be much more vulnerable in the reaction mixture prior to precipitation. Moreover, it is to be expected that cyclohexanone would compete poorly with chloramine for hydroxylamine. Quantitative rate data on the formation of cyclohexanone oxime are not available; the author's qualitative observations indicate it is slow. The rate of reaction in neutral solution of hydroxylamine with acetone,[2,3] which is much more soluble than cyclohexanone, is considerably slower than the reaction of hydroxylamine and chloramine. Both reactions are base catalyzed, but it is not certain whether the order of rates is altered in very concentrated sodium hydroxide solution.

The low yield of oxime does not appear to require any path other than equations 1 and 2 for the disappearance of chloramine, and all observations made here are consistent with this as the sole path. Since the completion of this work, the author has learned of a broad program of experimental work by Dr. L. F. Audrieth and co-workers at the University of Illinois which may ultimately show that this picture of the reaction is oversimplified and perhaps incomplete. The evidence obtained here does not exclude other reaction paths, but appears at least to establish that hydroxylamine is present as an intermediate during the reaction.

Preparation and Purity of Chloramine Solutions.— Chloramine solutions were prepared by the method of Coleman and Hauser,[4] using commercial sodium hypochlorite. In some cases the solutions were purified by vacuum distillation, but no gross difference in behavior of initial and purified solutions was observed so long as ammonium and bicarbonate ions were absent. Bicarbonate ion was found to hasten the decomposition of chloramine in a manner not related to pH. Ammonium ion appears to slow decomposition of chloramine by hydroxide or bicarbonate.

Acknowledgment.—The author is grateful to Dr. Turner Alfrey for helpful suggestions during this work, and to H. W. Rinn and R. F. Bremer for the X-ray analyses.

(2) S. F. Acree and J. M. Johnson, *Am. Chem. J.*, **38**, 258 (1907).

(3) E. Barrett and A. Lapworth, *J. Chem. Soc.*, **93**, 85 (1908).

(4) G. H. Coleman and C. R. Hauser, THIS JOURNAL, **50**, 1193 (1928).

PHYSICAL RESEARCH LABORATORY
THE DOW CHEMICAL COMPANY
MIDLAND, MICHIGAN

The Mercury-photosensitized Reactions of Tritium with Acetylene and Ethylene

BY LOUIS KAPLAN

RECEIVED NOVEMBER 20, 1953

As a part of a study of the feasibility of introducing tritium into organic molecules by reaction with hydrogen atoms produced by mercury photosensitization, experiments were performed on systems containing acetylene and ethylene. Since there appears to have been no previous investigation of the isotopic composition of the products obtained from either of these hydrocarbons by reaction with a mixture of hydrogen isotopes under these conditions, the results of these measurements are reported here.

Experimental

Apparatus.—The reaction vessel consisted of a quartz tube irradiated with two four-watt General Electric "Ger-micidal" lamps. The reaction mixture was circulated through the irradiated tube by means of a Toepler pump which also served as a mercury saturator. The system, which also included a manometer, had a volume varying from 300 to 600 cc., depending on the position of the mercury in the pump.

Reagents.—Tritiated hydrogen was prepared from tritiated water by reaction with heated zinc. After passage through a trap at $-195°$ it was diluted with electrolytic hydrogen which had been passed through a "Deoxo" catalytic purifier and then through silica gel at $-195°$. The final tritium content was about 10 microcuries per millimole.

Ethylene and acetylene obtained from the Matheson Chemical Co. were subjected to low-temperature fractional distillation and the center cuts were used in the reactions. The vapor pressures of these fractions remained unchanged by additional distillations.
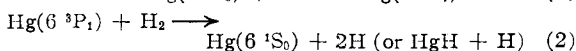
Procedure.—Hydrogen was used in large excess in order to minimize quenching by the hydrocarbons. The hydrocarbon and tritiated hydrogen were measured into the highly evacuated system, and were mixed by operation of the Toepler pump. The total pressure was in the range of 200 to 400 mm. The mercury vapor lamps were turned on and irradiation was continued, in the experiment with ethylene, until the reaction became constant, in order to avoid the difficulty of separating ethylene from ethane. With acetylene, the reaction was stopped short of completion to permit the determination of the tritium content of the residual acetylene. After irradiation, the hydrocarbons were removed by circulating the reaction mixture through a trap at $-195°$. (Ethane, ethylene and acetylene were shown to be separated quantitatively in this way from synthetic mixtures with hydrogen; methane is an insignificant product from either reaction and could have little effect on the measured quantity or specific activity of the hydrogen.) The volume of hydrogen was measured manometrically and an aliquot was taken for the determination of its tritium content. The condensed hydrocarbons were transferred to a fractionation train. After each run the entire apparatus was flamed while oxygen was passed through it, in order to prevent the accumulation of polymer on the walls.

Separation of Products.—The mixture of hydrocarbons was subjected to fractionation[1] at low pressure through a train of traps maintained at successively lower temperatures. Each fraction was checked for purity by attempts at further fractionation as well as by measurement of its vapor pressure at several temperatures. Known mixtures of ethane, acetylene and butane were found to be separated quantitatively by this procedure.

Determination of Tritium.—A 10-cc. aliquot of the hydrogen, or the entire sample of hydrocarbon, was introduced into a 250-cc. ionization chamber[2] which was then filled to atmospheric pressure with propane. The ion current at saturation voltage was measured[3] with a vibrating reed electrometer.

Results and Discussion

Reactions[4] between hydrogen and hydrocarbons in the presence of mercury vapor irradiated with the mercury resonance line at 2537 Å. are initiated by the reactions

$$Hg(6\ ^1S_0) + h\nu \longrightarrow Hg(6\ ^3P_1) \qquad (1)$$

$$Hg(6\ ^3P_1) + H_2 \longrightarrow$$
$$Hg(6\ ^1S_0) + 2H \text{ (or } HgH + H) \quad (2)$$

The hydrogen atoms then react with the hydrocarbon to give free radicals which may react further in a variety of ways, including recombination, disproportionation, and attack on other molecules. If HT is present in the hydrogen, tritium atoms

(1) E. C. Ward, *Ind. Eng. Chem., Anal. Ed.*, **10**, 169 (1938); J. J. Savelli, W. D. Seyfried and B. M. Filbert, *ibid.*, **13**, 868 (1941).

(2) C. J. Borkowski, Atomic Energy Commission document, MDDC-1099, declassified June 12, 1947.

(3) K. E. Wilzbach, A. R. Van Dyken and L. Kaplan, Argonne National Laboratory document, ANL-5143.

(4) Mercury photosensitized reactions of hydrocarbons are reviewed in E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1946.
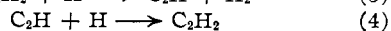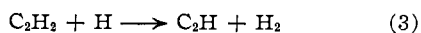
TABLE I

MERCURY-SENSITIZED HYDROGENATIONS

Reactants	Vol. cc.a	Mol. act.b	Vol. cc.a	Mol. act.b	Vol. cc.a	Mol. act.b	Vol. cc.a	Mol. act.b
C_2H_2	15.2		23.4		26.2			
C_2H_4							25.5	
H_2	129	1.00	213	1.00	220	1.00	225	1.00
Products								
H_2	127	1.00	196	1.02	202	1.03	210	1.01
C_2H_2	13.0	0.022	5.1	0.21	3.5	0.32		
C_2H_6	0.25		1.0	0.88	1.3	0.97	2.45	0.76
C_4H_{10}	0.25		0.6	1.4	0.75	1.5	8.0	0.64
"C_6" + "C_8"			0.75	1.04	0.92	1.03	2.4	0.55

a Cc. of gas at S.T.P. b Relative tritium content per mole of compound; initial $H_2 = 1.00$.
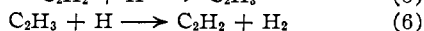
will be produced in reaction 2, and tritium may be introduced into the product either by reactions of tritium atoms or by reactions of free radicals with the HT molecules. Reactions involving HT molecules will, in general, occur more slowly than those involving H_2; tritium atoms may react either more or less rapidly than protium atoms.[5]

The results of several experiments are summarized in Table I. The distributions of reaction products are similar to those found in other investigations[6] of these reactions, except that the formation of the C_6- and C_8-hydrocarbons has not been reported previously. In the reaction with ethylene no polymer formation was observed and material and activity balances are good. In the acetylene reaction, large amounts of polymer formed on the quartz tube; from material balances, the ratio of H_2 to C_2H_2 in this polymer is about 0.6.

Perhaps the most unexpected result is the slowness of the exchange between hydrogen gas and acetylene compared to the rates of hydrogenation and polymerization. After 87% of the acetylene has been consumed, the ratio of the molar activity of acetylene to that of hydrogen is only 0.32; at equilibrium[7] this ratio should be about 3. This is in marked contrast to the reaction[8] of acetylene with deuterium atoms from a discharge tube which leads to almost complete exchange with little loss of acetylene. This difference in behavior is undoubtedly attributable to the much higher hydrogen atom concentration produced in the discharge tube, which favors the reactions[8]

$$C_2H_2 + H \longrightarrow C_2H + H_2 \qquad (3)$$
$$C_2H + H \longrightarrow C_2H_2 \qquad (4)$$

or

$$C_2H_2 + H \longrightarrow C_2H_3 \qquad (5)$$
$$C_2H_3 + H \longrightarrow C_2H_2 + H_2 \qquad (6)$$

whereas in the mercury photosensitized reaction the hydrogen atom concentration is kept so low by reaction 3 or 5 that the C_2H or C_2H_3 radical first formed has an opportunity to react with molecular hydrogen or acetylene.

It is of interest that the tritium content per mole of the ethane produced both from ethylene and

from acetylene is lower than that of the hydrogen in spite of the facts that the ethane from acetylene has incorporated two molecules of hydrogen, and that some of its tritium was introduced into the acetylene by exchange. The preferential incorporation of protium rather than tritium is in accord with expectation for reactions with molecular H_2 and HT; it might also result from a difference in the relative rate of production of protium and tritium atoms in reaction 2. Another point of interest is the ratio of the molar activity of butane to that of ethane. In the acetylene reaction this ratio is about 1.6, while in the ethylene reaction it is 0.8. From the postulate[9] that in both reactions the butane is formed by the recombination and the ethane by the disproportionation of ethyl radicals, it would be expected that these ratios would be the same, even though the molar activity of the ethyl radicals differed. The large difference between the observed ratios appears to be incompatible with such a postulate.

(5) J. Bigeleisen, J. Chem. Phys., 17, 675 (1949).

(6) D. J. LeRoy and E. W. R. Steacie, ibid., 12, 369 (1944); W. J. Moore and H. S. Taylor, ibid., 8, 504 (1940).

(7) Estimated from vibration frequencies in F. Halverson, ibid., 19, 87 (1947); using the method of calculation in H. C. Urey, J. Chem. Soc., 562 (1947).

(8) K. H. Geib and E. W. R. Steacie, Z. physik. Chem., B29, 215 (1935).

(9) Reference 4, pp. 261, 265, 268.

CHEMISTRY DIVISION
ARGONNE NATIONAL LABORATORY
LEMONT, ILLINOIS

Nitric Oxide Interference in Nitrogen Isotope Analyses with the Mass Spectrometer[1,2]

BY ROBERT L. ORY, J. M. PRESCOTT AND CARL M. LYMAN

While conducting biological studies involving N^{15} as a tracer, an abnormally high mass 30 peak was often encountered in the mass spectrometer curves particularly when large samples were oxidized by the Dumas method.[3] Of the two equations which may be employed to compute atom per cent. N^{15}, erratic values were obtained using the direct method, while the indirect method yielded consistent results. The former requires experimental values for mass 30 as well as for masses 28 and 29; the latter represents mass 30 in terms of masses 28 and 29 based on the statistical occurrence of the $N^{15}N^{15}$ molecule. Both methods should yield the same results within the experimental limits of the spectrometer. However, the

(3) J. B. Niederl and V. Niederl, "Organic Quantitative Microanalysis," John Wiley and Sons, Inc., New Yok,. N. Y. 1938, p. 60