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Gas Chromatographic Fractionations of the Carbon and Oxygen Isotopes of Carbon Monoxide

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Abstract

A high-precision gas chromatograph was used in conjunction with a quadrupole mass spectrometer and an on-line computer to study the fractionation of carbon and oxygen isotopes in carbon monoxide on silica and on finely divided nickel powder. Relative retentions were studied as a function of temperature using both natural abundances and isotopically enriched species. On silica, the values ranged from 0.99639 ± 0.00046 to 1.00152 ± 0.00089 for the $^{13}C/^{12}C$ pair and from 1.00054 ± 0.00057 to 1.00162 ± 0.00039 for the $^{16}O/^{18}O$ pair. The values on nickel were greater, average values being 1.037 for the $^{12}C/^{13}C$ pair and 1.009 for the $^{16}O/^{18}O$ pair. The larger values on nickel compared to those on silica reflect the much stronger interaction.

INTRODUCTION

Previous studies (*1–5*) have shown that fractionation of carbon and oxygen isotopes in a variety of molecules occurs. Bocola et al. (*3*), who studied methane and oxygen, and Shepard et al. (*4*), who studied carbon dioxide, observed that fractionation of oxygen isotopes is more pronounced on supports such as silica or alumina, while the fractionation of carbon isotopes is more pronounced on less polar supports.

Isotopic fractionations involving carbon monoxide were studied to see if they followed the same trends. CO should provide insight with respect to which molecular interactions are important in the fractionation of oxygen isotopes, because it is polarizable, but it shows little acid-base character in the form of hydrogen bonding ability. In addition, CO frac-

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tionations on an active metal surface were also studied because a chemical reaction can enhance fractionation. Nickel was chosen as the metal packing because of the ease with which it chemisorbs and subsequently desorbs CO and because of its relatively low cost (compared to ruthenium, palladium, or platinum, which behave similarly). The chemisorption of CO on those surfaces occurs through the carbon atom (*6–8*).

EXPERIMENTAL

Supports used were silica, 100/120 mesh (Davison Chemical Co.); alumina, 100/120 mesh (M. Woelm Chemicals); Carbopak B, 60/80 mesh (Supelco); Porapaks Q and R, 100/120 mesh (Waters Associates); nickel, 100/120 mesh (Alfa Chemicals); and Chromosorb P, 100/120 mesh (Alltech Associates).

Liquid phases used were β,β-oxydipropionitrile (American Cyanamid), hexamethylphosphoramide (Alltech Associates), Silar 5C (Supelco), diethanolamine (Alldrich Chemical Co.), and polyethyleneimine (Alltech Associates).

Natural abundance carbon monoxide (Matheson Co.) was used with every packing material studied. However, two different isotopically enriched carbon monoxide samples were also used with the nickel packing 20% C-13 carbon monoxide (Mound Laboratories, Monsanto Corp.) and 99% O-18 carbon monoxide (Bio-Rad Laboratories).

Helium carrier gas (Selox) was purified by passing it through copper turnings heated at 450°C and then through Linde molecular sieve 5A (Union Carbide Corp.). Hydrogen and argon (Selox) were used as received.

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APPARATUS

The overall experimental set-up has been described previously (*4*, *5*), but the following changes were made for this study. To obtain lower temperatures, a Dry Ice/methanol slurry was used in conjunction with the Flexicool (FTS Systems) and heater systems. This allowed a temperature of -77°C to be reached.

Chromatographic oven temperatures were measured and controlled by mounted MH series Stikon thermometers (RdF Corp.). Temperatures were stable within ±0.05°C for the elevated values and ±0.02°C for the subambient values.

Flow rate was controlled either by a Chromatrol dual-column electronic controller (Applied Materials) or by a Brooks model 5840 controller. Flow rates were constant within ±0.2%.

The mass spectrometer (UTI Model 100C) was controlled by a PDP 11/20 computer (Digital Equipment Corp.). Mass-to-charge ratios and sensitivities were selected for the isotopic pairs. The output signal was transferred through an 8-bit latch (*4*) to a Hewlett-Packard Model 2212A voltage-to-frequency converter. Individual sets of chromatograms were stored on tape (Digital Equipment Corp.).

PROCEDURES

Argon was used as the nonretained species in these studies and was monitored by observing the signal at m/e 40. Sample mixtures of 2:1, 1:1, 1:2, and 1:4 argon-to-carbon monoxide pressure ratios were used to check for changes in retention time due to changes in the concentration of CO. After no difference was observed, 1:4 mixtures were then used for the remainder of the study.

Columns of 2.2 mm i.d. × 3 m 316 stainless steel tubing (Alltech Associates) were used for all packings except nickel, where 2.1 mm × 3 m nickel tubing (Alltech Associates) was used. Before packing, the stainless steel tubing was treated by rinsing it successively with methanol, chloroform, and acetone. The nickel tubing was washed successively with 3 *M* nitric acid, water, acetone, chloroform, methanol, water, and acetone.

All columns were dry-packed using the "tap and fill" method. The Porapak Q and Porapak R columns were preconditioned by heating at 250°C using a helium flow rate of 5 mL/min for 4 hr. Alumina, activated carbon, and silica columns were heated at 325°C using a helium flow of 5 mL/min for 4 hr. The nickel powder was packed as received. It was treated *in situ* by heating at 300°C while passing a hydrogen flow of 5 mL/min for 1 hr.

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DATA ACQUISITION AND CALCULATIONS

Data were taken using multiple ion monitoring. In each experiment, 240 readings of intensity versus time were taken for each isotope in an eluting peak. Readings alternated between the two masses of the isotopic pair of interest. Data acquisition rates were 1 to 3 Hz.

At each temperature, 7 to 10 runs were made in the nickel study, and 12 to 18 runs were taken in the silica study. The standard deviation was calculated for each set.

Peak locations were calculated by using either 7 or 11 data points around the observed maximum in a Gram polynomial curve fit (*9*). The retention time was then computed as the time between the calculated peak maximum and sample injection. The retention time, α, was calculated using

$$\alpha = (t_{r2} - t_a)/(t_{r1} - t_a) = K_2/K_1$$

where t_{r2} and t_{r1} are times of calculated peak maxima, t_a is the calculated retention time for argon, and K_1 and K_2 are distribution ratios. Individual α values were obtained from each run to use an internal standard approach to minimize effects of any variations in carrier flow rate and column temperature.

RESULTS

Preliminary studies were performed on a variety of packing materials and liquid phases. Runs were performed at both ambient temperature (~20°C) and −77°C to see if retention of carbon monoxide occurred, and if so if any fractionation could be found. Either no retention of carbon monoxide or no observable fractionation was found on Chromasorb P, Porapak Q, Porapak R, β,β-oxydipropionitrile, hexamethylphosphoramide, Silar 5C, diethanolamine, and polyethylene imine.

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Alumina and Carbopack B showed some retention and some isotopic fractionation at −77°C. The values, however, were very small and nonreproducible, particularly for alumina where a change in activity between consecutive runs was apparent.

Silica showed isotopic fractionation of both C-13 and O-18 between −77 and 0°C (Table 1). Note that the elution order of the carbon isotopes changed at approximately −20°C. While the relative retentions for the oxygen isotopes decreased to virtually zero but did not reverse, retention times decreased from 950 to 280 sec as the temperature increased, and peak widths decreased from 65 to 30 sec. Separations of peak maxima ranged from 3.5 to 1.0 sec for the carbon isotopes and from 1.5 to 0 sec for the oxygen isotopes. Above 0°C, retention times became small, and fractionations were either very small or very difficult to measure accurately.

Carbon monoxide showed little retention on nickel at ambient temperature, but it was retained approximately 120 to 200 sec as the temperature changed from 115 to 180°C. As the temperature was increased, peak widths increased from 25 to 40 sec. The separation of isotopic peak maxima ranged from 1 to 4 sec for the carbon isotopes and from 0.5 to 1.5 sec for the oxygen isotopes. As the temperature increased above 145°C, the oxidation of carbon monoxide to carbon dioxide became significant, reducing greatly the amount of CO eluted. For example, at 170°C, approximately 80% of the CO was oxidized.

The isotopic fractionations of natural abundance CO are given in Table 2. The larger standard deviations observed on nickel as compared to

TABLE 1

Relative Retention as a Function of Temperature for the Isotopic Fractionation of Natural Abundance Carbon Monoxide on Silica

	Temperature (°C)	α
$^{13}C/^{12}C$	−3.47	1.00152±0.00089
	−5.85	1.00122±0.00072
	−16.29	1.00101±0.00067
	−24.12	0.99931±0.00048
	−33.64	0.99837±0.00057
	−41.76	0.99814±0.00043
	−46.86	0.99731±0.00053
	−56.72	0.99688±0.00048
	−67.86	0.99692±0.00064
	−76.55	0.99639±0.00046
$^{16}O/^{18}O$	+2.32	1.00054±0.00057
	−6.84	1.00068±0.00039
	−13.91	1.00086±0.00034
	−21.54	1.00087±0.00047
	−28.25	1.00109±0.00031
	−39.67	1.00131±0.00046
	−53.12	1.00148±0.00056
	−59.83	1.00169±0.00034
	−65.36	1.00183±0.00042
	−76.49	1.00162±0.00039

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TABLE 2

Relative Retention as a Function of Temperature for the Isotopic Fractionation of Natural Abundance Carbon Monoxide on Nickel

	Temperature (°C)	α
$^{12}C/^{13}C$	118.36	1.0180±0.0048
	124.34	1.0197±0.0120
	129.98	1.0153±0.0085
	137.08	1.0391±0.0125
	144.61	1.0366±0.0076
	152.42	1.0394±0.0087
	158.57	1.0215±0.0065
	167.17	1.0279±0.0062
$^{16}O/^{18}O$	124.34	1.0083±0.0043
	137.08	1.0078±0.0054
	144.61	1.0092±0.0064
	152.41	1.0106±0.0048
	158.57	1.0121±0.0067

TABLE 3

Relative Retention as a Function of Temperature for the Isotopic Fractionation of Isotopically Enriched Carbon Monoxide on Nickel

	Temperature (°C)	α
$^{12}C/^{13}C$	120.29	1.0078±0.0039
	127.24	1.0183±0.0042
	136.52	1.0288±0.0037
	144.93	1.0311±0.0032
	154.69	1.0323±0.0047
	160.43	1.0228±0.0039
	167.82	1.0192±0.0048
	175.39	1.0136±0.0059
$^{16}O/^{18}O$	121.78	1.0073±0.0029
	132.46	1.0089±0.0033
	143.09	1.0108±0.0027
	152.59	1.0117±0.0039
	160.62	1.0110±0.0042
	169.74	1.0096±0.0045

silica are principally due to the much shorter retention times. The relative retention values for the carbon isotopes increased with temperature starting at 118°C then passed through a maximum between 135 and 150°C before they decreased. In contrast, the values for the oxygen ratio showed a gradual increase over the temperature range of 125 to 160°C.

Isotopically enriched carbon monoxide samples were used for some runs on the nickel columns (Table 3) so as to improve the precision and to allow observation of any fractionation that might be obtained at a high temperature. The values from the enriched samples agreed with those found for the natural abundance material, but were somewhat more precise because of the better ability to measure the larger signal of the low abundance isotope. Both showed the maximum in the carbon isotope values and the same slight increase in the values for the oxygen isotopes.

DISCUSSION

We observed isotopic fractionations on alumina, activated carbon, silica, and nickel. Both alumina and activated carbon showed an elution order of $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$ at $-77°C$ but, as indicated earlier, the separations on alumina changed with time, while those on carbon were too small to be measured accurately.

Silica showed a very temperature-dependent fractionation in that, as the temperature was raised, the carbon isotope pair had a "cross-over"

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point around −20°C where the elution order changed from $^{12}C^{16}O$, $^{13}C^{16}O$ to $^{13}C^{16}O$, $^{12}C^{16}O$. The oxygen isotopic pair showed a decreasing fractionation with higher temperature, with $^{12}C^{18}O$ always eluting sooner than $^{12}C^{16}O$.

The longer retention of the oxygen-18 species of carbon monoxide on silica agrees with the previously observed behavior of O_2 (*3*) and CO_2 (*4*) on silica. Shepard et al. (*4*) compared the isotopic fractionations of CO_2 on Porapak Q and silica gel. Their average relative retention values were 1.0027 and 1.0031 for the carbon isotopes and 1.0011 and 1.0050 for the oxygen isotopes. The similar values for the carbon isotopes indicated that the change in packing had little effect on the fractionation. This was in contrast to our study where a change in packing from silica to nickel resulted in a change of average values from 1.002 to 1.025. This reflected the much stronger interaction of the nickel with the carbon atom.

Their average value of 1.0050 for the oxygen isotopes on silica and ours of 1.0021 were an indication of the stronger interaction of silica with the oxygen atoms in CO_2. Those oxygen atoms can hydrogen bond easily while those in CO cannot. In contrast, the oxygen ratio for CO on nickel was much larger, approximately 1.01. Hence the stronger interaction that differentiated the carbon isotopes on nickel was also reflected in the oxygen values.

The maxima observed in the carbon isotope fractionation on nickel implies that there is an optimal temperature for the enrichment. However, the enrichment obtained from fractions cut from carbon monoxide samples passed over nickel is small compared to the commercial Cyanex or cuprous ammonium chloride methods (*10*) and also suffers from the loss (and contamination) of the 5 to 10% that is oxidized to CO in this temperature range.

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