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CARBON-ISOTOPE FRACTIONATION DURING WET OXIDATION OF OXALIC ACID

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The usual procedure for the preparation of carbon dioxide from the oxalic-acid standard supplied by the National Bureau of Standards is wet oxidation by means of potassium permanganate in acid solution. The procedure is straightforward, but suffers from a certain difficulty in determining the end point of the reaction.

Craig (1961) measured the standard gas samples from several laboratories, prepared both by wet oxidation and by direct combustion in an oxygen stream. The δC^{13} values for the direct combustion ranged from -17.15 to -22.72 with a mean of $-19.3\%_0$ referred to the PDB standard. The values for the wet-oxidized carbon ranged from -18.37 to -31.37. After rejecting the four lowest values, the mean for wet-oxidized oxalic acid was -19.6. As Craig pointed out, the very low values are what one might expect if the oxidation had not gone to completion.

Fractionation during chemical reactions has long been known. For example, Lindsay et al. (1949) reported as much as 3.5% change in C^{13} istotope concentration during the decomposition of oxalic acid. Bernstein (1957) reported that the decomposition of formic acid by sulfuric acid provided a simple means of producing isotope effects up to 150%. Such effects are well known to physical chemists, but may not receive as much attention among radiocarbon dating laboratories as they deserve.

When routine C^{13} measurements in the University of Arizona laboratory on newly prepared CO_2 from oxalic acid revealed a δC^{13} value of -25.5, we reviewed our method of preparation to see what factors were responsible. The sample had been purified in two batches and the two parts had shown δC^{13} values of -31.3 and -23.6. At first it was thought that the two portions had had identical histories up to the time of partition for final purification. This history included the oxidation in solution, chemical washing, freezing and pumping, thawing and passing over hot copper, and freezing for a second time. The division for final purification over CaO was accomplished by partially thawing the contents of a cold trap and purifying the evolved gas, and then thawing and purifying the remaining portion.

The possibility of fractionation during freeze-thaw operations was tested, although it was felt, a priori, that such operations were too far from equilibrium to seriously affect isotopic composition. Nevertheless,

a sample was carried through a series of freeze-thaw operations designed to accumulate any fractionation effects. Successive δC^{13} measurements yielded values of -30.03, -29.96, -29.81, -29.72, and -29.51. While the trend was monotonic, the total fractionation was negligible.

Another batch of oxalic acid was oxidized and isotopic samples were taken at intervals. When cessation of bubbling and change of color in the reaction flask signaled the end of the reaction, the first part of the evolved sample was isolated. The reaction proceeded slowly from this point, and yielded appreciable additional CO_2. The end point of the reaction is not clearly defined, and only repeated testing will determine its completion.

The successive C^{13} samples taken during the processing revealed that the isotopic composition was becoming heavier, as might be expected from the nature of the reaction. The final .05-liter portion showed a δC^{13} value of $+61.5\%$! This represents a 16% concentration of C^{14} in the final aliquot. The value for the total combined gas sample was -19.0, which is adequately close to the accepted value.

It is clear that fractionation progresses steadily throughout the wet oxidation of oxalic acid and that the color change and cessation of bubbling are not adequate criteria for determining the end point. It is also important to note that freeze-thaw operations are essentially layer processes occurring at the cold-trap walls and may preserve serial fractionation through several cold-trap operations.

While this note adds nothing new to the science of isotopic chemistry, it is perhaps worthwhile as a reminder of the magnitudes of fractionation that can occur in the important oxalic-acid reaction, and of the necessity for continually monitoring the δC^{13} values of the standard gas. There is an element of art in the successful performance of the wet oxidation of oxalic acid that must be carefully impressed upon each generation of laboratory technicians. Dry combustion affords an effective alternative, but this too has problems.

REFERENCES

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