

Figure 1. Time-of-flight mass spectrum of C_nLa cluster complexes (open peaks) and bare C_n clusters (blackened peaks) produced by laser vaporization of a lanthanum-impregnated graphite disk in a pulsed supersonic nozzle. The bottom trace was taken at low (<0.01 mJ cm^{-2}) ionizing fluence from an ArF excimer laser (6.4 eV, 10 ns). The top trace was taken with much higher ArF laser fluence (1–2 mJ cm^{-2}). Here multiphoton-induced fragmentation has reduced the mass spectrum to only the most stable photoions. Except for the particularly stable C_{60} and C_{70} species corresponding to the blackened peaks in this figure, the most stable photoions are found to contain a single lanthanum atom.

ranging from 44 to more than 76. At the much higher ArF ionizing laser fluence used to produce the top mass spectrum in Figure 1, fragmentation induced by multiphoton processes reveals the C_nLa^+ species (and particularly $C_{60}La^+$) to be the most stable possible photoions other than C_{60}^+ . In fact, C_{60}^+ and C_{70}^+ are virtually the only bare carbon cluster ions detected. Note further that there is no evidence of any cluster picking up more than one La atom, suggesting that there is only one highly stable binding site in the C_n ligand.⁶

In accord with earlier workers,⁷ our experiments on graphite indicate that large even-numbered clusters of carbon are ejected intact in the laser vaporization process.⁸ This behavior is unique to graphite and probably results from the high stability of the graphite hexagonal sheets and the weak intersheet forces. Once in the gas phase, the even-numbered C_n clusters thus produced would not be expected to prefer the planar hexagonal structure of the bulk, since this leaves too many unsatisfied valences at the edges. Instead, these experiments suggest that these graphite fragments rearrange to a network of five- and six-membered rings, a process that bends the sheet back on itself with a curvature that ultimately produces a sphere of roughly 7-Å diameter.

As discussed elsewhere,¹ the most stable ultimate form, C_{60} , is thought to be a truncated icosahedron. Addition of an extra band of hexagons around the middle produces a reasonable candidate for the next most stable form: an egg-shaped C_{70} . Both these structures are closed, with all valences satisfied in a highly resonance-stabilized, rigid structure. Experiments such as those

(5) We assume species of the form C_nCl_x and C_nLaCl_x are also present in the beam but are not ionized to produce chlorine-containing photoions under these conditions.

(6) Similar results have now been obtained for C_nM clusters where $M = Ca, Ba, \text{ and } Sr$.

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of Figure 1 reveal that C_nLa complexes are also highly stable—particularly $C_{60}La$ —just as would be expected if these C_n species surround the metal atom much as an egg (shell) surrounds its yoke.

Such aromatic “egg shell” complexes of metal atoms may be stable enough to survive in normal condensed-phase chemical environments. If so, they would provide interesting starting materials for new classes of compounds, reagents, and catalysts.

Acknowledgment. This research was supported by the US Army Research Office and the Robert A. Welch Foundation and used a laser and molecular beam apparatus supported by the National Science Foundation and the U.S. Department of Energy. H.W.K. thanks the S.E.R.C (U.K.) for support.

Separation of Oxygen Isotopic Compounds by Reversed-Phase Liquid Chromatography on the Basis of Oxygen Isotope Effects on the Dissociation of Carboxylic Acids

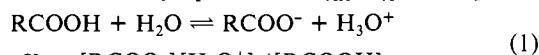
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Received June 14, 1985

Separation of isotopic compounds is of much interest in modern liquid chromatography. Reversed-phase liquid chromatography (RPLC) using a hydrophobic stationary phase and an aqueous mobile phase has enabled the separation of hydrogen isotopic compounds,¹ including the separation between C_6H_6 and C_6H_5D .^{1c} We wish to report here the first example of the separation of oxygen isotopic compounds by RPLC. The three isotopic benzoic acids,² $C_6H_5C^{16}O^{16}OH$ ($1-^{16}O_2$), $C_6H_5C^{16}O^{18}OH$ ($1-^{16}O-^{18}O$), and $C_6H_5C^{18}O^{18}OH$ ($1-^{18}O_2$), were completely separated by the ionization control technique in RPLC³ in about 20 h on the basis of the very slight difference in their acid dissociation constants.

The retention of solutes in RPLC is primarily determined by the hydrophobic property of the solutes.⁴ Thus, carboxylic acids in the undissociated form show much larger retention than the corresponding carboxylate ions.^{3,5c}

The retention (k' , or capacity factor) of a carboxylic acid in RPLC can be described by eq 2,³ where k'_{AH} , k'_{A^-} , and K_a stand



$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH]} \quad (1)$$

$$k' = \frac{k'_{AH}[RCOOH]}{[RCOOH] + [RCOO^-]} + \frac{k'_{A^-}[RCOO^-]}{[RCOOH] + [RCOO^-]} = \frac{k'_{AH}}{1 + K_a/[H_3O^+]} + \frac{k'_{A^-}K_a/[H_3O^+]}{1 + K_a/[H_3O^+]} \quad (2)$$

for the k' of the undissociated acid, the k' of the carboxylate ion, and the acid dissociation constant, respectively.

(1) (a) Tanaka, N.; Thornton, E. R. *J. Am. Chem. Soc.* **1976**, *98*, 1617–1619. (b) Cartoni, G. P.; Ferretti, I. *J. Chromatogr.* **1976**, *122*, 287–291. (c) Yamazaki, S.; Tanimura, T. Eighth International Symposium on Column Liquid Chromatography, Abstract 1a-44, New York, May, 1984.

(2) $1-^{16}O_2$ stands for ordinary benzoic acid without any isotopic enrichment, unless its separation from other isotopic benzoic acids is specifically indicated. $1-^{18}O_2$ and $1-^{16}O-^{18}O$ were prepared from α,α,α -trichlorotoluene and benzoyl chloride, respectively, by hydrolysis with $H_2^{18}O$ of 97% enrichment. No exchange reaction seemed to take place during the separation.

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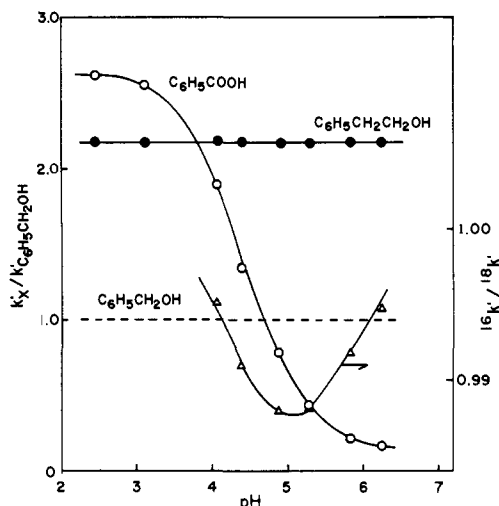


Figure 1. pH dependence of k' values of $1\text{-}^{16}\text{O}_2$ normalized by using the k' value of benzyl alcohol in each mobile phase, and the pH dependence of ^{18}O isotope effect on retention, $^{16}k'/^{18}k'$. The curves were drawn by using eq 2 by applying $k'_{\text{AH}} = 2.646$, $k'_{\text{A}^-} = 0.128$, $^{16}K_{\text{a}} = 3.631 \times 10^{-5}$, and $^{18}K_{\text{a}} = 3.561 \times 10^{-5}$, which were estimated from the results between pH 2.4 and 6.3.

Equation 2 indicates that the k' of a carboxylic acid is determined by the extent of ionization of the acid. The dissociation constant of benzoic acid containing ^{18}O is expected to be smaller than that of $1\text{-}^{16}\text{O}_2$.⁵ This will result in the lesser extent of ionization of $1\text{-}^{18}\text{O}_2$ and $1\text{-}^{16}\text{O}\text{-}^{18}\text{O}$ compared to $1\text{-}^{16}\text{O}_2$ at a pH near the $\text{p}K_{\text{a}}$. Therefore, the retention of benzoic acids containing ^{18}O is expected to be greater than that of $1\text{-}^{16}\text{O}_2$ in such a pH region. This assumes that the secondary oxygen isotope effects on k'_{AH} and k'_{A^-} are small compared to the equilibrium oxygen isotope effects on acid dissociation constants K_{a} , which influence the retention of the acid according to eq 2.

The present chromatographic system consisted of an octadecylsilylated silica stationary phase⁶ and a methanol-water mobile phase (20/80 v/v) containing acetic acid-sodium acetate buffer.⁷

$1\text{-}^{16}\text{O}_2$ and $1\text{-}^{18}\text{O}_2$ showed very similar k' values below pH 3 and above pH 6 (where the acids dissociate very little or dissociate almost completely). In the pH region near the $\text{p}K_{\text{a}}$, however, differences of up to 1.2% in k' values were found between $1\text{-}^{16}\text{O}_2$ and $1\text{-}^{18}\text{O}_2$. $1\text{-}^{18}\text{O}_2$ was actually retained longer than $1\text{-}^{16}\text{O}_2$. The maximum separation was achieved near pH 5, as shown in Figure 1.

From eq 2, where k'_{AH} and k'_{A^-} were found to be similar for the two isotopic acids, eq 3 can be derived, where $^{16}k'$ and $^{18}k'$

$$^{16}K_{\text{a}}/^{18}K_{\text{a}} = \frac{k'_{\text{AH}} - ^{16}k'}{^{16}k' - k'_{\text{A}^-}} \bigg/ \frac{k'_{\text{AH}} - ^{18}k'}{^{18}k' - k'_{\text{A}^-}} \quad (3)$$

stand for the capacity factors of $1\text{-}^{16}\text{O}_2$ and $1\text{-}^{18}\text{O}_2$, respectively. This equation yields the isotope effects, $^{16}K_{\text{a}}/^{18}K_{\text{a}}$, based on the k' values in RPLC, k'_{AH} at low pH, k'_{A^-} at high pH, and $^{16}k'$ and $^{18}k'$ at intermediate pH.

$^{16}K_{\text{a}}/^{18}K_{\text{a}}$ was found to be 1.020 ± 0.002 on the basis of the results between pH 4 and 6 in 20% methanol.⁸ The oxygen isotope effect on the dissociation of formic acid in water was reported

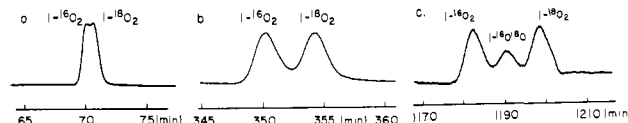


Figure 2. Separation of isotopic benzoic acids in recycle chromatography. Column: Cosmosil 5-C₁₈-P, 4.6-mm i.d., 15 cm × 4. Mobile phase: 20% methanol, 0.05 M acetic acid-sodium acetate buffer, pH 4.83. Flow rate: 0.8 mL/min. Temperature: 30 °C. (a) 1 cycle, (b) 5 cycles, (c) 17 cycles. Mass of samples: 0.5 μg each of $1\text{-}^{16}\text{O}_2$ and $1\text{-}^{18}\text{O}_2$ in (a) and (b); 0.25 μg of $1\text{-}^{16}\text{O}\text{-}^{18}\text{O}$ and 0.5 μg each of $1\text{-}^{16}\text{O}_2$ and $1\text{-}^{18}\text{O}_2$ in (c). A part of the tail of the $1\text{-}^{18}\text{O}_2$ peak was shaved off during the recycle operation in (c).

to be 1.022. Taking into account the presence of an organic solvent, the present results with benzoic acid agree well with the results for formic acid.^{5a} Thornton also estimated the oxygen isotope effect on the acidity of H_3O^+ to be about 2%.^{5b}

Column switching and solute recycling were utilized to resolve the three isotopic benzoic acids at pH 4.8. Two pairs of two 15-cm columns (60-cm total) were connected through a six-port valve.^{1c,9} The chromatograms after 1, 5, and 17 recycles, giving the effective column lengths of 0.6, 3.0, and 10.2 m, respectively, are shown in Figure 2. The chromatogram in Figure 2c shows the resolution of the three isotopic benzoic acids with about 340 000 theoretical plates. Figure 2a shows that partial separation can be achieved without any solute recycling.

The results suggest the possibility of the enrichment of minor isotopes in various dissociable compounds from the natural abundance to near 100% by the ionization control technique in RPLC.

Acknowledgment. We acknowledge Dr. J. W. Dolan for reviewing the manuscript.

Registry No. C₆H₅C¹⁶O¹⁶OH, 65-85-0; C₆H₅C¹⁶O¹⁸OH, 21048-30-6; C₆H₅C¹⁸O¹⁸OH, 17217-84-4.

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Separation of Nitrogen Isotopic Compounds by Reversed-Phase Liquid Chromatography on the Basis of Nitrogen Isotope Effects on the Dissociation of Amines

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Received June 27, 1985

Isotope separation has been one of the most interesting subjects in separation science, and the importance of isotopic separation is increasing due to the wide use of isotopes in energy and life science oriented applications. We have reported the measurement of oxygen isotope effects on the dissociation constant of benzoic acid and the separation of the three isotopic benzoic acids, C₆H₅C¹⁶O¹⁶OH, C₆H₅C¹⁶O¹⁸OH, and C₆H₅C¹⁸O¹⁸OH by ionization control in reversed-phase liquid chromatography (RPLC).¹ We wish to report here the first example of the separation of

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