PHYSICOCHEMICAL STUDIES OF THE
CARBAMATE-CO₂-SOLVENT SYSTEM

A Thesis

Presented to the Graduate Faculty
of the Department of Chemistry
Brooklyn College
City University of New York

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ABSTRACT

The formation of carbamate from CO_2 and the various amine solutions has been investigated for the purpose of elucidating the structure of the species generated in the reaction. The amine solutions used were 1 and 2 molar solutions of di-n-butylamine (DNBA) in triethylamine (TEA), pure DNBA and pure TEA. It has been found that the non-aqueous solvent participates in the formation of carbamate in 1 and 2M-DNBA/TEA solutions as a proton acceptor in DNBA-carbamate formation. However, due to the high concentration of the solutions and the basicities of the amines, a significant amount of DNBA which does not form the DNBA-carbamate anion is also found to be participating as a proton acceptor. Pure TEA absorbs only 1/60 of the absorption by pure DNBA. The extent of TEA participation in the CO_2 -absorption process other than as a proton acceptor in DNBA-carbamate is negligible. The formation of carbamic acid and zwitterion have been found unlikely.

TABLE OF CONTENTS

I.	Introduction	1
II.	Experimental	14
	1. Equilibration Apparatus	14
	2. Equilibration Procedure	17
	3. Determination of Equilibrium Gas Phase Composition	18
	4. Data Reduction	22
III.	Experimental	32
	1. Experimental Results of Equilibrium Constant Calculations	32
	2. Results on Carbamate Structure Using Instrumental Methods	50
	3. Correlation with Isotope Exchange Equilibria	55
IV.	Suggested Further Investigations	58
	1. Determination of Activity Coefficients	58
	Experimental	58
	Theoretical	59
	2. N. M. R. Studies	60
V.	Conclusion	61
VI.	Summary	62
VII.	References	64
VIII.	Acknowledgement	66

LIST OF TABLES

1) Summary of Least Squares Fit Used for Gas Chromatography.....	24
2) Physical Properties of Amines.....	31
3) Summary of the Total Equilibrium Pressure vs Mmoles of CO ₂ Added for 1M-DNBA/TEA, 2M-DNBA/TEA, DNBA, TEA at 25°C.....	33
4) Summary of Equilibrium Studies for Formation of Carbamate in 1M DNBA/TEA at 25°C.....	36
5) Summary of Equilibrium Studies for the Formation of Carbamate in 2M DNBA/TEA at 25°C.....	39
6) Summary of Equilibrium Studies for the Formation of Carbamate in Pure TEA at 25°C.....	45
7) Summary of Equilibrium Studies for the Formation of Carbamate in Pure DNBA at 25°C.....	48

LIST OF FIGURES

1)	α_{13} vs $1/T$ for 1M-DNBA-Carbamate in TEA.....	6
2)	Carbamate Reaction Vessel.....	15
3)	Carbamate Preparation and Equilibration System.....	16
4)	Chromatogram of Liquid Sample for 1M-DNBA/TEA Solution...	20
5)	Chromatogram of Gaseous Mixture of CO_2 and TEA.....	23
6)	Calibration Curve used for Gas Chromatographic Determination of CO_2 -TEA Mixture.....	25
7)	Flow Chart.....	27
8)	Total Pressure vs mmoles of CO_2 added at $25^\circ C$	34
9)	Equilibrium Constants for Formation of Carbamate in 1M-DNBA/TEA.....	37
10)	Equilibrium Constants for Formation of Carbamate in 2M-DNBA/TEA.....	40
11)	Comparison of $K(1:1:1)$ for 1 and 2 M-DNBA/TEA Solutions.....	41
12)	Equilibrium Constants for Formation of Carbamate in Pure TEA.....	46
13)	Equilibrium Constants for Formation of Carbamate in DNBA.....	49
14)	a. NMR Spectrum of Pure TEA.....	51
	b. NMR Spectrum of Pure DNBA.....	51
15)	a. NMR Spectrum of 2M-DNBA/TEA without CO_2	53
	b. NMR Spectrum of 2M-DNBA/TEA with CO_2	53

I. INTRODUCTION

The purpose of this study has been twofold. The first has been to experimentally determine physicochemical properties of the carbon dioxide-carbamate system and their effect on the separation factor for carbon-13. Secondly, it has been proposed to investigate the nature of the species present at equilibrium during carbamate formation.

Carbon-13 is a stable isotope that occurs at a natural abundance level of 1.11%. The fact that it is not a radioactive isotope has recently attracted the interest of scientists to its potential use as a tracer for carbon in medical and biological studies. Recent advances in ^{13}C NMR have made the use of this isotope particularly attractive since in trace studies not only will the path of ^{13}C be traceable, but its molecular environment can be determined as well.

Carbon-13 is currently being enriched up to 95.5% by means of cryogenic distillation of carbon monoxide¹; it has also been fractionated by thermal diffusion of methane². Low temperature distillation of carbon monoxide can produce large quantities of ^{13}C , but it requires rather sophisticated equipment, and substantial capital investment and operating cost.

The thermal diffusion process, originally devised by Clausius and Dickel³, has been used for isotope separation

purposes. This is due primarily to the simplicity of the apparatus; however this method is only capable of producing small quantities of enriched ^{13}C .

Another class of separation processes is the chemical exchange method. In an isotope exchange method, two compounds containing exchangeable isotopes are brought into contact with each other in a separation stage. The partially enriched and depleted streams of the two compounds out of the separation stage are used as input streams for the next higher and lower stages, respectively, in a cascade of stages. At each end of a cascade, the compound coming out of the terminal stage is chemically and quantitatively converted to the other compound, and the latter is then refluxed back into the cascade. In the ^{13}C exchange between HCN and CN^- developed by Urey and co-workers,⁴ which had been used by the Eastman Kodak Co, ^{13}C was enriched from its natural abundance by means of carbon isotope exchange between an aqueous solution of sodium cyanide and gaseous hydrogen cyanide:

The equilibrium constant was found to be 1.026 at room temperature, but the toxicity of the chemicals and their tendency to polymerize required special precautions. Chemical reflux also has the disadvantage of leading to costly chemical waste.

The recently developed method of laser activated isotope separation has a special advantage of being capable of yielding a large separation factor.⁵ At this stage of development, however, the material throughput is exceedingly limited due to the fact that laser activation has to be conducted in the gaseous state at very low pressures, typically of the order of 1 torr. This dilute system is a necessary requirement for the achievement of the extremely high isotope selectivity. The future of laser isotope separation seems to depend on a compromise between selectivity and throughput.

A system that consists of a cuprous chloride-ammonium chloride solution and carbon monoxide (COCO system), developed at Oak Ridge laboratories, employs thermal reflux.⁶ In a thermal reflux process, the refluxes at both ends of a cascade are achieved by thermal means rather than by means of chemical conversion. It avoids the use of chemicals for reflux and the unnecessary chemical byproducts. This is a very important consideration in an industrial size plant. The stage separation factor for this COCO system is 1.015 at room temperature, but its throughput is small.

Another system which employs thermal reflux is the carbon dioxide-carbamate exchange developed by T. I. Taylor and his students at Columbia University. It has been scaled up by Mound laboratories for enriching ¹³C from its natural abundance to about 93%, and has been operated until recently. The effective stage separation depends on the temperature,

flow rate, and choice of amine used in formation of carbamate.⁷

When carbamate is brought into contact with carbon dioxide, there is an exchange of carbon isotopes between the carbon dioxide and the carbamate, resulting in enrichment of ^{13}C in the liquid phase, carbamate, and depletion of ^{13}C in carbon dioxide:

The single stage separation constant, α , is defined as the ratio of $^{13}\text{C}/^{12}\text{C}$ in carbamate over the ratio of $^{13}\text{C}/^{12}\text{C}$ in carbon dioxide, and it is equal to K for the present system, as shown below:

$$\alpha = \frac{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{carbamate}}}{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{CO}_2}} = K \quad (2)$$

Ghate and Taylor found that the exchange between carbon dioxide and amine carbamate of di-n-dutylamine (DNBA) dissolved in triethylamine (TEA) gave substantially higher overall packed column separation of ^{13}C than other amines and solvents used.⁸ They also found that the basicity of the solvent very much affected the separation factor. When DNBA was used in triethylamine or pyridine, either of which has suitable solvent properties but different basicities, the overall column separation (S_{13}) was found to be higher in the former than the latter solvent; 2.05 and 1.74

for 1M DNBA in TEA and 1M DNBA in pyridine, respectively.⁹

Furthermore, experiments performed in this laboratory by Henry Wieck¹⁰ in order to obtain the single stage separation factor, α , indicated that there were some discrepancies between α 's obtained for 1 M-DNBA in TEA and 2 M-DNBA in TEA. Unlike the procedure used by Ghate and Taylor, the method used by Wieck, et al, did not employ the column technique to measure α , but rather a single stage equilibration method was used to obtain the single stage separation factor directly. The overall separation in a column, S , is given by the following:

$$S = \alpha^n$$

where n is the total number of effective theoretical plates. In a multistage technique such as this, there are uncertainties in the number of separating stages; this is due to the uncertainty on the stage efficiency, and therefore the single stage separation factor cannot be determined accurately.¹¹

Figure 1 shows experimentally determined α 's at different temperatures for a 1 M-DNBA in TEA solution.¹² For the amine solutions the isotope exchange equilibrium was approached from both sides of the equilibrium. From one side, carbamate prepared with natural abundance CO_2 was reacted with CO_2 having 20% ^{13}C content. From the other side carbamate prepared with CO_2 having 20% ^{13}C was reacted with natural abundance CO_2 . Enriched carbon-13

was used because if the absolute sensitivity of the mass spectrometer remained the same at different ^{13}C enrichment levels, i.e., between 1% and 10% ^{13}C , then the relative sensitivity of the isotope ratio determination at 10% ^{13}C level is tenfold higher than at 1% ^{13}C level.

The open circles in Figure 1 refer to results of reacting the enriched carbamate with natural abundance CO_2 , and the black circles refer to results of mixing the carbamate formed with natural abundance CO_2 with enriched carbon dioxide. The big open circles show the average α 's obtained at 25°C, 30°C, and 35°C; all of the α 's are within experimental error since the uncertainties of the Mass Spectrometer Model 21-201 used to obtain the data are within ± 0.001 . The slanted solid line marked "Theoretical" was obtained by Finston and Ishida using H_2NCO_2^- molecule for the theoretical calculations.¹³ The other slanting solid lines in the figure were calculated by increasing the indicated force constants by 5% over the values corresponding to the line marked "Theoretical". The slanting dashed lines in Figure 1 were calculated by increasing the values of the geometric parameters by 5% over the ones corresponding to the line marked "Theoretical". The agreement between the theoretically calculated values of α and the experimental values is surprisingly good, especially when considering that the calculated values are for H_2NCO_2^- -carbamate and the experimental values

are for DNBA-carbamate.

However, when α 's for 2 molar solutions of DNBA in TEA were measured the values were found to be somewhat lower than the ones shown in Figure 1, and the difference is probably significant. The average α 's calculated at 30°C for 1 and 2M solutions were ~ 1.01 and ~ 1.007 , respectively.¹⁴ The difference in α 's would indicate that some chemical species whose concentrations depend on the stoichiometric "carbamate" concentration might be significantly contributing to the exchange of carbon isotopes in the amine solutions.

For these reasons an investigation was undertaken to determine the physicochemical properties of carbamate, the species present at equilibrium when carbamate is formed, and to what extent, if any, the solvent is involved in the reaction.

The reaction of primary and secondary amines with CO₂ in non-aqueous solvents is thought to result in the formation of carbamate as shown below:

The secondary amine with its lone pair of electrons attacks the relatively electron deficient carbon in carbon dioxide

resulting in bond formation between the nitrogen and the carbon. The systems under observation are composed of 1 and 2 M solutions of DNBA in TEA, pure DNBA, and pure TEA.

Three possible forms of carbamate are a salt, a zwitterion, or undissociated carbamic acid. If carbamate exists as a salt, there are two possibilities: in the first, the proton is abstracted by a solvent molecule to form the salt shown below;

Secondly, another DNBA molecule is involved in taking up the proton forming the following salt:

The other two possible structures of carbamate are:

and

The importance of ascertaining the nature of the species present in carbamate that exchange carbon isotopes

with CO_2 is clear, since if more than one species significantly contribute to this exchange, then the experimental conditions such as the stoichiometric concentration of carbamate would greatly affect α .

A series of experiments were performed in order to obtain the equilibrium constant for the formation of carbamate in the various amine solutions. Depending on the identity of the "carbamate" species the formation reaction and the expression for the equilibrium constant would be different. By finding out which equilibrium constant remains constant one would be able to identify the dominant species present during carbamate formation.

If, upon addition of CO_2 to 1 or 2M solutions of DNBA in TEA, carbamate salt is formed, then there are two possibilities for the expression of the equilibrium constant. First, if only DNBA is involved in forming the salt, the equation for the equilibrium constant is given by

and K is given by:

$$K = \frac{[\text{R}_2\text{NCOO}^-][\text{R}_2\text{NH}_2^+]}{[\text{R}_2\text{NH}]^2[\text{CO}_2]} \quad , \quad (3b)$$

where the stoichiometric molar ratio of amine to carbon dioxide is 2:1.

The second possibility is that the non-aqueous solvent, in this case TEA, is involved in carbamate salt formation as shown by the following equation:

where the equilibrium constant is given by the following expression:

$$K = \frac{[R_2NCOO^-][R'_3NH^+]}{[R_2NH][R'_3N][CO_2]} \quad (4b)$$

where the stoichiometric ratio of DNBA/TEA/CO₂ is 1:1:1.

The formation of [TEAH]⁺ does not seem to be an unreasonable assumption since there is an excess of TEA, and the pK_b's for DNBA and TEA are 2.69 and 3.285 respectively.¹⁵ For these reasons, TEA is better equipped to pick up the proton generated by the reaction of CO₂ with the secondary amine.

If the zwitterion is formed, then the reaction will be given by

and K is given by

$$K = \frac{[R_2NH^+-COO^-]}{[R_2NH][CO_2]} \quad (5b)$$

and the stoichiometric molar ratio of amine to CO₂ will be 1:1.

If carbamic acid is formed, then the reaction will be

where the equilibrium constant is given by

$$K = \frac{[R_2NCOOH]}{[R_2NH][CO_2]} \quad (6b)$$

and the stoichiometric ratio of amine to CO_2 will again be 1:1.

When pure TEA is brought in contact with CO_2 the only possibility for carbamate formation is the zwitterion, and the reaction is as follows:

where K is given by

$$K = \frac{[\text{R}_3\text{N}^+\text{COO}^-]}{[\text{R}_3\text{N}][\text{CO}_2]} \quad , \quad (7b)$$

and the stoichiometric ratio of TEA to CO_2 is 1:1.

Another possibility is that CO_2 physically dissolves in the amine solution as a loosely solvated form but without any significant chemical reaction taking place; this possibility will be discussed more extensively later on.

When CO_2 is reacted with pure DNBA, the following possibilities arise: the salt is formed where a second molecule of DNBA reacts to pick up the proton, in which case the equilibrium constant will be given by equation 3b. If either the zwitterion or carbamic acid is formed, then the equilibrium constants will be given by 5b and 6b respectively.

The equilibrium constants for each of the systems, i.e., DNBA, TEA, and 1 and 2 M solutions of DNBA and TEA, have been determined for each of the possible formation reactions as discussed above by introducing varying amounts of CO_2 in the amine solutions. By checking the consistency in K with increasing amounts of CO_2 added to the solutions,

it has been possible to determine what carbamate species are dominantly present at equilibrium and which of the reactions mentioned above actually occurred to a significant extent. Since the equilibrium constant ideally should only depend on the temperature (which was kept constant at 25°C), any extreme fluctuation in an equilibrium constant would be regarded to indicate the non-existence of the corresponding equilibrium.

To further elucidate the chemical nature of the species present at equilibrium, a study using a T-60 NMR has been conducted; although further studies are needed, NMR spectroscopy proved to be an invaluable tool in determining the structure of carbamate.

II. EXPERIMENTAL

In this chapter, the experimental apparatus and procedure used in order to obtain data needed for the calculations will be outlined.

II-1. Equilibration Apparatus

The experimental apparatus consisted partly of 150 ml round bottom reaction vessels equipped with high vacuum stopcocks, such as the one shown in Figure 2, which were used in conjunction with a constant temperature bath and a vacuum system shown in Figure 3. Referring to Figure 2, an amine solution of known concentration was pipetted through the septum port before the septum was inserted, and was subsequently degassed several times. The standard 10/30 female tapered joint was degreased with benzene; the flask was then weighed to the nearest milligram and connected to the system shown in Figure 3 by means of the 10/30 joint, Q, and it was immersed in the constant temperature bath. The water in the bath was kept within $\pm 0.1^{\circ}\text{C}$ with a circulating pump (Model E-52 manufactured by Haake Co.) equipped with a thermoregulator; an additional mechanical stirrer was used to keep the temperature homogeneous throughout the bath.

The system used for the experiment is shown in Figure 3, and consists of four main parts: a) a manometer, b) a one liter carbon dioxide reservoir flask, c) a constant temperature bath which was kept at 25°C ,

Figure 2 Carbamate Reaction Flask

- K Kovar Seal
- L Stainless Steel Bellows
- Q $\frac{1}{8}$ 10 30 Joint
- V Reaction Vessel
- S Septum Port
- T Constant T Bath

Figure 3
Carbamate Preparation
and Equilibration
System

d) and a vacuum system.

II-2. Equilibration Procedure

An approximately known amount of pure CO_2 was frozen from the reservoir flask into the cold finger labelled X. The CO_2 was allowed to warm up to room temperature and to come in contact with the degassed amine solution in V. At this point stopcocks G, E, and D were kept closed, while stopcocks J and P were opened. The reaction vessel was manually shaken for several minutes taking advantage of the stainless steel bellows, L, installed to allow flexibility, until the pressure, which was constantly being monitored, became steady. This indicated that equilibrium had been reached; the equilibrium pressure was then recorded. The pressure usually became steady after about a minute of shaking, but the manual stirring was continued for a few more minutes.

The reaction vessel was subsequently detached from the system after stopcocks P, J, and D were closed, cleaned thoroughly to get rid of the water from the outside surface of the reaction vessel and the grease from the 10/30 joint, and was weighed. From the difference in the two weighings the total amount of mmoles of CO_2 introduced in the flask can be calculated. The weight difference was typically between 100mg and 900mg, so that the uncertainty of the order of milligram corresponds to 1% and .1% error in the amounts of CO_2 injected.

The total equilibrium pressure measured from the manometer was due to the partial pressures of CO_2 and amine vapors at equilibrium. In order to obtain the mole fractions of CO_2 and amine vapors present in the gas phase, gas chromatography was employed, and thus the equilibrium constants could be calculated.

II-3. Determination of Equilibrium Gas Phase Composition

The gas chromatographic column used for separation of CO_2 , TEA and DNBA was packed with Porapak Q (100-120 mesh), a porous polymer manufactured by Waters Associates Inc.; the polymer was coated with 5% w/w polyethylene imine (PEI) supplied by Kodak. Since the separation and quantitative determination of aliphatic amines on the untreated polymer is severely limited by tailing and peak asymmetry, Porapak Q was treated with PEI.¹⁶ These problems are also encountered in conventional gas liquid chromatographic separation of amines and have been overcome by the treatment of the solid support by coating with an inorganic or organic base. The peak tailing observed with the untreated polymer indicates that there are sites on the surface of the solid which strongly absorb amines. Also, because transition metals are used in the production of polymers, it is possible that traces of these ions might complex with the amines causing tailing and peak asymmetry.

Hollis¹⁷ showed that when aromatic polymers were coated with PEI, the symmetry of the peaks from amines was greatly improved.

The retention times of aliphatic amines depend on the structure of the amine; this indicates that the separation is brought about principally by absorption on the nonpolar polystyrene, and not the polyamine since changing the amount of base on Porapak Q from 1 to 5% w/w has little effect on the retention times of the amines.¹⁸ The retention times of the amines were determined on a Varian Aereograph 90-P gas chromatograph equipped with a hot wire detector coupled to a Fisher 5000 recorder. A stainless steel column 6 ft. by 1/8 inch i.d. was used, and the flow rate of helium was kept at 75 ml/min. The column was prepared by dissolving a weighed sample of PEI in excess methanol, and a known weight of polymer beads was added to the solution. The mixture was evaporated to dryness under reduced pressure, and the column material was conditioned at 200°C under a helium flow for several hours.

Figure 4 shows a chromatogram of a 1 M solution of DNBA in TEA. The column temperature was 195°C, and the recorder speed was set at 0.5 inch/min. The adjusted retention times of TEA and DNBA were 3.0 min and 17.3 min, respectively. Unfortunately, because the vapor pressure of DNBA is very small (0.0061 atm at 25°C), the chromatograms

Figure 4

Chromatogram of Liquid sample
for 1M-DNBA/TEA Solution
Column-Porapak Q with 5% PEI
Column Temperature-195°C
Carrier Flow Rate-75 ml NTP Helium/min
Chart Speed-0.5 inch/min

of the gas phase for 1 and 2 M solutions of DNBA in TEA did not show a DNBA peak useful for quantitative measurements.

A calibration curve needs to be used in gas chromatography because the hot wire detector has different sensitivities for CO_2 and TEA since the thermal conductivity of the two chemicals is different. The calibration curve was constructed by using a series of standard gas phase solutions of CO_2 and TEA at different concentrations which were obtained in the following manner. An exactly known amount of CO_2 was degassed and introduced in the reaction vessel of Fig. 2. Approximately 60 mgs of liquid TEA was weighed with a Mettler balance to the nearest milligram and introduced through the septum port with a syringe. The amount of liquid introduced was small enough so that, at room temperature, it completely vaporized as soon as it was injected in the flask. The number of moles of TEA injected was kept constant and the amount of CO_2 introduced in the flask was varied. This procedure permitted taking several gas samples from the same flask for chromatographic analysis without changing the CO_2 /TEA ratio since TEA was present only in the gas phase. If liquid TEA were present in the flask, then the amount of CO_2 would decrease each time a gas sample would be removed, while the loss of TEA vapor would be replenished by the evaporation of additional liquid. Therefore the

CO₂/TEA ratio would be different for each sample.

A chromatogram of CO₂ and TEA is shown in Figure 5. The needle of the gas syringe contained air, so that CO₂ had to be separated from air. This was achieved with the polymer column by keeping the column temperature at 90°C, while all other parameters were kept constant; after separation of CO₂ and air was obtained, the column temperature was raised to 195°C. Since the separation between CO₂ and TEA was so great, there was enough time to obtain a stable baseline at the new temperature even at high sensitivities before TEA eluted from the column into the detector, making possible highly precise quantitative measurements.

A calibration curve using known concentrations of CO₂ and TEA was made using the procedure described above and is shown in Figure 6; the slope and intercept were determined by a least squares fit calculation. Calculations of areas under the curves were made with a planimeter, and several chromatograms using the same concentration of CO₂ and TEA were obtained in order to reduce operator error. The chromatograms of the gas phase in the reaction vessels for the various amine solutions were taken, and the mole fractions of CO₂ and TEA thereby determined.

II-4. Data Reduction

In order to compute the equilibrium constants a Fortran program was written; the flow chart is shown in

Figure 5

Chromatogram of Gaseous
Mixture of CO_2 and TEA
Column-Porapak Q with 5% PEI
Column Temperature-90°C at CO_2
Elution and 195°C at TEA Elution
Carrier Flow Rate-75 ml NTP Helium/min
Chart Speed- 1 inch/min

TABLE 1

Summary of Least Squares Fit
Used for Gas Chromatography

<u>Mole Fraction of CO₂</u>	<u>Area of CO₂</u> <u>Area of CO₂ + Area of TEA</u>
.4132	.3843
.5502	.5276
.6418	.6226
.7271	.7425
.8418	.8521
.9120	.9006
.9516	.9465
.9700	.9669

Slope = 1.0464

Intercept = -0.42923×10^{-1}

Column size - 6 ft. by 1/8 inch i.d.

Packing material - Porapak Q with 5% w/w PEI

Carrier flow rate - 75 ml NTP helium/min

Temperature of column at CO₂ elution - 90 °C

Temperature of column at TEA elution - 195 °C

Recorder speed - 1 inch/min

Figure 7. The known experimental facts were: the total equilibrium pressure (P), the volume occupied by the gas phase in the reaction vessel (V_g), the temperature (T), the number of mmoles of DNBA and TEA in the reaction vessel before any reaction had taken place (n_{DNBA} and n_{TEA}), the total amount of CO_2 (n_{CO_2}), and the mole fractions of CO_2 and TEA in the gas phase at equilibrium, (Y_{CO_2} and Y_{TEA}). The equilibrium pressure was obtained from the manometer, and the volume of the gas, V_g , was calculated by subtracting the volume of the liquid amine solution from the volume of the reaction vessel. The total volume of the flask was obtained by first evacuating it and weighing it. Then, the flask was filled with water at a known temperature and was weighed again. From the density of water at a known temperature and an appropriate buoyancy correction the volume was calculated. The mole fractions of CO_2 and TEA in the gas phase were obtained by gas chromatography.

From these data the approximate pressure due to CO_2 (p_{CO_2}) can be calculated as the product of the total pressure and the mole fraction of CO_2 in the gas phase. This is only an approximation since the amount of DNBA in the gas phase (p_{DNBA}) was not yet known and was totally neglected when calculating p_{CO_2} . The number of mmoles of CO_2 in the gas phase was calculated using the ideal gas law, and subsequently the number of mmoles of CO_2

Figure 7
Flow Chart

in the liquid phase was known. From this information the number of mmoles of carbamate formed was calculated; obviously the number of mmoles of carbamate formed is dependent on which "carbamate" species are assumed to be generated by the reaction: the zwitterion, carbamic acid, or the salt with and without TEA participation. The concentration of each alternative species mentioned was calculated and the mole fraction of the unreacted DNBA in the liquid phase (X_{DNBA}) was obtained, again taking into account all of the possible stoichiometric ratios.

Since the vapor pressure of pure DNBA at 25°C was known and the mole fraction of unreacted DNBA in the liquid phase was obtained, Raoult's law was used in order to calculate the partial pressure due to DNBA; the pressure due to CO_2 was then recalculated more accurately. If the difference between the newly calculated pressure of CO_2 and the old one was small enough, K was computed; if not, the computer went through the same cyclic process until the difference became sufficiently small. The threshold difference between the successive values of calculated pressures of CO_2 was set equal to 1 torr since the manometer can only be read to within ± 1 torr. This cyclic procedure was needed because the number of moles of CO_2 in the gas phase originally calculated was overestimated. However, in the successive reiterative calculations, more accurate values of $n_{\text{CO}_2}(\text{g})$ are obtained

and inserted in the expression for the number of moles of CO_2 absorbed in the liquid phase, thereby eliminating the error of the original assumption that no DNBA vapors were present in the gas phase.

The procedure for calculating the equilibrium constants outlined above was used only for 1 and 2 M solutions of DNBA in TEA. For pure TEA the method used was essentially the same. However, because no DNBA was present, the steps used in calculating X_{DNBA} and P_{DNBA} were bypassed; also no cyclic or repetitive calculations were necessary since there was no need to approximate the partial pressure of DNBA.

For pure DNBA no gas chromatography was necessary and, therefore, the pressure of CO_2 was assumed to be equal to the total equilibrium pressure as a first approximation rather than to the product of P and Y_{CO_2} ; the cyclic process was then repeated until the difference in the calculated pressures for CO_2 was equal to or less than 1 torr.

The computer-calculated equilibrium quantities were used to compute the equilibrium constants for 1 and 2 M DNBA/TEA solutions and pure DNBA in the following manner. For a DNBA/TEA/ CO_2 ratio of 1:1:1,

$$K(1:1:1) = \frac{V_g \cdot n_{\text{CO}_2}^2(1)}{n_{\text{CO}_2}(g) \left[n_{\text{DNBA}} - n_{\text{CO}_2}(1) \right] \left[n_{\text{TEA}} - n_{\text{CO}_2}(1) \right]} \quad (8)$$

For a DNBA/CO₂ ratio of 2:1,

$$K(2:1) = \frac{Vg \cdot n_{CO_2}^2(1)}{n_{CO_2}(g) [n_{DNBA} - 2.0 \cdot n_{CO_2}(1)]^2} \quad (9)$$

For DNBA/CO₂ ratio of 1:1,

$$K(1:1) = \frac{Vg \cdot n_{CO_2}(1)}{[n_{DNBA} - n_{CO_2}(1)] n_{CO_2}(g)} \quad (10)$$

For pure TEA the equilibrium constants calculated for a stoichiometric ratio of TEA/CO₂ of 1:1 is

$$K(1:1) = \frac{Vg \cdot n_{CO_2}(1)}{n_{CO_2}(g) [n_{TEA} - n_{CO_2}(1)]} \quad (11)$$

and for TEA/CO₂=2:1,

$$K(2:1) = \frac{Vg \cdot [n_{CO_2}(1)]^2}{[n_{TEA} - 2.0 \cdot n_{CO_2}(1)]^2 n_{CO_2}(g)} \quad (12)$$

Following is a table of physical properties for DNBA and TEA which are needed for these calculations as well as other computations in this study. The densities of the solutions were measured at 25.0°C using a hydrometer; the uncertainties in the density measurements were within ± 0.001 grams/ml. Before each density measurement, the amine solutions were kept at 25.0°C by immersing them in the constant temperature bath for several hours. The vapor pressure measurements were made using the manometer on the vacuum system shown in Figure 3 with the reaction vessel immersed in the bath to keep the temperature constant.

Table 2
Physical Properties of Amines

	<u>DNBA</u>	<u>TEA</u>
Formula	$C_8H_{19}N$	$(C_2H_5)_3N$
Mol. Weight	129.25	101.19
Density (25°C)	0.753 g/ml ^a	0.718 g/ml ^a
Vapor Pressure (25°C)	0.006 atm ^a	0.089 atm ^a
pK _b (25°C)	2.69 ^b	3.285 ^b
Dielectric Constant	2.978 (20 °C) ^b	2.42 (25°C) ^b
Normal Boiling Point	156-158 °C	88-90 °C
Origin	Eastman Kodak	Eastman Kodak
	<u>1 M-DNBA/TEA</u>	<u>2 M-DNBA/TEA</u>
Density (25°C)	0.725 g/ml ^a	0.732 g/ml ^a

a) Measured in this laboratory

b) A. Riddick and Bunger, Organic Solvents, Wiley-Interscience N. Y. (1970)

c) Unless otherwise stated, data taken from "Handbook of Chemistry and Physics", 53rd Edition, Chemical Rubber Co., (1972)

III. RESULTS AND DISCUSSION

This chapter is comprised of three parts. Section III-1, which follows, will contain results and discussion of the equilibrium constant calculations. In the second part of this chapter, section III-2, results and discussion obtained using instrumental analytical techniques in order to gain more information on the chemical structure of the carbamate species will be presented. In section III-3, a qualitative discussion for correlating the present findings and Wieck's experimental values of $^{13}\text{C}/^{12}\text{C}$ exchange equilibria will be attempted.

III-1. Experimental Results of Equilibrium Constant Calculations

Table 3 contains the summary of the total equilibrium pressure as a function of the amounts of CO_2 added to the reaction vessels containing 1 and 2 M-DNBA/TEA solutions, and for pure TEA and DNBA. Figure 8 shows a plot of the data in Table 3. From this graph it can be seen that, for 1 M-DNBA in TEA, 2 M-DNBA in TEA, and pure DNBA, as carbon dioxide is charged in the amine solutions, the total equilibrium pressure does not change very much when DNBA is in excess, or the amount of CO_2 charged is relatively small. But, as more CO_2 is injected in the reaction vessel, and the amine solution approaches saturation, the addition of a small amount of CO_2 gives a relatively large change in the equilibrium pressure. None of the curves in Figure 8

Table 3

Summary of the Total Equilibrium Pressure vs Mmoles
of CO₂ Added for 1M-DNBA/TEA, 2M-DNBA/TEA, DNBA, TEA at 25°C

<u>1M DNBA/TEA</u>		<u>2M DNBA/TEA</u>		<u>DNBA</u>		<u>TEA</u>	
<u>CO₂ Charged</u> <u>(Mmoles)</u>	<u>Press.</u> <u>(Torr)</u>	<u>CO₂ Charged</u> <u>(Mmoles)</u>	<u>Press.</u> <u>(Torr)</u>	<u>CO₂ Charged</u> <u>(Mmoles)</u>	<u>Press.</u> <u>(Torr)</u>	<u>CO₂ Charged</u> <u>(Mmoles)</u>	<u>Press.</u> <u>(Torr)</u>
1.55	93.0	2.23	66.7	4.07	13.3	1.52	221.6
1.84	101.4	2.50	68.3	5.02	23.2	2.59	328.3
2.18	106.5	3.54	84.0	5.25	26.9	3.07	390.2
2.48	140.9	4.57	118.2	6.27	77.3	3.95	429.7
2.73	132.8	4.77	114.0	6.36	82.9	4.16	498.6
2.93	132.8	4.82	120.4	7.50	172.2	4.64	542.7
2.99	154.6	6.00	173.3	8.04	205.8	5.45	626.8
3.11	160.9	6.34	192.1	9.50	248.6		
3.52	188.7	6.57	182.9	10.01	375.8		
3.73	202.4	7.54	269.8	11.50	564.2		
4.82	275.1	7.54	272.0				
5.34	331.6	7.57	278.0				
5.41	334.3	7.93	306.1

Figure 8. Total Pressure vs mmols of CO₂ added at 25°C

have sharp breaks at any point; such a sharp break would have indicated an irreversible carbamate formation reaction. If a sharp break occurred in the curves, it would also have indicated that the equilibrium constant was very large. For TEA all points fall into a straight line, showing that there is very little absorption of CO_2 by the amine.

Table 4 summarizes the results of computer calculations of the various equilibrium constants for the runs in which varying amounts of CO_2 were added to 5 ml of 1M-DNBA in TEA solutions at 25°C. In this table, K (1:1:1) and K (2:1) were calculated for the equilibria of Eqs. (4a) and (3a) respectively, and K (1:1) was computed for the reaction of Eq. (5a) or (6a). Figure 9 shows a plot of the equilibrium constants vs mmoles of CO_2 added for carbamate formation in the amine solutions. The points in the triangles represent the equilibrium constants obtained for salt formation assuming no TEA involvement. The stoichiometric molar ratio of DNBA/ CO_2 is 2:1. The circles represent the equilibrium constants obtained assuming carbamate salt formation with TEA participating in the reaction; the stoichiometric ratio of DNBA/TEA/ CO_2 is 1:1:1. The points enclosed by the crossed circles represent the equilibrium constants for zwitterion or carbamic acid formation, where the stoichiometric ratio of DNBA/ CO_2 is 1:1. From this Figure it can be seen that when TEA is assumed to participate in carbamate salt

TABLE 4

Summary of Equilibrium Studies for
Formation of Carbamate in 1M DNBA/TEA at 25°C*

<u>CO₂ Charged (mmoles)</u>	<u>K (1:1:1:)x10¹ (liter/mole)</u>	<u>K (2:1) (liter/mole)</u>	<u>K (1:1)x10² (liter/mole)</u>
1.55	0.76	1.59 x 10 ²	1.80
1.84	0.89	2.71 x 10 ²	1.80
2.18	1.49	1.02 x 10 ³	2.41
2.48	0.79	4.95 x 10 ²	1.30
2.73	1.07	1.57 x 10 ³	1.56
2.93	1.68	3.10 x 10 ⁴	2.91
2.99	1.16	5.30 x 10 ³	1.55
3.11	1.32	3.22 x 10 ⁴	1.67
3.52	1.01	3.28 x 10 ⁵	1.23
3.73	1.21	9.29 x 10 ³	3.20
4.82	1.30	5.63 x 10 ²	1.00
5.34	0.93	5.35 x 10 ²	0.93
5.41	1.32	3.00 x 10 ²	0.51

* 5 ml of amine solution was used.

Figure 9. Equilibrium Constants for Formation of Carbamate in LM-DNBA/TEA

- DNBA/TEA/CO₂ (1:1:1) left vertical axis
- △ DNBA/CO₂ (2:1) right vertical axis
- ⊕ DNBA/CO₂ (1:1) left vertical axis

formation and is accounted for in the equilibrium constant expression, K is more constant than for any of the other possibilities mentioned earlier.

Table 5 and Figure 10 show the data and plot for the equilibrium constants vs mmoles of CO_2 added for 2M-DNBA in TEA solutions. The circles represent the equilibrium constants for carbamate salt formation assuming that TEA participates in the reaction. The triangles represent the equilibrium constants with varying amounts of CO_2 injected in the reaction vessel assuming that the stoichiometric molar ratio of DNBA/ CO_2 is 2:1, and the cross circles are the equilibrium constants for carbamic acid or zwitterion formation. Figure 10 shows that, again, the best consistency is given assuming that the stoichiometric ratio of DNBA/TEA/ CO_2 is 1:1:1. The equilibrium constant, $K(1:1)$, for the zwitterion formation in 1M and 2M solutions is more dependent on the concentration of carbamate than $K(1:1:1)$. However, the agreement between the K -values in 1M and 2M solutions is better for $K(1:1)$ than for $K(1:1:1)$. On this ground, therefore, zwitterion formation cannot be completely excluded. On the other hand, the fact that the isoelectric point of α and β amino acids is of the order of $\text{pH} = 6$ reduces the possibility of existence of a zwitterion in the amine solutions. Similarly, the undissociated form of the acid in the basic solutions is very unlikely.

TABLE 5

Summary of Equilibrium Studies for the
Formation of Carbamate in 2M DNBA/TEA at 25°C*

<u>CO₂ Charged (mmoles)</u>	<u>K (1:1:1) x 10¹ (liter/mole)</u>	<u>K (2:1) (liter/mole)</u>	<u>K (1:1) x 10² (liter/mole)</u>
2.23	4.00	2.09 x 10 ²	3.99
2.50	3.25	1.92 x 10 ²	2.91
3.54	5.58	7.06 x 10 ²	3.37
4.57	4.32	1.55 x 10 ³	2.07
4.77	4.03	1.96 x 10 ³	1.85
4.82	4.32	2.47 x 10 ³	1.94
6.00	4.35	-----	1.59
6.34	3.31	7.15 x 10 ⁴	1.20
6.57	4.45	5.33 x 10 ³	1.50
7.54	3.83	1.16 x 10 ³	1.19
7.54	3.87	1.04 x 10 ³	1.19
7.57	3.66	1.09 x 10 ³	1.13
7.93	3.47	7.45 x 10 ²	1.00

* 5 ml of amine solution was used.

Figure 10. Equilibrium Constants for Formation of Carbamate in 2 M-DNBA/TEA

○ DNBA/TEA/ CO_2 (1:1:1)
 △ DNBA/ CO_2 (2:1)
 ⊕ DNBA/ CO_2 (1:1)

The comparison of the equilibrium constants calculated for carbamate formation assuming TEA as being one of the reactants for 1M and 2M-DNBA/TEA solutions is shown in Figure 11. The average K for the 1M solution is 11.8 liter/mole, while for the 2M solution it is 40.3 liters/mole. This discrepancy may be accounted for by the fact that in the expression for the equilibrium constants, molar concentrations are used rather than activities of the species present at equilibrium. For 2M-DNBA/TEA the activity coefficients of the charged species would be smaller than the activity coefficients in a 1M solution of DNBA in TEA, since in the former solution the concentration of the charged species is greater than for the latter amine solution. Also, in solutions where the dielectric constant of the solvent is relatively low, i. e., 2.42 at 25°C for TEA, the existence of molecular association which is stronger than in aqueous solutions is expected. This effect would be more pronounced at higher concentrations, and such association into ion pairs would drastically lower the value of the effective ionic activity coefficients.

The carbamate salt is composed of the alkyl ammonium ion and the carbamate anion, and the concentrations of both of these ions appear in the numerator of the equilibrium constant expression. Therefore, if activities were used in the expression, then the K 's for 2M solutions would be closer to the K 's for 1M solutions than Figure 11 indicates. The activities of the uncharged species,

DNBA and TEA, would be less affected by the change in molar concentrations. Thus, substituting activities for the concentrations of TEA and DNBA would not offset the effect of the ionic activities described above. The only other conceivable explanation for the difference in $K(1:1:1)$ is that at the higher concentration a significant fraction of the total DNBA might be involved in accepting the proton generated by the carbamate reaction.

In order to determine whether the protonated solvent is actually the cationic species which is dominant in the carbamate salt, the ratio of the concentrations of $[TEAH]^+$ and $[DNBAH]^+$ was determined using the following procedure. For the reaction shown below,

the equilibrium constant is given by:

$$K = \frac{[R_2NH][R_3\ddot{N}H]}{[R_2\ddot{N}H_2][R_3\ddot{N}]}$$

If the pK_b 's of DNBA and TEA for aqueous media are used and substituted in the above equation, K is found to be 0.254 for this system. With this data and the proton balance, it was possible to calculate the $[R_3\ddot{N}H]/[R_2\ddot{N}H_2]$ ratios for 1 and 2M DNBA/TEA solutions. It was found that the ratios were 5.8:1 and 2.4:1 for 1 and 2M-DNBA/TEA, respectively. Although the pK_b 's used for the amines were determined in aqueous solutions, these ratios show that there is a significant amount of $[DNBAH]^+$ being generated in the carbamate reaction, and this amount increases substantially in the more concentrated solution. However, the consistency of K 's obtained assuming no TEA involvement, i.e. $K(2:1)$, is poor, which again

supports the conclusion that TEA must be significantly involved in carbamate formation as a proton acceptor.

In order to determine whether all of the CO_2 that goes into the amine solutions has reacted to form carbamate, or if some of it (if not most) is just being physically absorbed, or involved in some side reaction with the solvent, pure TEA was charged with CO_2 . Table 6 shows the results of runs in which varying amounts of CO_2 were added to 5 ml of pure TEA at 25°C , and Figure 12 shows the plot for the equilibrium constants vs CO_2 charged in the reaction flask. The triangles represent the equilibrium constants obtained for zwitterion formation, where the stoichiometric molar ratio of TEA to CO_2 is 1:1. The circles represent the equilibrium constants for the following reaction:

where A and B are some products. This is simply to see how much an equilibrium constant for a reaction other than zwitterion formation might vary. It is noted that no carbamic acid formation is possible in TEA. It is seen from Figure 12 that the equilibrium constants for both reactions are very small; this shows that the amine needs a mobile hydrogen attached to the nitrogen in order to form a relatively stable N-C bond leading to carbamate formation. Figure 12 also shows that the consistency of the K's calculated for the zwitterion

TABLE 6

Summary of Equilibrium Studies for
The Formation of Carbamate in Pure TEA at 25°C*

<u>CO₂ Charged (mmoles)</u>	<u>K (2:1) x 10⁻³ (liter/mole)</u>	<u>K (1:1) x 10⁻¹ (liter/mole)</u>
1.52	4.71	7.6
2.59	7.42	7.30
3.07	4.60	5.22
3.95	23.0	9.83
4.16	8.28	5.97
4.64	5.61	4.70
5.45	9.12	4.20

* 5 ml of amine solution was used.

Figure 12. Equilibrium Constants for Formation of Carbamate in Pure TEA

formation reaction is better than for the equilibrium constants obtained assuming a TEA/CO₂ ratio of 2:1; however, part of the CO₂ could also have been physically absorbed by the amine. In any case, whether CO₂ is physically absorbed, or is involved in forming the zwitterion, or both, the extent of CO₂ absorption is very small. Since the equilibrium constants in pure TEA are only 1 to 2% of K (1:1:1) in the DNBA/TEA systems, the effect of any side reactions involving the TEA solvent in DNBA/TEA on the values of K involving DNBA would be negligible.

Data for the equilibrium constants for pure DNBA are shown in Figure 13 and Table 7. The circles represent the equilibrium constants calculated assuming that the stoichiometric ratio of DNBA to CO₂ is 2:1. The triangles represent K's for zwitterion or carbamic acid formation. It is seen in Figure 13, that neither of the two possibilities give constant K's. A very likely possibility is that more than one reaction is occurring at the same time: carbamate salt formation and zwitterion formation. This could be conceivable as the amount of CO₂ added to the amine becomes larger. The DNBA molecules left at equilibrium have to solvate the salt formed, and, as more CO₂ is added, more DNBA is needed for solvation and participation in the reaction. If the equilibrium is shifted toward more zwitterion formation, there

TABLE 7

Summary of Equilibrium Studies
For the Formation of Carbamate in Pure DNBA at 25°C

<u>CO₂ Charged (mmoles)</u>	<u>K (2:1)x10³ (liter/mole)</u>	<u>K (1:1) x10² (liter/mole)</u>
4.07	1.79	9.42
5.02	4.91	6.47
5.25	7.03	5.85
6.27	46.6	2.33
6.36	50.9	2.18
7.50	35.3	1.17
8.04	3.87	1.09
9.50	1.43	0.68
10.1	0.64	0.69
11.5	0.49	0.45

would be more DNBA available for solvation.

III-2. Results on Carbamate Structures Using Instrumental Methods

In order to find what the molecular environments for the species present at equilibrium in the carbamate reaction are, a series of NMR studies were performed. The carbamate solutions were prepared in a manner similar to that described above for the equilibrium constant studies. After a solution was saturated with CO_2 , a portion of the liquid sample was taken through the septum of port S of the reaction flask with a syringe equipped with a shut-off valve on the needle. The liquid was then injected into an NMR tube prefilled with CO_2 to one atmosphere through a septum. This procedure avoided contact of the carbamate solution with air and moisture, thus preventing the hydrolysis of carbamate. The spectra were taken with a Varian Model T-60.

Figures 14a and 14b show the NMR spectra of pure TEA and pure DNBA, respectively. Different protons and corresponding peaks have been labelled with identifying letters. The peak labelled x, with a chemical shift (τ) of 0.63 ppm, is assigned to the hydrogen attached to the nitrogen atom of DNBA. This assignment is confirmed by the disappearance of the peak when a few drops of heavy water are added to the amine. The fact that the proton is well shielded is due to the effect of hydrogen bonding.

Figures 15a and 15b show the NMR spectra of a solution of 2M-DNBA/TEA without CO_2 and a 2M solution of DNBA/TEA saturated with CO_2 . (See Figure 14 for proton identification). The peak labelled x in DNBA disappears upon formation of carbamate, indicating that either (1) the N-proton is removed from nitrogen or (2) the charge density around the nitrogen is strongly affected.

The downfield shift of DNBA's α proton peak upon carbamate formation can be taken as evidence for bond formation between nitrogen and the carbonyl group. The loss of resolution in peaks b, c and a for the spectrum of carbamate points to the fact that DNBA is shifting rapidly between two states at equilibrium, thus producing a blurring of the spectral lines.

Evidence supporting the presence of $[\text{TEAH}]^+$ ion in the CO_2 saturated DNBA/TEA solutions has not been found, although this is not unusual since the effect of the quadrupole moment of nitrogen is to broaden the N-nitrogen peak in such a way that, even if higher sensitivity were used, the peak would still not be noticeable. No peaks were found downfield, at about $\tau = 12$ ppm, which indicates that no carbamic acid is formed; zwitterion formation can neither be proven nor disproven with this technique due to the quadrupole moment effect of nitrogen.

In order to gain more information on the system, the

use of other NMR techniques is necessary. Amines with ^{15}N rather than ^{14}N should be used in proton NMR study, other solvents (both polar and non polar), and the use of low temperatures to sharpen the blurred peaks due to rapid equilibrium reactions should be employed. Also, ^{15}N magnetic resonance studies should be conducted since with this technique the charge density around the nitrogen can clearly be determined.

To obtain more information on the fate of the proton during carbamate formation, infrared spectroscopy was used. Infrared spectra of 1M solutions of DNBA in TEA with and without addition of CO_2 were taken and the following results obtained. The 1M-DNBA/TEA solution contains a single N-H band at 3300 cm^{-1} ; a second lower band arising from the hydrogen bonded form of DNBA is not seen presumably because it is masked by other bands in the spectrum. The N-H band disappears with addition of CO_2 , and two more bands appear, at 2450 cm^{-1} and 1680 cm^{-1} . The first is characteristic of salts of secondary and tertiary amines having $>\text{NH}_2^+$ and $>\text{NH}^+$ groups which have broad absorptions in the range of $2250\text{--}2700\text{ cm}^{-1}$.¹⁹ The second absorption band is characteristic of the carbonyl group. For further identification purposes of the $>\text{NH}_2^+$ and $>\text{NH}^+$ groups the study of deformation modes in the 1600 cm^{-1} region is necessary; however this area of the spectrum is

sandwiched by large absorption bands due to the alkyl groups of TEA and DNBA and the carbonyl group.

III-3. Correlation with Isotope Exchange Equilibria

As mentioned in the introductory chapter, the value of the carbon isotope exchange equilibrium, Eq.(1), between carbon dioxide and the carbamate of DNBA is somewhat less in the 2M-DNBA/TEA solution than in the 1M-DNBA/TEA solution. The present study has shown that, by far, the most dominant carbamate species is the DNBA-carbamate anion, coupled with the TEA-ammonium cation. It has also been shown that the carbamate formation equilibrium constant based on the (1:1:1) stoichiometry and the assumption of the ideal solution lead to a slightly higher K value in 2M-DNBA/TEA solution than in 1M-DNBA/TEA solution, and that the difference shown in Figure 11 may disappear if the activity coefficients are used in calculating the K values.

The equilibrium constant of Eq.(1) can be calculated by using the Bigeleisen-Mayer function²⁰, $(s/s')f$, as

$$K_{13}^{eqm} = \frac{(s/s')f \left[\text{carbamate-}^{13}\text{C} / \text{carbamate-}^{12}\text{C} \right]}{(s/s')f \left[^{13}\text{CO}_2 / ^{12}\text{CO}_2 \right]} \quad (14)$$

To the first order, the value of K_{13} calculated by means of this statistical mechanical procedure is independent of the identity of the ammonium ion, so that the identity of the proton acceptor in carbamate formation is immaterial as far as K_{13} is concerned. Again, to the

first order, the value of the statistical mechanical K_{13} depends on the intramolecular forces around the isotopically exchangeable carbon atom only, and any effects of the molecular structure and molecular forces away from the carbonyl carbon is of second order importance.²¹ the larger the sum of diagonal harmonic force constants directly related to the motion of the carbonyl carbon, the larger the value of $(s/s')f$ for carbamate. Thus, one would expect a larger K_{13} with the carbamate anion participating in the exchange reaction than with either the zwitterion or carbamic acid participating in the reaction because the electronic density around the carbonyl carbon in the carbamate anion is greater than for the other carbamate species.

If α_{13} is in fact smaller at the higher carbamate concentration, then this must be attributed to a higher level of participation in the isotope exchange by zwitterion/carbamic acid at the higher concentration. The only other conceivable explanation is the concentration dependent effect of the intermolecular forces upon $(s/s')f$. Such an effect may increase or decrease $(s/s')f$ because the contribution of internal vibrations to $(s/s')f$ usually decreases when a molecule comes under an influence of an external force, while such a force creates a new, positive, term which is attributable to translational and rotational motions of the molecule.²² Thus, usually, the vapor pressure of the heavier isotopic molecule is

lower than that of the lighter isotopic molecule; this situation corresponds to a larger $(s/s)f_c$ for the condensed phase than $(s/s)f_g$ of the gaseous phase. This is the normal vapor pressure isotope effect. However, the situation is often reversed, and the vapor pressure of the lighter molecule is lower than that of the heavier molecule. This is the inverse vapor pressure isotope effect. The examples are the D/H effects in liquid methane²³ and ethylene.²⁴ The shift in $(s/s)f$ upon condensation is typically of the order of ± 0.01 out of the total magnitudes of 1~5 for the deuterium effects in the hydrocarbons at 300°K, while the corresponding shift for $^{13}\text{C}/^{12}\text{C}$ effect is of the order of ± 0.001 out of 0.1~0.2 at room temperature.²⁵

If the observed tendency of decreasing $\alpha_{1,2}$ with increasing carbamate concentration is real, then it could be due to the change in the external forces felt by the carbamate anions, and the decrease in $\alpha_{1,2}$ by 0.003 is well within the magnitudes of such external effects. This fact is obvious especially when one notes that the external effects for the ionic species must be stronger than that for the non-polar molecules.

IV. SUGGESTED FURTHER INVESTIGATIONS

This chapter is composed of two parts. Section IV-1 will contain a short discussion of suggested further study for determining experimentally and theoretically the activity coefficients for the systems studied. The second part of this chapter contains suggestions for further NMR studies.

IV-1. Determination of Activity Coefficients

Experimental. Activity coefficients can be calculated for a solution containing a salt using the freezing point depression. The formula for the freezing point depression is given by:

$$\theta = K_f m (1-j) \quad (15)$$

where K_f $\equiv$ freezing point depression constant

m $\equiv$ molality of the solution

$(1-j)$ $\equiv$ osmotic coefficient

The following formula relates the activity coefficient of the solute to experimentally determinable parameters:

$$\ln \gamma = -j - \int_0^m (j/m) dm \quad (16)$$

From experimental values of θ and m , j can be calculated using equation 15, j/m vs m can be plotted, and the area under the curve, which is equal to the integral, can be determined. After obtaining the value of γ , the activity

can be calculated using the relation $a = m \cdot \gamma$.

However, since carbamate formation is an exothermic reaction, the equilibrium will be shifted towards more carbamate formation as the solution cools down, and the concentration of the salt will differ from that calculated in this experiment at 25°C. The concentration of carbamate salt formed at the temperature where the solvent begins to crystallize out of solution will have to be determined by pressure measurements in a manner similar to that employed in the present study. However, newly developed apparatus will be needed to ensure vigorous stirring so that the measured pressure will be representative of the equilibrium pressure.

Theoretical. The Debye-Hückel limiting law for obtaining the activity coefficients was used in this experiment. However, due to the low dielectric coefficients of the amines and the high concentration of the salt at equilibrium, ridiculously low activity coefficients were obtained. Since the Debye-Hückel theory is intended for use in very dilute systems, typically in aqueous solutions for which the dielectric constant is 78.54, it is not surprising that the activity coefficients calculated do not reflect the true values.

The basic flaw in the Debye-Hückel model is in the assumption that ions will rarely be close together. However, this is only true in extremely dilute solutions

for which the dielectric constant of the solvent is relatively high, such as water. In such a case, the interionic potential is usually small, much less than the average thermal energy, and the solution of the limiting law is based on this assumption. If an ion is surrounded by an ionic atmosphere at a distance which is less than the diameter of one solvent molecule, the assumption that the interionic potential energy is much smaller than the thermal energy is no longer true, and the solution of the Debye-Hückel theory no longer valid. The Poisson-Boltzmann equation must be reconsidered to give solutions for activity coefficients which would suit concentrated solutions with low dielectric coefficients, such as the ones investigated in this study.

IV-2. NMR Studies

To obtain more information on the carbamate systems, the use of other magnetic resonance techniques is necessary. Nitrogen-15 magnetic resonance should be used so that the charge density around the nitrogen atoms can be determined. If proton magnetic resonance studies are conducted, different polar and non polar solvents and amines with ^{15}N rather than ^{14}N , to eliminate the quadrupole moment effect, should be employed. Low temperatures should also be used for carbamate spectra so that the splittings of the peaks which are blurred due to fast equilibrium reactions can be determined.

V. CONCLUSION

The following conclusions can be drawn from this study. TEA does participate in the formation of carbamate in 1 and 2M-DNBA/TEA solutions by abstracting the proton generated in the formation of the DNBA-carbamate anion. A significant fraction of DNBA also participates in the proton abstraction. The amount of TEA-carbamate formed, or the amount of physically dissolved CO_2 , is negligible. Thus, the DNBA-carbamate is primarily a salt in which DNBA forms a bond with the carbon of CO_2 . We should then expect a relative insensitivity of the carbon-13 separation factor to the choice of solvent used.

VI. SUMMARY

Physicochemical properties of the carbamate-CO₂-solvent system have been investigated for the purpose of elucidating the chemical nature of the species present at equilibrium during carbamate formation. For this purpose equilibrium constants for carbamate formation were determined for pure di-n-butylamine (DNBA), triethylamine (TEA), and for 1 and 2 molar solutions of DNBA in triethylamine; gas chromatography was used to determine the composition of the gas phases. Furthermore NMR spectroscopy was employed to better elucidate the structure of carbamate. It was found that when TEA was taken into account in the expression for the equilibrium constant, K, it did not fluctuate as much with varying amounts of CO₂ and the amines as when TEA was assumed not to be involved in the reaction. Therefore, it was concluded that TEA, when used as a solvent, participates in carbamate salt formation by abstracting the hydrogen from DNBA after CO₂ has reacted with the secondary amine to form $\left[R_3NH \right]^+$. It was also found that when TEA was charged with CO₂, very little absorption of carbon dioxide occurred. The ratio of the number of moles of amine to that of CO₂ absorbed was about 60 times larger for DNBA than for TEA; correspondingly the equilibrium constants for 1 and 2 M solutions of DNBA in TEA were much larger than for pure TEA. This confirmed the fact that the amine needs a mobile hydrogen attached

to the nitrogen in order to form a relatively stable N-C bond between the amine and carbon dioxide. No peaks were found with a chemical shift at about 12 ppm for the NMR spectra of carbamate, indicating that there is no carbamic acid formation. The isoelectric point of α and β amino acids is of the order of $\text{pH} \approx 6$, so that the existence of a zwitterion is highly unlikely in the amine solutions. NMR evidence supporting the presence of $\left[\left(\text{C}_2\text{H}_5\right)_3\text{NH}\right]^+$, or $\left[\text{TEAH}\right]^+$, after addition of CO_2 to 1 and 2 M solutions of DNBA in TEA was not found, although this is not unusual due to the quadrupole moment effect of nitrogen.

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