

Chapter 25

Synthesis of Benzene for Low-level ^{14}C Measurement: A Review

R. Burleigh, A. D. Hewson and K. J. Matthews

Research Laboratory, The British Museum, London, U.K.

INTRODUCTION

The conversion of sample carbon to benzene before measurement of the ^{14}C activity is now a standard procedure in four low-level measurement laboratories in this country and in many more overseas. Techniques have been developed and refined by many workers and it seems appropriate to take stock of the progress made. This paper is the result of such a review of the methods we use in our own laboratory.

CHEMICAL SYNTHESIS

There are a number of different ways of introducing sample carbon into a counting vial and it is generally sensible to choose the most convenient. For low-level natural ^{14}C measurements, however, convenient methods are not always capable of incorporating large enough amounts of the specimen into the counting cocktail. Several grams of sample carbon in the cocktail is the minimum requirement to provide a satisfactory count rate and hence $\pm 1\%$ precision in the measurement. As a result it is necessary to consider chemical conversion of the sample material prior to counting. Such a chemical conversion should give a high yield, a pure resultant material and be routinely reproducible.

If a wide variety of materials are to be dealt with then the simplest method of extracting carbon is to burn the sample and collect the carbon dioxide produced. Many instruments have been developed to combust samples of less than 1 g easily and automatically. For larger samples and those containing only a small proportion of carbon, two separate methods which ensure complete combustion have been developed and each has its own protagonists.

The first, invented in 1830 by Justus von Liebig of Giessen, is to heat the sample in a quartz tube in the presence of an oxygen stream. Nitrogen is used as a carrier gas. To ensure complete oxidation of carbon monoxide to carbon dioxide the vapours are passed over heated cupric oxide in an after-burning zone. Catalytic oxidation over platinum is also recommended. The nitrogen and oxygen flow rates must be carefully regulated but the technique is easy to apply after a little practice. The principal disadvantage is the need to char materials containing volatile components before they are burnt.

The second method based on a combustion bomb also has an ancient pedigree having been invented by Bertholet in 1881 who used it to measure calorific values. The principle is to place the sample in contact with a filament in a crucible suspended inside a steel vessel. The vessel is pressurized with oxygen and then combustion is initiated by passing a current through the filament.

Several workers⁹⁻¹⁴ have constructed bombs based on Bertholet's and all are agreed that a relatively large volume is required (about 5 l for a 20 g sample) so that (a) combustion products are removed without reducing the oxygen concentration at the sample surface and (b) the flame is not quenched by the proximity of the wall of the vessel. About 25 ml of distilled water is placed in the bottom of the vessel to assist the removal of oxides of nitrogen and sulphur. Pressures used vary between 100 and 400 psi. Experience has shown that there is a slight danger of a dust explosion if the sample is finely divided and so it is recommended that samples are moistened and compressed before combustion. Additionally a bursting disc or some similar device incorporated in the body of the bomb and designed to blow out if the pressure in the vessel rises excessively ensures that the equipment is fail safe. Samples with a total carbon content of as little as 5% have been successfully burnt by this method.¹³

In both techniques the products of combustion and the excess oxygen are bled into a vacuum line and separated. This takes about one hour and a semi-automatic method of separation has been described.¹⁴

Before considering the synthesis of benzene, methods of producing other sample derivatives suitable for introduction into a scintillation cocktail may be mentioned. A suitable derivative should contain a substantial proportion of carbon and ideally it should be a good counting solvent. If it is not a good solvent then the degree of quenching introduced into the cocktail by the derivative should be small so as to provide the maximum counting efficiency.

Methanol may be synthesized by the reduction¹⁵ of carbon dioxide using lithium aluminium hydride in diethylene glycol diethyl ether.¹⁵ A complete apparatus for the reaction has been described.¹⁶ The methanol must¹⁶ be purified by fractional distillation and yields of over 60% have been claimed.^{16,17} Methanol is a diluent and contains 37% by weight of carbon. Therefore not much more than 2 g of sample carbon can be counted in a 20 ml counting vial and this at a rather reduced efficiency.

A further conversion of methanol to trimethyl borate with a 71% yield through the esterification of boric oxide and separation^{18,19} of the resultant methanol-trimethyl borate azeotrope has been described.^{18,19} Trimethyl borate contains 64% by weight of carbon and up to 3 g of sample in 20 ml can be counted at an acceptable efficiency in this way.

Carbon dioxide may also be converted to ethylene and then to paraldehyde. A yield of 30% overall has been claimed for this reaction.²⁰ Paraldehyde is a diluent containing 54% carbon and a counting cocktail containing 40% sample carbon or about 8 g in 20 ml has been described.

An obvious²¹ step is to attempt to incorporate carbon dioxide directly into the cocktail. Barendsen²¹ found carbon dioxide under pressure at -20°C to be 'unlimitedly soluble' in toluene. In practice, quenching effects limited the amount of carbon dioxide to about 30% or about 1.4 g of sample carbon in 20 ml.

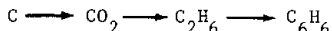
Carbon dioxide may be converted to acetylene with good yields (see below). Audric and Long^{22,23} investigated the possibility of counting acetylene¹ in toluene at -78°C and 1 atmosphere pressure. They found that a solution of 3 g l⁻¹ of PPO in toluene containing 2% ethanol would readily absorb over 100 times its own volume of acetylene with a change in counting efficiency of approximately 20%. Thus a 20 ml vial could contain about 2 g of sample carbon.

The synthesis of toluene containing seven specimen carbon atoms is very long-winded. In contrast, incorporation of sample carbon dioxide into toluene via a Grignard reaction with phenyl magnesium bromide followed by a reduction of the benzoic acid produced is straightforward. Toluene synthesized in this way contains 13% sample carbon or about 2.2 g in 20 ml. The excellent counting characteristics of toluene need not be reiterated here.

BENZENE SYNTHESIS

Benzene is a good counting solvent and, providing all six carbon atoms come from the sample, contains 92% sample carbon.

All methods of synthesizing benzene published to date, with the exception of the direct reaction of the sample with lithium (see below), use the route



Several authors describe the conversion of carbon dioxide to acetylene via strontium carbide.²⁴⁻²⁷ The procedure is to collect the carbon dioxide in 10% ammonium hydroxide and to precipitate strontium carbonate with strontium chloride. The precipitate is washed several times out of contact with air with carbon dioxide-free water, then dried, ground and blended with magnesium powder. The blended powder is placed in a stainless steel tube which is then evacuated. The tube is heated externally to initiate the reaction which proceeds exothermically to completion in about 5 min. Yields of 90-100% are reported.

Several cautionary remarks are worth making about this reaction:

- (a) The strontium chloride and the magnesium powder should be free of radon-producing impurities.
- (b) Commercial magnesium powder is often produced by the reduction of magnesium salts by carbon and so the purity of the magnesium should be determined.
- (c) A large amount of heat is produced in the reaction which without adequate precautions can get out of hand. Tamers *et al.*²⁶ give a comprehensive description of experimental procedure.

An alternative, more direct method of converting carbon dioxide to acetylene was first suggested by Arrol and Glascock in 1947.²⁸ They heated 40 mg of barium in a stainless steel vacuum-tight furnace filled with 50-500 microlitre-atmospheres of carbon dioxide to 600 °C for 5-10 min. The furnace was cooled and water added liberating H_2 , C_2H_2 , NH_3 , water vapour and a maximum of 2% ethylene. Yields were in the range 79-98%.² They noted lower yields for small quantities of carbon dioxide. They warned against the use of a mild steel furnace as they had been able to produce acetylene under 'blank' conditions from the carbon within the steel. They also noted a lower yield when acetylene, ammonia and water vapour were condensed together in the presence of mercury, possibly due to the formation of the acetylde.

Barker²⁹ modified their procedure to give a method for the large-scale synthesis of acetylene. He reacted carbon dioxide with an excess of lithium at 700 °C in a stainless steel furnace. Good yields were favoured by using a large excess of lithium and allowing the exothermic reaction to proceed at as high a temperature as possible. He also recommended using a large excess of water for the subsequent hydrolysis to give a final concentration of lithium hydroxide of about 5% as the rate of evolution of acetylene was markedly less at higher concentrations.

Subsequent literature^{8,13,30-33} disputes the necessity of a large excess of lithium or water and also whether the reaction temperature should be precisely controlled or not. There is general agreement, however, that some of the carbon dioxide is reduced to carbon and that fresh lithium must be brought into contact with such carbon in order to achieve a high yield. Hence continued heating after all the carbon dioxide has been absorbed is generally recommended, as is active evacuation of the furnace to remove any radon introduced with either the lithium or the carbon dioxide.

Some samples may be converted direct to lithium carbide by heating the sample material with lithium.⁴¹ Since it is not possible to determine the yield of this reaction it is necessary to check the $^{13}\text{C}:^{12}\text{C}$ ratio of the benzene produced to ensure that possible fractionation of the carbon isotopes does not pass undetected.

The conversion of acetylene to benzene can be achieved by the action of heat alone -- temperatures of the order of 400-600 °C being necessary. Benzene is not the only product of pyrolysis and so the resulting mixture must be fractionally distilled before counting. Tamers and Bibron³⁴ reported the presence of a strong quenching agent, 1,3-cyclohexadiene, which boils at 80.5 °C and therefore could not be removed by distillation. They removed it by reacting it with bromine and distilling once again.

Clearly a catalytic conversion of acetylene to benzene is more convenient. Such a conversion was described by Shapiro and Weiss³⁵ who used a silica-alumina support activated by diborane. Noakes *et al.*,²⁷ using this technique, obtained yields of as

much as 60%. However diborane is toxic, inflammable and unstable at ambient temperatures and is therefore not pleasant to work with.

In a search to improve yields and improve the handling of the catalyst Noakes *et al.*³⁰ activated a selection of silica-alumina supports with various transition metal oxides. They concluded that the activating agent should contain metal ions in valence state of +5 or greater and be present in the support at a concentration of up to 20% of the total weight. The support should also have a large surface area. Commercial catalysts are now available for the trimerization reaction and excellent yields (95% or more) are reported.^{13,32,36-39}

The synthesized benzene is reasonably pure and contains negligible amounts of quenching agents. It can therefore be counted without prior fractional distillation. A recent investigation of the impurities in benzene routinely synthesized in seven laboratories⁴⁰ revealed that the major contaminant was toluene at a maximum level of 1100 ppm. Small amounts of quenching agents were detected at a maximum level of 180 ppm.

Hence we see that synthesizing benzene is a practical if time consuming, proposition. The density of benzene is 0.88 and so up to 16 g of carbon may be counted at a high efficiency in this form.

ALTERNATIVES TO LIQUID SCINTILLATION COUNTING

Apart from gas proportional counting, other techniques for measuring low levels of ¹⁴C activity have been proposed such as the use of nuclear track plates⁴² or thermoluminescence dosimetry.⁴³ Neither of these methods can offer the simplicity of the liquid scintillation method.

Recently interest has arisen in the possibility of direct measurement of natural ¹⁴C concentrations. Conventional mass spectrometry is incapable of registering concentrations at the level of one part in 10¹⁴ as is possible when measuring decay rates. However, a method of selectively⁴⁴ enriching synthesized formaldehyde using a finely tuned laser is under development with the intention of measuring the product in a mass spectrometer. An alternative, also under investigation,^{45,46} is to accelerate ¹⁴C introduced as carbon dioxide or elemental carbon to high energies in cyclotron or a tandem van der Graaf generator and count individual ¹⁴C ions. None of these methods seems likely to supplant the more conventional radiochemical techniques for ¹⁴C measurement, in particular liquid scintillation counting, in the immediate future.

REFERENCES

1. L.G. Hubner and W.E. Kisielecki, *Atompraxis* 16, 1 (1970).
2. J.I. Peterson, *Anal. Biochem.* 31, 204 (1969).
3. J.I. Peterson, F. Wagner, S. Seigel and W. Nixon, *Anal. Biochem.* 31, 189 (1969).
4. N. Kaartinen, *Packard Tech. Bull.* 18, (1969).
5. L. Hunt and B. Bastomsky, *Clin. Chem.* 17, 10 (1971).
6. E. Rapkin, in *Liquid Scintillation Counting* Vol 3 (M.A. Crook and P. Johnson, Eds) Heyden, London, 1974, p.132.
7. J.E. Noakes, in *Liquid Scintillation Counting: Recent Developments* (P.E. Stanley and B.A. Scoggins, Eds) Academic Press, London, 1974, p.125.
8. H.A. Polach and J.J. Stipp, *Int. J. Appl. Radiat. Isot.* 18, 359 (1967).
9. H. Barker, R. Burleigh and N. Meeks, *Nature (London)* 221, 49 (1969).
10. V.R. Switsur, M.A. Hall and R.G. West, *Radiocarbon* 12, 590 (1970).
11. R. Burleigh, in *8th Int. Conf. on Radiocarbon Dating* (T.A. Rafter and T. Grant-Taylor, Eds) R. Soc. New Zealand, Wellington, 1972, p.11.
12. V.R. Switsur, in *8th Int. Conf. on Radiocarbon Dating* (T.A. Rafter and T. Grant-Taylor, Eds) R. Soc. New Zealand, Wellington, 1972, p.11.
13. D.D. Harkness and H.W. Wilson, in *8th Int. Conf. on Radiocarbon Dating* (T.A. Rafter and T. Grant-Taylor, Eds) R. Soc. New Zealand, Wellington, 1972, p.1102.
14. R. Burleigh, in *Liquid Scintillation Counting*, Vol 3 (M.A. Crook and P. Johnson, Eds) Heyden, London, 1974, p.295.
15. R.F. Nystrom, W.H. Yanko and W.G. Brown, *J. Am. Chem. Soc.* 70, 441 (1948).
16. C.F.G. Delaney and J.R. McAulay, *Sci. Proc. R. Dublin Soc.* A1, 1, 1 (1959).
17. R.W. Pringle, W. Turchinets and B.L. Funt, *Rev. Sci. Instrum.* 26, 859 (1955).
18. H.I. Schlesinger, *J. Am. Chem. Soc.* 72, 513 (1953).

19. R.W. Pringle, W. Turchinets, B.L. Funt and S.S. Danyluk, Science 125, 69 (1957).
20. C. Leger, G. Delibrias, L. Pichat and C. Baret, in Liquid Scintillation Counting (C. Bell and F.N. Hayes, Eds) Pergamon, London, 1958, p.261.
21. G.W. Barendsen, Rev. Sci. Instrum. 28, 430 (1957).
22. B.N. Audric and J.V.P. Long, Nature (London) 173, 992 (1954).
23. B.N. Audric and J.V.P. Long, in Radioisotope Conference, Vol 2, Butterworths, London, 1954, p.134.
24. H. Suess, Science 20, 5 (1954).
25. M.A. Tamers, Science 132, 668 (1960).
26. M.A. Tamers, J.J. Stipp and J. Collier, Geochim. Cosmochim. Acta 24, 266 (1961).
27. J.E. Noakes, A.F. Isbell, J.J. Stipp and D.W. Hood, Geochim. Cosmochim. Acta 27, 797 (1963).
28. W.J. Arrol and R. Glascock, Nature (London) 159, 810 (1947).
29. H. Barker, Nature (London) 172, 63 (1953).
30. M.A. Tamers, in Proc. 6th Int. Conf. on Radiocarbon and Tritium Dating, Washington, 1965, p.53.
31. J.E. Noakes, S. Kim and J.J. Stipp, in Proc. 6th Int. Conf. on Radiocarbon and Tritium Dating, Washington, 1965, p.68.
32. M.A. Geyh, Int. J. Appl. Radiat. Isot. 20, 463 (1969).
33. R. Burleigh, in Liquid Scintillation Counting, Vol 2 (M.A. Crook and P. Johnson, Eds) Heyden, London, 1972, p.139.
34. M.A. Tamers and R. Bibron, Nucleonics 21, 90 (1963).
35. I. Shapiro and H.G. Weiss, J. Am. Chem. Soc. 79, 3294 (1957).
36. S. Ikeda and A. Tamaki, Radioisotopes 12, 368 (1963).
37. F. Pietig and H.W. Scharpenseel, Atompraxis 12, 2 (1966).
38. H. Polach, J. Gower and I. Fraser, in 8th Int. Conf. on Radiocarbon Dating (T.A. Rafter and T. Grant-Taylor, Eds) R. Soc. New Zealand, Wellington, 1972, p.B36.
39. D.D. Coleman, C.L. Liu, D.R. Dickerson and R.R. Frost, in 8th Int. Conf. on Radiocarbon Dating (T.A. Rafter and T. Grant-Taylor, Eds) R. Soc. New Zealand, Wellington, 1972, p.B50.
40. I. Fraser, H.A. Polach, R.B. Temple and R. Gillespie, in Liquid Scintillation Counting: Recent Developments (P.E. Stanley and B.A. Scoggins, Eds), Academic Press, London, 1974, p.173.
41. E.R. Swart, Experientia 20, 47 (1963).
42. D. Jeffreys, D. Larson and J.D. French, Am. J. Phys. 40, 1400 (1972).
43. J. Winter, Archaeometry 14, 281 (1972).
44. E.T. Hall and R.E.M. Hedges, Archaeometry Conference, Philadelphia, 1977, unpublished work.
45. R.A. Muller, Science 196, 489 (1977).
46. A.E. Litherland, University of Toronto, unpublished work.

DISCUSSION

G.W.A. NEWTON: Have you studied the pressure dependence of the conversion of acetylene to benzene by catalysis?

A.D. HEWSON: Not in detail, though we are aware that the acetylene must be exposed to the catalyst at a pressure of not less than 0.5 atm in order to ensure a satisfactory reaction rate.

R.L. OTLET: I should like to comment on a point you raised regarding the advantages of direct reaction of the carbon substance with lithium. In addition to that of saving time over the usual method, I think a possible source of fractionation is also removed. As you indicated, the conversion to lithium carbide from carbon dioxide works either by a direct one-step reaction or via the intermediate process producing firstly elemental carbon and secondly lithium carbide. Isotope fractionation is always a risk in such a branching process unless yields are 100%. In practice much care has to be taken to achieve yields close to 100% and success is not always guaranteed. In direct conversion of the carbon substance to lithium carbide there are no intermediate or branch steps. Where it reacts the conversion is complete. If overall yields are less than 100% any unconsumed material at the end of the process is still in its original form and no fractionation will have occurred.