Decomposition of Mono- and Diethanolamine Carbamate in Glycerol Solution

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Monoethanolamine (MEA) and diethanolamine (DEA) provide excellent methods to remove acidic gases from natural and refinery gases. At normal temperatures these amines have strong affinity for the gases, while at higher temperatures these amines are recovered by expulsion of the acidic gases.

Many papers have been published on the absorption reaction of carbon dioxide with MEA or DEA$^{1-5)}$, and a few on the reverse reaction$^{6,7)}$. However, no kinetic study of the decomposition of the MEA and DEA carbamate or carbonate has hitherto been carried out.

The present paper reports the activation energies for decomposition and absorption obtained from the rate of decomposition, and the heats of formation, together with equilibrium constants, over the temperature range of 110 to 140°C.

Experimental

Chemicals. — MEA, DEA and glycerol were of reagent grade and fractionally distilled in vacuo. Solvents such as xylene, *n*-butyl acetate, *n*-butyl alcohol, acetic acid, and toluene were also of reagent grade. Carbon dioxide from a steel cylinder was purified by passing through concentrated sulfuric acid and anhydrous calcium chloride.

Preparation of Samples. — MEA (1 part) was dissolved in glycerol (2 parts). The reaction between the solution, n_D^{20} 1.4680, d_{20}^{20} 1.187, and carbon dioxide took place by bubbling the latter through the former gently for 3 hr. The sample thus obtained had carbon dioxide 0.06385 g./g. sample (0.334 mol. CO_2/mol. MEA), n_D^{20} 1.4803, d_{20}^{20} 1.250. The DEA glycerol solution (1 : 2 by vol.), n_D^{20} 1.4729, d_{20}^{20} 1.211, was treated with the same procedure as above; 0.02485 g. CO_2/g. sample (0.220 mol. CO_2/mol. DEA), n_D^{20} 1.4779, d_{20}^{20} 1.228.

Apparatus and Technique. — The apparatus for the decomposition of the sample was shown in Fig. 1. The reaction tube R was a 50 ml. test tube, 2.5 cm. in diameter, charged with glass rods, 0.4 cm. $\phi \times 1.0$ cm. The manometer M was provided with an entraining liquid, a saturated aqueous solution of sodium chloride acidified with sulfuric acid containing a few drops of methyl orange. The cooling zone N was an effective, comparatively large, about 100 ml., heat exchanger, and the temperature of it was maintained constant by circulating water at 20°C. The graduated glass tube G, 3 mm. in diameter, lying horizontally, was calibrated exactly by measuring the length of mercury of known weight.

The experiment was carried out as follows: the apparatus consisting of R, M, N and G, was filled with pure carbon dioxide. About 9 g. of mercury was employed to stop the open end of the graduated glass G. The reaction temperature was maintained within ±0.2°C by the vapor of the boiling solvent which was heated by an oil-bath thermostat O regulated to ±1°C. When the system reached an equilibrium, as shown by a steady state of the colored solution inside the U-tube M and the mercury plug P, all the variables—barometric pressure, temperatures of cooling water T_5, of the room T_3, of the reaction tube T_2, and of the solvent vapor T_1—were recorded. Then the plug was set to zero

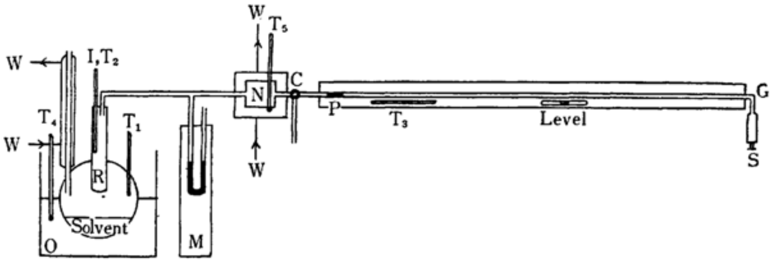

Fig. 1

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1) J. W. Mason and B. F. Dodge, *Trans. Am. Inst. Chem. Engrs.*, **32**, 27 (1936).

2) D. S. Cryder and J. O. Maloney, ibid., **37**, 827 (1941).

3) A. L. Shneerson and A. G. Leibush, *J. Appl. Chem.*, (*U. S. S. R.*), **19**, 867 (1946); *Chem. Abstr.*, **41**, 4340 (1947).

4) D. W. Van Krevelen and P. J. Hoftijzer, *Chem. Eng. Prog.*, **44**, 529 (1948).

5) F. Goodridge, *Trans. Faraday Soc.*, **49**, 1324 (1953); **51**, 1703 (1955).

6) R. M. Reed and W. R. Wood, *Trans. Am. Inst. Chem. Engrs.*, **37**, 363 (1941).

7) H. C. Paulsen et al., U. S. Pat. 2701750 (1955).

by means of a two way cock C and a syringe S. A weighed sample was poured from 2 ml. syringe into the reaction tube through an open glass tube I. The glass tube was closed with a rubber plug. It took less than 3 seconds. The temperature in the tube did not substantially decrease. The sample began to evolve carbon dioxide pushing the mercury plug. The syringe S was operated manually to maintain the inside and outside pressures equal at all times by reading the manometer M. The position of the mercury plug, time, and other variables were recorded at short intervals. The experiment was repeated two or three times at the same temperature.

Gravimetric analyses of carbon dioxide of the fresh and the heated samples which still retained carbon dioxide were carried out. The apparatus and technique were the same as those of Knorr's method[8].

Results and Discussion

Figures 2 and 3 are graphs of the increase in volume of the gases formed as a function of time due to the decomposition of the samples over the temperature range of about 110 to 140°C. It can not be assumed that the increase in volume was due only to the evolution of carbon dioxide. Vapor of the amines and the solvent, the change of atmospheric pressure and room temperature may affect the measurements. The temperature and the pressure were substantially constant during the experiments. As to the vapor of the amines and the solvent, a blank test showed that the vapor increased the volume by about 0.3 ml./g. sample at 136°C for the initial period of the reaction, in about half a minute. After that period the reaction system reached an equilibrium.

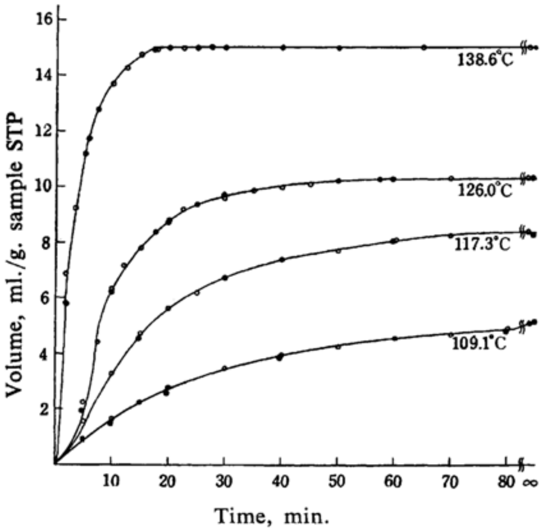

Fig. 2. Rate of decomposition of MEA carbamate in glycerol solution at constant pressure.
● Theoretical
○ Experimental

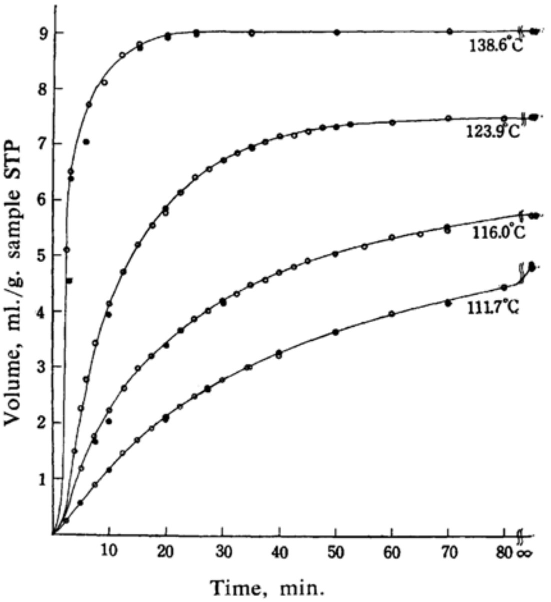

Fig. 3. Rate of decomposition of DEA carbamate in glycerol solution at constant pressure.
● Theoretical
○ Experimental

The results of gravimetric and volumetric analyses at equilibrium were listed in Table I.

TABLE I. THE AMOUNT OF CARBON DIOXIDE, EVOLVED AND RESIDUAL (ml. CO_2/g. sample STP)

Temp., °C	Vol. of evolved gas, u_e (volumetric)	Vol. of residual CO_2 (gravimetric)
MEA 138.6	15.0±0.5	17.3 ±0.2
126.0	10.3±0.4	22.0 ±0.1
117.3	8.4±0.2	23.8 ±0.1
109.1	5.1±0.2	27.2 ±0.1
At room temp.	—	32.27±0.05
DEA 138.6	9.1±0.3	3.5 ±0.1
123.9	7.5±0.2	5.1 ±0.1
116.0	5.8±0.1	6.8 ±0.1
111.7	4.9±0.2	7.7 ±0.1
At room temp.	—	12.58±0.05

Concerning the reaction mechanism of the amines and carbon dioxide, Van Krevelen and Hoftijzer suggested that in aqueous solution the complete reaction took place in two steps, the first being a dissociation of the amine and the second the combination of the fragments, and the reaction was a third order[4]. As to

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[8] W. W. Scott, "Scott's Standard Method of Chemical Analysis", D. Van Nostrand Co., Inc., New York (1939), p. 235.

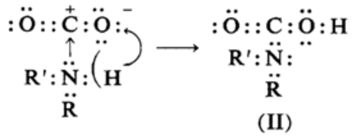
the reaction order a similar conclusion was reached by Cryder and Maloney[2], and Smola[9]. The work of Mason and Dodge[1], and of Shneerson and Leibush[3], showed that the concentration of carbon dioxide in aqueous solution of the amine at equilibrium varied about 0.5 to 0.9 mol. per amine as the temperature decreased from about 75 to 0°C, and the absorption would take place as follows:

$$2RR'NH+H_2O+CO_2 \rightleftarrows (RR'NH_2)_2CO_3$$

$$(RR'NH_2)_2CO_3+CO_2+H_2O \rightleftarrows 2RR'NH_2HCO_3$$

$$R=HOCH_2CH_2;\ R'=R \text{ or } H$$

Goodridge interpreted the reaction in terms of zero order as tentative, and presented the following mechanism in the absence of water[5]:



(II)

The amine carbamates in glycerol solution were decomposed, according to the following reactions:

$$RR'NCOONH_2RR' \underset{k_2}{\overset{k_1}{\rightleftarrows}} 2RR'NH+CO_2 \qquad (1)$$

MEA $R=HOCH_2CH_2,\ R'=H$

DEA $R=R'=HOCH_2CH_2$

The partial pressure of carbon dioxide was constant at 1 atmospheric pressure. The reaction was reversible as the formula 1, and the following differential equation will be valid:

$$du/dt=k_1(a_0-u)-k_2(a_0'+2u)^2p_{CO_2} \qquad (2)$$

$$=k_1(a_0-u)-k_2'(a_0'+2u)^2 \qquad (3)$$

where

a_0 = initial concentration of MEA or DEA carbamate, mol./g. sample,

a_0' = initial concentration of MEA or DEA, mol./g. sample,

k_1 = rate constant of decomposition of the carbamate,

k_2 = rate constant of absorption of the MEA or DEA,

u = moles of the decomposed carbamate at the time t, and

p_{CO_2} = partial pressure of carbon dioxide.

When $u=0$ at $t=0$ and $u=u_e$ at $t=\infty$, the solution of the Eq. 3 is:

$$(Ka_0-a_0'^2)/u=(\sqrt{K^2+8K(2a_0+a_0')/2})\cdot \coth(k_2't\sqrt{K^2+8K(2a_0+a_0')/2}) + (K+4a_0')/2 \qquad (4)$$

where $K=k_1/k_2'=(a_0'+2u_e)^2/(a_0-u_e) \qquad (5)$

$$k_2'=k_2p_{CO_2} \qquad (6)$$

A relation between rate constants, k_1 and k_2', and equilibrium constant K, should be expressed as $k_1/k_2'=K^{1/\nu(r)}$, where $\nu(r)$ = the number of occurrence of a rate determining step necessary to complete an overall reaction formula[10]. At present, however, $\nu(r)=1$, as will be explained.

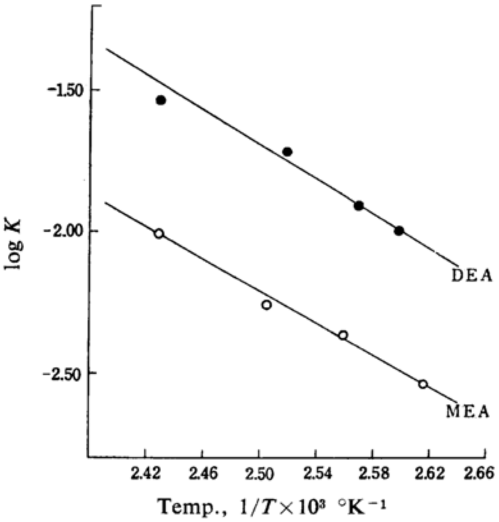


Fig. 4. Temperature dependence of equilibrium constant K; $\log K$ vs. $1/T$ ($\times 10^{-3}$).

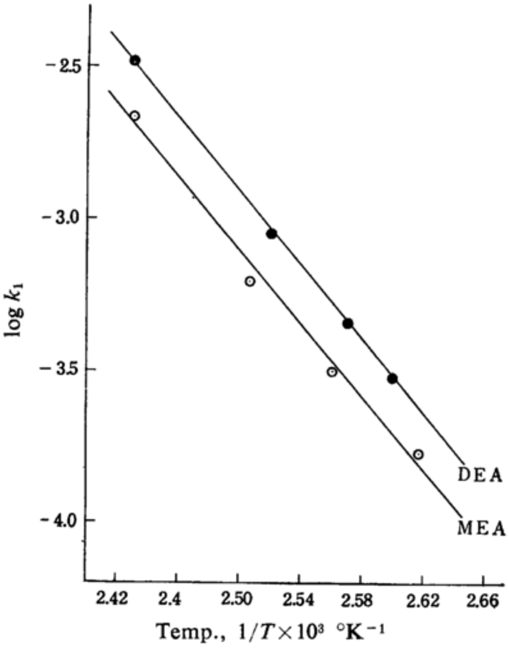


Fig. 5. Temperature dependence of rate constant k_1; $\log k_1$ vs. $1/T$ ($\times 10^{-3}$).

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9) A. Smola, *Mitt, chem. Forsch.*, 2. 38 (1948); 2, 43 (1948).

10) J. Horiuti, *Chem. & Chem. Ind.* (*Kagaku to Kogyo*) **9**, 355 (1956).

On the basis of the amount of carbon dioxide at equilibrium, equilibrium constants were calculated. The temperature dependence of the equilibrium constants was shown in Fig. 4. From the slopes of the lines the heats of the reaction were calculated by the van't Hoff's equation, and were found to be 12.9 and 13.4 kcal./mol. CO_2 for MEA system and DEA system, respectively. Since a_0, a_0', K, t and u were known by the experiment, the rate constants, k_1 and k_2', at each temperature, were calculated. After the initial period the values of the rate constants became equal within the limits of experimental error. The calculated values of u obtained from Eq. 4, using these rate constants and the others, were plotted against the time. The agreement with the experimental values supports the validity of Eqs. 1 to 6. The values of $\log k_1$ and $\log k_2'$ were plotted against the reciprocals of corresponding absolute temperatures, as shown in Figs. 5 and 6, and the Arrhenius' energies of activation of the decomposition and the absorption were calculated over the temperature range of 110 to 140°C, and were found to be 27.5 and 14.4 kcal./mol. for the MEA system, 27.8 and 13.6 kcal./mol. for DEA system, respectively.

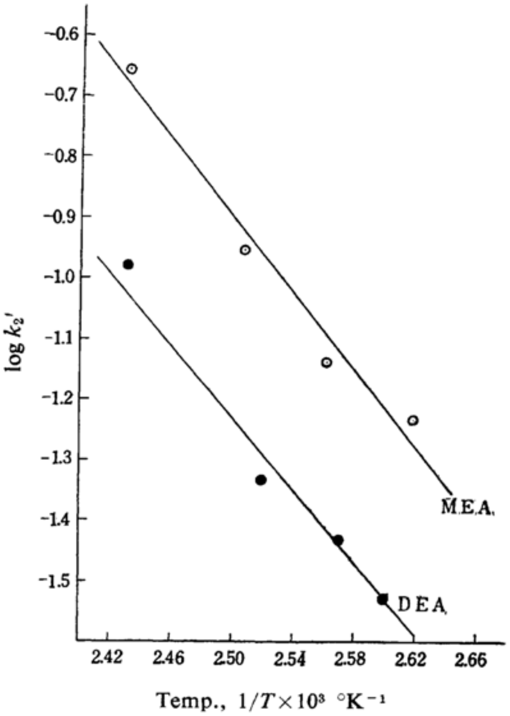

Fig. 6. Temperature dependence of rate constant k_2'; $\log k_2'$ vs. $1/T$ ($\times 10^{-3}$).

As to the samples, the reaction products should have the formula $RR'NCOONH_2RR'$ (I), since the solution had still excess amine which would eventually change the products of the type $RR'NCOOH$ (II), if present, to the type (I).

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