was faster than diffusion. (3) The rate of exchange of hydrogen chloride gas is faster than the rate of exchange of methylene chloride (expt. 3a, b, c, d) (other halogenated methanes which we have tested show much faster exchange, however). (4) Detectable exchange of hydrogen chloride gas with aluminum chloride occurs at −80° and the temperature coefficient of the exchange is low (expt. 4). (5) The exchange may be observed with vacuum sublimed commercially produced aluminum chloride (expt. 6) as well as with aluminum chloride synthesized *in situ* (expt. 1, 2, 3, 4, 5).

Because of the fact that negative results have been reported in an attempt to measure the exchange[1] we have sought tests which would be as conclusive as possible in demonstrating that the results which we have observed are not due to causes other than exchange. Thus, the fact that hydrogen chloride picks up more activity than methylene chloride, when exposed to the same aluminum chloride surface at the same pressure and transferred in the system in the same way, eliminates the possibility that bulk transfer of aluminum chloride to the counter or other physical effects are involved. Transfer of aluminum chloride as a spurious indication of exchange is also eliminated by the fact that exchange was observed when the activity was initially in the hydrogen chloride, and yet again by an analysis for aluminum in the hydrogen chloride fraction from expt. 2. The latter analysis showed aluminum equivalent to only 0.25% of the aluminum used in the reaction. In order to demonstrate the absence of radioactive hydrogen chloride which would have been produced by hydrolysis if water were present as an impurity in expt. 2 the aluminum chloride reactant was analyzed for aluminum and chlorine after the reaction. The ratio was found to be 0.256 in agreement with the calculated value of 0.2535 for $AlCl_3$.

The absence of exchange in the experiments of Richardson and Benson at room temperature may have been due to the method of preparation of their aluminum chloride. An example of the sensitivity of such surfaces to small differences in treatment is the fact that aluminum chloride prepared *in situ* by our method and subsequently exposed briefly in a "dry-box" to nitrogen which had been dried by passage through magnesium perchlorate always exchanged chlorine with carbon tetrachloride much less readily than aluminum chloride which had not been so exposed.[5] This presumably was due to small amounts of residual moisture in the dry-box atmosphere, since no effect on the reactivity was observed as a result of exposing a similar surface in a vacuum system to air dried by passing through a long train of phosphorus pentoxide.[2]

In order to determine whether aluminum chloride prepared by the *in situ* synthesis we have used has a greater ability to form a stable compound with hydrogen chloride than that investigated by other workers,[1,6] Mr. James Reavis of our laboratory has made adsorption measurements of the pressure–volume type. These show that there is no reaction at room temperature and 500 mm. pressure in excess of that which might be expected from slight physical adsorption.

It is impossible to state the mechanism of the exchange reported here on the basis of the facts available. The difficulty of obtaining identical aluminum chloride surfaces with which to test the influence of pressure and temperature of hydrogen chloride is a complicating factor in making quantitative studies. It seems clear from the work of Brown and Pearsall[6] and Richardson and Benson[1] and of more recent work in our laboratory, however, that the equilibrium concentration of $HAlCl_4$ must be extremely low.

It has been suggested[2] that the exchange between alkyl chlorides and solid aluminum chloride may be due to the fact that the aluminum chloride is an ionic crystal with localized spots of unsaturated charge on the surface which can adsorb molecules with permanent or induced dipoles by coulombic attraction. There is then the possibility that when the species leaves the surface it will do so with a different chlorine atom than came on. It may be that a process of this type is involved in the exchange of hydrogen chloride with aluminum chloride.

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[5] C. W. Herrmann, Ph.D. thesis, University of Wisconsin, 1949.

[6] H. C. Brown and H. Pearsall, THIS JOURNAL, **73**, 4681 (1951).

Tritiation of Multiple Bonds—Synthesis of Tritiated Styrene

BY IRVING A. BERSTEIN, WINIFRED BENNETT AND MELVIN FIELDS

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Tritium labeled styrene has been prepared by the reduction of acetophenone with tritium and subsequent dehydration of the methylphenylcarbinol. The reduction was carried out at room temperature and atmospheric pressure over platinum oxide. Dehydration of the carbinol in the presence of *p*-toluenesulfonic acid[1] gave a 79% yield of styrene of specific activity 0.66 mc./mm.

An apparatus for tritiation has recently been described.[2] A simpler, more convenient apparatus of general application is reported here that permits efficient utilization of tritium. The significantly different reaction rates of tritium and protium make it essential to use a reduction mixture as rich in tritium as possible. By the Toeplering procedure outlined below the effects of the differences in diffusion rates of tritium and protium are avoided and a very efficient transfer of tritium from the low pressure ampoule to the hydrogenation vessel is accomplished. Tritium assay of benzoic acid obtained from the oxidation of the tritiated styrene indicates that 9% of the total tritium in the styrene was introduced by exchange with protium on the benzene ring.

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[1] Procedure developed by M. A. Leaffer of this Laboratory.

[2] D. L. Williams and A. R. Ronzio, THIS JOURNAL, **72**, 5787 (1950).

Experimental

Apparatus and Procedure for Tritiation of Multiple Bonds.—The tritiation apparatus employed is illustrated in Fig 1. The hydrogenation bottle containing catalyst and material to be tritiated was placed in a mechanical shaker. The entire system with stopcock E open was evacuated with a water aspirator through stopcock A and flushed several times with tank hydrogen through stopcock G. An atmosphere of "cold" hydrogen is left in the bottle by closing stopcock B. With the system evacuated at 15–20 mm. pressure, stopcocks C and F closed, and the mercury at the top of the 350-ml. buret at stopcock D, the tritium ampoule is opened at the break seal. The mercury in the buret is pulled down with the Toepler pump at the base of the buret in order to transfer the tritium from the ampoule into the buret. Stopcock D is then closed and the pressure in the ampoule brought to 1 atm. with tank hydrogen. The gas in the ampoule was then pulled into the buret and Toeplered back and forth between buret and ampoule twice to ensure thorough mixing. This process was repeated until about 150 ml. of gas at 1 atm. pressure was contained in the buret. The shaker was then started, and after this quantity of gas was used in the reduction, stopcock B was closed and the above procedure repeated. In all, this method of removal of tritium and reduction with portions of 150 ml. of gas was carried out five times. The buret was then filled completely with tank hydrogen and the reduction allowed to go to completion. The apparatus should be employed in an efficient hood and since once used for tritiation it becomes contaminated; thereafter, it should be used for tritiation experiments only.

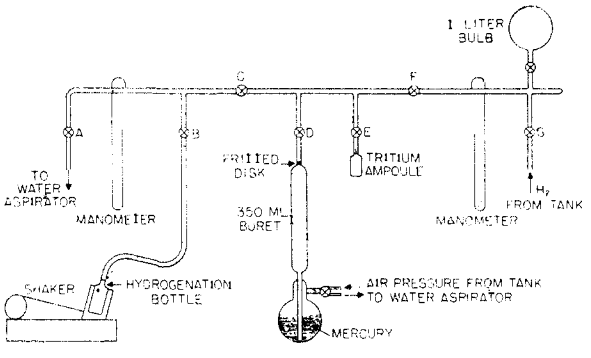

Fig. 1.—Tritiation apparatus.

Methylphenylcarbinol.—In a Parr hydrogenation bottle were placed 5.0 ml. of distilled acetophenone (b.p. 44–45°, 1 mm.) and 0.30 g. of platinum oxide catalyst. The reduction was carried out by the procedure described above employing a tritium ampoule containing 50 mc. (Oak Ridge value). The hydrogenation stopped by itself after 1158 ml. of gas was absorbed in 3.5 hr. (Theoretical uptake of hydrogen for reduction of acetophenone to carbinol was 1102 ml.). The organic material was dissolved in ether and filtered to remove the catalyst. After most of the ether had been distilled off at atmospheric pressure, the last traces were removed *in vacuo*. In a comparable cold run methylphenylcarbinol (b.p. 88°, 13.5 mm.) ($n^{25.5}_{\mathrm{D}}$ 1.5260) was isolated in 92% yield.

Dehydration of Methylphenylcarbinol to Styrene.—In the hot run, the tritiated methylphenylcarbinol, after the last traces of ether had been removed from it, was dehydrated directly without distillation.

To the flask containing the methylphenylcarbinol were added 10 mg. of picric acid and 5 mg. of *p*-toluenesulfonic acid and to the receiver 10 mg. of picric acid. With the bath temperature at 155–190°, the water and styrene distilled at 42–68° at 100 mm. pressure. After drying over anhydrous magnesium sulfate, 3.54 g. of styrene b.p. (62.5–63.5°, 60 mm.) ($n^{27}\mathrm{D}$ 1.5409) was obtained which represented a 79% yield based on acetophenone.

Analysis of this material for tritium indicated a specific activity of 0.66 mc./mm.

Oxidation of Styrene to Benzoic Acid.—In order to determine whether any tritium had been introduced into the styrene by exchange of tritium with protium on the benzene ring, the tritiated styrene was oxidized to benzoic acid with potassium permanganate[3] and the benzoic acid analyzed for its tritium content.

To remove any tritium that might have exchanged with the carboxyl hydrogen during the oxidation, the benzoic acid was dissolved in 5% sodium hydroxide solution and allowed to stand for 30 minutes. The solution was acidified with sulfuric acid and chilled in an ice-bath for 30 minutes. The white solid was filtered, washed with cold water and again dissolved in sodium hydroxide. This process was carried out four times in all. The benzoic acid thus obtained was dried in an Abderhalden pistol (m.p. 122.8–123.0°).

Analysis for tritium content indicated 0.06 mc./mm. which would correspond to 9% of the total tritium in the styrene.[4]

Tritium Analyses.—Analyses for tritium were accomplished by combustion of the organic compound on a semimicro scale and conversion of the tritiated water to tritium.[5] The tritium gas was then counted in an ionization chamber in conjunction with a Lindemann–Ryerson electrometer.[6] The equivalence of rate of discharge of the electrometer (mv./sec.) per millicurie of tritium was established with aliquots of tritium obtained by manometric dilution of several tritium ampoules of given activity as supplied by Oak Ridge National Laboratory.

Acknowledgment.—We wish to thank Mr. John J. Rohan for valuable assistance on the manometric dilutions of the tritium gas.

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(3) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 164.

(4) If there were no preferential formation of C–T bond over C–H bond, then calculating from the values of the specific activities of the tritiated styrene and the tritiated benzoic acid, the specific activity of the carbinol should have been 1.26 mc./mm. Even if all of the 50 mc. of tritium in the ampoule had been introduced into the acetophenone, theoretically the maximum value of the specific activity of the carbinol would have been 1.16 mc./mm.

This observed discrepancy between the theoretical and computed values of the specific activity of the carbinol can be attributed to one or more of the following factors: (a) The values assigned by Oak Ridge for the tritium content of the 50 mc. ampoule and for several ampoules used in the standardization of the analytical procedure may have been in error. (b) The error of the analytical procedure employed is within ±5–10%. (c) There may be a preferential formation of the C–T bond or O–H bond over a C–H bond and O–T bond in the reduction of acetophenone with H–T.

L. C. Anderson and N. W. MacNaughton (THIS JOURNAL, **64**, 1456 (1942)) have reported preferential formation of the C–D bond in the reduction of the carbonyl group with H–D over Raney nickel. However, they observed no such selectivity with a platinum catalyst at room temperature. They established that the observed effects were not due to exchange reactions under the conditions of the hydrogenation.

A preferential reaction of H–T with a carbonyl group would seem possible. If less than 100% of the tritium were introduced into the acetophenone, as is likely, the effect is even more significant. It is hoped that further work will help determine whether in catalytic reductions of carbonyl compounds with H–T such preferential formation of C–T bond actually occurs.

(5) F. C. Henriques, Jr., and C. Margnetti, *Ind. Eng. Chem.*, **18**, 420 (1946).

(6) C. D. Janney and B. J. Moyer, *Rev. Sci. Instruments*, **19**, 667 (1948).

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The Heat of Formation of Ferrocene

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Ferrocene has been prepared[1] by reaction of cyclopentadienylmagnesium bromide with ferric chloride, and also, by the direct action of cyclopentadiene on a "doubly-promoted Haber cat-

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(1) T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).