RECOIL-ACTIVATED AND THERMAL EXCHANGE REACTIONS BETWEEN SULFUR-35 AND CARBON DISULFIDE

Sir:

Two interesting exchange reactions have been observed in research on the preparation of S^{35}-tagged CS_2 (CSS*). Each reaction presents an interesting chemical phenomenon, namely, the exchange of a free sulfur atom or ion with one bound in the CS_2 molecule, and each is applicable to the preparation of CSS*. Such *atomic* exchange reactions, involving energetic covalent bonds, have been found in the past to be much slower.

The activation energy in the first of these reactions is supplied by the specific nuclear process which results in formation of S^{35}. Two experiments have been performed to date, each utilizing the n,p reaction on Cl^{35} to make the 87-day S^{35}. In the first experiment, a solution of CS_2 in CCl_4 (10 volume per cent. CS_2) was placed in the stray neutron field near the Massachusetts Institute of Technology cyclotron for one month. The total S^{35} activity and that present as CS_2 were assayed by Carius analysis. For the CS_2 analysis, exhaustive extraction with Na_2CO_3 solution was followed by distillation of the mixture to remove the other S^{35}-containing compounds ($CSCl_2$ etc. No effort was made to separate CCl_4 and CS_2). About 50% of the S^{35} formed in compounds not volatile below room temperature was present as CSS*. In the second experiment, a solution of one gram of C_2Cl_6 in 1 ml. of CS_2 was sealed in a quartz vial for a thirty-day bombardment in the Oak Ridge pile, and assayed as described above, except that upon receipt, the sample was kept frozen until aliquoted for total S^{35} analysis to avoid loss of the more volatile compounds (of $BaCS_3$). In this case, 12% was recovered as CSS*. The lower value in the second experiment may be attributed (a) to the precaution taken to recover volatile compounds, and (b) to the greater variety and number of radiation-induced side reactions possible in the higher neutron flux of the pile. The specific activity of S^{35} as CSS* in the Oak Ridge sample attained a value of greater than one millicurie per gram.

The second reaction, now being studied, is the exchange of sulfide ion in aqueous solution with CS_2 as a separate phase. The reaction proceeds through sulfide exchange with thiocarbonate ion ($CS_3^=$), and like the electron transfer reactions of thallium[1] and iron[2] recently reported appears to be catalyzed by precipitation (of $BaCS_3$). On the other hand, when the $CS_3^=$ is decomposed with acid and the resulting CS_2 extracted with CCl_4 and analyzed, this exchange shows a half-time of about forty minutes (sulfide concentration about 0.5 M, thiocarbonate about 0.15 M, pH 9.5, 30°). Investigation of the kinetics of this reaction continues.

(1) R. J. Prestwood and A. C. Wahl, THIS JOURNAL, **70**, 880 (1948).

(2) L. Van Alten and C. N. Rice, *ibid.*, **70**, 883 (1948).

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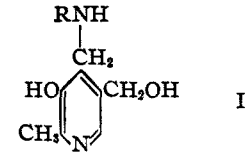
PYRIDOXYLAMINES

Sir:

Pyridoxal has been reductively coupled with certain amines, including several pressor amines, to give compounds of structure I. For example,



I

β-phenylethylamine, tyramine, tryptamine, isobutylamine, histamine (amines derived from naturally occurring amino acids), as well as benzylamine reacted with pyridoxal to give yellow Schiff bases, which were hydrogenated over a platinum catalyst to give pyridoxyl-β-phenylethylamine dihydrochloride, II (m. p. 227–228°, dec.), pyridoxyltyramine dihydrochloride, III (m. p. 238–239°, dec.), pyridoxyltryptamine hydrochloride, IV (m. p. 222–223°, dec.), pyridoxylisobutylamine hydrochloride, V (m. p. 204–205°, dec.), pyridoxylhistamine dihydrochloride, VI (m. p. 236–237°, dec.), and pyridoxylbenzylamine dihydrochloride, VII (m. p. 220–221°, dec.). These new compounds as well as the intermediary Schiff bases were also analytically characterized.

These pyridoxylamines, which are derivatives of both pyridoxine and the pressor amines, are being studied for vitamin B_6 activity and for pressor activity.

The tests of these compounds for vitamin B_6 activity in deficient rats were made by Dr. Gladys Emerson and Miss Elizabeth Wurtz of the Merck Institute for Therapeutic Research, who have found that compounds II, III, IV and VII show activities which range between 50 and 100% of the activity of a molar equivalent of pyridoxine. Such high biological activity for these new compounds is in contrast to the low activity which has been found for previous structural modifications of the vitamin B_6 group.[1]

(1) Unna, *Proc. Soc. Exptl. Biol. Med.*, **43**, 122 (1940); Harris and Wilson, THIS JOURNAL, **63**, 2526 (1941); Harris, *ibid.*, **63**, 3363 (1941).