

Experimental

Triphenylacetic Acid-1-C¹⁴ (II).—The apparatus, assembled with ¹⁴/₂₀ standard taper joints, consisted of a 10 ml. generator flask and a 100 ml. reaction vessel, each equipped with a separatory funnel and interconnected through a drying tube (Drierite) with a stopcock on the reaction vessel side. The vacuum line, also with stopcock, led from the reaction vessel.

Ten and seven-tenths millicuries of BaC¹⁴O₃ in 600 mg. of total barium carbonate were introduced into the generator flask, and the system was swept free of atmospheric gases with dry nitrogen fed through the generator separatory funnel. After partial evacuation, the carbon dioxide was liberated by the dropwise addition of 30% perchloric acid and frozen (liquid air) into the reaction vessel. The latter was then isolated from the rest of the system, the liquid air bath removed, and 30 ml. (1.2 molar proportions) of a 0.1 *N* solution of triphenylmethyl sodium (I)⁶ in ether was added immediately and rapidly from the separatory funnel. It is essential that oxygen be excluded from I in the course of preparation and manipulation, in accordance with the technique described by Renfrow and Hauser.⁶ The reaction vessel was then brought to room temperature, and the contents were shaken vigorously for two minutes. On removal from the system, an equal volume of 10% ammonia was added, and the ethereal phase was extracted twice again with dilute ammonia. The combined alkaline solutions, after one ether wash, were acidified to precipitate from 780 to 800 mg. (90–92% yield) of triphenylacetic acid-1-C¹⁴ (II), melting at 267° and exhibiting a specific radioactivity of 12.5 million counts per mg. per min., as determined in the windowless flow gas counter operating at approximately 40% efficiency. Schlenk and Marcus⁷ report m. p. 267° for the C¹² product obtained in unstated yield through the same reaction.

Triphenylacetamide-1-C¹⁴ (III).—The acid II (800 mg.) in purified thionyl chloride (5 ml.) was refluxed 2.5 hours. After evaporation to dryness in vacuum on the bath, the solid acid chloride was pulverized under 10 ml. of concentrated ammonia and let stand for 30 minutes when the amide was collected and dried (780 mg., melting at 246–248° in agreement with the literature).⁸

Triphenylacetoneitrile-1-C¹⁴ (IV).—The amide III (780 mg.) in dry toluene (15 ml.) was heated under reflux for 50 hours with 5 g. phosphorus pentoxide. After addition of water, the aqueous phase was separated and washed four times with benzene. The combined organic extracts were dried over potassium hydroxide, and the solvents distilled to yield 730 mg. of crude IV as a brownish crystalline residue melting at 115–125°. Recrystallization from dilute acetone raised the m. p. to the reported¹⁰ 127–128°.

Other dehydrating agents were found to be less satisfactory. Oxalyl chloride failed to effect the conversion, and phosphorus pentachloride gave a lower yield than phosphorus pentoxide. While the yield with thionyl chloride was excellent, the product was contaminated with traces of a tenacious sulfur-containing impurity which remained in the final cyanide.

Sodium Cyanide-C¹⁴ (VI).—The crude nitrile IV (730 mg.) in 9.5 ml. of dry ethanol contained in a 50-ml. standard taper flask fitted with a sealed-in gas inlet tube (closed) was refluxed with 1 g. of sodium added in ten portions over a period of 30–40 minutes. As a precautionary measure to prevent the loss of any free hydrogen cyanide at the beginning of the reaction, the effluent gases from the reflux condenser were passed through sodium hydroxide solution. At the end of the operation, the aqueous alkali from the trap was added to the reaction mixture [when triphenylmethane (V) precipitates], and the vessel was fitted to a dropping funnel carrying a gas exit tube from the interior of the system to the distillation condenser, the outlet from which protruded below the surface of the receiving 1 *N* sodium hydroxide solution (20% excess). The apparatus was swept with a slow stream of nitrogen introduced through the inlet tube

to the reaction vessel, and excess dilute sulfuric acid was added dropwise from the separatory funnel. The contents of the flask were then boiled gently until approximately 15 ml. of distillate had collected. A slight turbidity in the latter was cleared by one washing with ether, and the alkaline solution was made to known volume and an aliquot was taken for titration of its cyanide content by the usual argentimetric method. For storage, the solution was taken to dryness in vacuum at room temperature.

In many runs, each from 600 mg. of barium carbonate and without purification of the intermediates, the yields of NaC¹⁴N ranged from 103 to 109 mg. (68–72%).

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A Derivation of the Concentration Distribution Equation for the Craig Counter Current Apparatus

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The development of the Craig counter-current distribution apparatus, with subsequent successful application to widely varied problems of separation, isolation and identification, has created a need for an equation which relates the distribution coefficient of a solute with the solute concentration in any tube, *r*, after *n* transfers have been completed. This equation has been obtained from consideration of the terms of a binomial expansion of degree *n* and by drawing an analogy between diffusion and the distribution process.²

It is the purpose of this note to present a derivation of the concentration distribution equation based solely upon probability considerations.

We shall discuss a system of a solute and two mutually saturated immiscible phases, where the solute has a linear distribution coefficient, *K*, between the phases. The coefficient, *K*, is defined as *Y/X*, where *Y* and *X* are the equilibrium solute concentrations in the upper and lower phases, respectively. Then, if *n* be the number of transfers performed, *r* the number of the tube under consideration, and if we give our attention to one molecule in tube number 0, we can derive the expression for the probability that this molecule will be in the tube *r* after *n* transfers.

The probability that the molecule will be in the upper (mobile) phase at the time a transfer occurs is equal to the ratio of the equilibrium amount of solute in the upper phase to the total amount of solute present in the tube.

Letting the amount of solute present in tube number 0 at the start of the procedure be one arbitrary unit and denoting the ratio of the volumes, *V*₁ and *V*₂, of the upper and lower phases by *Z*, we see that the probability of successful transfer, *p*, which is the same as the probability of being in the mobile phase, is given by

$$p = V_1 Y / (V_1 Y + V_2 X)$$

(1) Public Health Service Research Fellow of the National Heart Institute.

(2) Williamson and Craig, *J. Biol. Chem.*, **168**, 687 (1947).

(10) Vorländer, *Ber.*, **44**, 2468 (1911).

Here, $V_1Y + V_2X$ is the total amount of material added to tube number 0 and $K = Y/X$. Combining and rearranging we find that

$$p = KZ/(1 + KZ)$$

The probability, q , that the molecule will fail to advance to the next tube at the time of transfer is

$$q = 1 - p = 1/(1 + KZ)$$

The probability, $P_{n,r}$, that in n transfers the molecule under consideration will reach tube r is equal to the product of the probability of r successful transfers, $n - r$ failures and the number of ways in which r successes and $n - r$ failures can be combined.

$$P_{n,r} = \frac{n!}{r!(n-r)!} p^r q^{n-r}$$

If r and $n - r$ are greater than five and if p is between 0.1 and 0.9, it is possible to express $P_{n,r}$ with LaPlace's binomial approximation

$$P_{n,r} = \frac{1}{\sigma \sqrt{2\pi}} e^{-(r-r_m)^2/2\sigma^2}$$

where

$$r_m = np = \frac{nKZ}{1 + KZ}$$

and

$$\sigma = \sqrt{npq} = \sqrt{\frac{nKZ}{(1 + KZ)^2}}$$

By definition, r_m is the number of the tube in which the given molecule has the maximum probability of occurrence, and σ is the usual standard deviation of the distribution curve.

The general concentration distribution equation for a system containing g_0 grams of solute then becomes

$$g_{n,r} = \frac{g_0}{\sqrt{2\pi} \frac{nKZ}{(1 + KZ)^2}} e^{-(r-r_m)^2/2(nKZ/(1 + KZ)^2)}$$

For the special case where the volumes of the two phases are equal this general equation reduces to the final expression given by Williamson and Craig.

Illustrations of the precision of this equation under various values of p , n and r are given by Fry.³

The properties of the distribution curve now can be employed to obtain information about the purity, homogeneity, identity and optimum separation conditions of the solutes under examination.

To find the conditions for optimum separation of multicomponent mixtures we plot $\log KZ$ against r_m/n . From this plot it is apparent that optimum separation will occur if the $\log KZ$ values for the components are symmetrically distributed about zero.

The position of the maximum, $r_m = np$, of an experimental concentration curve may be an

(3) Fry, "Probability and its Engineering Uses," D. Van Nostrand Company, Inc., New York, N. Y., 1928, p. 213.

aid in establishing the identity of a component, by yielding the distribution coefficient

$$K = r_m/(n - r_m)Z$$

In addition, the geometry of the curve yields the standard deviation. The relation between σ and K is

$$K = \frac{\frac{n}{\sigma^2} - 2 \pm \sqrt{\frac{n^2}{\sigma^4} - 4 \frac{n}{\sigma^2}}}{2Z}$$

A test of homogeneity of sample can be made by normalizing the concentration curve and fitting it to a normal distribution curve, similar to the manner in which diffusion curves are treated.⁴

(4) Bevilacqua, Bevilacqua, Bender and Williams, *Ann. N. Y. Acad. Sci.*, **46**, 309 (1945).

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A Convenient Synthesis of Acetyl Sulfide

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The literature records¹ conflicting claims in the preparation of acetyl sulfide. Several authors, using various methods of preparation, obtained a product boiling around 119°. On the other hand, by action of phosphorus pentasulfide on acetic anhydride, or of acetyl chloride on lead thioacetate, Davies obtained² mixtures which he fractionated into thioacetic acid, acetic acid and a liquid, b. p. around 157°. The latter gave an analysis close to that calculated for acetyl sulfide. Davies suggested that the samples previously reported to boil around 119° were largely acetic acid, but offered no proof of this point. A recent need for acetyl sulfide has prompted us to develop a new and convenient synthesis for this substance, to substantiate its structure by reductive desulfurization, and to demonstrate conclusively the correctness of Davies' claim that acetic acid had been obtained by previous workers.

An attempt was made to duplicate the preparation of Jacquemin and Vosselmann³ using acetyl chloride and potassium sulfide. Regardless of the mode of mixing, moderate yields of a liquid, b. p. 118° on careful fractionation through a $\frac{3}{4} \times 24$ inch helix-packed column, were obtained, accompanied by extensive decomposition and tar formation. These findings accord with those of Jacquemin and Vosselmann. The main product was shown to be acetic acid by its boiling point, d_{20}^{20} 1.041, n_{20}^{20} 1.3728, its water solubility, and the fact that it produced benzylthiuronium acetate in the same yield as did pure acetic acid on reaction with benzylthiuronium chloride. When the reaction was conducted by adding potassium sulfide to refluxing acetyl chloride, a substantial

(1) Beilstein, "Handbuch der organischen Chemie," Vol. 2, p. 232 (101).

(2) Davies, *Ber.*, **24**, 3551 (1891).

(3) Jacquemin and Vosselmann, *Compt. rend.*, **49**, 372 (1859).