Of the radicals HO, HO_2 and HO_3, rapid exchange seems possible only for HO.

More complete experimental results will be presented in a later report, containing also data on related systems.

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RECEIVED JUNE 7, 1952

TRACER STUDIES ON SOME REACTIONS OF THIOSULFATE AND TETRATHIONATE

Sir:

The oxidation of thiosulfate to tetrathionate with iodine, the reduction of tetrathionate to thiosulfate with sulfide, and the decomposition of both thiosulfate and tetrathionate with mercuric chloride in presence of bisulfite and excess formaldehyde have been studied with the aid of S^{35}.

In order to separate the products of the reactions with mercuric chloride, three successive precipitations were made: $HgCl_2 \cdot 2HgS$ (from thiosulfate) and $HgCl_2 \cdot 2HgS + S$ (from tetrathionate) were precipitated in the cold by means of a large excess of concentrated buffered mercuric chloride and addition of some ammonia after one hour (I), sulfate was precipitated, also in the cold, with acetic acid and barium chloride (II), finally the protected bisulfite was oxidized with potassium hypobromite and precipitated as barium sulfate (III). Radioactive contamination of III was excluded by an intermediate scavenging operation which consisted of the addition of inactive thiosulfate or tetrathionate, mercuric chloride and barium chloride. These intermediate precipitates were checked to be practically inactive.

If thiosulfate labeled at the central S-atom was treated in this way the activity distribution was: 1% in I, 95% in II, none in III.

If the same thiosulfate was titrated to tetrathionate with iodine, and analyzed in the same manner, again 1% was found in I, and 95% in II, but this time 2–3% entered into III.

Save for the infrequent side-reaction which caused the formation of radioactive sulfite during the decomposition of tetrathionate, the reactions may be assumed to proceed according to

$$2SS^*O_3^{=} + 3HgCl_2 + 2H_2O \longrightarrow HgCl_2 \cdot 2HgS + 2S^*O_4^{=} + 4Cl^- + 4H^+$$

$$2SS^*O_3^{=} \longrightarrow O_3S^*SSS^*O_3^{=} + 2e^-$$

$$2O_3S^*SSS^*O_3^{=} + 3HgCl_2 + 4H_2O \longrightarrow HgCl_2 \cdot 2HgS + 4S^*O_4^{=} + 4Cl^- + 8H^+ + 2S$$

If tetrathionate, obtained by titration of the same thiosulfate with iodine, was reduced immediately with inactive sulfide (in presence of inactive bisulfite and excess formaldehyde), the sulfur formed was inactive. The filtrates from this reaction were analyzed with mercuric chloride both directly, and after they had been titrated back to tetrathionate. In the first case the activity distribution was found to be: 1% in I, 96% in II, 1–2% in III; in the second case: 1% in I, 95% in II and 3% in III.

The activities found in all fractions I may well be introduced into the thio-S of the thiosulfate by side-reactions during its formation.

If tetrathionate was prepared from thiosulfate labeled at the thio-S, 2–3% of the total activity was always found in the solid sulfur; if inactive tetrathionate was reduced with active sulfide, 97% was found in the sulfur.

The results indicate that, save for a minor side-reaction, the reduction of tetrathionate with sulfide proceeds according to

$$O_3S^*S^\dagger S^\dagger S^*O_3^{=} + S^- \longrightarrow 2S^\dagger S^*O_3^{=} + S$$

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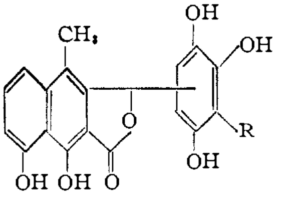
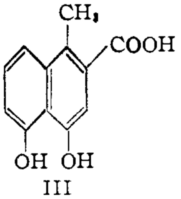
TERRAMYCIN. V. STRUCTURE OF TERRINOLIDE. AN ACID DEGRADATION PRODUCT OF TERRAMYCIN

Sir:

Among the products formed by the degradation of terramycin[1] in dilute hydrochloric acid at elevated temperatures is terrinolide (I), $pK_{a_1} = 4.6$, $pK_{a_2} = 7.5$ (dimethylformamide–water); $[\alpha]_D$ $-16.0°$ (c 1% in 1:1 methanol–0.1 N hydrochloric acid). *Anal.* Calcd. for $C_{20}H_{15}NO_8$: C, 60.45; H, 3.81; N, 3.53. Found: C, 60.46; H, 4.10; N, 3.52. On hydrolysis in hot 12 N sulfuric acid, terrinolide loses ammonia and carbon dioxide to yield a nitrogen-free, optically-inactive compound, decarboxamidoterrinolide (II),[2] $pK_{a_1} = 4.7$, $pK_{a_2} = 10.2$ (dimethylformamide–water). *Anal.* Calcd. for $C_{19}H_{14}O_7$: C, 64.41; H, 3.98; C-methyl, 4.25. Found: C, 64.10; H, 4.41; C-methyl, 3.82. Pentamethyldecarboxamidoterrinolide: m.p. 152–153°, *Anal.* Calcd. for $C_{24}H_{24}O_7$: C, 67.91; H, 5.70; CH_3O, 36.55. Found: C, 67.85; H, 5.74; CH_3O, 35.95. Terrinolide and decarboxamidoterrinolide have been assigned structures I and II, respectively.



I, R = $CONH_2$
II, R = H



III

Alkali fusion of II yields 1,8-dihydroxy-4-methyl-3-naphthoic acid (III).[3] I, II and III enhance the

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(1) P. P. Regna, I. A. Solomons, K. Murai, A. E. Timreck, K. J. Brunings and W. A. Lazier, THIS JOURNAL, **73**, 4211 (1951).

(2) Terrinolide and decarboxamidoterrinolide were originally assigned the formulas $C_{18}H_{17}NO_8$ and $C_{18}H_{12}O_6$, respectively, in our first Communication (R. Pasternack, P. Regna, R. Wagner, A. Bavley, F. Hochstein, P. Gordon and K. Brunings, THIS JOURNAL, **73**, 2400 (1951)). The formation of stable solvates and a tendency of these compounds to decompose under conditions of molecular weight determination complicated the assignment of the molecular formulas.

(3) F. A. Hochstein, *et al.*, to be published.