CO_2SO_3H + C_6H_6 \longrightarrow C_6H_5SO_3H + CH_3COOH \qquad (5)$$

After an extensive study in aromatic sulfonation kinetics, Cerfontain and his co-workers[6,16–18] introduced a mechanistic model (see Figure 1) that is believed to be applicable for sulfonation with sulfur trioxide in both solvents which act as a Lewis base for SO_3, e.g. nitrobenzene, SO_2, nitromethane and in aprotic solvents without Lewis base character, e.g. halo alkanes. Results from kinetic experiments concerning sulfonating of chlorobenzenes with SO_3 in nitromethane, as an example of a solvent of the first type[16,17] and with $CFCl_3$, as a solvent of the latter type[6,16] were shown to be in agreement with the model presented.

The reaction sequence (6–8), known as primary sulfonation, results in arenepyrosulfonic acid as the primary reaction product. Although pyrosulfonic acids have not been isolated as such,[19] the existence of methanepyrosulfonic acid in solution has been shown by Raman spectra.[20] At present, the occurrence of pyrosulfonic acids in aromatic sulfonation is generally accepted.[19,21] Because of instability, arenepyrosulfonic acids react further to arenesulfonic acids, arenesulfonic

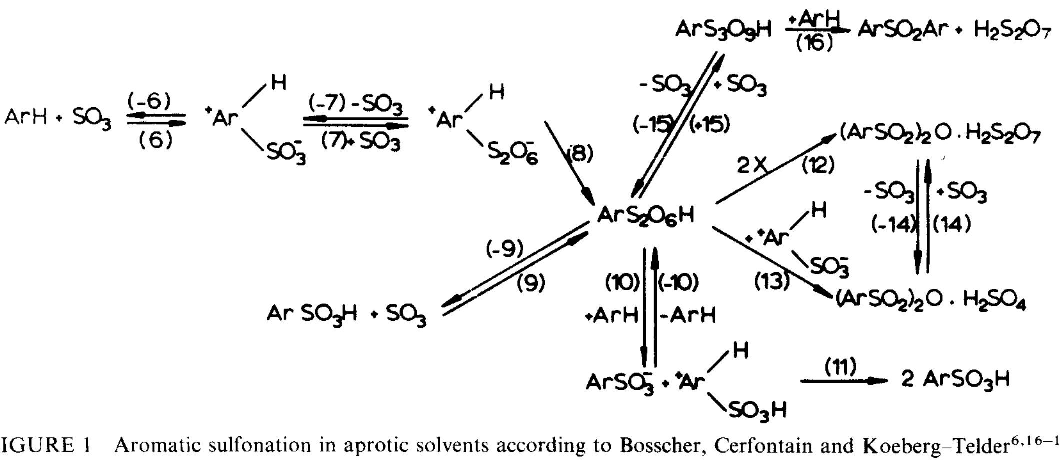


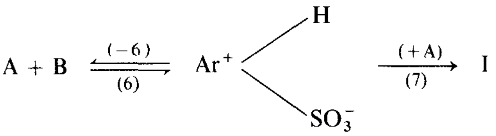
FIGURE 1 Aromatic sulfonation in aprotic solvents according to Bosscher, Cerfontain and Koeberg-Telder[6,16–18]

anhydrides and diaryl sulfones. If the conversion rate of pyrosulfonic acid is comparable to, or slower than its production rate, then the pyrosulfonic acid concentration may reach appreciable values.[6] Pyrosulfonic acid may act as a sulfonating agent via reactions (10, 11),[18] this is called secondary sulfonation. The main sulfonation routes shown in Figure 1, i.e. primary and secondary sulfonation, anhydride formation and sulfone formation, are briefly discussed in the following section.

Primary Sulfonation

The proposed primary sulfonation mechanism allows for monomeric SO_3 as the primary sulfonating agent which is widely accepted at present.[1,4,5,21]

The absence of a significant hydrogen isotope effect has proved that the reaction steps including proton removal from the aromatic ring (e.g. in reactions 8, 16, 11) were not rate limiting in sulsulfonation of benzene. This holds without a solvent,[22,23] with a Lewis base as a solvent[16,24,25] and with a non-Lewis base as a solvent.[16,25] These reaction steps are also not rate limiting in *p*-dichlorobenzene sulfonation in a complexing[16,17] and in a non-complexing solvent.[6,16] These observations indicate that equilibrium (7) lies far to the right; thus the general rate equation for primary sulfonation follows from[6,16]



$$A + B \underset{(6)}{\overset{(-6)}{\rightleftharpoons}} Ar^+\!\!<^{H}_{SO_3^-} \xrightarrow[(7)]{(+A)} I$$

The result is[6,16]

$$-r_A = \frac{k_6 k_7 c_A^2 c_B}{k_{-6} + k_7 c_A} \qquad (17)$$

Without a Lewis base as a solvent, the observed r_A is proportional to $c_A c_B$, indicating that $k_{-6}/k_7 c_A$ is much smaller than one. This has been shown to be the case for *p*-dichlorobenzene sulfonation in $CFCl_3$.[6,16]

On the contrary, with a Lewis base as a solvent, the observed r_A is proportional to $c_A^2 c_B$. This was shown for halobenzenes in nitromethane,[16,17,26] benzene in nitrobenzene,[13] nitrobenzene without a solvent,[14] and for halobenzenes and *p*-nitrotoluene in nitrobenzene.[12,13] These results are explained by the large affinity between SO_3 and a Lewis base solvent which causes the numerical value of the group $k_{-6}/k_7 c_A$ to increase from much smaller to much larger than one.[16]

In comparing the kinetics of benzene and *p*-dichlorobenzene sulfonation, k_7 is not expected to be much influenced by the effects of ring substitution.[6] Besides, k_{-6} for benzene is thought to be smaller than, or at least of the same order of magnitude as that for *p*-dichlorobenzene.[6] From these considerations we conclude that primary sulfonation of benzene without a solvent, or in the non-complexing solvent 1,2-dichloroethane, proceeds following sequence (6, 7, 8) and is of first order in both SO_3 and benzene concentration.[6]

It should be mentioned that concerning the conversion rate of sulfur trioxide, reaction (9) possibly competes with reactions (6–8) at higher aromatic conversions.

$$ArSO_3H + SO_3 \rightleftharpoons ArS_2O_6H \qquad (9)$$

On the basis of a comparison with the systems H_2SO_4–$H_2S_2O_7$ and CH_3SO_3H–$CH_3S_2O_6H$, the equilibrium of reactions (9) is expected to lie far to the right-hand side in aprotic sulfonation.[18]

Secondary Sulfonation

In secondary sulfonation, pyrosulfonic acid acts as the sulfonating agent for the aromatic.[18] Secondary sulfonation reactions are considered to be slow compared to primary sulfonation.[18] This is concluded from the strong decrease in aromatic conversion rate in initially 1–1 SO_3-aromatic mixtures for an aromatic conversion above $\zeta = 0.5$; that is, after 2 moles SO_3 have reacted with 1 mole benzene. Concerning this aspect, data are available on sulfonation of nitrobenzene,[12] 4-nitrotoluene,[27] iodobenzene in nitromethane[26] and benzene and halobenzenes in nitrobenzene.[13] These observations may indicate, but not prove, that secondary sulfonation is also slow compared to primary sulfonation, in sulfonating neat benzene, or benzene diluted with the non-complexing solvent 1,2-dichloroethane.

An additional argument follows from interpretation of experimental results obtained by Koeberg-Telder *et al.*[18] They sulfonated toluene by bubbling gaseous SO_3 diluted with N_2 through the liquid (25°C), and measured after hydrolysis of the reaction mixture, a change in isomer distribution with increasing toluene conversion. From this observation it was concluded that secondary

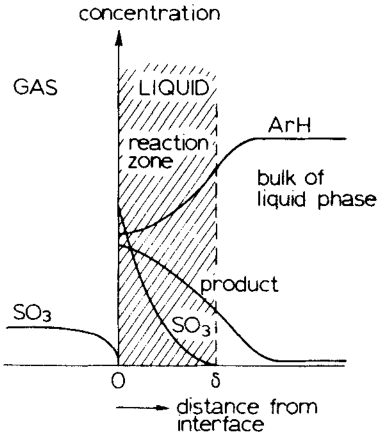


FIGURE 2 Concentration profiles near gas-liquid interface.

sulfonation according to reactions (10–11) was not significant for toluene conversion below 1%. We have shown[10] that the overall true kinetic rate of the reactions (6–8) in sulfonation of benzene with SO_3 is fast compared to the rate of the SO_3 absorption process, at least at room temperature in a solvent that does not de-activate SO_3 and with benzene concentrations above the order of 20% by volume. Therefore, the concentration profiles of the reactants SO_3 and benzene (ArH) near the gas-liquid interface are qualitatively as presented in Figure 2.[10] Due to the high reactivity, all SO_3 that absorbs from the gas phase into the liquid phase is converted in the hatched zone close to the interface (Figure 2) and practically no unconverted SO_3 is found beyond a certain distance δ from the interface. As only in the hatched area SO_3 and benzene are both present, reaction between these substances is restricted to this zone exlusively; it is called the reaction zone. The thickness of this zone is in the order of 10^{-4} m or smaller.[28–29] Transport of ArH to and product from the reaction zone near the gas-liquid interface is effected by diffusion. Toluene behaves in a similar way as benzene because it is even more reactive than benzene.[4] If secondary sulfonation according to reactions (10, 11) is fast compared to primary sulfonation, then pyrosulfonic acid should convert immediately after it has been formed, that is, fast in comparison to the rate by which the product diffuses away from the reaction zone, beyond δ. However, as mentioned above, Koeberg-Telder[15] found the conversion rate of pyrosulfonic acid to be relatively low compared to the conversion rate of toluene when toluene conversions were below 1%. This indicates that for toluene secondary sulfonation is not fast in comparison to the mass transfer process. Therefore the product that accumulates at the interface is pyrosulfonic acid and not sulfonic acid. Pyrosulfonic acid diffuses from the interface into the bulk of the liquid where it reacts relatively slowly to form the product sulfonic acid, though the secondary sulfonation rate still may be fast enough to maintain a low pyrosulfonic acid concentration in the bulk liquid. If the data on sulfonation of toluene as presented above, can be extended to sulfonation of benzene, then these results suggest that secondary sulfonation of benzene is slow compared to both primary sulfonation and the mass transport process. We expect that this extension is allowed because of chemical similarity of the two secondary sulfonation reactions.

Anhydride Formation

With an initial SO_3/aromatic ratio >0.5 and at a low reaction temperature, sulfonic anhydride is the ultimate main product in sulfonation of halobenzenes. This has been found with SO_3 solved in nitromethane below 0°C[17,21] and with SO_3 solved in trichlorofluoromethane below −10°C.[6]

At a higher reaction temperature less anhydride is formed. In sulfonation of iodobenzene at 40°C with an initial SO_3/aromatic ratio <0.5, anhydride formation is below 10% with respect to converted aromatic.[21]

Reaction (12) has been proposed for a solvent of Lewis base type[17,21] and rejected for non-complexing solvents.[6] Reaction (13) is proposed for the latter case[6] but is believed to be also possible in solvents with Lewis base character.[17] In sulfonation of *p*-dichlorobenzene two moles of SO_3 are consumed per mole of aromatic. This indicates that $(ArSO_2)_2O \cdot H_2S_2O_7$ is the main product.[6,17]

In sulfonation of toluene with SO_3, anhydride formation plays a minor role due to the much higher reactivity of toluene which favours reaction (10) with respect to reaction (13).[18] This same argument may hold for benzene though quantitative information is not found in the open literature.

To investigate the formation of anhydride in benzene sulfonation, we sulfonated both neat and diluted benzene (30 vol.% in 1,2-dichloroethane) in a round bottom flask by bubbling a sulfur trioxide-nitrogen mixture through the liquid. In these experiments, 10^{-4} m^3 of reaction mixture was poured into 10^{-3} m^3 of cold (0°C), diluted sulfuric acid (37%). It was expected that if anhydride was present, a precipitate would form analogous to *p*-dichlorobenzenesulfonic anhydride (which precipitates from reaction mixtures with trichlorofluoromethane as a solvent after adding cold diluted sulfuric acid[16]) and to toluenesulfonic anhydride (which precipitates after diluting the reaction mixture with water[18]). Neat benzene was sulfonated at room temperature until $c_P/c_{B_0} =$ 0.008 and 0.2, respectively and diluted benzene until $c_{PcB_0} = 0.19$, 0.36, 0.72 and 0.75, respectively. In none of these experiments was a precipitate observed after quenching. To check the possibility that some anhydride remained in the dichloroethane phase, the organic phase of the $c_P/c_{B_0} =$ 0.75 mixture was separated from the aqueous layer and the amount of sulfonic acid still present in the organic phase was measured. The mixture was then diluted with an equal amount of water and refluxed for 30 minutes in order to hydrolyze any solved anhydride.[18] After re-measuring the amount of sulfonic acid, it was found that 0.34% anhydride could have formed relative to benzenesulfonic acid.

From these results, we conclude that anhydride formation is not important in sulfonation of benzene for the given conditions of temperature and conversion.

Sulfone Formation

Sulfone formation according to reactions (15) and (16) differs in several aspects from Rueggeberg's hypothesis (reaction (3)). Among these differences is the predicted relationship between sulfone formation rate and SO_3 concentration. Bosscher and Cerfontain[6,16,17] proved that the reaction sequence (15, 16) explains the observed sulfone formation in homogeneous sulfonation of chlorobenzenes in both a complexing (nitromethane) and a non-complexing solvent (trichlorofluoromethane), while reaction (3) does not.

In connection with the hypothesis of ArS_3O_9H as an intermediate, Bosscher and Cerfontain[6] refer to the existence of $H_2S_3O_{10}$ in fuming sulfuric acid.

Reaction sequence (15, 16) also has been suggested for the sulfonylation of benzene.[6] Moreover, the absence of a kinetic isotope effect in sulfonylation of (1,3,5-$^2H_3$) benzene indicates that the proton removal step in reaction (16) is not rate limiting.[25]

REACTION RATE

Kinetic rate expressions for the sulfonation of benzene and chlorobenzenes in various solvents are reviewed in Table II. Only two reaction rate studies on sulfonation of benzene with sulfur trioxide are known.[13,30] These are the studies of Desel *et al.* (Table II, entry No. 1) on the sulfonation of benzene in a complexing solvent ($C_6H_5NO_2$) and of Ratcliff (Table II, entry No. 3) in a non-complexing solvent (ClC_2H_4Cl). We expect Ratcliff's rate equation (entry No. 3) to predict a sulfonation rate which is too low for benzene in a non-complexing solvent such as dichloroethane. Our arguments are:

1) The sulfonation rate of chlorobenzene is approximately 10^5 times faster than the sulfonation rate of *p*-dichlorobenzene (see Table II, entries No. 5 and 6). Sulfonation of benzene is still faster (compare entries No. 2 and No. 4). Hence, sulfonation of benzene in a non-complexing solvent (ClC_2H_4Cl) is expected to be very much faster than sulfonation of *p*-dichlorobenzene in the same type of solvent. However, Ratcliff's equation only predicts a small difference for typical experimentally applied concentrations[30] (compare entries No. 3 and No. 7).

2) Complexing solvents as CH_3NO_2 and $C_6H_5NO_2$ reduce SO_3 reactivity considerably.[31] Therefore, sulfonation of *p*-dichlorobenzene is about 10^5 times faster in a non-complexing solvent than in a complexing one (see entries No. 6 and and No. 7). Such a difference in rate may be expected for benzene too. According to Ratcliff's equation, however, sulfonation in non-complexing dichloro ethane is not or not much faster than in complexing $C_6H_5NO_2$ (see entries No. 1, 2 and 3).

3) The kinetic orders measured by Ratcliff as

$$-r_A = 5.11 c_A^{1.24} c_B^{0.57} \tag{18}$$

are not in agreement with theory on primary sulfonation in a non-complexing solvent which predicts first order kinetics with respect to both reactants. We showed[32] that the apparent orders observed may have been influenced by diffusion limitation. According to the theory of combined mass transfer with reactions[28,29] true 1,1-kinetics will actually be observed as

$$r_A \sim c_A \sqrt{c_B} \tag{19}$$

provided that the reaction rate is much faster than the mixing rate and that the reaction occurs

TABLE II

Kinetic rate expressions for sulfonation of benzene and chlorobenzenes in various solvents

Entry No.	ArH	Solvent	T [°C]	Rate expression [kmol/m³ s]	k	Experimental conditions	Reference
1	C_6H_6	$C_6H_5NO_2$	3.1	$-r_A = kc_A^2c_B$	17.2	$(c_B = 0.05;$	Dresel[13]
2	C_6H_6	$C_6H_5NO_2$	40.1	$-r_A = kc_A^2c_B$	48.8	$0.04 < c_A < 0.16)$	Dresel[13]
3	C_6H_6	ClC_2H_4Cl	25	$-r_A = kc_A^{1.24}c_B^{0.57}$	5.11	$(0.04 < c_B < 0.2; 0.015 < c_A < 0.04)$	Ratcliff[30]
4	C_6H_5Cl	$C_6H_5NO_2$	40	$-r_A = kc_A^2c_B$	2.4		Dresel[13]
5	C_6H_5Cl	CH_3NO_2	3.5	$-r_A = kc_A^2c_B$	0.6		Bosscher[17]
6	p-$C_6H_4Cl_2$	CH_3NO_2	20	$-r_A = kc_A^2c_B$	$17\ 10^{-6}$	$(0.75 < c_B < 2.5; 0.2 < c_A < 0.8)$	Bosscher[17]
7	p-$C_6H_4Cl_2$	$CFCl_3$	20	$-r_A = kc_Ac_B$	1.2	$(5 \cdot 10^{-3} < c_B < 0.1; 5\ 10^{-2} < c_A < 0.25)$ extrapolated from −10°C and −28°C	Bosscher[16]

mainly in the liquid elements that contained benzene before mixing occurred.

Equation (18) agrees with Eq. (19) within the range of experimental error. Therefore the apparent reaction orders, as found by Ratcliff, can be explained by completely diffusion limited, 1,1-order kinetics. Accepting the fact that sulfonation of benzene with SO_3 in a non-complexing solvent is first order in both reactants and taking as a minimum value $-r_A$ as predicted by Eq. (18) results in

$$-r_A = k_6 c_A c_B \tag{20}$$

with

$$k_6(25^\circ C) \geq 5.11 \frac{c_A^{0.24}}{c_B^{0.43}} \tag{21}$$

The inequality sign in Eq. (21) is to include the possibility that the observed reaction rate has been influenced by diffusion limitation, which, if it occurs, always lowers the conversion rate.

In Ratcliff's experiments $c_A \leq 0.04\ \mathrm{kmol/m^3}$ and $c_B \geq 0.04\ \mathrm{kmol/m^3}$. Therefore:

$$k_6(25^\circ C) \geq 9.4\ \mathrm{m^3/kmol\ s}. \tag{22}$$

SELECTIVITY

In the sulfonation of benzene, a strong dependence is found between the percentage of sulfone obtained and the manner in which the reactants are brought together (Table I).

This phenomenon, while not yet completely understood, must relate, at least in part, to the mass transport limitation which plays a role in sulfonation of benzene. The argument is as follows. For the case of homogeneous kinetics with sulfonic acid formation according to

$$\mathrm{ArS_2O_6H + ArH \longrightarrow 2ArSO_3H} \tag{10}$$

and sulfone formation following

$$\mathrm{ArS_2O_6H + SO_3 \rightleftharpoons ArS_3O_9H} \tag{15}$$

$$\mathrm{ArS_3O_9H + ArH \longrightarrow Ar_2SO_2 + H_2S_2O_7} \tag{16}$$

maximum by-product formation $(1 - \eta)$ is expected in those experiments in which the SO_3/benzene ratio is, on an average, at its highest. This may be understood directly from the proposed kinetics (10, 15, 16) or indirectly by applying steady state theory with respect to the intermediates ArS_2O_6H (I) and ArS_3O_9H (I′). For the latter route:

$$0 = \frac{dc_I}{dt} = k_6 c_A c_B - k_{10} c_B c_I - k_{15} c_A c_I + k_{-15} c_I' \tag{23}$$

$$0 = \frac{dc_{I'}}{dt} = k_{15} c_A C_1 - k_{-15} c_{I'} - k_{16} c_B c_1' \tag{24}$$

$$\frac{dc_X}{dt} = k_{16} c_B c_I' \tag{25}$$

$$\frac{dc_P}{dt} = 2k_{10} c_B c_I \tag{26}$$

From Eqs. (23–26) it follows that

$$\frac{dc_X}{dc_P} = \frac{k_{15} k_{16} c_A}{2k_{10}(k_{-15} + k_{16} c_B)} \tag{27}$$

Comparing the liquid bulk concentration ratio c_A/c_B, averaged over the conversion ζ, in the two sulfonation methods A and B described in Table I, it is evident that this ratio is higher in method B, in which benzene is added drop wise to sulfur trioxide, than in method A, in which the reverse procedure is applied. Therefore, for the case of true homogeneous kinetics highest sulfone formation is expected with method B according to Eq. (27). The contrary is observed from Table I. This indicates that the reported $(1-\eta)$ from Table I cannot be understood from true homogeneous kinetics according to Eqs. (10, 15, 16).

In the preceding section we concluded that it is difficult to realize homogeneous kinetics for this reaction because of the high reaction rate relative to the mixing rate. Therefore we expect that the reported selectivities in Table I are influenced by mass transport limitation of reactants. However, insufficient information on the micro-concentration history in the experiments presented in Table I, prevents an explanation of the observed differences in sulfone yield. For this reason, we systematically studied the influence of mass transfer on selectivity in sulfonation of liquid benzene with gaseous SO_3. The results of this investigation will be summarized in the next section.

EXPERIMENTAL RESULTS

We sulfonated liquid benzene with gaseous sulfur trioxide in a stirred cell reactor (see Figure 3), a co-current tube reactor (see Figure 4) and in a cyclone reactor (see Figure 5). A more extensive description of the reactors and of the experimental

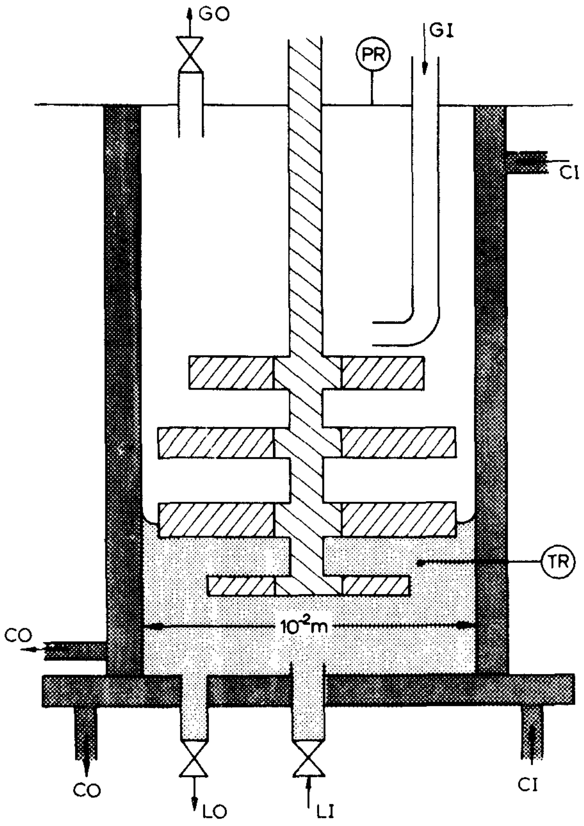


FIGURE 3 Stirred cell reactor (scale drawing). C = coolant; G = gas; I = inlet; L = liquid; O = outlet; P = pressure; R = recorder; T = temperature.

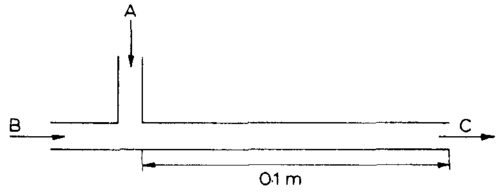


FIGURE 4 Tube reactor. A = gas inlet; B = liquid inlet; C = outlet diamater: 8 10^{-3}m.

set-up has been presented elsewhere.[10,11] In the stirred cell, the liquid surface is only slowly stirred and therefore the liquid side mass transfer coefficient (k_L) is relatively low in this reactor compared to conventional gas liquid reactors.[10] The cyclone reactor is a new gas-liquid reactor which has a tangential liquid inlet (see Figure 6). This reactor especially has been developed to realize very high k_L values.[9] In the tube reactor, k_L values are intermediate.[11] Table III summarizes typical values of the liquid side mass transfer coefficient of non-viscous solutions in the various reactors. Experimental results on selectivity obtained with the sulfonation of 30 vol % benzene in 1,2 dichloroethane with gaseous sulfur trioxide in the various reactors have been summarized in Figure 7. References 10 and 11 give additional data.

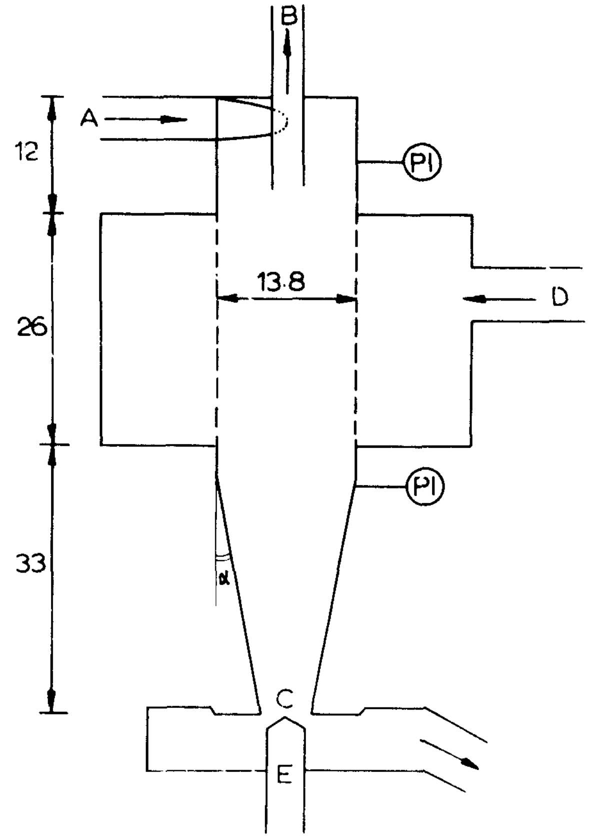


FIGURE 5 Cyclone reactor. Unit of length: 10^{-3}m. A = liquid inlet (4 10^{-3}m); B = gas outlet (3 10^{-3}m); C = liquid outlet (8.66 10^{-6} m^2); D = gas inlet; E = cone (120°); PI = pressure indicator; $\alpha = 8°$; dashed lines indicate cylindrical porous, gas permeable, section of cyclone wall.

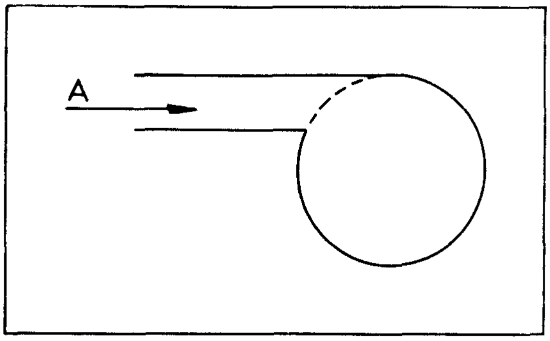


FIGURE 6 Liquid inlet of cyclone reactor.

The values of k_L shown in Figure 7 were obtained with a 2.07 M NaOH solution as a liquid and a CO_2-nitrogen mixture as a gas at corresponding hydrodynamical conditions as used in the sulfonation experiments. The actual k_L value during sulfonation could not be derived but is expected to be lower due to an increase of viscosity near the gas-liquid interface which is caused by accumulation of pyrosulfonic acid at this interface.[10,11]

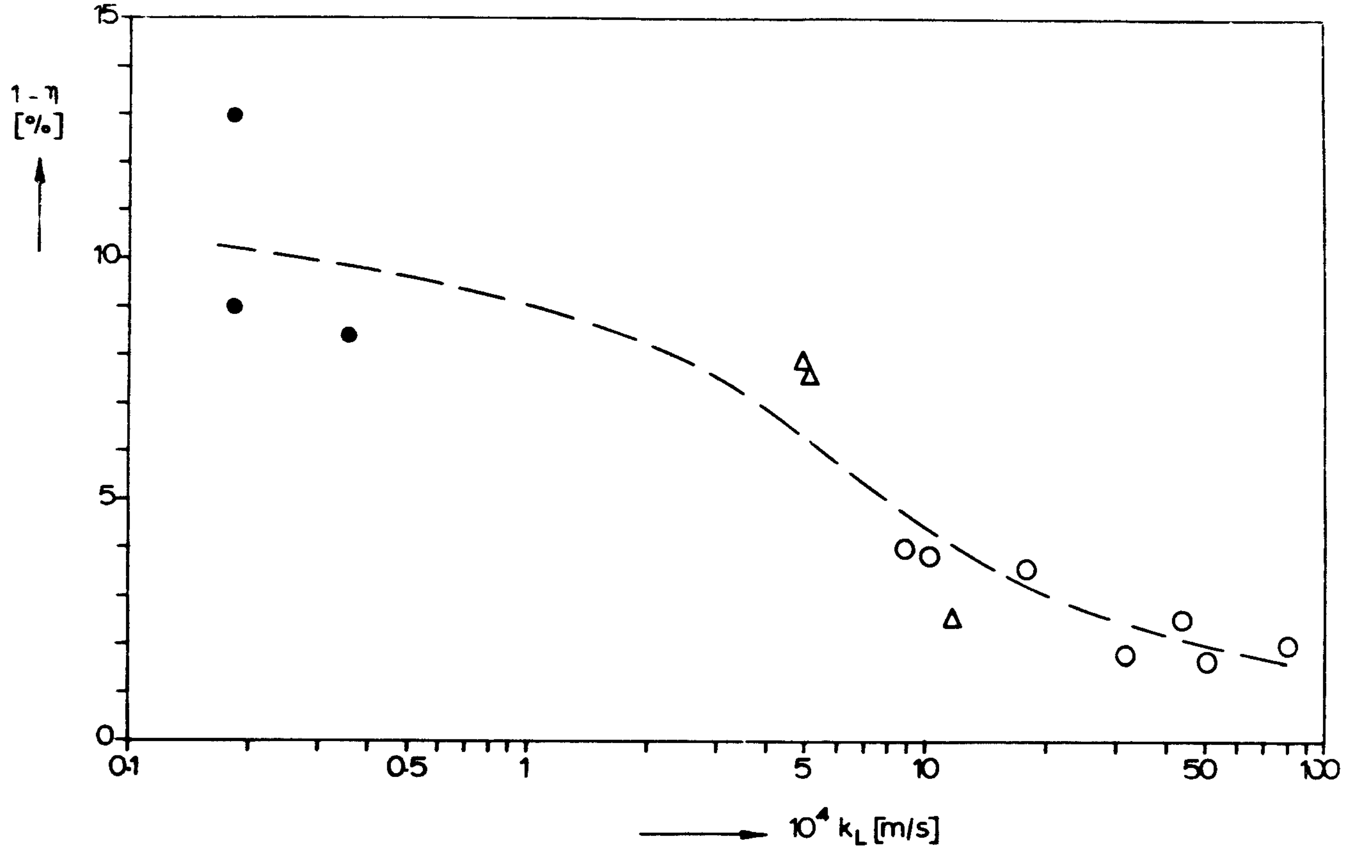


FIGURE 7 Diphenyl sulfone formation $(1 - \eta)$ in sulfonation of 30 vol. % benzene in 1,2-dichloroethane at ≃20°C and benzene conversion $\ll 1$, presented as a function of a liquid side mass transfer coefficient (k_L). ● = stirred cell reactor; Δ = co-current tube reactor; ○ = cyclone reactor.

TABLE III

Typical values of mass transfer coefficients (k_L) in the various experimental reactors

Reactor	k_L (m/s)
Stirred cell	$10^{-5} - 10^{-4}$
Tube reactor	$10^{-4} - 10^{-3}$
Cyclone reactor	$10^{-3} - 10^{-2}$

Although the k_L values from Figure 7 can only be considered as a relative measure for the actual mass transfer rate, it is possible to draw conclusions based on the kinetics discussed above.

DISCUSSION

If reactions (9) and (−15) don't play a major role, it follows from the preceding review on kinetics that sulfonation of benzene proceeds according to the scheme

$$A(G) \longrightarrow A(L) \qquad (28)$$

$$A(L) + zB(L) \longrightarrow zI(L);\ -r_B = zk_6 c_A c_B \qquad (29)$$

$$A(L) + I(L) \longrightarrow I'(L);\ r_{I'} = k_{15} c_A c_I \qquad (30)$$

with $A = SO_3$, $B =$ benzene, $I =$ pyrosulfonic acid, $I' = ArS_3O_9H$ and $z = \frac{1}{2}$. Without a solvent or in a non-complexing solvent such as 1,2-dichloroethane, reaction (29) is first order in both reactants.

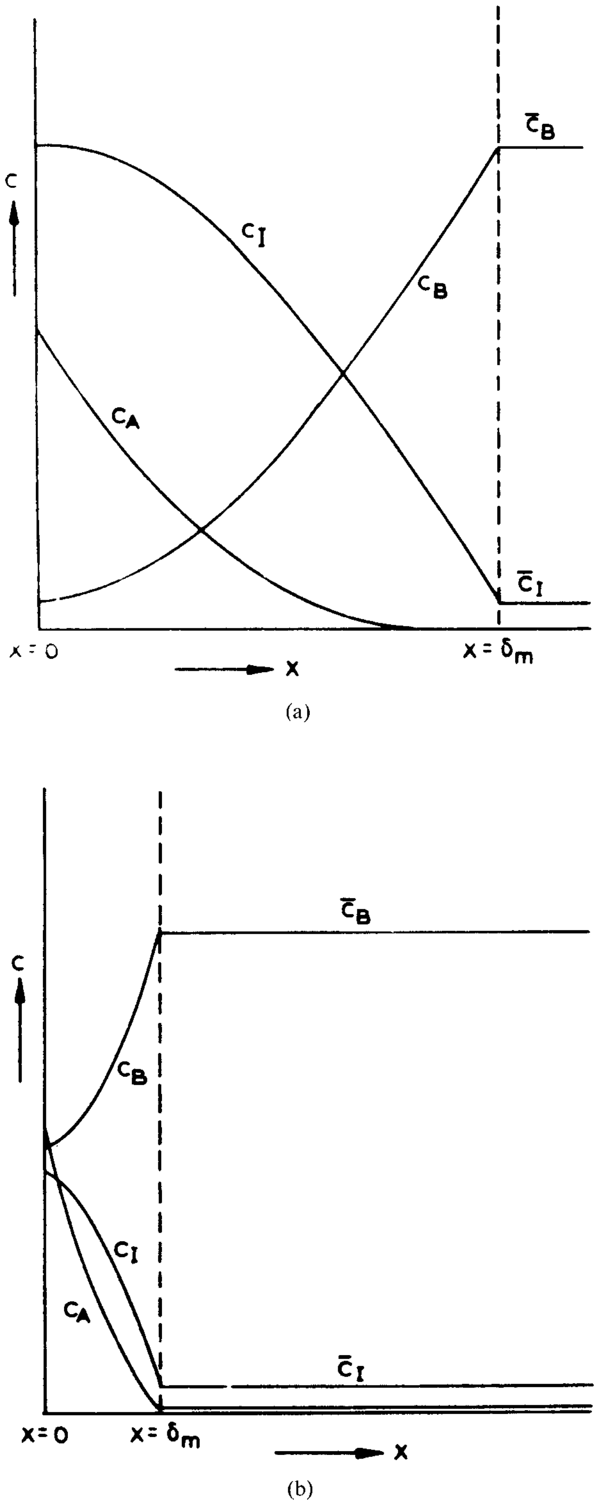
In principle, the reaction scheme is complicated by the following additional, consecutive reactions

$$I(L) + B(L) \longrightarrow 2P(L)$$

$$I'(L) + B(L) \longrightarrow X(L) + H_2S_2O_7$$

with $P =$ benzenesulfonic acid and $X =$ diphenyl sulfone. From the minimum value of k_6, as given by Eq. (22) and from data on SO_3 solubility and k_L, we used the available theory on mass transfer combined with reaction to show that reaction (29) is fast with respect to the mass transfer process.[10] In an earlier section we concluded that reaction (31) is slow compared to (29) and proceeds in the bulk of the liquid.

According to the film theory[28,29] the absorption of SO_3 into the benzene solution can be described by assuming a stagnant liquid film at the gas-liquid interface of thickness δ_m and an adjacent, well mixed liquid bulk beyond thickness δ_m (see Figure 8). Mass transport in the stagnant film is caused by diffusion as a result of concentration



(a)

(b)

FIGURE 8a, 8b Liquid phase concentration profiles near the interface at relatively low k_L (8a) and at relatively high k_L (8b).

gradients. Film thickness and mass transfer coefficient are related via[28,29]

$$\delta_m = \frac{D}{k_L} \tag{33}$$

Thus, a larger k_L is equivalent to a smaller film thickness δ_m.

As reaction (29) is fast with respect to the rate of mass transfer, all sulfur trioxide reacts within the stagnant film and no SO_3 will reach the well mixed bulk of the liquid. In the film, benzene is consumed and pyrosulfonic acid produced. Therefore, the benzene concentration in the stagnant film is lower and the pyrosulfonic acid concentration higher than in the bulk of the liquid. As shown qualitatively in Figure 8, the concentration differences in the film increase with increasing film thickness δ_m and thus with decreasing mass transfer coefficient k_L. Reactions (29) and (30) only occur in the zone in which SO_3 is present, i.e. in the reaction zone. The selectivity realized varies with the distance from the interface. In this region, local differential selectivity (η') follows from

$$1 - \eta' \equiv \left|\frac{2r_{I'}}{r_B}\right| = \frac{2k_{15}c_I}{k_6 c_B} \tag{34}$$

Comparison of the concentration profiles of c_B and c_I in the reaction zone for relatively low k_L (Figure 8a) and high k_L (Figure 8b) indicates that when k_L is low, c_B is relatively low while c_I is relatively high. This explains an increase of by-product formation with a decrease of the mass transfer coefficient k_L which indeed has been observed experimentally (Figure 7).

CONCLUSIONS

Available kinetic data on aromatic sulfonation with sulfur trioxide have been reviewed. Investigation of the literature value for the rate constant of sulfonation of benzene with sulfur trioxide in 1,2-dichloroethane revealed that this value is probably too low due to a low reactant mixing rate compared to the reaction rate. It was shown by experiment that sulfonation with sulfur trioxide of neat benzene and of 30 vol.% benzene in 1,2-dichloroethane, produced less than 1% of benzenesulfonic anhydride when benzene conversion was below 0.75. The main product was benzene-sulfonic acid with diphenyl sulfone as the by-product. It was further shown by experiment that formation of the by-product decreased with increasing mass transfer coefficient in sulfonation with gaseous sulfur trioxide of 30 vol.% benzene solved in 1,2-dichloroethane. In particular it should be noted that by-product formation was considerably suppressed in the cyclone reactor. A qualitative explanation for the relationship between by-product formation and mass transfer coefficient was put forth. Increasing the mass transfer coefficient could be a practically important procedure for improving industrial sulfonation processes. A technical economical analysis should be made however to prove economical feasibility for each process.

NOMENCLATURE

c	concentration, kmol/m^3
D	diffusion coefficient, m^2/s
G	Gas phase
k_L	liquid phase mass transfer coefficient, m/s
k_i, k_{-i}	reaction rate constants of reactions (i) and ($-i$), respectively
L	Liquid phase
r	rate of formation, kmol/m^3 s
t	time, s
T	reaction temperature, °C
x	distance from gas-liquid interface, m
z	stoichiometric coefficient from Eq. (29)
δ_m	thickness of stagnant diffusion film near gas-liquid interface, m
ζ	conversion of aromatic, fraction of aromatic that is converted
η	selectivity, fraction of converted aromatic that is converted to arenesulfonic acid
η'	differential selectivity ($-r_P/r_B$)

Subscripts

A	sulfur trioxide
Ao	initial sulfur trioxide
B	benzene
Bo	initial benzene
I	arenepyrosulfonic acid (arenesulfonic acid, monoanhydride with sulfuric acid)
I′	ArS_3O_9H (arenesulfonic acid, monoanhydride with disulfuric acid)
P	benzenesulfonic acid
X	diphenyl sulfone

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