Organic Process Research & Development **1999**, *3,* 357–362

Technical Notes

A Kinetic Model of the Choline Chloride Synthesis

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Abstract:

The process of ethylene oxide interaction with trimethylamine hydrochloride, giving choline chloride, has been studied. The reactions that proceed in the system were established. A kinetic model adequately describing the experimental data was developed.

Introduction

Choline chloride (ChCh) is a biologically active species, which plays a major role in cell metabolism, and is used in many pharmaceuticals.[1−3] It is also a base of many nutrition and feed additives.[4−6] The simplest method of its manufacture[7−11] is a direct synthesis from trimethylamine hydrochloride (TMAH) and ethylene oxide (EO) in an aqueous medium

$$(CH_3)_3NHCl + C_2H_4O \rightarrow [(CH_3)_3NCH_2CH_2OH]^+Cl^- \quad (I)$$

This method is well-known and realized in industry, but we cannot find a complete mathematical model of this process in the literature. We think that such a model would be useful to find the optimal technological conditions of the synthesis of choline chloride.

It is known[12−17] that this reaction is accompanied by side-processes of EO hydrolysis and hydrochlorination resulting in ethylene glycol (EG) and ethylene chlorohydrin (EChG) formation

$$C_2H_4O + H_2O \rightarrow HOCH_2CH_2OH \quad (II)$$

$$C_2H_4O + HCl \rightarrow HOCH_2CH_2Cl \quad (III)$$

Also in the system there is always free trimethylamine (TMA) present whose amount depends on the ratio of reactions I and III. The quality of the product is strongly influenced by the presence of these impurities (especially EChG, which is a harmful substance).

The general dependencies of EO reaction with amines are well known.[18−21] The kinetics of EO hydrolysis also has been described. However, these investigations were carried out under different conditions, and the results could not be used to describe the choline chloride synthesis along reaction I without some corrections. Thus, to elucidate the reaction mechanism and obtain a valid model, we had to investigate the kinetics of processes running during the EO reaction with TMAH in an aqueous solution.

The Kinetic Model. It is known[12−21] that the formation of the main products of the EO reaction with TMAH in an aqueous solution is the result of trimolecular reaction of nucleophiles (H_2O, HO^-, Cl^-, and $(CH_3)_3N$) with EO activated by proton donors (H_2O and $(CH_3)_3NH^+$).

The activation of EO is the result of the following equilibria:

$$C_2H_4O + H_2O \overset{K_1}{\rightleftharpoons} C_2H_4O\text{-----}HOH \quad (IV)$$

$$(CH_3)_3N^+H + C_2H_4O \overset{K_2}{\rightleftharpoons} C_2H_4O\text{-----}N^+H(CH_3)_3 \quad (V)$$

These equilibria are established quite rapidly and values of K_1 and K_2 are low. So, the concentrations of activated

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10.1021/op980080f CCC: $18.00

EO can be described by the following equations:

$$[C_2H_4O\text{-----}HOH] = K_1[C_2H_4O][H_2O] \qquad (1)$$

$$[C_2H_4O\text{-----}N^+H(CH_3)_3] = K_2[C_2H_4O][(CH_3)_3N^+H] \qquad (2)$$

According to the literature,[22] the TMA basicity constant determined by the equation

$$(CH_3)_3N + H_2O \overset{K_B}{\rightleftharpoons} (CH_3)_3N^+H + HO^- \qquad (VI)$$

is $K_B = 6.3\ 10^{-5}$ (p$K_B = 4.2$). Then pH of the 1 M aqueous solution of TMAH according to the equilibrium

$$(CH_3)_3N^+H + H_2O \rightleftharpoons (CH_3)_3N + H_3{}^+O(VII) \qquad (VII)$$

is 4.9. During the EO reaction with TMAH the pH always exceeds 7. It is the result of HCl binding by EO according to the overall reaction

$$(CH_3)_3NHCl + C_2H_4O \rightarrow (CH_3)_3N + HOCH_2CH_2Cl \qquad (VIII)$$

Ethylene chlorohydrine and free amine are formed as the result of the nucleophilic attack by Cl^- on EO activated according to eqs IV and V

$$Cl^- + C_2H_4O\text{-----}HOH \xrightarrow{k_1} HOCH_2CH_2Cl + HO^- \qquad (IX)$$

$$Cl^- + C_2H_4O\text{-----}N^+H(CH_3)_3 \xrightarrow{k_2} HOCH_2CH_2Cl + (CH3)_3N \qquad (X)$$

OH^- ion formed in the reaction IX yields a free amine reacting with TMAH according to VI.

The sum of the reactions IV, IX, and VI together with V and X gives VIII. The overall kinetic equation of the two EO parallel reactions IX and X is

$$r_{12} = K_1k_1[Cl^-][H_2O][C_2H_4O] + K_2k_2[Cl^-][HN^+(CH_3)_3][C_2H_4O] \qquad (3)$$

According to experimental data (Table 2) the concentration of the EChG formed is negligible compared with sum of concentrations of TMAH and ChCh. Thus, the Cl^- concentration in the course of the reaction can be assumed constant and equal to the initial TMAH concentration $[TMAH]_0$, also

$$[HN^+(CH_3)_3] = [TMAH]$$

Then if $K_1k_1 = k'_1$ and $K_2k_2 = k'_2$, we obtain

$$r_{12} = (k'_1[H_2O] + k'_2[TMAH])[TMAH]_0\,[C_2H_4O] \qquad (4)$$

The free amine formed in the reaction VIII is practically a catalyst of the main reaction and yields ChCh in the reaction with the EO activated by eqs IV and V

$$(CH_3)_3N + C_2H_4O\text{-----}HOH \xrightarrow{k_3} (CH_3)_3N^+CH_2CH_2OH + HO^- \qquad (XI)$$

$$(CH_3)_3N + C_2H_4O\text{-----}N^+H(CH_3)_3 \xrightarrow{k_4} (CH_3)_3N^+CH_2CH_2OH + (CH_3)_3N \qquad (XII)$$

Hydroxide ion formed in reaction XI regenerates free amine according to VI. So the sum of reactions IV, VI, and XI together with V and XII yields the main reaction that is catalysed by the free amine

$$(CH_3)_3NHCl + C_2H_4O \xrightarrow{(CH_3)_3N} [(CH_3)_3NCH_2CH_2OH]^+Cl^- \qquad (XIII)$$

Its rate is described by the following overall kinetic equation:

$$r_{34} = K_1k_3[(CH_3)_3N][H_2O][C_2H_4O] + K_2k_4[(CH_3)_3N][HN^+(CH_3)_3][C_2H_4O]$$

or

$$r_{34} = (k'_3[H_2O] + k'_4[TMAH])[TMA][C_2H_4O] \qquad (5)$$

Free amine, catalysing the reaction XIII, can be obtained also by the equilibrium reaction VI adding NaOH before the reaction. Without adding NaOH free amine is formed only in the reactions IX and X, and the equilibrium VI determines the existence of the alkaline media in the course of the process. Concentrations of hydroxide ion and free amine can be calculated from the equilibrium and balance equations:

$$K_B = \frac{[(CH_3)_3\ N^+H][HO^-]}{[(CH_3)_3N]} = \frac{[TMAH]\ [HO^-]}{[TMA]}$$

$$[EChG] = [TMA] + [HO^-] \qquad (6)$$

whereas

$$[HO^-] = K_B[EChG]/([TMAH] + K_B) \qquad (7)$$

$$[TMA] = [EChG][TMAH]/([TMAH] + K_B) \qquad (8)$$

Under alkaline conditions the reacting species undergo other transformations besides reactions VIII and XIII. The most significant of them are the reverse formations of EO from EChG

$$HOCH_2CH_2Cl + HO^- \xrightarrow{k_5} H_2O + Cl^- + C_2H_4O \qquad (XIV)$$

and choline chloride formation

$$HOCH_2CH_2Cl + (CH_3)_3NH \rightarrow [(CH_3)_3NCH_2CH_2OH]^+Cl^- \qquad (XV)$$

The free amine is spent in these reactions in equimolar amounts. According to[23,24] the rate of reaction XIV is

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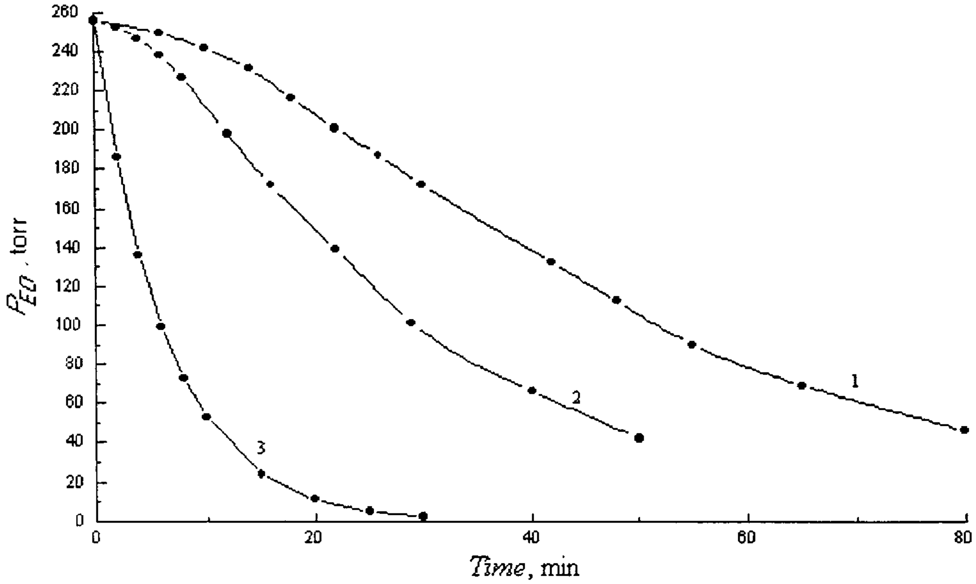

Figure 1. **The change of P_{EO} with time: 1 and 2, without catalyst; 3, with catalyst ([NaOH] = 0.028mol/L).**

described by the equation which according to dependence

$$r_5 = k_5[\mathrm{EChG}][\mathrm{HO}^-] = \exp(26.9 - 9444/T)[\mathrm{EChG}][\mathrm{HO}^-]$$

for concentration of a hydroxyl ion (eq 7) accepts the following kind:

$$r_5 = \exp(26.9 - 9444/T)K_B[\mathrm{EChG}]^2/([\mathrm{TMAH}] + K_B),\quad \mathrm{mol/(L \times s)} \qquad (9)$$

The rate of reaction XV is described by the equation

$$r_6 = k_6[\mathrm{TMA}][\mathrm{EChG}]$$

The other side process is hydrolysis of EO yielding EG by the uncatalysed and base-catalysed reactions

$$C_2H_4O + H_2O \xrightarrow{k_0} HOCH_2CH_2OH \qquad (XVI)$$

$$C_2H_4O + H_2O \xrightarrow{k'_0,\ OH^-} HOCH_2CH_2OH \qquad (XVII)$$

It is described by the overall equation[25]

$$r_0 = (k_0 + k'_0[\mathrm{HO}^-])[C_2H_4O] \qquad (10)$$

The ratio of k_0 and k'_0 allows to neglect the member k'_0[HO] at pH < 11 in eq 10. In these conditions the rate of hydrolysis is pH-independent and is described by the equation

$$r_0 = k_0[C_2H_4O] = \exp(18.37 - 9712/T)[C_2H_4O],\quad \mathrm{mol/(L \times s)} \qquad (11)$$

When pH > 11 it is necessary to take into account the second member of eq 10, $k'_0 = \exp(24.954 - 8907/T)$.

Summing up all the above we proposed the following kinetic model of the choline chloride synthesis:

$$d[\mathrm{EChG}]/d\tau = r_{12} - r_5 - r_6 = r_{12} - k_5K_B[\mathrm{EChG}]^2/([\mathrm{TMAH}] + K_B) - r_6 \qquad (12)$$

$$d[\mathrm{ChCh}]/d\tau = r_{34} + r_6 = (k'_3[H_2O] + k'_4[\mathrm{TMAH}])\,[C_2H_4O]\,[\mathrm{EChG}]\,[\mathrm{TMAH}]/([\mathrm{TMAH}] + K_B) + r_6 \qquad (13)$$

$$d[C_2H_4O]/d\tau = -d[\mathrm{EChG}]/d\tau - d[\mathrm{ChCh}]/d\tau - r_0 \qquad (14)$$

$$d[\mathrm{TMAH}]/d\tau = -r_{12} + r_5 - r_{34} \qquad (15)$$

Experimental Section

Materials. TMAH and NaOH were purchased from commercial suppliers and used without further purification. EO was purified by distillation under solid NaOH.

Apparatus. The EO order investigating experiments were carried out in manometric setup, described in the literature.[26] The other experiments were carried out in the isothermic batch autoclave, equipped with an automatic temperature controller.

Analysis. The TMAH concentration was determined by potentiometric titration. The EChG concentration was determined by GLC. The analysis was carried out on chromatograph "CHROM-5" (made in Czechoslovakia) equipped with flame ionization detector. A 1 m × $3 \cdot 10^{-3}$ m glass column packed with 15% FFAP on INERTON AW-DMCS (0.2−2.25 mm) was used for the analysis. The column temperature was 100 °C, the sample input temperature was 150 °C, the detector temperature was 150 °C, the carrier gas (nitrogen) flow rate was 30 cm^3/min, the air flow rate (for detector flame) was 300 cm^3/min, the hydrogen flow rate (for detector flame) was 30 cm^3/min, the input sample volume was 1×10^{-6} dm^3.

Results and Discussion

To test the adequacy of the proposed model and determine its parameters we carried out several series of runs in the

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Table 1. **Experimental (expt) and calculated (calcd) values of k_{eff}**

expt no.	initial concentrations mol/L $[C_2H_4O]_0$	$[TMAH]_0$	$[H_2O]_0$	[NaOH]	temp, °C	$k_{eff} \times 10^3$, s^{-1} expt	calcd
1	0.782	5.297	25.29	0.1115	30	3.93	4.23
2	0.745	5.310	25.33	0.098	30	3.52	3.73
3	0.792	1.245	46.78	0.1033	30	2.82	2.92
4	0.787	1.234	46.88	0.0886	30	2.38	2.50
5	0.753	2.622	39.60	0.0902	30	3.00	2.85
6	0.928	2.588	39.14	0.1209	30	4.07	3.77
7	0.732	1.247	46.96	0.0878	40	5.63	5.57
8	0.805	3.377	35.41	0.1143	40	8.67	8.53
9	0.752	6.562	18.84	0.0277	40	2.62	2.55
10	1.136	1.223	46.05	0.1056	20	1.25	1.24
11	0.792	2.659	39.29	0.0972	20	1.30	1.30
12	0.777	5.299	25.30	0.1039	20	1.77	1.67

manometric setup in conditions of the prevailing course of some of the listed above reactions. The preliminary experiments showed that curves of EO consumption are S-like. It is in an agreement with the proposed reaction scheme and kinetics of eq 12. According to them there should be an autocatalytic acceleration in the starting period thanks to accumulation of the free amine. It is formed in an equimolar amount with EChG by the reactions VI, IX, and X according to the balance eq 6. The addition of free amine or alkali to the starting mixture results in the full accordance with this equation in the reaction acceleration and change of the observed reaction order. There is no autocatalytic period when the free amine or alkali concentration is above 0.02 mol/L (Figure 1).

To simplify the kinetic model by excluding eq 12, we carried out the first series of experiments in the range of [NaOH] = 0.02−0.12 mol/L. In this concentration range there is no amine accumulation. Moreover, under these conditions pH < 10 and $k'_0[HO^-] \ll k_0$ in eq 10, and $k_0[C_2H_4O]$ in eq 14 is so negligible that the following equation is true:

$$-d[C_2H_4O]/d\tau = d[ChCh]/d\tau$$

Then eq 13 can be transformed to

$$-d[C_2H_4O]/d\tau = d[ChCh]/d\tau = (k'_3[H_2O] + k'_4[TMAH])\,[TMA]\,[C_2H_4O] \quad (16)$$

When $[TMAH]_0 > [C_2H_4O]_0$ eq 15 would have a first order on EO

$$-d[C_2H_4O]/d\tau = k_{eff}[C_2H_4O] \quad (17)$$

The experimental obtained value of k_{eff} in these conditions is described as

$$k_{eff} = (k'_3[H_2O] + k'_4[TMAH]_0)[NaOH] \quad (18)$$

Table 2. **Dependence of experimental and calculated TMAH and EChG concentrations vs time**

	Calculated Values of Rate Constant k'_1			
	[TMAH], mol/L		[EChG], mol/L	
time, min.	calcd	expt	calcd	expt
Experiment 1. $[TMAH]_0 = 1.439$ mol/L; $[C_2H_4O]_0 = 1.516$ mol/L; $t = 40$ °C				
5	1.255	1.185	0.0128	0.0134
8	1.042	1.014	0.0190	0.0180
10	0.891	1.031	0.0224	0.0210
12	0.748	0.898	0.0252	0.0199
15	0.559	0.299		
22	0.252	0.279		
$k'_1 = (2.044 \pm 0.248) \cdot 10^{-5}$, $L^2/(mol^2 \cdot min)$				
$k_6 = 2.0$ L/(mol min)				
Experiment 2. $[TMAH]_0 = 1.611$ mol/L; $[C_2H_4O]_0 = 1.698$ mol/L; $t = 40$ °C				
2	1.561	1.445	0.0069	0.0109
5	1.354	1.381	0.0162	0.0154
8	1.074	1.182	0.0236	0.0135
11	0.082	0.824	0.0291	0.0157
15	0.510	0.370		
20	0.265	0.276		
30	0.0338	0.0466		
$k'_1 = (2.079 \pm 0.143) \cdot 10^{-5}$, $L^2/(mol^2 \cdot min)$				
$k_6 = 2.1$ L/(mol min)				
Experiment 3. $[TMAH]_0 = 1.344$ mol/L; $[C_2H_4O]_0 = 1.442$ mol/L; $t = 50$ °C				
2	1.237	1.183	0.00889	0.00460
5	0.859	0.954	0.0194	0.0110
8	0.496	0.519	0.0257	0.0250
11	0.249	0.188	0.0293	0.0230
14	0.102	0.086		
$k'_1 = (3.94 \pm 0.27) \cdot 10^{-5}$, $L^2/(mol^2 \cdot min)$				
$k_6 = 3.0$ L/(mol min)				
Experiment 4. $[TMAH]_0 = 1.602$ mol/L; $[C_2H_4O]_0 = 1.684$ mol/L; $t = 30$ °C				
5	1.552	1.624	0.00624	0.00320
8.5	1.471	1.421.	0.01036	0.00710
12	1.363	1.356	0.0142	0.00910
16	1.218	1.321	0.0180	0.0103
20	1.066	1.141	0.0214	0.0177
30	0.714	0.675		
40	0.446	0.394		
50	0.262	0.220		
$k'_1 = (7.64 \pm 0.37) \cdot 10^{-6}$, $L^2/(mol^2 \cdot min)$				
$k_6 = 1.5$ L/(mol min)				

To obtain the values of k'_3 and k'_4 and activation parameters we carried out a series of runs in a manometric setup at 20, 30, and 40 °C, [TMAH] = 1.2−6.5 mol/L, $[C_2H_4O]$ = 0.73−1.13 mol/L, [NaOH] = 0.027−1.12 mol/L. The obtained dependencies of EO partial pressure vs time were linearised in the first-order coordinates, thus confirming our assumptions. The values of the first-order constants are listed in the Table 1. Supposing that the constants k'_3 and k'_4 in eq 18 have an Arrhenius temperature dependence, we determined activation parameters from all of the 12 experiments minimising the deviation squares.

It is seen that the calculated and experimental constant values are in a good accord. Maximum deviation does not

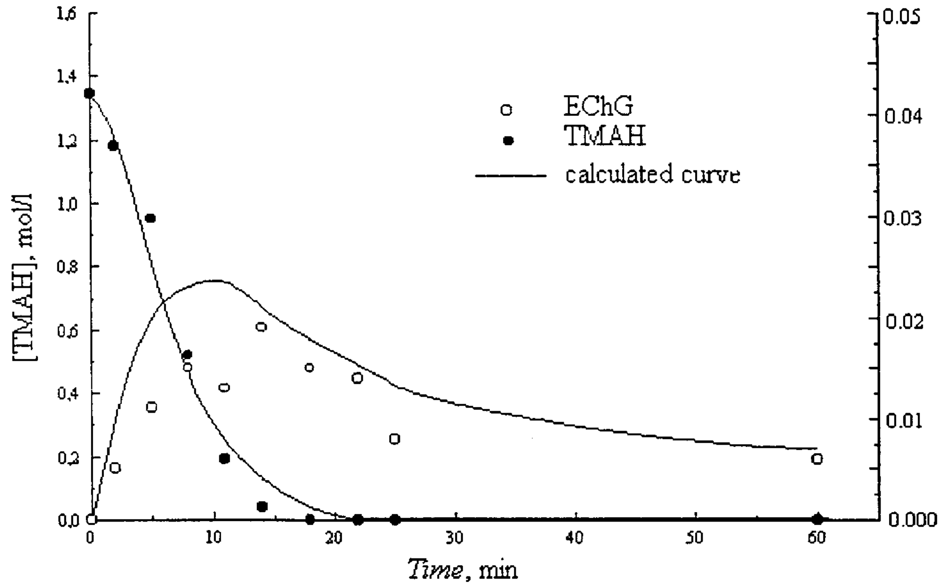

Figure 2. **Experimental and calculated dependencies. (Experiment number 3 from Table 2).**

exceed 7%. The obtained equation for k_{eff} is

$$k_{\mathrm{eff}} = \exp((17.59 \pm 0.06) - (7651 \pm 355)/T)([\mathrm{H_2O}] + (10.4 \pm 1.3)[\mathrm{TMAH}]_0)[\mathrm{NaOH}] \quad (19)$$

The ratio $k'_4/k'_3 = 10.4 \pm 1.3$ and is temperature-independent.

To check the adequacy of the complete kinetic model (eqs 12−15) and to determine the unknown parameters we carried out the series of experiments with the almost equimolar reagent ratio. Reaction was carried out in the isothermic batch reactor. The rate was monitored measuring the change TMAH and EChG concentrations with time. Results and conditions are listed in Table 2 and Figure 2. The experimental data were treated according to eqs 12−15. Equation 19 was used for the determination of k'_3 and k'_4. The ratio k'_2/k'_1 reflects the relative contribution of water and TMAH to reaction of EO with $\mathrm{Cl^-}$ (reactions IX and X). Having in mind the like reactions with amine participation, it was assumed to be equal to 10.4.

Thus, the following system of equations was used for the calculation of current reagent concentrations:

$$\mathrm{d[EChG]}/\mathrm{d}\tau = k'_1([\mathrm{H_2O}] + 10.4[\mathrm{TMAH}])[\mathrm{TMAH}]_0 - k_5K_\mathrm{B}[\mathrm{EChG}]^2/([\mathrm{TMAH}] + K_\mathrm{B}) - k_6[\mathrm{EChG}]^2\,[\mathrm{TMAH}]/([\mathrm{TMAH}] + K_\mathrm{B}) \quad (20)$$

$$\mathrm{d[ChCh]}/\mathrm{d}\tau = \exp(17.59 - 7651/T)([\mathrm{H_2O}] + 10.4[\mathrm{TMAH}])[\mathrm{C_2H_4O}][\mathrm{EChG}][\mathrm{TMAH}]/([\mathrm{TMAH}] + K_\mathrm{B}) + k_6[\mathrm{EChG}]^2 \times [\mathrm{TMAH}]/([\mathrm{TMAH}] + K_\mathrm{B}) \quad (21)$$

$$\mathrm{d[C_2H_4O]}/\mathrm{d}\tau = -\mathrm{d[EChG]}/\mathrm{d}\tau - \mathrm{d[ChCh]}/\mathrm{d}\tau - (k_0 + k'_0[\mathrm{HO^-}])[\mathrm{C_2H_4O}] \quad (22)$$

$$\mathrm{d[TMAH]}/\mathrm{d}\tau = -\mathrm{d[EChG]}/\mathrm{d}\tau - \mathrm{d[ChCh]}/\mathrm{d}\tau \quad (23)$$

Table 3. **Experimental and calculated values of total vapour pressure above aqueous solutions of EO and TMAH**

expt no.	vapor pressure, Torr		concentration, mol/L		temp, °C
	calcd	expt	[$\mathrm{C_2H_4O}$]	[TMAH]	
1	367	397	0.791	5.364	30
2	383	411	0.830	5.364	30
3	304	296	1.163	1.164	30
4	270	284	0.540	5.650	30
5	385	372	0.801	5.651	30
6	493	501	1.047	5.651	30
7	336	322	1.157	1.993	30
8	283	277	1.149	0.693	30
9	153	157	0.549	0.714	30
10	292	315	0.596	5.580	30
11	280	309	0.580	5.437	30
12	509	507	0.789	5.674	40
13	368	367	0.542	5.674	40
14	289	300	0.404	5.674	40
15	317	332	0.874	0.996	40
16	345	350	1.009	0.715	40
17	130	149	0.338	5.667	20
18	222	243	0.613	5.667	20
19	283	293	0.798	5.667	20
20	246	262	0.688	5.667	20
21	246	262	0.684	5.667	20

The unknown parameters k'_1 and k_6 were determined by nonlinear least-squares fit. Using the obtained k'_1 and k_6 values we determined the Arrhenius parameters. The obtained temperature dependencies of k'_1 and k_6 are described by the equations

$$k'_1 = \exp((15.2 \pm 1.9) - (9336 \pm 61)/T),\ \mathrm{L^2/(mol^2\ min)} \quad (24)$$

$$k_6 = \exp((7.5 \pm 1.0) - (3385 \pm 34)/T),\ \mathrm{L/(mol\ min)} \quad (25)$$

Data of Table 2 and Figure 2 show that system of eqs 20−23 including temperature dependencies 24 and 25 is a complete kinetic model of the process. This model describes all of the above-mentioned kinetic dependencies. To test this model further we carried out a series of experiments under

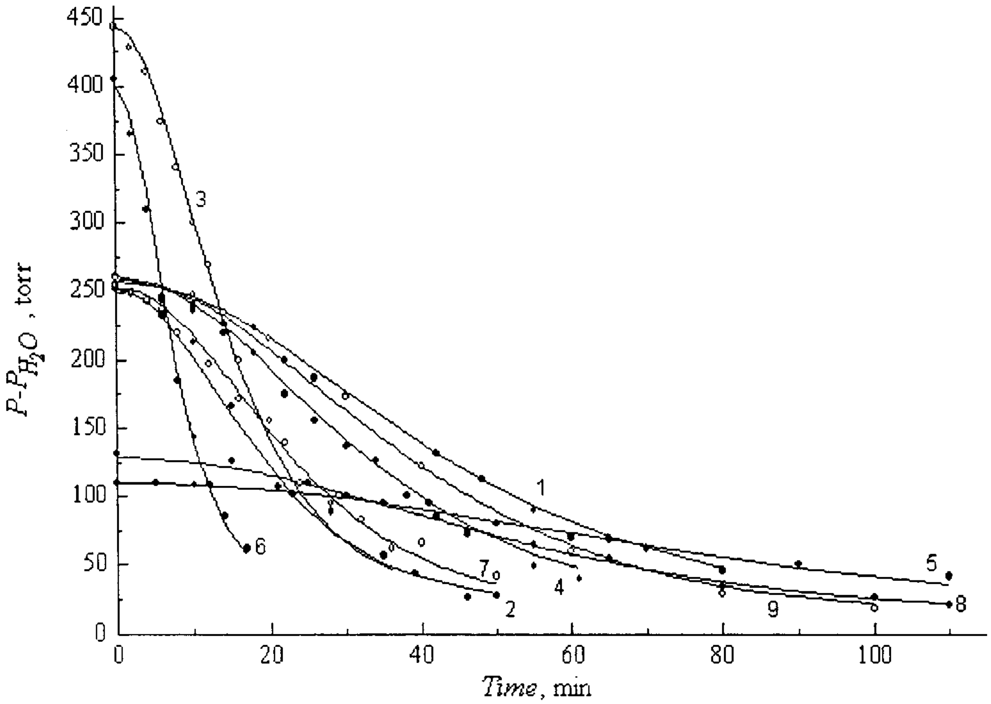

Figure 3. **The experimental (points) and calculated (lines) time-dependencies of vapour pressure above the reaction mixture. The initial conditions listed in the Table 3.**

other initial conditions without addition of the free base, i.e., when no equation or fragment of the model can be neglected.

These experiments were carried out at 20−40 °C, $[TMAH]_0 = 0.7-5.6$ mol/L, $[C_2H_4O]_0 = 0.4-1.15$ mol/L using the manometric setup. Under these conditions in contrast to the first series the reaction is not first-order on EO. This makes it necessary to calculate component concentrations from pressure differences. The vapour pressure above the reaction mixture is changed during the reaction due to formation of the free amine (reactions VI and X) and EO consumption. Henry's law adequately describes the dependence of pressure of TMA vapours above its aqueous solutions upon its concentration

$$P_{TMA} = \exp(17.91 - 3537/T)[TMA] \text{ Torr} \qquad (26)$$

A similar equation describes the same dependence for EO. However, in this case the Henry constant is significantly influenced by the amine salt. The growth of its concentration results in the increase in the EO partial pressure. We have obtained the equation linking the partial EO pressure above the reaction mixture with its concentration at different temperatures and amine salt concentrations. The experimental data are listed in Table 3.

The obtained equation is as follows:

$$P_{EO} = P - P_{H_2O} = \exp(13.51 + 0.144[TMAH]_0 - 2492/T)[C_2H_4O] \text{ Torr} \quad (27)$$

It is seen that calculated P_{EO} values are quite close to the experimental ones. During the treatment of the experiments cited below the ΔP values were calculated according to the equation

$$\Delta P = P - P_{H_2O} = P_{EO} + P_{TMA} \qquad (28)$$

The calculated and experimental dependencies of ΔP vs time are listed in the Figure 3. It is seen that there is a good agreement of calculated and experimental data in the wide range of initial conditions and temperatures. It serves as additional confirmation of the validity of eqs 20−23. Thus, these equations, possessing a good degree of reliability, can be used for the construction of the mathematical model of the reaction unit of choline chloride manufacture, for the unit optimisation, and for the determination of optimum conditions.

Received for review October 15, 1998.

OP980080F