tion of Animal Bones." In any case, for 55 years anthropology has been deprived of an important objective argument in favor of the antiquity of man in America.

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The Formation of Free Alkoxy ($RO\cdot$) Radicals in Solution

Many investigators,[1] on the basis of indirect evidence, have postulated the formation of alkoxy ($RO\cdot$) free radicals in the course of the decomposition of hydroperoxides by ferrous salts. Direct evidence of the formation of such radicals in the aqueous phase has been obtained by carrying out the decompositions in the presence of butadiene. The products identified are accounted for by reaction sequences of the following type.

$$ROOH + Fe^{++} \rightarrow RO\cdot + FeOH^{++} \qquad (1)$$

$$RO\cdot + H_2C{=}CHCH{=}CH_2 \rightarrow ROCH_2CH{=}CHCH_2\cdot \qquad (2)$$

$$2ROCH_2CH{=}CHCH_2\cdot \rightarrow (ROCH_2CH{=}CHCH_2—)_2 \qquad (3)$$

The yields of dimer vary somewhat with the nature of the hydroperoxide decomposed. With butadiene the best yield (85%) was obtained by decomposing *t*-butyl hydroperoxide; decomposition of α-cumyl hydroperoxide and hydrogen peroxide yielded, respectively, 65% and 30% of the dimeric products.

Butadiene forms, in addition to the dimer formulated in equation 3, smaller amounts (15–20%) of isomeric products—probably $[ROCH_2(H_2C{=}CH)CH—]_2$, together with some $ROCH_2CH{=}CHCH_2CH(CH{=}CH_2)CH_2OR$. These isomeric products have been separated from the principal dimeric product $[(ROCH_2CH{=}CHCH_2—)_2]$ by fractional distillation under reduced pressure.

The carbon-hydrogen content and the molecular weight of the principal dimer are consistent with the empirical formula given above. Evidence of structure has been obtained by ozonolysis and oxidation to succinic acid (isolable to the extent of 80% of the calculated amount), and by hydrogenation and subsequent hydrolysis of the saturated diether. These procedures gave the 1,8 glycol, which was identified by conventional methods.

It is of interest that, when hydroperoxide decomposition is carried out in the presence of a polyamine (e.g., triethylenetetramine) and traces of an iron salt, the butadiene product formed is of the type $ROCH_2CH{=}CHCH_2OH$.[2] This fact suggests that, under the specified conditions, the intermediate free radical (formed as indicated in equation 2) reacts with the hydroperoxide.

$$ROCH_2CH{=}CHCH_2\cdot + ROOH \rightarrow ROCH_2CH{=}CHCH_2OH + RO\cdot \qquad (4)$$

Additions of alkoxy free radicals to isoprene, to simple 1-alkenes, and to allyl alcohol have also been studied. They will be reported in detail in the near future.

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[1] For leading references see: Kharasch, Fono, and Nudenberg, *J. Org. Chem.*, **15**, 763 (1950).

[2] These experiments were carried out with E. H. White.

Formation of Colloidal Sulfur

THE recent article by Akiya, Nomato, and Okui (*Science*, **112**, 463 [1950]) concerning the effect of ultrasonic waves and nitrous acid on the production of colloidal sulfur prompts the writer to report on some work done at the University of Wisconsin by C. H. Sorum and the undersigned.

The kinetics of the reaction between thiosulfate ion and nitrite ion in dilute aqueous acid were studied, using the change in pH with time and the change in thiosulfate ion concentration with time. The rate law was found to be

$$\frac{-d[S_2O_3^{=}]}{dt} = k[NO_2^{-}]^{1.0}[S_2O_3^{=}]^{0.2}[H^{+}]^{2.0}.$$

Since both iodine titer and hydrogen ion concentration decreased in the course of this reaction, indicating the formation of $S_4O_6^{=}$, it is hard to reconcile these data with the conclusions of the authors of the above-mentioned article (for their mechanism would hold if the iodine titer and hydrogen ion concentrations increased).

In our studies, the reaction was observed to take up hydrogen ions quite rapidly in acid solution, for the half-life of the reaction at pH 4.0 is less than 1 min. The formation of elemental sulfur is dependent on the concentrations of thiosulfate ion and hydrogen ion, a fact well demonstrated by the work of La Mer and co-workers (Kenyon and La Mer, *J. Colloid Sci.*, **3**, 163 [1949] and preceding papers). If one assumes the following stoichiometry,

$$2HNO_2 + 2S_2O_3^{=} + 2H^{+} \rightarrow S_4O_6^{=} + 2NO + 2H_2O,$$

a simple and consistent explanation for the retardation of colloidal sulfur formation by nitrous acid is obtained.

The yellow color, which was ascribed to an unstable intermediate in the first-mentioned article, was observed in our kinetic investigation. Since the rate of its appearance qualitatively followed the reaction rate law for thiosulfate oxidation, we feel it is probably nitrogen dioxide formed by oxygen and nitric oxide.

If desired, further details may be obtained from the writer, or from the thesis filed in the library of the University of Wisconsin at Madison, Wisconsin. As much work remains to be done before a satisfactory mechanism can be postulated, we are not planning any publication of our material at this time.

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