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Fractionation of Oxygen-18 and Carbon-13 Isotopes by Chemical Exchange of Carbon Dioxide with Amine Carbamates

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Fractionation of Oxygen-18 and Carbon-13 Isotopes by Chemical Exchange of Carbon Dioxide with Amine Carbamates*

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Summary

The distribution of ^{18}O and ^{13}C isotopes in a chemical exchange system of carbon dioxide and amine carbamates has been studied. A comparison of isotope separation by 15 amines shows little dependence on the nature of the amine. Effect of amine concentration indicates that diffusion of the reacting species plays a significant role in these systems. This is in conformity with our observation that the viscosity of the amine solutions saturated with carbon dioxide increases rapidly with amine concentration.

INTRODUCTION

The lack of suitable radioactive isotopes of oxygen and carbon has led to the use of their stable isotopes, such as ^{18}O and ^{13}C, as tracers for the study of reaction mechanisms and the kinetic isotope effects (*1*). Many other applications exist; for example, the use of ^{13}C in hyperfine splitting (*2*), in NMR studies (*3*), in nuclear research (*4*), and the application of ^{18}O as tracer and in palaeotemperature technique (*5*). At the

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present time, ^{18}O is mainly enriched by the distillation of water (*6*) or nitric oxide (*7*). Similarly, ^{13}C is enriched by the distillation of carbon monoxide (*8*). Thermal and gaseous diffusion have also been used (*9*). Chemical exchange between cyanide ion and hydrogen cyanide has been used (*10*) for the enrichment of ^{13}C. Various nitric oxide systems exist for ^{18}O separation (*11*, *12*). Most of these systems have limitations that need not be discussed here.

The fractionation of stable isotopes of oxygen, nitrogen, carbon, and hydrogen in systems containing an amine and carbon dioxide under distillation was reported by Holmberg (*13*). Subsequently, Taylor (*14*) reported a system in which ^{18}O and ^{13}C could be separated by chemical exchange between amine carbamates and carbon dioxide. In this paper, results of the dependence of separation of ^{18}O and ^{13}C on the nature of amine and other process variables are described. A subsequent paper will describe separation of ^{13}C in greater detail (*15*).

ENRICHMENT FACTORS

The exchange reactions studied in the present work are:

$$^{13}CO_2 + R_2N^{12}CO^-_2 \rightleftarrows {}^{12}CO_2 + R_2N^{13}CO^-_2$$
$$C^{16}O_2 + R_2NC^{16}O^{18}O^- \rightleftarrows C^{16}O^{18} + R_2NC^{16}O^-_2$$

In these equations $R_2NCO^-_2$ is a part of a carbamate ion pair represented by $R_2NCO^-_2\ {}^+H_2NR_2$. The single stage enrichment factor α_{18} for ^{18}O for the exchange of carbon dioxide with monoethanolamine is (*14*) 1.013 at 25°C. From the results of the simultaneous separation of ^{18}O and ^{13}C in a column operating at total reflux the value of α_{13}, the single stage enrichment factor for ^{13}C, can be calculated as 1.01 at 25°C. These values are, therefore, experimental values. Theoretical values (*16*), however, cannot be computed due to the present unsatisfactory assignments (*17*) of the vibration frequencies of the carbamates.

EXPERIMENTAL

The exchange column used for these experiments, shown in Fig. 1, was made of glass, 196 cm long, 10 mm i.d. packed with a stainless steel, Helipak 3012 (Podbielniak Inc., Chicago, Ill.) packing, and had a concentric jacket. Carbon dioxide was admitted at the lower end of the column and rose countercurrently to the amine carbamate solution. At

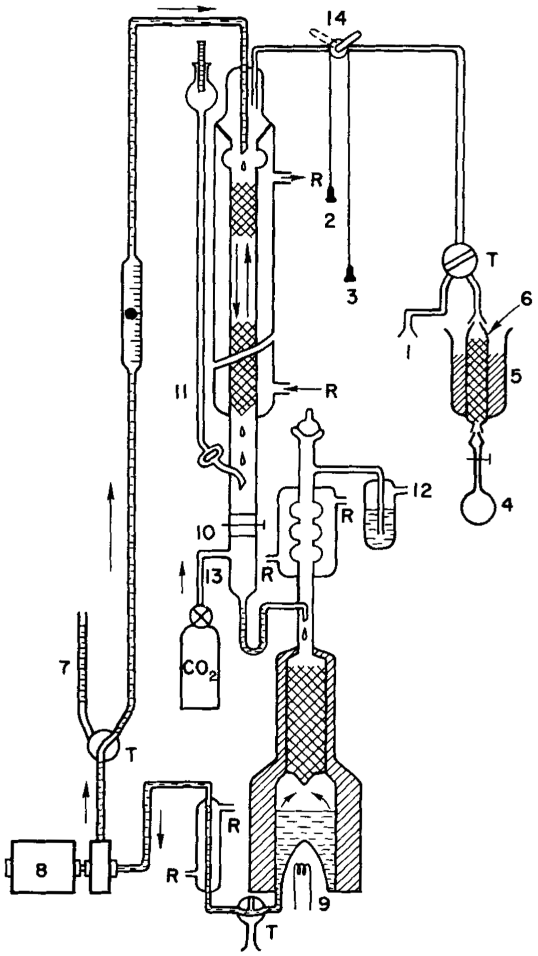

FIG. 1. Exchange column (196 × 1 cm i.d.) packed with Helipak (3012) for the carbamate–carbon dioxide exchange system: (1) to vacuum pump; (2) and (3) remote control cords for toggle valve; (4) sample tube; (5) Dry-Ice bath; (6) silica-gel tube; (7) buret; (8) finger pump; (9) heating coil; (10) Teflon section with a screw clamp; (11) line for flooding the column; (12) exit for waste carbon dioxide; (13) inlet for feeding CO_2; (14) toggle valve. (T) indicates three-way Teflon stop cocks and (R) indicates the entrance and exit of the refrigerant.

the bottom of the column the carbon dioxide was stripped from the amine solution by boiling and the solution was recirculated to the top of the column by means of a sigmamotor finger pump. Here it absorbed the ascending carbon dioxide to form the amine carbamate.

Before starting a run the packed bed was washed by pumping commercial methanol into the top end and discarding it at the bottom end. An initial charge of amine solution was prepared and used to flood the column. The column was flooded in such a manner that the solution rose from the bottom to the top and displaced the air present in the column. Once the column was flooded, it was drained very slowly while at the same time the solution was being pumped in at the top of the bed. Carbon dioxide was next admitted and, at the same time, the stripper and its heat exchanger were both allowed to start operating. If at any time solution flow was found interrupted, the column had to be flooded in order to assure good wetting of the packing. The toggle valve at the top of the column was left open for the first hour of column operation in order to drive off all air. The experiment was assumed to have started at the time this valve was closed. Samples of carbon dioxide were withdrawn from the top of the column through a capillary tube. Before admitting the sample to an evacuated sample tube, it was passed through a small silica gel section at Dry Ice temperature in order to remove any solvent or amine vapors. A 60° sector Nier Type single collector mass spectrometer was used for the isotopic analysis. In all these experiments ^{18}O concentrated and ^{13}C depleted in gas phase at the top of the column.

During the course of a run the flow rate, molarity of amine, and temperature were frequently checked and carefully controlled. Trace amount of water in the recirculating solution was determined periodically by gas chromatography. In these experiments the amines used were those supplied by Fischer Scientific Co. without further purification except monoethanolamine which was redistilled and isobutylamine which was dehydrated by sodium metal or calcium hydride and distilled. The carbon dioxide was supplied by J. T. Baker Chemical Co. Its purity was stated as 99.9%. Methanol used was obtained from Mallinckrodt Chemical Works and contained less than 0.1% water.

RESULTS AND DISCUSSION

Following points of interest emerge as a result of this investigation.

Nature of Amine

The over-all separation $S_{13}^{\max}$ and $S_{18}^{\max}$ for 15 amines are given in Table 1 under almost identical operating conditions of flow rate, molar-

TABLE 1

Comparison of Over-all Separations, $S_{13}^{\max}$ and $S_{18}^{\max}$ for 15 Different Amines (1 *M*) at Room Temperature in Methanol at a Flow Rate of ~0.8 ml/cm²-min. Column: 196 cm × 1 cm i.d.

Amine	$S_{13}^{\max}$	$S_{18}^{\max}$	$S_{18}^{\max}/S_{13}^{\max}$
Butylamines			
Normal	1.78	2.32	1.30
Iso	1.96	2.32	1.18
Secondary	1.57	2.05	1.31
Tertiary	1.50	1.97	1.31
Di-normal	1.75	2.08	1.19
Di-iso	1.61	2.04	1.27
Di-secondary	1.54	1.88	1.22
Tri-normal	1.63	1.40	0.86
Monoethanol	1.83	2.40	1.31
Monopropanol	1.66	1.76	1.06
Normal hexyl	1.73	1.76	1.02
Normal propyl	1.63	1.63	1.00
Piperidine	1.86	1.65	0.89
Pyrrolidine	1.52	1.45	0.95
Morphine	1.68	1.55	0.92

ity of amine, and temperature. The superscript max in $S_{13}^{\max}$ indicates the over-all separation S_{13} for ^{13}C at steady state and in $S_{18}^{\max}$ the maximum over-all separation S_{18} for ^{18}O, since the S_{18} starts decreasing after attaining a certain peak value. On the basis of $S_{13}^{\max}$ one can see that normal and isobutylamine give higher separations than other amines. Generally, separation appears to decrease for butylamines with increasing steric hinderance. From Table 1 it can be seen that amines as diverse as piperidine and monoethanolamine gave almost equal $S_{13}^{\max}$. Most amines differ widely in their basicity constants and their rate constants for reaction with carbon dioxide to form carbamates. Furthermore, the carbamates have very different stability constants. Even so, from Table 1 it can be seen that $S_{13}^{\max}$ depends rather weakly on the nature of the amine. A detailed discussion based on the properties of amines has been documented elsewhere (*18*). It is sufficient to say here that diffusion plays a more important role than rate of reaction in the isotope exchange reaction. In some experiments addition of catalytic amounts of hemin or cupric chloride at steady state increased the over-

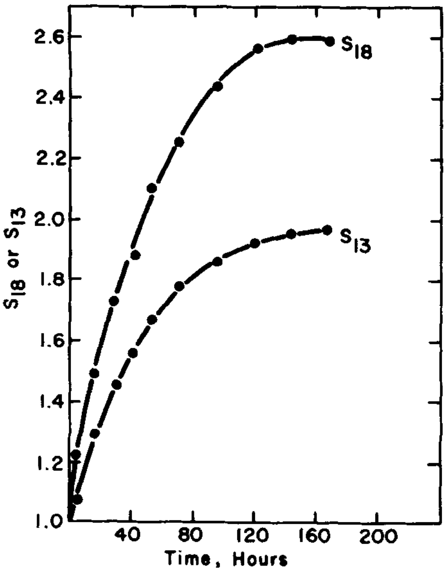

FIG. 2. Over-all separations for 1 *M* isobutylamine in methanol containing 0.04 *M* cupric chloride as a function of time at 25°C and flow rate 0.8 ml/cm²-min.

all separation somewhat, indicating that the rate of reaction is also significant. Thus in Fig. 2 data are shown for 1 *M* isobutylamine containing 0.04 *M* anhydrous cupric chloride. The $S_{13}^{\max}$ was now 2.58 as compared with 2.32 reported in Table 1 for the same amine without any catalyst. Therefore, the small differences among the amines are probably related to differences in their diffusivities as well as reaction rates. A comparison of the three most effective amines (*18*) shows that $S_{13}^{\max}$ followed the order isobutylamine > monoethanolamine ≥ *n*-butylamine. In most experiments, even if the water content of the system was kept below 0.1% (as monitored by gas chromatography), S_{18} always started to decrease after attaining a maximum value. This decrease is presumably caused by the formation of parasitic species which can exchange oxygen irreversibly resulting in an incomplete reflux of ^{18}O. As a consequence, the ratio $S_{18}^{\max}/S_{13}^{\max}$, which should be about 1.2 to 1.3 in this system, deviates significantly from its expected value as shown in Table 1. A possible source of parasitic species such as water and/or an ether is the slow aminolysis of alcohols by the amines (*19*).

Temperature

A variation of temperature in the carbamate–carbon dioxide exchange system results in a change of reaction rate, separation factor, viscosity, diffusion coefficients, and phase composition. As a consequence, the observed effect of temperature on separation is a composite effect. In Fig. 3, $S_{13}^{\max}$ has been plotted at different temperatures for 1 *M* isobutylamine in methanol. The over-all separation was highest at about 25°C which was close to the ambient temperature. In another experiment using *n*-butylamine in benzene, $S_{13}^{\max}$ was higher at 12°C compared to its values at 25 and 45°C. A detailed study of the dependence of the over-all separation on different types of solvents will be necessary to understand this behavior.

Flow Rate

For a system operating at total reflux with a separation factor α close to unity, the over-all separation $S_{13}^{\max}$ is given by Cohen (*20*) as:

$$\ln S_{13}^{\max} = \frac{k_t a Z(\alpha - 1)}{L'}$$

where we have used $k_t a$ instead of k alone. Here $k_t a$ is an interphase transfer rate in moles/cm^3-sec, L' is the flow of carbamate in moles/cm^2-sec, Z is the length of the column in cm, and a is the interfacial

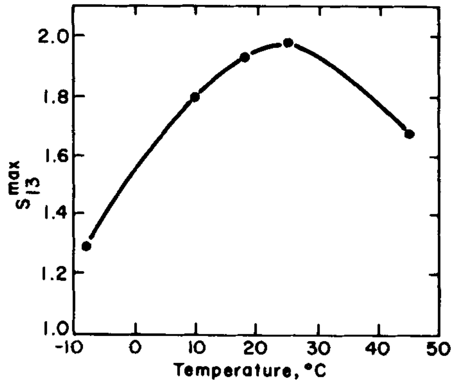

FIG. 3. Over-all separation $S_{13}^{\max}$ for 1 *M* isobutylamine in methanol as a function of temperature at a flow rate 0.8 ml/cm^2-min.

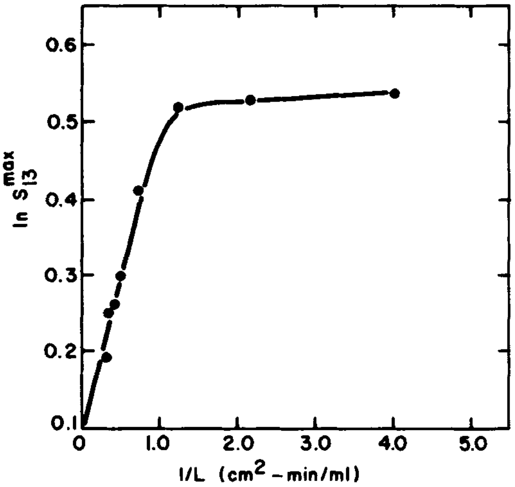

FIG. 4. Variation of ln S_{13}^{max} with the reciprocal of the flow rate L (ml/cm^2-min) for 1 M n-butylamine in methanol at 25°C.

area cm^2/cm^3 of the column packing. Figure 4 shows the results of experiments with 1 M n-butylamine in methanol at 25°C. We have used $1/L$ as abscissa instead of $1/L'$. Here L' is approximately equal to $10^{-5}L$, where L is the volumetric flow of the solution in cm^3/cm^2-min. The graph shows that ln S_{13}^{max} increases linearly with $1/L$ up to a cer-

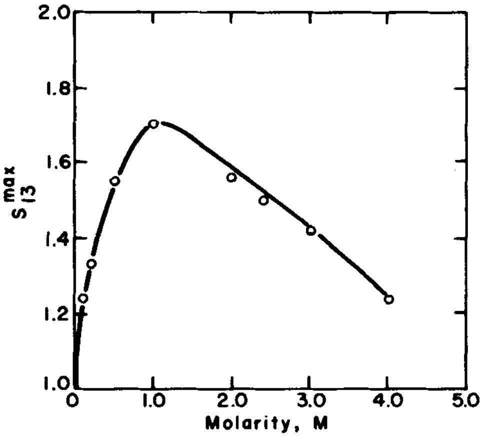

FIG. 5. Variation of S_{13}^{max} as a function of molarity of n-butylamine in methanol at a flow rate 0.8 ml/cm^2-min and 25°C.

tain point. At very low values of L, $S_{13}^{\max}$ tends to level off. Assuming an effective interfacial area of Helipak 3012 packing to be 1 to 2 cm^2/cm^3, the value of k_t from the initial ascending portion of the graph turns out to be about 3.1×10^{-6} moles/cm$_2$-sec which compares well with the value reported (*21*) for the absorption of carbon dioxide by a 1.6 *M* aqueous solution of diethanolamine in a disk column where the interfacial area was known. The decrease in ln $S_{13}^{\max}$ at low flow rates may be due to a decrease in a as a result of inadequate wetting of the packing.

Concentration of Amine

The effect of concentration of a typical amine such as *n*-butylamine is shown in Fig. 5. The optimum concentration of amine was found to be between 1.0 and 1.2 *M*. Figure 6 shows a plot of k_ta obtained from Cohen's equation using our data on over-all separation as a function of the concentration of amine. This curve shows that the transfer rate falls off at higher concentrations. This is probably related to changes in transport parameters with increase in amine concentration. For example, it is known (*22*) that the diffusivity of monoethanolamine is decreased threefold by a fourfold increase in its molarity in aqueous solu-

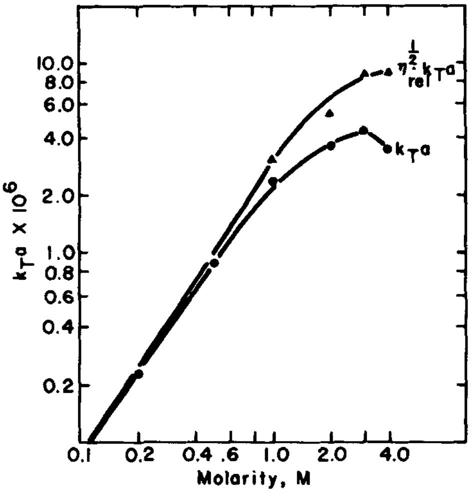

Fig. 6. Effect of concentration of *n*-butylamine on interphase mass transfer rate k_ta. The upper curve was obtained from the lower curve by multiplying the values of k_ta by $(\eta_{rel})^{1/2}$.

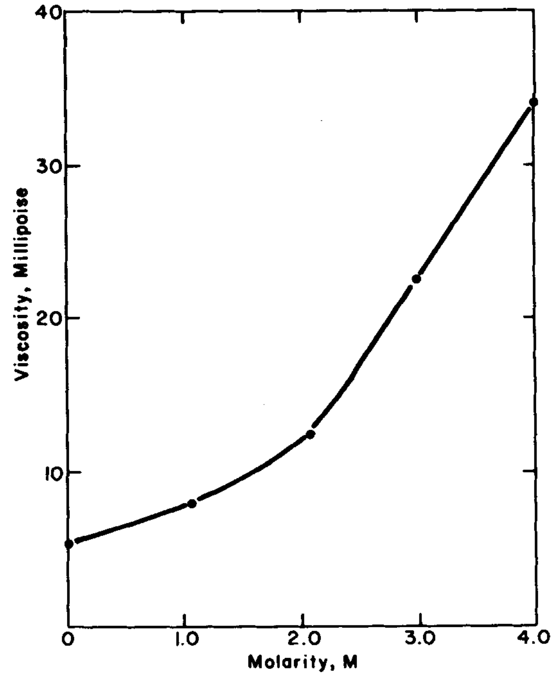

FIG. 7. Variation of the viscosity of solutions of *n*-butylamine in methanol saturated with carbon dioxide as a function of molarity of the amine.

tions. In the present work the viscosity of solutions of *n*-butylamine in methanol were measured using an Ostwald viscometer at 25°C after saturating each solution with carbon dioxide. As shown in Fig. 7, viscosity increases markedly at concentrations greater than 2 *M*. This is expected to affect not only the diffusivities but also the effective interfacial area per cubic centimeter of the packing. These factors are probably responsible for the slower increase of $k_t a$ at higher concentrations in Fig. 6. Since diffusion coefficients vary approximately inversely as the viscosity, the over-all film coefficient (*23*) should vary approximately as $\eta_{\text{rel}}^{1/2}$, where η_{rel} is the viscosity relative to that of the solvent. The upper curve in Fig. 6 is obtained from the lower after correcting for viscosity by multiplying the ordinates by $\eta_{\text{rel}}^{1/2}$. There is still a significant curvature at the higher concentrations, which is presumably due to the effect of viscosity on *a*, the interfacial area per cubic centimeter of the column packing.

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