

observed in acid hydrolysis (conversion of 4-chloro- and 4-phenoxy-derivatives into 4-hydroxy-compounds) and in various replacement reactions (conversion of 4-chloro- into 4-methoxy-, 4-phenoxy- and 4-anilino-derivatives; conversion of 4-phenoxy- into 4-amino-compounds).

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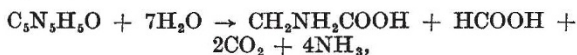
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² Keneford, Morley, Simpson and Wright, *J. Chem. Soc.*, 1356 (1949).
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A Source of Error in Amino-Acid Analysis

THE quantitative determination of amino-acids in proteins and tissues generally involves hydrolysis of the latter with acids, usually hydrochloric acid at a strength of about 6 *N* under a reflux condenser (about 108° C.) for 20–40 hr., or in a sealed tube at 120° C. for 10–12 hr.

In the last century it was shown by Strecker¹ and by Wulff² that purines are decomposed when heated with acid at high temperatures, giving rise to glycine, formic acid, carbon dioxide and ammonia. This reaction, represented for the case of guanine by the equation:



does not appear to be very widely known, although it has been made use of occasionally by chemists interested in purines and related substances, for example, by Abrams, Hammarsten and Shemin³, to determine the position of labelled carbon in guanine. Although Strecker and Wulff both used temperatures of about 180° C. in their experiments, we find that the reaction proceeds at lower temperatures, and that it is almost complete after 6 hr. at 120° C. Under these conditions, therefore, nucleic acids, which contain both adenine and guanine, will give rise to glycine, and when appreciable amounts of nucleic acid are present, as is often the case, serious errors in the amino-acid analyses may result. For example, we may consider the analyses of the *E. coli* bacteriophage *T*₄. Polson and Wyckoff⁴ find that after hydrolysis with 20 per cent hydrochloric acid, the glycine content of this bacteriophage is 7.34 per cent of the total amino-acids found. Its desoxyribose nucleic acid content is probably the same as that of the closely related *T*₂ bacteriophage, namely, 37 per cent by weight⁵. Assuming that the purines and pyrimidines in the nucleic acid are approximately equivalent (as in thymus nucleic acid), the purines alone could account for some 6 per cent glycine, that is, about 80 per cent of the total glycine found. The nucleic acid content of bacteriophages is exceptionally high, but many other analyses have been reported in which the nucleic acid glycine should be taken into account when computing the glycine content. These include some carried out on whole bacteria^{6,7,8}, yeast cells⁹, influenza viruses A and B¹⁰, tobacco mosaic virus¹¹, and investigations on the glycine content of whole chick embryos¹².

In general, it would seem that the simplest way of avoiding trouble from this source would be to remove the nucleic acid before hydrolysis.

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A Radioactive Tracer Method for the Analysis of Mixtures of Short-lived Free Radicals

THIS note gives a brief account of a radioactive tracer technique for the detection and estimation of the short-lived aliphatic free radicals; it is being used in both dynamic and static experiments. In a different way, radioactive indicators have previously been used in the study of free radicals by P. A. Leighton¹, who succeeded thus in refining the mirror technique of Paneth and Hofeditz.

The free radicals are allowed to react with iodine labelled with 8-day iodine-131, and the resulting alkyl iodides, likewise labelled, are frozen out in liquid air. At the conclusion of the experiment, excess iodine is removed, and about 1 c.c. of carrier for each of the alkyl iodides involved is added. After separation by fractional distillation, and conversion of each fraction into silver iodide, simple β-particle counts give directly the relative proportions of the various radicals initially present.

In the dynamic experiments, propyl radicals have been made by the 'sodium flame' technique of Polanyi², by the reaction of the vapours of propyl bromide and sodium. After passage through a furnace tube at a known temperature, iodine vapour is injected into the gas stream, and the products finally frozen out. With the furnace cold, activity is found only in the propyl iodide fraction; at 400° C., however, roughly equal activities are found in the methyl iodide and propyl iodide fractions. From measurements at different temperatures, a value for the activation energy for the decomposition reaction:



can be obtained; preliminary results yield a value of 19 k.cal./mole.

We are also investigating the photodecomposition of ketones in a static system by the method of Gorin³, elaborated by the use of radioactive iodine. So far, we have examined the ratio of methyl to ethyl radicals in the primary products of the low-temperature photolysis of methyl ethyl ketone. Using light of wave-length 2537 Å., results so far obtained indicate that reaction (1) is more probable than reaction (2), although the ratio of the alkyl radical yields is only of the order of 2.5 to 1.