EXCHANGE REACTIONS WITH RADIOSULFUR

Sir:

Using a radioactive isotope, we studied the interchange of sulfur between a number of its inorganic compounds in aqueous solutions. The radioactive sulfur (S^{35}) was produced by neutron bombardment of carbon tetrachloride [E. B. Andersen, *Z. physik. Chem.*, **B32**, 237 (1936)], and also by deuteron bombardment of sulfur (thanks are due to Professors E. O. Lawrence and E. M. McMillan and Dr. J. J. Livingood of the Radiation Laboratory of the University of California for the radiosulfur). It was freed of radioactive impurities by oxidation to sulfate, addition of phosphate and precipitation of ammonium phosphomolybdate. Activities were determined in a screen-walled counter constructed so that zero readings could be taken with the sample in place [Libby, *Phys. Rev.*, **46**, 196 (1934)].

Sulfide and sulfate did not show appreciable interchange in thirty-six hours at 100°. In the experiment sodium sulfide was added to an oxygen-free, alkaline solution of radioactive sulfate, and the mixture was heated to 100°. After the stated time it was acidified and the hydrogen sulfide was removed and oxidized. The barium sulfate from the sulfide gave a count of 0 ± 16/min. while that from the sulfate gave 680 ± 30/min.

An interchange between sulfite and sulfate, involving only a shift of an oxygen atom, seemed somewhat more probable, but it likewise did not occur. The experiment was carried out in much the same fashion as that with sulfide, again using a radioactive sulfate. After thirty-six hours at 100° the products showed the following activities: $BaSO_4$ from SO_3^{--}, 5 ± 8/min.; $BaSO_4$ from SO_4^{--}, 446 ± 40/min.

Sulfide and thiosulfate might be expected to show an effect, and it was found that they did. Active hydrogen sulfide was generated from barium sulfide produced by reduction of barium sulfate with carbon, and was passed with a stream of purified nitrogen into an alkaline thiosulfate solution. The oxygen-free solution was sealed in a Pyrex flask, heated for the desired time, and cooled. The sulfide was precipitated as lead sulfide and the thiosulfate was oxidized to sulfate and precipitated as barium sulfate. The results are tabulated, the numbers being counts/min.

Time, hrs.	*Temp.*, °C.	PbS	$BaSO_4$
28	20	234 ± 40	0 ± 14
24	57	154 ± 30	0 ± 20
2	100	230 ± 40	0 ± 20
23	100	228 ± 12	198 ± 16
25	100	44 ± 12	28 ± 12

Because the radioactivity of sulfur is very soft (beta particles of about 125,000 volts upper limit), the self-absorption error is high and the counts lack quantitative significance. However, it is certain that the exchange is not appreciable in less than two hours at 100°. This slow interchange contrasts sharply with the rapid exchange of oxygen between trisodium phosphate and water, which Blumenthal and Herbert [*Trans. Faraday Soc.*, **33**, 849 (1937)] found to be complete in two hours at room temperature. The mechanism of both interchanges may involve a substitution reaction of the type $S^{*--} + S_2O_3^{--} = S^*SO_3^{--} + S^{--}$, but in the case of the thiosulfate a mechanism involving the reaction $S_2O_3^{--} + S^{--} = SO_3^{--} + S_2^{--}$ seems possible.

That the latter reaction could be effective in the sulfide–thiosulfate interchange was shown by an experiment on polysulfide. An oxygen-free solution of ammonium sulfide was prepared. Radioactive sulfur was added, and the solution was shaken and heated at 100° until the sulfur had dissolved. This took nearly an hour. The solution was then acidified and the hydrogen sulfide was passed into lead acetate solution. The sulfur precipitated was oxidized to sulfate. The counts, 582 ± 50/min. for the lead sulfide from the S^{--} and 332 ± 40 for the barium sulfate from the S, indicated complete interchange.

It is planned to continue the experiments, and also to study gaseous reactions where some of the circumstances are simpler.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

H. H. VOGE
W. F. LIBBY

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