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Jitendra P. Agrawal[a][b]
[a] CHEMISTRY DEPARTMENT, COLUMBIA UNIVERSITY, NEW YORK, NEW YORK [b] E. I. du Pont de Nemours and Co., Wilmington, Delaware

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Enrichment of Carbon-13 by Chemical Exchange of Carbon Dioxide with Amine Carbamates in Nonaqueous Solvents*

JITENDRA P. AGRAWAL†

CHEMISTRY DEPARTMENT
COLUMBIA UNIVERSITY
NEW YORK, NEW YORK 10027

Summary

Enrichment of ^{13}C by the exchange of carbon dioxide with its amine carbamates in nonaqueous solvents has been further studied. Optimum operating conditions for the fractionation of ^{13}C in a packed countercurrent column have been determined. A comparison of the method with other competitive methods indicates that the process is fairly attractive at its present stage of development.

INTRODUCTION

The carbon isotope of mass 13 has found many applications in the fields of chemical, biological, medical, and industrial research. At the present time it is produced by the fractional distillation of carbon monoxide (*1–3*) and thermal diffusion of methane (*4*) although the latter is not favored over thermal diffusion of carbon monoxide (*5, 6*). Separation factors for ^{13}C in the distillation of chloroform, carbon tetrachloride, benzene, and methanol have been reported (*7*). Other methods described

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† Present address: E. I. du Pont de Nemours and Co., Wilmington, Delaware 19898.

in the literature include gas–gas exchange (*8*) and exchange on resins (*9*). Highly enriched ^{13}C is primarily produced by thermal diffusion of methane (*10*). Fractionation of ^{13}C and ^{18}O in a countercurrent column

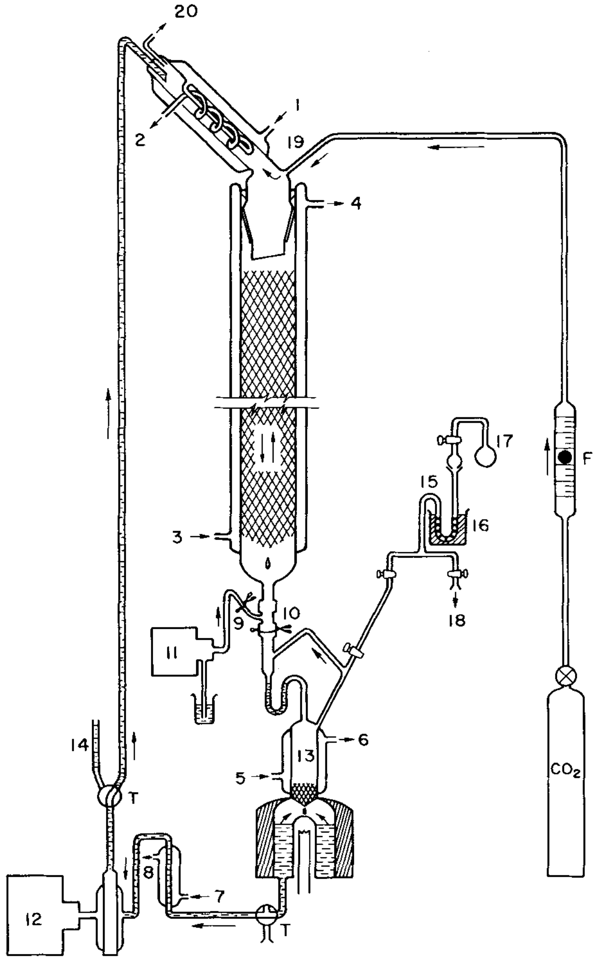

Fig. 1. Exchange column 250 cm long and 2.5 cm i.d. packed with Helipak 3013 (Podbielniak Inc., Chicago, Ill.). (1) to (8) Entrance and exits for cooling water; (9), (10) Teflon sections with pinch clamps; (11) pump to flood the column; (12) sigmamotor finger pump; (13) stripper; (14) buret; (15) silica-gel tube; (16) Dry-Ice bath; (17) sample tube; (18) to vacuum pump; (19) CO_2 feed port; (20) waste CO_2 exit.

by chemical exchange between carbon dioxide and amine carbamates was reported by Taylor (*11*). Recently a more complete investigation of this process has been described (*12*). Further examination of the data obtained so far has shown that the process appears to be satisfactory for the production of highly enriched ^{13}C and partially enriched ^{18}O. The present work describes new results on the effect of viscosity and nature of the solvent on the enrichment of ^{13}C. A qualitative comparison of the carbamate method with other existing methods for the separation of ^{13}C is also included.

EXPERIMENTAL

The exchange system used in the present work is shown schematically in Fig. 1. It contained a 250-cm long, 25 mm i. d. glass column packed with a stainless steel Helipak 3013 (Podbielniak Inc., Chicago, Ill.) packing. The column had a concentric jacket to maintain a constant temperature. It was equipped with a CO_2 inlet at the top, a product refluxer at the bottom, a sampling system consisting of silica gel and Dry Ice traps, vacuum line, a flooding line, heat exchangers at both ends, and a waste end. The operation of the column was similar to the one described before (*12*), the only difference being the reversal of product and feed ends. In order to ensure adequate wetting of the packing the column was flooded and drained in the manner described elsewhere (*12*). In most experiments, cold tap water was adequate for the heat exchangers at both ends of the column. Commerical carbon dioxide was fed into the column after passing through a dehydrating tube. The rate of carbon dioxide feed was in excess of that required for the saturation of the amine solution. During the course of the experiment the flow rates, temperature, and amine concentration were monitored and controlled within narrow limits. Samples of carbon dioxide withdrawn at the bottom of the column were analyzed by a 60° sector, Nier type mass spectrometer. In all experiments ^{13}C concentrated and ^{18}O depleted at the bottom, the product end of the column.

RESULTS AND DISCUSSION

Optimum Operation

The optimum operating conditions for a typical ^{13}C enrichment experiment are given in Table 1. The single stage separation factor α_{18}

TABLE 1

Summary of Optimum Operating Conditions and Performance of a Column for Enriching ^{13}C by Monoethanolamine Carbamate–Carbon Dioxide Exchange in Methanol Solutions

Column length, cm	250
Column diameter, cm	2.54
Packing	Helipak 3013
Temperature, °C	25
Solution flow rate, ml/min	4.5
Solution flow rate, ml/cm²-min	0.9
Throughput L (mg. atom carbon)/cm²-min	0.5
63% Equilibrium period, hr	50
Holdup in column, mg atoms carbon	62
Over-all separation, S_{13}	2.8
Enrichment factor α_{13}	1.01
Stages, n	104
HETP, cm	2.4
Holdup per stage (mg atom carbon)/stage	0.6
Processing time, min/stage	0.25

for ^{18}O in these systems has an experimental value of 1.013 at 25°C (*11*). For a system operating at total reflux, one can show that

$$\ln S_{13}/\ln S_{18} = \ln \alpha_{13}/\ln \alpha_{18}$$

where S represents over-all separation in a column, α the single stage separation factor, and the subscripts 13 and 18 refer to ^{13}C and ^{18}O, respectively. Therefore, one can calculate an experimental value of α_{13} from the above equation using experimental vaules of S_{13} and S_{18} from a column experiment. This value of α_{13} turns out to be 1.01 at 25°C.

From Table 1 it is clear that although a reasonably small stage height can be attained, the transport is too low for purposes of production in pilot plants. Further experiments were designed to increase the throughput without significantly increasing the HETP.

Effect of Solvent

Previous investigation (*12*) showed that isotope separation followed the order isobutylamine > monoethanolamine ≥ *n*-butylamine. Isobutylamine cannot be used in 2 *M* solutions due to the lower solubility of its carbamate. Monoethanolamine is preferred over other amines because of its high boiling point and consequent lower losses due to

TABLE 2

Over-all Separation S_{13} for ^{13}C in a 250-cm Long, 2.5-cm Inner Diameter Column Packed with Helipak 3013 by the Exchange of Carbon Dioxide with Its Carbamates in Various Solvents

Run No.	Amine	Solvent[a]	Molarity	Flow (ml/cm^2-min)	Temp. (°C)	$S_{13}{}^{\max}$	HETP (cm)
E-2	NBA	M	1.09	0.75	25	2.16	3.1
E-3	NBA	B	0.96	0.8	25	2.71	2.5
E-5	MEA	M	1.0	0.8	25	2.81	2.4
E-11	MEA	M	4.4	0.8	25	1.19	14.2
E-11	MEA	M	4.4	0.8	40	1.20	14.2
E-21	MEA	M	1.0	2.0	25	1.85	4.0
			1.0	1.0	25	2.6	2.6
			2.0	2.0	25	1.4	7.35
			2.0	1.0	25	2.0	3.6
			1.0	0.8	25	2.95	2.3[b]
E-23	MEA	MB-1	1.0	2.0	25	2.05	3.5
E-23	MEA	MB-1	1.0	0.8	25	2.8	2.4
E-24	MEA	MB-2	2.0	2.0	25	1.5	6.1
E-26	MEA	MB-2	2.0	1.0	25	2.2	3.2
E-25	MEA	MB-2	3.2	2.0	25	1.37	7.8
E-8R	MEA	MC	0.95	0.8	25	2.1	3.35
E-9	MEA	MC	0.9	0.8	52	1.92	3.8
E-12R	MEA	I	1.0	0.8	25	2.0	3.6
E-13	MEA	MI	1.0	0.8	25	1.72	4.55
E-16	MAE	M	1.3	0.8	25	2.38	2.9
E-17	MAE	M	1.06	0.8	25	2.65	2.55

[a] B = benzene; I = isopropanol; M = methanol; MAE = methylaminoethanol; MB-1 = 50:50 by volume mixture of methanol and benzene; MB-2 = 60:40 by volume mixture of methanol and benzene; MC = methyl cellosolve; MEA = monoethanolamine; MI = 10% methanol + 90% isobutanol by volume; NBA = *n*-butylamine.

[b] 0.4 *M* $CuCl_2$ was present for this data.

evaporation. Therefore, monoethanolamine appears to be superior to all from a practical standpoint. Methylaminoethanol gave about the same separation as monoethanolamine although the former reacts four times faster with CO_2 than monoethanolamine in at least aqueous solutions (*13*). Table 2 shows that the over-all separation for *n*-butylamine was higher in benzene as compared with methanol. A decrease in the over-all separation with increase in viscosity was found for monoethanolamine when different alcoholic solvents were used. This is shown in Fig. 2. In case of monoethanolamine a 50:50 by volume mixture of benzene and methanol give a lower HETP when compared with methanol alone as the solvent. Catalytic amounts of cupric chloride gave slightly higher S_{13}, indicating some reaction rate control as reported before (*12*).

Comparison with Other Methods

In order to examine the present system critically, calculations were made for four existing processes to produce 1 g/day of 90% ^{13}C starting from a natural abundance of about 1.1%. These calculations are summarized in Table 3. Since different packings were used in all cases, a reliable comparison of the three chemical exchange methods cannot be made. The principal differences in the size of the plant arise from the differences in HETP values provided the flow per unit area and holdup per unit volume of the packing are all about the same. The HETP for

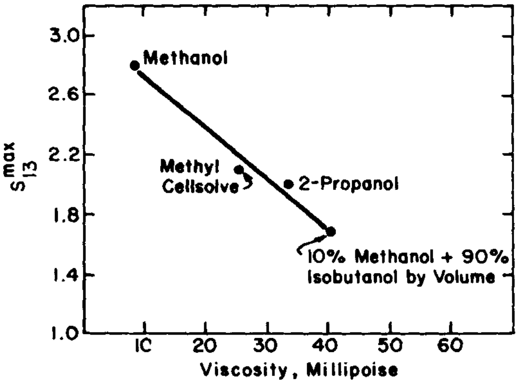

FIG. 2. Effect of viscosity on over-all separation S_{13} for ^{13}C in 1 *M* monoethanolamine at 25°C in a 250 × 2.5 cm i.d. column packed with Helipak 3013. Flow rate = 0.8 ml/cm^2-min.

TABLE 3

Comparison of Carbamate–CO_2 Exchange Method with Bicarbonate, Cyanide (Exchange) and Carbon Monoxide Distillation for the Production of 90% ^{13}C at the Rate of 1 g/Day in a Square Cascade Consisting of a Single Column

Process variables	Carbamate–CO_2 process	Bicarbonate process	Cyanide process	CO distillation
Temperature	25°C	25°C	25°C	75°K
Concentration, moles/liter	1	—	—	—
Packing	Helipak 3013	Etched Haydite	Glass helices	Dixon rings (1/16 in.)
α	1.01	1.012	1.012	1.01
Over-all separation	810	810	810	810
HETP, cm	2.4	45	6.1	1.6
Minimum number of stages	676	570	570	676
Minimum length of column, *m*	17.2	256	35	10.8
L_{min}/P, reflux ratio	8250	6900	6900	8250
Interstage flow, mg atom C/min	495	415	415	495
Flow (mg atom C/cm^2-min)	0.45	16	10	45
Minimum area of column, cm^2	1100	26.0	41.5	11
Minimum volume of column, liters	1890	665	145	11.9
Processing time λ, min/stage	0.27	2.36	0.32	0.08
Relative equilibrium time, $[\lambda/(\alpha - 1)^2] \times 10^{-3}$	2.7	16.4	2.24	0.8
References	*14, 15*	*16–18*	*16, 17, 19–24*	*1, 25, 26*

the bicarbonate process is very large. The HETP values for the cyanide and carbamate processes will probably be equal for the same packing material. However, the toxicity of HCN and the need for chemicals in the reflux systems give the carbamate system some advantage. At the present time the best method listed in Table 3 appears to be the low temperature distillation of carbon monoxide. New developments in this area have been reported (*27*) by Mound Laboratories operated by Monsanto Research Corporation which is a subsidiary of the Monsanto Company. The simplicity in the operation of the carbamate system along with the possibility of also concentrating ^{18}O in the same system makes its further development worthwhile. Such a development has been recently reported (*28*). A glance at the second column in Table 3 shows that the area of the system required is too large. In practice a cascade of several columns is preferred over a single column owing to large space requirements and long relaxation times. A typical calculation shows that to produce 100 mg/day of 90% ^{13}C the cascade will consist of three stages each about 7.5 m in length.

Interest on the part of industry in the carbamate method is indicated by the activities at Monsanto. While routine production of ^{13}C has been going on using CO distillation and thermal diffusion of methane (*27*) progress has been made to construct a multistage cascade (*29*) for the production of highly enriched ^{13}C using the carbamate process.

After the conclusion of the manuscript, the author came across a carbon monoxide-cuprous chloride called the COCO process, reported by Palko, Landau, and Drury (*30*). This process appears to be quite competitive with the carbamate process. However, recent developments in the carbamate process (*28*, *29*) indicate that the carbamate method may have certain advantages such as simplicity of equipment and less toxicity of process chemicals.

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