[Radiocarbon, Vol 25, No. 2, 1983, P 529-532]

STABLE ISOTOPE FRACTIONATION DURING BENZENE SYNTHESIS FOR RADIOCARBON DATING *

HECTOR O PANARELLO, MIGUEL C ALBERO, and
FERNANDO E ANGIOLINI

Instituto de Geocronología y Geología Isotópica (INGEIS)
Pabellón 2, Ciudad Universitaria
1428 Buenos Aires, Argentina

ABSTRACT. ^{13}C isotope analyses of different stages of benzene synthesis have been made to study partial isotope fractionation. More than 60 analyses of carbonates, charcoal, carbon dioxide, and benzene were made in a double collector mass spectrometer. In the first stage of the synthesis (conversion to carbon dioxide) little or no fractionation was observed, beyond the analytical error of the method. Later stages of the process, show a greater and systematic fractionation. The experimental techniques are described.

INTRODUCTION

Routine ^{14}C samples were isotopically analyzed for carbon isotope fractionation. The results obtained will be used to correct ^{14}C ages and to control the general behavior of the benzene synthesis line (Tamers, 1975). The $\delta^{13}C$ values obtained in the Stable Isotopes Laboratory (SIL) on the CO_2 released from the samples by H_3PO_4 (100 %) (carbonate samples) or V_2O_5 oxidation (organic samples) are used as reference to evaluate fractionation in successive stages of benzene synthesis.

TECHNICAL PROCEDURE

In order to produce CO_2 from different samples, the following procedures are carried out.

BENZENE SAMPLES. 1) 4µl of benzene are introduced in a ca 3ml quartz vial, containing 120mg of previously vacuum-baked V_2O_5, by using a microsyringe; 2) Ten quartz vials are connected by means of PVC tubes to a stainless steel manifold. While the samples are frozen with liquid nitrogen, the gases are pumped out until a vacuum of ca 10^{-4} mbar is achieved; 3) The vials are then introduced into the purification line by breaking the vial into the vacuum. The CO_2 is released, purified and the yield is estimated.

---

* Contribution no.65 of the Instituto de Geocronología y Geología Isotópica (INGEIS), supported by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET)

CARBONATE SAMPLES. These samples are processed according to the technique of McCrea (1950) and Panarello *et al* (1980).

SOLID ORGANIC MATERIAL SAMPLES. These samples are processed according to Hoefs and Schidlowski (1967). The CO_2 obtained in this manner is then measured against a Carrara Marble reference in a Micromass 602-D mass spectrometer. The results are expressed as $\delta^{13}C$ ‰ vs PDB, defined as

$$\delta^{13}C = \left[\frac{Rs}{Rstd} - 1\right] x\ 1000\ ‰$$

Where Rs: $^{13}C/^{12}C$ in the sample
Rstd: $^{13}C/^{12}C$ in the PDB standard defined by Craig (1957).

RESULTS AND DISCUSSION

Table 1 shows the values obtained for the analyzed samples. In column 1, the $\delta^{13}C$ obtained on CO_2 by H_3PO_4 (100 %) dissolution of carbonates or V_2O_5 oxidation of organic samples are listed. In 2, the $\delta^{13}C$ of CO_2 obtained on the first stage of the benzene synthesis are shown.

The two sets of values show the lack of isotope fractionation in this first stage. The mean value of the difference between these two columns is (0.16 ± 0.49) ‰.

The "t" Student test:

$$t = \frac{\bar{d} - 0}{s/(n-1)^{1/2}} \qquad \text{in the zero point}$$

Where $\bar{d}$: 0.16 mean value of the difference
s: 0.49 standard deviation
n: 23 number of samples
gives t: 1.532, inside the critical interval defined by $t_{.95,\ 22} = 2.074$ (2 tails).

Column 3 shows the $\delta^{13}C$ values of benzene. The systematic difference between these values and those in column 2, shows an isotope depletion in the CO_2 conversion to benzene.

The mean value of the difference among 23 samples is now (-1.72 ± 0.87) ‰.

The "t" Student test:

$$t = \frac{\bar{d} - 0}{s/(n-1)^{1/2}} \qquad \text{in the zero point}$$

Where $\bar{d}$: -1.72 mean value of the difference
s: 0.87 standard deviation
n: 23 number of samples
gives t: -9.27 outside of the critical interval defined $t_{.95,\ 22} = 1.72$ (1 tail)

TABLE 1. $\delta^{13}C$ values in the different stages of benzene synthesis

		(1)*	(2)**		(3)†		
Sample no.	Material	$\delta^{13}C \pm 0.1$ ‰	$\delta^{13}C_{CO_2} \pm 0.1$ ‰	(2) - (1) ‰	$\delta^{13}C_{Bz} \pm 0.3$ ‰	Yield %	(3) - (2) ‰
AC0352	Marine shell	1.3	1.6	0.3	-1.3	83	-2.9
AC0379	" "	0.3	-0.6	-0.9	-2.0	82	-1.4
AC0383	" "	1.4	1.3	-0.1	-0.2	82	-1.5
Ac0343	" "	0.6	1.0	0.4	-0.9	83	-1.9
AC0371	Freshwater shell	-0.3	-0.8	-0.5	-2.1	89	-1.3
AC0344	Marine shell	1.5	1.5	0.0	-0.8	86	-2.3
AC0384	" "	2.8	2.6	-0.2	1.5	82	-1.1
AC0340	Freshwater shell	0.3	0.2	-0.1	-2.0	89	-2.2
AC0307	" "	-6.2	-6.4	-0.2	-8.2	75	-1.8
AC0339	Marine shell	1.7	1.8	0.1	-1.8	78	-3.6
AC0390	" "	1.5	1.5	0.0	-1.1	76	-2.6
AC0391	" "	2.8	3.1	0.3	0.6	84	-2.5
AC0323	Sediment	-4.5	-4.8	-0.3	-5.8	81	-1.0
AC0375	Marine shell	0.0	-0.1	-0.1	-1.2	85	-1.1
AC0326	" "	1.8	2.2	0.4	-0.2	86	-2.4
AC0333	" "	0.9	1.6	0.7	-0.2	80	-1.8
AC0334	" "	1.2	1.3	0.1	-1.7	80	-3.0
AC0345	" "	-2.1	-2.1	0.0	-4.0	84	-1.9
AC0077	Vegetal charcoal	-23.0	-22.2	0.8	-23.2	83	-1.0
AC0080	" "	-23.4	-22.1	1.3	-22.9	76	-0.8
AC0217	" "	-23.0	-22.0	1.0	-22.7	81	-0.7
AC0273	" "	-9.5	-9.0	0.5	-9.3	80	-0.3
Secondary Standard							
$BaCO_3$ ‡		-26.0	-26.2	0.2	-26.7	85	-0.5
$\bar{x} \pm s$		-	-	0.16 ± 0.49	-	-	-1.72 ± 0.87

*$\delta^{13}C$: H_3PO_4 (100 %) attack or V_2O_5 oxidation in the SIL

**$\delta^{13}C_{CO_2}$: first stage, $HClO_4$ (70 %) attack or O_2 stream combustion, in ^{14}C laboratory

†$\delta^{13}C_{Bz}$: Benzene + V_2O_5 in SIL

‡ See Angiolini & Albero (1983)

Therefore, a systematic fractionation can be assumed. The benzene yield, about 80 %, may cause this fractionation; however, the error it introduces into the ^{14}C activity measurement is much lower than the statistical error of the activity. Similar errors introduced by fractionation in sample and standard cancel each other out in age calculations.

Two conclusions can be made: 1) Benzene yields around 80% do not result in major fractionation, and thus do not cause appreciable errors in activity measurements. 2) The correction for isotopic fractionation needed in the activity measurement will not change noticeably by using either the $\delta^{13}C$ from the CO_2 released from the sample in the first stage or the $\delta^{13}C$ of the CO_2 evolved from the benzene by catalytic combustion.

ACKNOWLEDGMENTS

The autors thank the Stable Isotopes Laboratory members who assisted in this research. Also thanks are due to E Linares, who supported this research.

REFERENCES

Angiolini, FE and Albero, MC, 1983, A Secondary standard for radiocarbon dating, in Stuiver, M and Kra, RS, eds, Internatl ^{14}C Conf, 11th, Proc: Radiocarbon, v 25.

Craig, H, 1957, Isotopic standards for carbon and oxygen and correction factors for mass spectrometric analysis of carbon dioxide: Geochim et Cosmochim Acta, v 12, p 133-150.

Hoefs, J and Schidlowski, M, 1967, Carbon isotope composition of carbonaceous matter from the Precambrian of the Witwatersrand system: Science, v 155, p 1096-1097.

McCrea, JM, 1950, The isotopic chemistry of carbonates and a paleotemperature scale: Jour Chem Physics, v 18, p 849-857.

Panarello, HO, García, CM, Valencio, SA, and Linares, E, 1980, Determinación de la composición isotópica del carbono en carbonatos. Su utilización en Hidrogeología y Geología: Rev Asoc Geol Argentina, v 35, no. 4, p 460-466.

Tamers, M, 1975, Chemical yield optimization of benzene synthesis for radiocarbon dating: Internatl Jour Appl Radiation Isotopes, v 26, p 676-682.