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Kinetic Study of COS with Tertiary Alkanolamine Solutions. 1. Experiments in an Intensely Stirred Batch Reactor

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proached and exceeded by conducting DPO at conventional pressures (~6 MPa) but at unusually high temperatures (530–730 vs 450 °C). Also important according to the model was short reaction time (on the order of tens to hundreds of milliseconds) to prevent combustion.

The model predictions for conditions roughly corresponding to our experiments (550 °C, 6.2 MPa, 13–15% O₂ in the feed, and 13–15% CH₄ conversion) indicated that ~45–50% CH₃OH selectivity might be expected (assuming that our estimated residence times—as low as ~1500 ms—were sufficiently short). The dominance of C₂⁺ in the present study's results suggest that further testing of the model's predictions in other experimental configurations (e.g., empty tubes with very low surface/volume ratios) would be desirable to determine if its chemical basis requires modification.

Conclusions

At elevated pressure (6.2 MPa), significant amounts of C₂⁺ oxidative coupling products could be obtained without a catalyst (~35% carbon selectivity at ~15% methane conversion) at temperatures much lower than those of conventional catalytic operation (550–600 vs 750–900 °C). However, the observed selectivity behavior is typical of much of the conventional catalytic low-pressure, high-temperature data at similar conversion. This observation, coupled with a modest influence on selectivity by samarium oxide catalyst when run at the same atypical conditions, supports the view that noncatalytic gas-phase radical reactions play a strong role in conventional oxidative coupling.

At the elevated pressure and moderate temperatures investigated, the direct conversion of CH₄ to CH₃OH and C₂⁺ appears to depend upon the relative contributions of two parallel pathways: increasing oxygen partial pressure and/or temperatures favors the C₂⁺ path while reducing

these parameters favors CH₃OH production.

Registry No. CO, 630-08-0; CO₂, 124-38-9; CH₃OH, 67-56-1; CH₃CH₃, 74-84-0; CH₂=CH₂, 74-85-1; HC≡CH, 74-86-2; H(C₂H₅)₃, 74-98-6; CH₄, 74-82-8.

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Kinetic Study of COS with Tertiary Alkanolamine Solutions. 1. Experiments in an Intensely Stirred Batch Reactor

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The reaction between COS and various tertiary alkanolamines in aqueous solutions has been studied in an intensely stirred batch reactor. Experiments for TEA, DMMEA, and DMEA were carried out at 303 K; the reaction between COS and aqueous MDEA has been studied at temperatures ranging from 293 to 323 K. A two-step reaction mechanism has been proposed which describes all observed phenomena. This mechanism can be regarded as the base-catalyzed analogue of the reaction mechanism for the hydrolysis of COS. The proposed reaction mechanism was confirmed by absorption experiments into nonaqueous solutions of tertiary alkanolamines.

1. Introduction

Removal of sulfur-containing components like H₂S and COS from natural and industrial gases is a frequently encountered operation in process industry. For this operation usually amine processes are applied in which the acid gaseous components are absorbed into a basic alka-

noamine solution. From both technical and economical points of view coabsorption of CO₂ is preferred to be minimized, and consequently, selective absorption of H₂S, being the main sulfur compound, has received a lot of attention. The selectivity for H₂S can be improved by applying tertiary alkanolamines like methyldiethanolamine (MDEA) which react rather slowly with CO₂ in comparison with primary and secondary alkanolamines (see, e.g., Blauwhoff et al., 1985). However, COS reacts much more slowly with amines than CO₂ and the attainable sulfur selectivity tends to become hampered by the decreased

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COS absorption capacity. Also, stricter environmental regulations stress the need for sufficient COS removal in combination with a high sulfur selectivity.

For an adequate design of acid gas treating units knowledge of reaction kinetics and mechanism is indispensable. The reaction between CO₂ and tertiary alkanolamines has been studied extensively (see, e.g., Littel et al., 1990b), whereas the reaction between COS and tertiary alkanolamines has received almost no attention. Recently, Al-Ghawas et al. (1989) presented kinetic data for the reaction between COS and MDEA in aqueous solutions at temperatures ranging from 293 to 313 K. Their kinetic data were applied to describe absorption experiments for the simultaneous absorption of H₂S, COS, and CO₂ into aqueous MDEA solutions (Al-Ghawas and Sandall, 1991).

Considering the lack of experimental data for the reaction between COS and tertiary alkanolamines and the increasing importance of (selective) COS removal, reaction kinetics and the reaction mechanism for the reaction between COS and tertiary amines in both aqueous and nonaqueous solutions have been studied extensively in the present work. In this article experiments will be described which were carried out in an intensely stirred batch reactor. In this reactor the kinetics between COS and various tertiary alkanolamines could be studied under saturated bulk conditions. Kinetic experiments at various temperatures were carried out with triethanolamine (TEA), MDEA, dimethylmonoethanolamine (DMMEA), and diethylmonoethanolamine (DEMEA). The observed overall reaction rate differed substantially from the experiments reported by Al-Ghawas et al. (1989).

In part 2 (Littel et al., 1992a) stirred cell experiments for the absorption of COS in aqueous solutions of MDEA and DEMEA are presented. The amine concentrations applied in the stirred cell experiments extend the concentration range covered in this article. The absorption experiments were interpreted by means of a numerically solved absorption model and were found to be in reasonable agreement with the kinetic experiments presented in this article. The absorption model was subsequently applied to investigate the discrepancies between the present work and the work of Al-Ghawas et al. (1989).

2. Literature

The hydrolysis of COS in aqueous solutions has been studied by Thompson et al. (1935), Philipp and Dautzenberg (1965), and Sharma (1965). Philipp and Dautzenberg (1965) investigated the hydrolysis of COS by means of polarography and proposed a two-step mechanism:



They reported that reaction step 2 is rate determining under ambient conditions. The overall reaction rates observed by Thompson et al. (1935) and Sharma (1965) agree reasonably well with the data of Philipp and Dautzenberg (1965).

Al-Ghawas et al. (1989) studied the reaction between COS and MDEA in aqueous solutions at temperatures ranging from 293 to 313 K. All their kinetic experiments were carried out in a wetted sphere absorber. They observed a first-order behavior of the overall reaction rate in both COS and amine concentrations. On the basis of these observations they proposed the following reaction mechanism for the reaction between COS and tertiary amines:

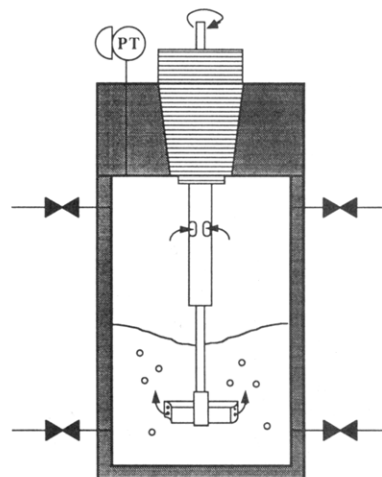


Figure 1. Intensely stirred batch reactor.

This mechanism can be regarded as the base-catalyzed version of the first step of the reaction mechanism proposed by Philipp and Dautzenberg (1965) for the hydrolysis of COS. Al-Ghawas et al. (1989) observed no evidence for the occurrence of the second step of this hydrolysis mechanism (reaction 2).

Reaction mechanism 3 is the analogue of the reaction mechanism proposed by Donaldson and Nguyen (1980) for the reaction between CO₂ and tertiary amines, which has been widely accepted in literature (see, e.g., Yu et al., 1985; Versteeg and van Swaaij, 1988a; Tomcej and Otto, 1989; Littel et al., 1990b). The reaction rates observed by Al-Ghawas et al. (1989) for the reaction of COS with MDEA are only 5 times lower than those reported for CO₂. This seems remarkable considering the large difference between the reaction rates of COS and CO₂ with primary and secondary amines (Sharma, 1965; Littel et al., 1992c).

Recently Al-Ghawas and Sandall (1991) reported experiments for the simultaneous absorption of H₂S, COS, and CO₂ in a stirred cell reactor. These experiments appear to confirm the kinetic data reported by Al-Ghawas et al. (1989), although it should be noted that the sensitivity of the experiments toward the reaction kinetics for COS was not very strong.

It is claimed in the literature that some heterocyclic tertiary amines show a relatively high absorption rate for COS in comparison to the more common tertiary alkanolamines (Ernst and Chen, 1988; Ernst et al., 1990; Reilly et al., 1990).

3. Experimental Section

3.1. Setup and Experimental Conditions. All kinetic experiments described in this article were carried out in an all-glass thermostated reactor (see Figure 1). The total volume of the reactor is about 1225 mL, and four 8-mm baffles increase the effectiveness of the high intensity gas stirrer (Medimex), which agitates gas and liquid phase vigorously. The operation is batchwise with respect to both gas and liquid phase. During an experiment the pressure decrease of COS is recorded as a function of time by means of a pressure transducer which is connected to an Apple IIe computer.

Under the assumption of saturated bulk conditions for COS, this pressure decrease is proportional to the overall reaction rate:

$$V_g \frac{d[\text{COS}]_g}{dt} = -R_{\text{COS}} V_L \quad (4)$$

$$t=0: \quad [\text{COS}]_g(t=0) = [\text{COS}]_g^0 \quad (5)$$

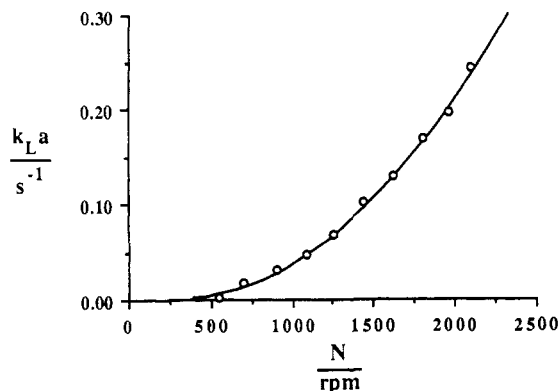


Figure 2. Volumetric mass-transfer coefficient as a function of stirring rate (COS absorption into water, $T = 298$ K, $V_L = 705 \times 10^{-6}$ m³).

The overall reaction rate was found to be first order in the COS concentration and, assuming ideal gas properties, solving eqs 4 and 5 yields:

$$\ln \left\{ \frac{P_{\text{COS}}(t)}{P_{\text{COS}}^0} \right\} = -k_{\text{app}} \frac{m_{\text{COS}} V_L}{V_g} t \quad (6)$$

The validity of assuming saturated bulk conditions can be checked by condition 7:

$$(Al - 1)Ha^2 \ll 1 \quad (7)$$

with

$$Ha = (k_{\text{app}} D_{\text{COS}})^{1/2} / k_{L,\text{COS}} \quad (8)$$

$$Al = k_{L,\text{COS}} / aD_{\text{COS}} \quad (9)$$

Condition 7 is a ratio between the pseudo-first-order reaction rate constant and the volumetric liquid-phase mass-transfer coefficient, and in order to check this condition physical mass-transfer experiments have to be carried out (see also Westerterp et al., 1984).

Measurement of reaction kinetics under saturated bulk conditions does have some advantages over kinetic measurements in the chemically enhanced regime ($E = Ha$) as encountered in stirred cell experiments: no diffusivity data are required for the interpretation of the kinetic experiments and the measured absorption flux is proportional to k_{app} , whereas in the chemically enhanced regime the absorption flux is proportional to $k_{\text{app}}^{1/2}$. Condition 7, however, shows that kinetic experiments under saturated bulk conditions are only feasible for reactions which are slow in comparison to mass transfer.

The solubility data needed for the interpretation of the kinetic experiments were obtained via a COS-N₂O analogy (Littel et al., 1992b). Solubility data for N₂O in aqueous solutions of tertiary amines were presented by Versteeg and van Swaaij (1988b) and Littel et al. (1992b).

All amines (TEA, MDEA, DMMEA, DEMEA, TREA) were obtained from Janssen Chimica and used as received. The amine purity for TEA was 97%; the purity of the other amines used was at least 99%. Chemical analysis of the pure amines showed that the remaining impurities consisted primarily of water. COS with a minimum purity of 97.5% was obtained from UCAR.

3.2. Reactor Characterization. The present reactor configuration has been characterized by means of physical absorption experiments. The influence of liquid volume and stirring rate on the volumetric liquid-phase mass-transfer coefficient, $k_L a$, has been investigated.

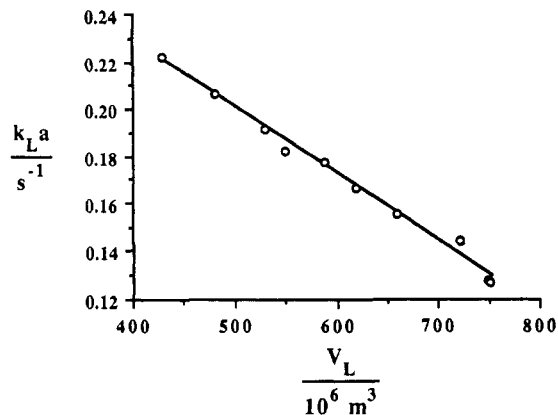


Figure 3. Volumetric mass-transfer coefficient as a function of liquid volume (N₂O absorption into water, $T = 298$ K, $N = 1600$ rpm).

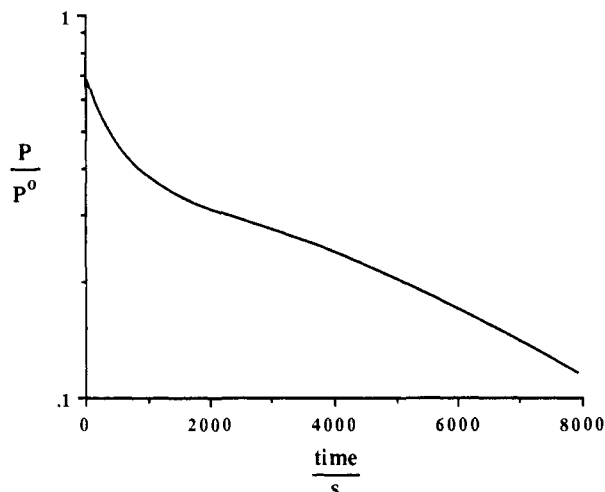


Figure 4. Typical pressure versus time behavior for COS absorption into aqueous MDEA ($[MDEA] = 200$ mol m⁻³, $T = 303$ K, $N = 1600$ rpm).

During physical absorption experiments the pressure decrease is recorded as a function of time. From this pressure decrease the $k_L a$ can be calculated:

$$\ln \left\{ \frac{P_g(t) - P_g(t=\infty)}{P_g(t=0) - P_g(t=\infty)} \right\} = - \frac{(mV_L + V_g)}{V_g} k_L a t \quad (10)$$

Typical experimentally determined $k_L a$ values are presented in Figures 2 and 3 as a function of stirring rate and liquid volume, respectively. All kinetic experiments were carried out at a stirring rate of 1600 rpm and with liquid volumes ranging from about 450×10^{-6} to 550×10^{-6} m³. Condition 7 was easily fulfilled for all kinetic experiments.

4. Reaction Mechanism

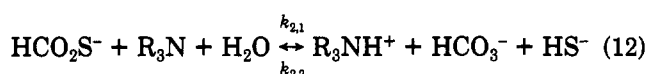
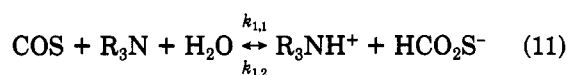
All kinetic experiments for the absorption of pure COS in aqueous solutions of tertiary alkanolamines showed a same pattern with regard to the pressure decrease as a function of time. A representative absorption experiment is given schematically in Figure 4, in which the pressure decrease is plotted as a function of time according to eq 6. Figure 4 shows that, after the presaturation of the liquid (first 20–30 s), initially the COS pressure decreases rather rapidly and that subsequently an equilibrium appears to be reached, after which the pressure decreases much more slowly. Eventually almost all COS is absorbed providing the capacity of the liquid is sufficient. It should be noted that the relative COS pressure shown in Figure 4 is equal

Table I. Survey of COS Absorption Experiments, Validating the Proposed Reaction Mechanism

solvent	amine	<i>m</i>	observations
ethanol		9.2 ± 0.3	no reaction
ethanol	1 M DEMEA	9.1	no reaction
ethanol	0.5 M MDEA	9.2	no reaction
octanol		8.1 ± 0.1	no reaction
octanol	0.5 M MDEA	8.2	no reaction
water	0.2 M TREA		rapid reaction
water	0.3 M TREA		rapid reaction

to 1 at $t = 0$ (owing to the time scale this is not clearly shown).

The general pressure-time profile shown in Figure 4 can be explained by the base-catalyzed analogue of the reaction mechanism for the COS hydrolysis as proposed by Philipp and Dautzenberg (1965):



The initial, rather rapid, pressure decrease corresponds to the first step of this reaction mechanism. The first step reaches equilibrium, and subsequently, the pressure decrease is primarily determined by the second step. The equilibrium constant of reaction 12 appears to be very high as almost total absorption of COS occurred in all experiments. The reaction mechanism proposed by Al-Ghawas et al. (1989) for the reaction between COS and aqueous MDEA consisted only of eq 11. This may have resulted from the low amine conversions applied by Al-Ghawas et al. (1989), in which case reaction 11 would have been entirely rate determining.

In order to obtain additional information for the validity of the proposed reaction mechanism represented by reactions 11 and 12, some absorption experiments have been carried out in nonaqueous solutions, because the presence of H_2O appears to be essential for the progression of the reaction between COS and tertiary amines. A survey of the absorption experiments of COS into solutions of MDEA and DEMEA in ethanol and octanol is presented in Table I. Only physical absorption was observed for COS absorption into nonaqueous solutions of tertiary alkanolamines, which is in good agreement with the proposed reaction mechanism.

It is reported in the literature that COS reacts with ethanol in alkaline solutions (Ferm, 1957). In order to check that the observed reactivity between COS and tertiary alkanolamines does not stem from a reaction between COS and the alcohol groups of the alkanolamines, some absorption experiments were carried out for COS into aqueous solutions of triethylamine (TREA). Although TREA does not have any alcohol groups, a rapid reaction between COS and aqueous TREA was observed (see Table I), and actually the reaction was so rapid that the reaction rate could not be determined in the present reactor configuration as condition 7 was not fulfilled. These absorption experiments validate that the alcohol groups of the alkanolamines investigated are not reactive toward COS within the pH range (about 7–10) covered in the present work. This confirms the proposed reaction mechanism.

Additional confirmation of reaction mechanism 11 and 12 was obtained from the analysis of concentrated aqueous amine solutions with high COS concentrations by means of $^1\text{H-NMR}$. In Figure 5 the spectrum of a DEMEA solution without COS is compared to a DEMEA solution

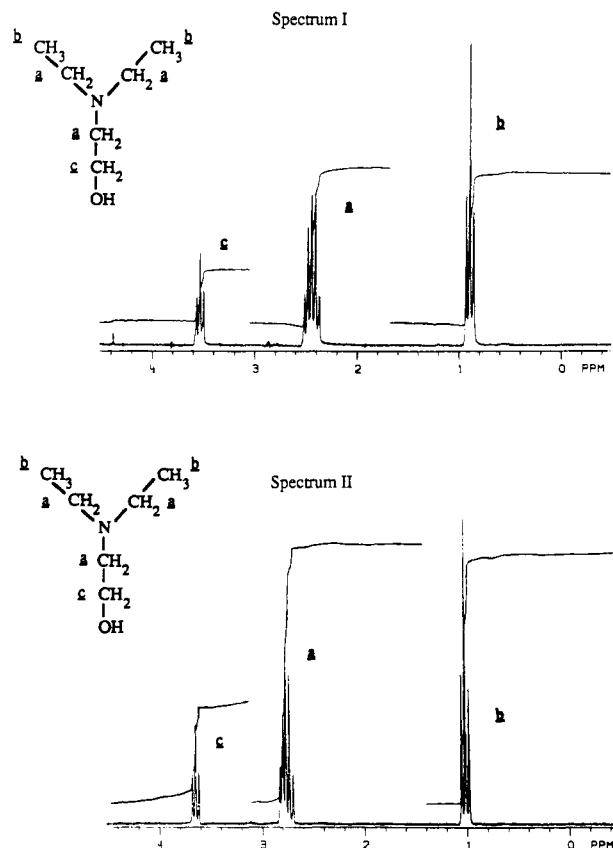


Figure 5. $^1\text{H-NMR}$ spectra for DEMEA- H_2O (spectrum I) and COS-DEMEA- H_2O (spectrum II) (spectrum I, 90 wt % DEMEA, 20% sample in acetone; spectrum II, 90 wt % DEMEA, 20% amine conversion, 20% sample in acetone).

with an amine conversion of about 20%. No new peaks occurred after reaction with COS, and for corresponding peaks only a small peak shift is observed. The extent of this peak shift is related to the position of the H-atoms with respect to the N-atom and can only be explained from a protonation of the N-atom. Due to rapid exchange this proton cannot be detected directly by means of NMR. The NMR spectra in Figure 5 are in good agreement with the proposed reaction mechanism.

5. Modeling

In order to deduce reaction rate constants from the COS absorption experiments into aqueous amine solutions, an absorption model has been developed. This transient absorption model, which takes into account the reversible reactions 11 and 12, consisted of eqs 13–19:

$$\frac{d[\text{COS}]_g}{dt} = -k_L a (m_{\text{COS}}[\text{COS}]_g - [\text{COS}]_L) \frac{V_L}{V_g} \quad (13)$$

$$\frac{d[\text{COS}]_L}{dt} = k_L a (m_{\text{COS}}[\text{COS}]_g - [\text{COS}]_L) - R_{1,1} + R_{1,2} \quad (14)$$

$$\frac{d[\text{R}_3\text{N}]}{dt} = -R_{1,1} + R_{1,2} - R_{2,1} + R_{2,2} \quad (15)$$

$$\frac{d[\text{HCO}_2\text{S}^-]}{dt} = R_{1,1} - R_{1,2} - R_{2,1} + R_{2,2} \quad (16)$$

$$\frac{d[\text{R}_3\text{NH}^+]}{dt} = R_{1,1} - R_{1,2} + R_{2,1} - R_{2,2} \quad (17)$$

$$\frac{d[\text{HS}^-]}{dt} = \frac{d[\text{HCO}_3^-]}{dt} = R_{2,1} - R_{2,2} \quad (18)$$

with

$$R_{1,1} = k_{1,1}[\text{COS}]_L[\text{R}_3\text{N}]$$

$$R_{1,2} = k_{1,2}[\text{HCO}_2\text{S}^-][\text{R}_3\text{NH}^+]$$

$$R_{2,1} = k_{2,1}[\text{HCO}_2\text{S}^-][\text{R}_3\text{N}]$$

$$R_{2,2} = k_{2,2}[\text{HS}^-][\text{HCO}_3^-][\text{R}_3\text{NH}^+]$$

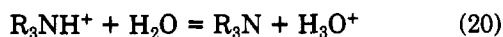
The initial conditions are given by

$$[\text{COS}]_g = \frac{P_{\text{COS}}^0}{RT}$$

$$[\text{COS}]_L = [\text{HCO}_2\text{S}^-] = [\text{HS}^-] = [\text{HCO}_3^-] = 0$$

$$[\text{R}_3\text{N}] = [\text{R}_3\text{N}]^0 \quad [\text{R}_3\text{NH}^+] = [\text{R}_3\text{NH}^+]^0 \quad (19)$$

The initial concentrations for free amine and protonated amine follow from an equilibrium model in which equilibria 20 and 21 were taken into account:



The absorption model represented by eqs 13–19 was solved by means of a fourth-order Runge–Kutta procedure.

The absorption model does not take into account all reactions which will take place in an aqueous amine solution during the absorption of COS. However, the contribution to the overall reaction rate of side reactions like the equilibrium reactions 20 and 21 and the bicarbonate–carbonate equilibrium was initially accounted for in the absorption model but was found to be negligible. The desorption of H_2S and CO_2 due to high concentrations of HS^- and HCO_3^- was also not taken into account. This desorption, however, is not substantial as long as amine conversions remain rather low, and the assumption that the pressure is proportional to the COS concentration appears to be very reasonable for all kinetic experiments. On the basis of work by Philipp and Dautzenberg (1965) on the hydrolysis of COS and some presently carried out absorption experiments of COS into water, the contribution of the direct reaction between COS and OH^- was considered to be negligible within experimental accuracy.

A Levenberg–Marquardt fitting procedure was used to infer kinetic rate constants from the absorption experiments. For each absorption experiment seven pressure–time points were selected at regular (but not necessarily equal) time intervals. Rate constants could be deduced from one absorption experiment or from a set of absorption experiments. All rate constants reported in the present work are based on a set of at least 6 absorption experiments at various amine concentrations (i.e., rate constants are based on at least 42 data points selected over the entire COS pressure and amine concentration ranges applied in the present work). For all absorption experiments the backward reaction rate of reaction 12 was found to be negligibly small.

6. Results

Kinetic experiments for the reaction between COS and TEA, DMMEA, and DEMEA in aqueous solutions were carried out at 303 K. The reaction between COS and aqueous MDEA was studied at temperatures ranging from 293 to 323 K. A survey of the experimental conditions applied in the kinetic experiments is provided in Table II.

In all kinetic experiments a pressure versus time behavior was observed similar to the pressure profile depicted in Figure 4. Some typical pressure versus time profiles for various amines are presented in Figure 6. Kinetic rate

Table II. Experimental Conditions in Kinetic Experiments

amine	T, K	[Am] _{tot} , mol m ⁻³	[COS] _L ⁰ , mol m ⁻³	no. of expts
TEA	303	201–1504	68–125	9
MDEA	293	153–1011	89–125	10
MDEA	303	101–803	22–129	27
MDEA	313	152–803	90–103	9
MDEA	323	99–798	79–106	8
DMMEA	303	99–997	83–120	7
DEMEA	303	100–501	84–119	10

⁰Total brutto COS concentration at the end of the kinetic experiment.

Table III. Fitted Reaction Rate Constants

amine	T, K	pK _a	k _{1,1} , 10 ⁵ m ³ mol ⁻¹ s ⁻¹	k _{1,2} , 10 ⁵ m ³ mol ⁻¹	k _{2,1} , 10 ⁶ m ³ mol ⁻¹ s ⁻¹
TEA	303	7.78	1.70	7.81	0.85
MDEA	293	8.73	1.25	2.96	2.14
MDEA	303	8.53	2.59	2.55	0.97
MDEA	313	8.34	5.80	5.20	1.40
MDEA	323	8.16	14.1	14.8	4.77
DMMEA	303	8.99	5.23	1.95	2.59
DEMEA	303	9.47	15.6	2.25	3.54

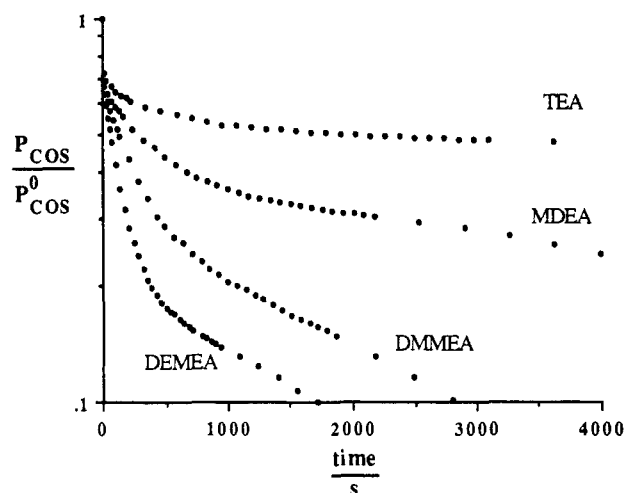


Figure 6. Typical COS pressure versus time profiles for various tertiary amines ($T = 303$ K, $[\text{R}_3\text{N}] = 200$ mol m⁻³).

constants for reactions 11 and 12 were deduced from sets of absorption experiments by means of the absorption model. The fitted reaction rate constants are presented in Table III.

The fitted reaction rate constants describe the pressure versus time profiles for most kinetic experiments within about 5% (MDEA, DMMEA, DEMEA). Only the kinetic experiments at low amine concentrations in combination with high COS concentrations were fitted worse. This must probably be attributed to the violation of the assumption that no (desorbed) H_2S or CO_2 is present in the gas phase. Therefore kinetic experiments at low amine concentrations in combination with high COS loadings (i.e., amine conversions >50%) were not taken into account in the deduction of kinetic rate constants from the experiments. For TEA the fitted reaction rate constants describe the measured pressure versus time profiles within about 10–15%. The causes for this larger imprecision are not clear but must probably also be attributed to minor desorption of H_2S and CO_2 to the gas phase, because the basicity of TEA is much lower than the basicity of the other amines used.

Since the initial pressure decrease is rather strong and primarily determined by the forward reaction rate of reaction 11, the precision of the fitted forward reaction rate

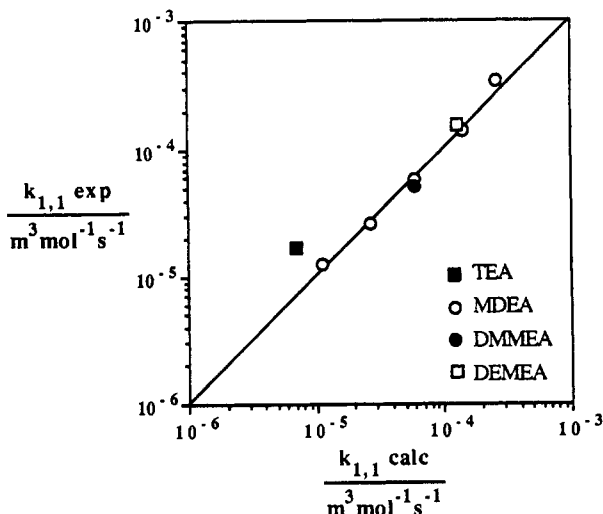


Figure 7. Parity plot for Brønsted relationship 23 ($k_{1,1}$ values).

constants ($k_{1,1}$) appears to be rather high. The fitted rate constants $k_{1,2}$ and $k_{2,1}$ are less accurate as they are primarily determined by the slower pressure decrease which takes place after the initial pressure decrease. It should be noted, however, that each region of the observed pressure versus time profile depended, more or less, on all three fitted rate constants. On the basis of the spread in the fitted rate constants for each absorption experiment, the accuracy of $k_{1,1}$ is estimated to be about 15% and the accuracies of $k_{1,2}$ and $k_{2,1}$ are estimated to be typically about 50%.

7. Discussion

The reaction between COS and aqueous MDEA has been studied as a function of temperature. The effect of temperature on the fitted reaction rate constant $k_{1,1}$ can be described by an Arrhenius type relationship:

$$k_{1,1} = 2.35 \times 10^6 \exp(-7624/T) \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (22)$$

The first step of the proposed reaction mechanism (reaction 11) is very similar to the reaction mechanism for CO_2 with aqueous tertiary amines. For CO_2 a Brønsted relationship has been developed which describes the forward reaction rate constant as a function of temperature and amine basicity (Littel et al., 1990b). A similar Brønsted relationship was found to describe the dependence on temperature and amine basicity for the fitted forward reaction rate constants $k_{1,1}$ for the reaction between COS and aqueous tertiary alkanolamines:

$$\ln k_{1,1} = -10896/T + 1.765pK_a + 10.37 \quad (23)$$

Information on the pK_a values for various tertiary alkanolamines as a function of temperature is provided by Littel et al. (1990a). The pK_a values used in the derivation of expression 23 are listed in Table III. In Figure 7, the reaction rate constants calculated according to expression 23 are compared to the experimentally obtained reaction rate constants. Expression 23 is found to fit almost all experimentally obtained rate constants within 15%; only the experimental value for TEA is underestimated by about a factor of 2. The reasons for this latter discrepancy are not entirely clear but must probably be attributed to small experimental inaccuracies which can have a rather large effect on the fitted reaction rate constants. Nevertheless, expression 23 offers the possibility to estimate the forward reaction rate constant of reaction 11 for tertiary alkanolamines not yet investigated.

In fitting the experimental absorption data by means of the absorption model, not only the forward reaction rate

Table IV. Calculated K_{COS_1} Equilibrium Constants

amine	T, K	K_{eq}	$10^{18}K_W$	$10^{11}K_A$	$K_{\text{COS}_1}, \text{m}^3 \text{mol}^{-1}$
TEA	303	0.22 ± 0.1	4.7	30	252 ± 116
MDEA	293	0.42 ± 0.1	4.1	3.4	112 ± 26
MDEA	303	1.0 ± 0.2	4.7	5.3	209 ± 41
MDEA	313	1.1 ± 0.2	9.1	8.3	183 ± 33
MDEA	323	0.95 ± 0.3	31	13	128 ± 40
DMMEA	303	2.7 ± 0.3	4.7	1.8	191 ± 21
DEMEA	303	6.9 ± 2.2	4.7	0.59	164 ± 52

constant of reaction 11 has been determined but also the backward reaction rate constant. The equilibrium constant for reaction 11 can be obtained from the ratio of forward and backward reaction rate constant:

$$K_{\text{eq}} = \frac{k_{1,1}}{k_{1,2}} = \frac{[\text{HCO}_2\text{S}^-][\text{R}_3\text{NH}^+]}{[\text{COS}][\text{R}_3\text{N}]} \quad (24)$$

Equilibrium 24 can be rewritten as a function of three elemental equilibria:

$$K_{\text{eq}} = \frac{k_{1,1}}{k_{1,2}} = K_{\text{COS}_1} \frac{1}{K_A} K_W [\text{H}_2\text{O}] \quad (25)$$

with

$$K_{\text{COS}_1} = \frac{[\text{HCO}_2\text{S}^-]}{[\text{COS}][\text{OH}^-]}$$

$$K_A = \frac{[\text{R}_3\text{N}][\text{H}_3\text{O}^+]}{[\text{R}_3\text{NH}^+][\text{H}_2\text{O}]} \quad K_W = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} \quad (26)$$

The values for the equilibrium constants K_A and K_W can be obtained from the literature, and consequently, the values for K_{COS_1} , which are not available in the literature, can be calculated from the reaction rate constants obtained in the present work. The calculated K_{COS_1} values are reported in Table IV. At 303 K, the values calculated for K_{COS_1} from the kinetic rate constants for TEA, MDEA, DMMEA, and DEMEA should be identical because the influence of the amine on equilibrium 24 is entirely represented by K_A . The mean K_{COS_1} values presented in Table IV are not entirely independent of the amine type but decrease slightly with increasing amine basicity: going from TEA to DEMEA this decrease is about 50%. However, considering the variation of more than a factor of 30 in the experimentally determined K_{eq} values and considering the accuracy of the K_{eq} values for the various alkanolamines, this decrease in the mean K_{COS_1} values seems minor and is well within the experimental accuracy. This provides additional proof for the validity of the proposed reaction mechanism and shows that the experimental data for the four amines studied at 303 K are reasonably consistent with each other. Although the temperature dependence of K_{COS_1} is not unambiguously clear from the present work, the data in Table IV seem to suggest that K_{COS_1} decreases with temperature.

The forward reaction rate constants obtained for the second step of the proposed reaction mechanism (reaction 12), except the $k_{2,1}$ value for MDEA at 293 K, are shown to increase with temperature and amine basicity (see Table III). This suggests that these reaction rate constants can probably be summarized by a Brønsted type relationship. Tentative fitting of the experimental data for $k_{2,1}$ yielded a Brønsted type relationship which fitted all data, except the $k_{2,1}$ value for MDEA at 293 K, within about 40%:

$$\ln k_{2,1} = -6891/T + 1.06pK_a \quad (27)$$

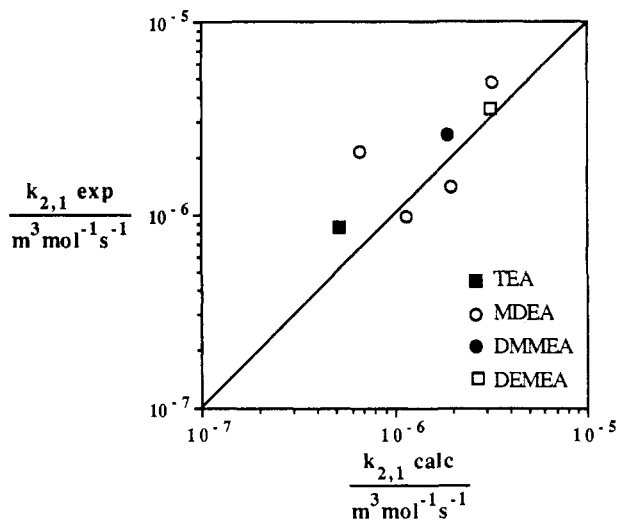


Figure 8. Parity plot for Brønsted relationship 27 ($k_{2,1}$ values).

In Figure 8, the rate constants calculated according to expression 27 are compared to the experimentally obtained rate constants. For MDEA at 293 K expression 27 predicts a $k_{2,1}$ value which is about a factor of 3 lower than the experimentally obtained value. It should be realized, however, that the $k_{2,1}$ values have been determined from that part of the pressure versus time profile where the absolute pressure decrease is low and that therefore the sensitivity of the $k_{2,1}$ values is rather large toward slight experimental variations.

Al-Ghawas et al. (1989) studied the reaction between COS and aqueous MDEA in a wetted sphere absorber. They observed only the first step of the reaction mechanism proposed in the present work. This may be explained from the low amine conversions applied by Al-Ghawas et al. (1989), in which case reaction 11 would have been entirely rate determining. However, the reaction rate constants reported by Al-Ghawas et al. (1989) are about a factor of 30 higher than the rate constants for reaction 11 observed in the present work. This discrepancy will be investigated in detail in part 2 of the present work (Littel et al., 1992a).

8. Conclusions

The reaction between COS and various tertiary alkanolamines in aqueous solutions has been studied in an intensely stirred batch reactor. Experiments for TEA, DMMEA, and DEMEA were carried out at 303 K; the reaction between COS and aqueous MDEA has been studied at temperatures ranging from 293 to 323 K.

A two-step reaction mechanism has been proposed which describes all observed phenomena (reactions 11 and 12). This mechanism can be regarded as the base-catalyzed analogue of the reaction mechanism proposed by Philipp and Dautzenberg (1965) for the hydrolysis of COS. The proposed reaction mechanism was confirmed by absorption experiments into nonaqueous solutions of tertiary alkanolamines.

The fitted forward reaction rate constants for the first step of the proposed reaction mechanism could be summarized by a Brønsted type relationship which describes the reaction rate constants as a function of temperature and amine basicity. From the ratio of the reaction rate constants of forward and backward reactions of the first step (reaction 11), a value for the $\text{COS}/\text{HCO}_2\text{S}^-$ equilibrium constant could be calculated. At 303 K this value was shown, within experimental accuracy, to be fairly independent of the amine type. This is in good agreement

with the proposed reaction mechanism and shows the consistency among the experimental data for the various tertiary alkanolamines.

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Nomenclature

a = specific interfacial area, (m^2 interfacial area)/(m^3 liquid volume)

Al = Hinterland ratio (eq 7)

D = diffusivity, $\text{m}^2 \text{s}^{-1}$

Ha = Hatta number (eq 6)

k_{app} = apparent pseudo-first-order reaction rate constant, s^{-1}

k_L = liquid-phase mass-transfer coefficient, m s^{-1}

$k_L a$ = volumetric liquid-phase mass-transfer coefficient, s^{-1}

m = dimensionless solubility

N = stirring rate, rpm

P = pressure, Pa

R = ideal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

t = time, s

V = volume, m^3

Subscripts/Superscripts

0 = initial condition

g = gas phase

L = liquid phase

Amine Abbreviations

DEMEA = diethylmonoethanolamine

DMMEA = dimethylmonoethanolamine

MDEA = *N*-methyldiethanolamine

TEA = triethanolamine

TREA = triethylamine

Registry No. COS, 463-58-1; TEA, 102-71-6; DMMEA, 108-01-0; DEMEA, 100-37-8; MDEA, 105-59-9.

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Kinetic Study of COS with Tertiary Alkanolamine Solutions. 2. Modeling and Experiments in a Stirred Cell Reactor

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Absorption experiments of COS into aqueous solutions of MDEA and DEMA at 303 K have been carried out in a stirred cell reactor. An absorption model, based on Higbie's penetration theory, has been developed and applied to interpret the absorption experiments, using the kinetic data obtained in part 1 of the present work. Experimental and calculated absorption rates agreed reasonably well at relatively low amine concentrations but deviated increasingly with increasing amine concentration. These deviations must very probably be attributed to an underestimation, by the COS-N₂O analogy, of the COS solubility in rather concentrated amine solutions. The absorption model has been applied to investigate the discrepancies between the present work and kinetic data for MDEA reported in the open literature. It has been shown that these discrepancies were possibly due to small amounts of rapidly reacting contaminants.

1. Introduction

In part 1 (Littel et al., 1992b) kinetic data have been presented for the reaction of COS with aqueous solutions of triethanolamine (TEA), methyldiethanolamine (MDEA), dimethylmonoethanolamine (DMMEA), and diethylmonoethanolamine (DEMEA) at various temperatures. These kinetic experiments were carried out in an intensely stirred batch reactor. On the basis of experiments in aqueous and nonaqueous solutions, a reaction mechanism for the reaction of COS with tertiary amines has been proposed which can be regarded as the base-catalyzed analogue of the reaction mechanism proposed by Philipp and Dautzenberg (1965) for the COS hydrolysis. The observed overall reaction rates were about a factor of 30 lower than those reported by Al-Ghawas et al. (1989) for the absorption of COS into aqueous MDEA solutions in a wetted sphere absorber.

In this article experimental data are presented for the absorption of COS into aqueous solutions of MDEA and DEMA which were obtained by means of the stirred cell technique. The amine concentrations applied in these absorption experiments were substantially higher than those used in part 1. An absorption model, based on Higbie's penetration theory, was developed to interpret the absorption experiments, using the kinetic data obtained

in part 1 (Littel et al., 1992b). The absorption model was also applied to investigate the discrepancies between the present work and the kinetic data reported by Al-Ghawas et al. (1989).

2. Experimental Section

The kinetic experiments for MDEA and DEMA were carried out in a stirred cell reactor. The experimental setup and procedure have been described in detail elsewhere (see, e.g., Blauwhoff et al., 1984).

For the interpretation of the kinetic experiments solubility and diffusivity data are required which generally cannot be measured in a direct way in a reactive system. The solubility data were estimated by means of a COS-N₂O analogy (Littel et al., 1992a). This analogy appears to be valid only for relatively diluted aqueous solutions (Littel et al., 1992a, 1992c), which might result in an underestimation of the COS solubility for the amine solutions applied in the present work. Solubility data for N₂O in aqueous MDEA and DEMA solutions were reported by Versteeg and van Swaaij (1988b) and Littel et al. (1992a), respectively. The diffusivity of COS in amine solutions was calculated from the COS diffusivity in water with the help of the modified Stokes-Einstein relationship developed by Versteeg and van Swaaij (1988b). The COS diffusivity in water at 303 K was estimated from the COS diffusivity at 298 K (Littel et al., 1992a), assuming the same activation energy as reported by Versteeg and van Swaaij (1988b) for the diffusivity of CO₂ in water.

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