LETTERS TO THE EDITORS

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Radiochemical Studies on Free Radicals

WHEN the first attempt was made to determine the coefficient of accommodation of free organic radicals, a 'guard mirror' of lead was placed in front of a second mirror ; by gradually reducing the length of the guard mirror until the second mirror was attacked, it was possible to show with a fair degree of accuracy that free radicals reacted with a lead mirror at every first impact. On a clean glass wall no more than about one in a thousand radicals was not reflected[1].

We have tried to simplify, and at the same time to increase the accuracy of these experiments by a radiochemical technique. The use of radioactive mirrors in free radical studies is not new. Leighton and Mortensen[2] employed invisible mirrors of radium D and E to detect very low concentrations of free radicals produced by photolysis. Using a β-electroscope, they were unable to measure directly the change in activity of the mirror ; but they could trap and measure the radioactive products. The advantages of this radioactive mirror method over the visual observations were doubtful, so that in later studies the authors returned to the old method. We have improved the radioactive technique by using a Geiger counter instead of an electroscope, and a 'slit' method for measuring the activity of the mirror.

A lead block (6 cm. × 6 cm., of 1 cm. thickness) was provided in the middle with a slit of adjustable width, and with a groove on the under side, so that, placed on the reaction tube, it could be moved smoothly along its length. A small Geiger tube was fitted on top of the slit, which was at right angles to the groove. The aperture could be narrowed to less than 1 mm., thus making it possible to measure small cross-sections of the mirror. With this arrangement the distribution of radioactivity along the mirror could be measured by taking sectional counts. The extent of change in this distribution due to the action of free radicals on one mirror gives immediately the length of mirror necessary to reduce the concentration of free radicals to zero, thus making the runs with guard mirrors of different lengths unnecessary.

The first indicator to be tried was antimony-124 ; but, because of its penetrating γ-radiation, sharp definition could not be obtained. Radium E was then chosen, because of its pure β-emission ; it proved to be quite suitable. Unlike Leighton and Mortensen, we separated the radium E electrochemically and used it as the indicator for a heavy bismuth mirror. This ensures that throughout the experiments the conditions offered to the impinging radicals remain the same.

With this device it was easy to determine exactly the limit which ethyl radicals reached on the mirror. It was gratifying to find with the bismuth mirrors a full confirmation of the result obtained by Paneth and Herzfeld with lead mirrors and a different technique, namely, an accommodation coefficient of 1 for the impact of the radicals on the metal[3]. A further advantage of the method is that the number of free radicals reacting can be determined without much difficulty. As we know now that with a suitable mirror every radical is combining, it is only necessary to measure the radioactivity removed from a sufficiently long and heavy mirror of known specific radioactivity in order to find the quantity of bismuth ethyl $(Bi(C_2H_5)_3)$ formed, and hence the number of free radicals present. This procedure is easier than the microchemical methods hitherto employed[4,5].

Radioactive indicator methods have been shown, or promise, to be useful, also in other free radical studies. Durham, Martin and Sutton, in this laboratory, have developed a general radiochemical method for the identification of free radicals and the determination of the yield in which they are produced[6]. It seems promising, too, to use radioactive indicators for the study of the half-life of free radicals in solution, although preliminary experiments indicate that a much more elaborate technique will be necessary. Also, the still more difficult investigation of the electric and magnetic moments of free radicals may well be undertaken by radioactive tracer techniques. Experiments on these lines are under way in this laboratory.

A more detailed report is being submitted to *Transactions of the Faraday Society*.

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[1] Paneth, F. A., and Herzfeld, K., *Z. Elektrochem.*, **37**, 577 (1931).

[2] Leighton, P. A., and Mortensen, R. A., *J. Amer. Chem. Soc.*, **58**, 488 (1936). See also Burton, M., Ricci, J. E., and Davis, T. W., *J. Amer. Chem. Soc.*, **62**, 265 (1940).

[3] For details, see Ph.D. thesis of Hollis, A. (University of Durham, 1950).

[4] Paneth, F. A., Hofeditz, W., and Wunsch, A., *J. Chem. Soc.*, 372 (1935).

[5] Feldman, M. H., Ricci, J. E., and Burton, M., *J. Chem. Phys.*, **10**, 618 (1942).

[6] Durham, R. W., Martin, G. R., and Sutton, H. C., *Nature*, **164**, 1052 (1949).

An Alkaloid Related to Dehydrolaudanosoline

FROM the oxidation of laudanosoline, Robinson and Sugasawa[1], and independently Schopf and Thierfelder[2], isolated an optically inactive quaternary ammonium salt which they showed had the structure (I) and which was named 'dehydrolaudanosoline'. Since the oxidation proceeded so readily and so smoothly, the latter authors suggested that it might reasonably be assumed that it also occurred in the plant cell, but they were unable to cite any alkaloid which was, or could be, a derivative of (I). Later, Folkers, Koniuszy and Shavel[3] ascribed to certain alkaloids of *Eyrthrina* species structures based on the ring system of (I) ; but recent work of Carmack, McKusick and Prelog[4] has shown that other structures are more likely.

However, a simple derivative of (I) has now been obtained from a natural source. From the bark of *Cryptocarya bowiei* (Hook.) Druce, collected in northern Queensland, a water-soluble alkaloid,