hydrogen peroxide in 150 ml. of acetic acid was heated at 100° for 10 min. The solution turned very dark. After evaporation, the resinous residue was chromatographed on a column of 300 g. of neutral Woelm alumina (grade I). The fractions eluted with benzene were crystallized from acetone to give 1.5 g. of XIII (9%): m.p. 230–232°; infrared (KBr) 3200 (N–H), 1660 (carbonyl), and 1032 cm.$^{-1}$ (sulfoxide); ultraviolet inflection at 238 mμ (ϵ 8000).

Anal. Calcd. for $C_{10}H_{11}NO_2S$ (209.27): C, 57.39; H, 5.30; N, 6.69; S, 15.32. Found: C, 56.88; H, 5.50; N, 6.66; S, 15.22.

2,3,4,6-Tetrahydro-1H-5,1-benzothiazocine Hydrochloride (XII) from XI.—To a solution of 4 g. of lithium aluminum hydride in 400 ml. of anhydrous tetrahydrofuran was added slowly at 0° a solution of 3.9 g. of XI in 220 ml. of anhydrous tetrahydrofuran. The mixture was stirred 24 hr. at room temperature. After cooling in an ice bath, a saturated solution of sodium sulfate was added slowly until hydrogen evolution ceased; then crystalline sodium sulfate was added, and the mixture was filtered. The solution was evaporated, and the starting material was separated as material insoluble in ether (1 g., m.p. 188–192°). The ether solution was evaporated, the oily residue was dissolved in acetone, and an ethereal solution of hydrogen chloride was added. After evaporation to dryness, the residue was crystallized from 95% ethanol to give 1.1 g. of XII (25%): m.p. 216–220° with transformation above 205°; infrared (KBr) 2900, 2860, 2800 (–CH_2–), 2720–2410 (amino salt), and 1580 cm.$^{-1}$ (anilino C–N); ultraviolet λ_{max} 245–255 mμ (ϵ 5300) and 309–310 mμ (ϵ 1300).

Anal. Calcd. for $C_{10}H_{13}NS \cdot HCl$ (215.75): C, 55.67; H, 6.54; Cl, 16.43; N, 6.49; S, 14.86. Found: C, 55.44; H, 6.54; Cl, 16.36; N, 6.46; S, 14.99.

3-(2-Nitrobenzylsulfonyl)propionic Acid (XIV) from IX.—A solution of 4.8 g. of IX and 5 ml. of 30% hydrogen peroxide in 100 ml. of acetic acid was heated for 4 hr. at 100° and then evaporated. The crystalline residue was recrystallized from ether to give 5.2 g. of XIV (96%): m.p. 126–127°; infrared (KBr) 2700, 2570, 1700 (–COOH), 1524, 1342 (–NO_2), 1316, and 1130 cm.$^{-1}$ (–SO_2–); ultraviolet λ_{max} 251–258 mμ (ϵ 4900).

Anal. Calcd. for $C_{10}H_{11}NO_6S$ (273.27): C, 43.95; H, 4.06; N, 5.13; S, 11.73. Found: C, 44.00; H, 4.17; N, 4.93; S, 11.72.

3-(2-Aminobenzylsulfonyl)propionic Acid (XV) from XIV.—A solution of 5.2 g. of XIV in 300 ml. of methanol was hydrogenated over 0.5 g. of 10% palladium-on-carbon catalyst at room temperature and 90–115 p.s.i. pressure; then it was filtered and evaporated. The residue was crystallized from a methanol–ether mixture to give 4.6 g. of XV (99%): m.p. 168–172°; infrared (KBr) 3400, 3330 (–NH_2), 2740, 2640, 2530, 1710 (–COOH), 1318, and 1105 cm.$^{-1}$ (–SO_2–); ultraviolet λ_{max} 240–241 mμ (ϵ 7800) and 294–295 mμ (ϵ 3200).

Anal. Calcd. for $C_{10}H_{13}NO_4S$ (243.29): C, 49.37; H, 5.39; N, 5.76; S, 13.18. Found: C, 49.65; H, 5.46; N, 5.76; S, 13.47.

1,3,4,6-Tetrahydro-2H-5,1-benzothiazocin-2-one 5,5-Dioxide (XVI) from XV.—A boiling solution of 4.5 g. of XV in 1000 ml. of xylene was distilled slowly over 2 hr. After cooling, the crystalline starting material (4.2 g., m.p. 166–172°) was filtered, and the solution was evaporated. Recrystallization of the residue from acetone gave 100 mg. of XVI, m.p. 287–292°. The same cyclization occurred by melting XV at 200° for 10 min. From 3 g. of XV, 0.6 g. of XVI (22%) was obtained in this way. The spectral data for XVI are: infrared (KBr) 3200 (N–H), 1668 (carbonyl group), 1317, and 1115 cm.$^{-1}$ (–SO_2–); ultraviolet inflections at 234–235 mμ (ϵ 6500), 270 mμ (ϵ 490), 277 mμ (ϵ 320), and 300 mμ (ϵ 130).

Anal. Calcd. for $C_{10}H_{11}NO_3S$ (225.27): C, 53.32; H, 4.92; N, 6.22. Found: C, 53.82; H, 5.19; N, 6.19.

Acknowledgment.—We are indebted to Dr. A. Steyermark for the microanalyses, to Dr. V. Toome for the ultraviolet spectra, and to Mr. S. Traiman for the infrared spectra.

The Reaction of Carbon Tetrachloride in a Radiofrequency Glow Discharge[1a]

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The action of a glow discharge produced by radiofrequency energy on carbon tetrachloride in the gas phase at room temperature produces a chlorinated polymer, hexachloroethane, tetrachloroethylene, dichloroacetylene, hexachlorobenzene, and chlorine. These products are formed primarily through the initial generation of a trichloromethyl radical. Any dichlorocarbene is not present in sufficient amounts to be detected.

Several methods are generally available for the generation of free radicals in the gas phase.[2-7] This may be conveniently accomplished by electron impact in an electric discharge, thermally, or by photolysis. Electron impact in an electric discharge may be obtained by several known techniques: electrical discharge tubes, low-frequency discharge, radiofrequency discharge, and microwave discharge.[8] Little or no work on the decomposition of organic compounds in a radiofrequency discharge has been carried out and there are only a few reports of decomposition of organic compounds in a microwave discharge.[9]

Decomposition of carbon tetrachloride at reduced pressure over activated carbon at 1200–1350° has been carried out.[10,11] The preliminary report,[10] which disclosed the isolation of dichlorocarbene, was later corrected[11] to show that the dichlorocarbene reported was actually a mixture of dichloroacetylene and chlorine in equal molar amounts. The trichloromethyl radical was demonstrated to be the primary decomposition fragment, as is the case in the thermal decomposition of carbon tetrachloride under reduced pressure without a catalyst.[12,13] The mass spectral analysis of the particles from the decomposition of carbon tetrachloride

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(1) (a) Presented at the International Symposium on Organic Reaction Mechanisms, Cork, Ireland, July 20–25, 1964; Abstracts of Papers, p. 53; (b) to whom correspondence concerning this paper should be sent.

(2) G. Glockler and S. C. Lind, "The Electrochemistry of Gases and Other Dielectrics," John Wiley and Sons, Inc., New York, N. Y., 1939.

(3) C. L. Thomas, G. Egloff, and J. C. Morrell, *Chem. Rev.*, **28**, 1 (1941).

(4) E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. I and II, Reinhold Publishing Corp., New York, N. Y., 1954.

(5) G. J. Minkoff, "Frozen Free Radicals," Interscience Publishers, Inc., New York, N. Y., 1960.

(6) A. M. Bass and H. P. Broida, Ed., "Stabilization of Free Radicals at Low Temperature," National Bureau of Standards Monograph 12, U. S. Government Printing Office, Washington, D. C., 1960.

(7) Papers presented at the Fourth International Symposium on Free Radicals Stabilization, Trapped Radicals at Low Temperature, Uppsala, Sweden. Aug. 31, Sept. 1 and 2, 1959.

(8) A. M. Bass and H. P. Broida, Ed., "Formation and Trapping of Free Radicals," Academic Press Inc., New York, N. Y., 1960.

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(10) M. Schmeisser and H. Schröter, *Angew. Chem.*, **72**, 349 (1957).

(11) M. Schmeisser, H. Schröter, H. Schildre, J. Massonne, and F. Rosskopt, *Ber.*, **95**, 1648 (1962).

(12) G. LeMoan, *Compt. rend.*, 2462 (1962).

(13) L. A. Errede and J. P. Cassidy, *J. Phys. Chem.*, **67**, 69 (1963).

under reduced pressure on a tungsten ribbon at 1000–1800° has revealed, however, a CCl_2 species.[14]

In the present work, we report the radiofrequency decomposition reaction of carbon tetrachloride.

Experimental

Apparatus.—The apparatus (Figure 1) was made up of Pyrex glass. The radiofrequency generator[15] was built to develop a maximum output of 600 w. at a fixed frequency of 14 Mc. It consists of a 7-Mc. crystal-controlled oscillator, a frequency doubler, final amplifier, and appropriate power supplies. The output can be continuously adjusted from 0 to 600 w. by means of a variable transformer that energizes the high-voltage power supply for the final amplifier and can be varied through the full range of power without influencing the frequency to which the unit is tuned. The final amplifier is also designed to operate under a wide range of loads without affecting the tuning. The alternating current output of the generator flows through a coil of copper tube (B) that surrounds the glass reaction tube (C). The ends of the coil are connected to the amplifier through capacitors for insulation from the high voltage that energizes the final stage. The reaction tube (C) is connected to a series of traps which are set at −20 (D), −40 (E), −80 (F), and −196° (G). A mercury pump is connected to the end of the series of traps and to a manometer.

Radiofrequency Decomposition Reaction of Carbon Tetrachloride.—The reactant was frozen at −80°, the Dry Ice–actone bath was removed, and an empty dewar flask was placed around the tube containing reactant. Once the reduced pressure of 1 μ was reached, the generator was turned on, carbon tetrachloride was introduced into the reaction tube, and a dim glow discharge was maintained. The vacuum pump was then turned off.

After 6 hr., 2.1 g. (0.0135 mole) of carbon tetrachloride had passed through the radiofrequency field. The compound in the −20 and −40° traps was hexachloroethane. The infrared spectra of the hexachloroethane from the reaction and that of the authentic sample were identical. The melting point of a mixture of the unknown compound with the authentic sample was not depressed (186–187°).

The mixture of compounds from the −80° trap (F) was analyzed by means of the gas chromatograph (F & M Model 500). A diisodecyl phthalate column at a column temperature of 125° with a flow rate of helium gas of 30 cc./min. was used. Two components were observed. By comparing the retention times and infrared spectra of the unknown compounds with the authentic samples, the two peaks were identified as carbon tetrachloride and tetrachloroethylene.

The compounds from the −196° trap (G) were analyzed by a gas chromatograph (Perkin-Elmer Model 154). A diisodecyl phthalate column at a column temperature of 25° with a flow rate of helium gas of 30 cc./min. was used. Two components were observed. By comparing the retention times with the authentic samples and the infrared spectra of the mixture with an authentic mixture, the two compounds were identified as chlorine and phosgene. Dichloroacetylene was not isolated from the −196° trap (G) by vapor fractometry since it was rapidly converted to phosgene by small amounts of air.[11] An infrared spectrum of the mixture of chlorine and dichloroacetylene directly from trap (G) was obtained, however; the spectrum corresponded to that reported for dichloroacetylene.[11]

In one experiment, the gaseous products from the −196° trap were aged at room temperature in the absence of air for 1 month. Upon gas chromatographic analysis of the products using a diisodecyl phthalate column and the same operation conditions as before, hexachloroethane and hexachlorobenzene were found.

The yields[16] of all the products from a typical run of the radiofrequency decomposition reaction of carbon tetrachloride are polymer 1.4%, hexachloroethane 23.8%, tetrachloroethylene 4.3%, chlorine 11%, dichloroacetylene (as phosgene) 21%, and carbon tetrachloride 38.5%. Another run in which the reactant was kept frozen at −80° throughout the whole reaction, which provided a lower pressure, a slower rate of passage, and thus a higher ratio of power per fragment in the discharge zone, produced a 95% conversion to products as follows: polymer 20%, hexachloroethane 24.5%, tetrachloroethylene 15.5%, chlorine 17%, and dichloroacetylene (as phosgene) 18%.

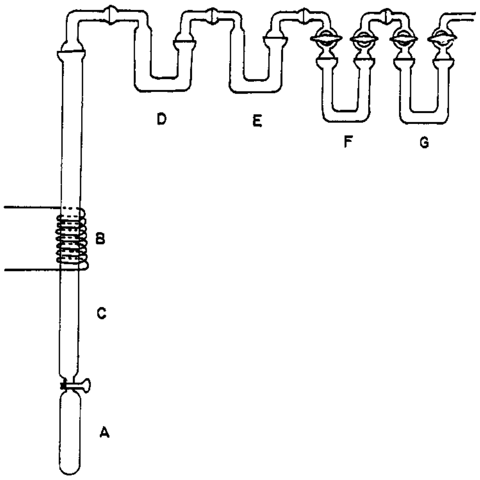

Figure 1.

Dichlorocarbene Trapping Experiments.—Carbon tetrachloride was frozen at −80° and the trapping agent, tetramethylethylene, was cooled to −50° so that an excess of carbon tetrachloride compared to tetramethylethylene would be introduced into the reaction tube at a position just above the radiofrequency field. Only two traps (−80 and −196°) were used. A dim blue glow discharge was maintained.

After 5 hr., 0.51 g. (0.61 mmole) of tetramethylethylene and 4.76 g. (3.36 mmoles) of carbon tetrachloride had passed through the reaction tube. The products in the −80° trap were analyzed by a gas chromatograph (F & M Model 500). The operating conditions were the same as those used to analyzed the products from the −80° trap from the carbon tetrachloride radiofrequency decomposition reaction. Five major peaks were found and the products were separated. None of the products was 1,1-dichloro-2,2,3,3-tetramethylcyclopropane. An authentic sample[17] of the cyclopropane derivative was injected into the gas chromatograph, but its retention time did not correspond to any one of the five peaks. Chloroform was found to be one of the products from this trapping experiment.

In a second experiment, a reaction tube with a liquid nitrogen cold finger positioned just downstream from the discharge zone was used. Tetramethylethylene was first condensed on the cold finger, carbon tetrachloride was then passed through the radiofrequency field, and the decomposition products were also condensed on the cold finger. The radiofrequency generator power was turned to a minimum and the liquid nitrogen was allowed to evaporate. The warm-up products were transferred into the −80° trap under reduced pressure. After condensation of the tetramethylethylene the radiofrequency reaction was then resumed in the same manner as before. This process was repeated until 2.59 g. of the products was collected in the −80° trap. The products were analyzed as in the first experiment and the same number of product was found to be produced. 1,1-Dichloro-2,2,3,3-tetramethylcyclopropane was not one of the products.

Discussion

The reaction of carbon tetrachloride in a glow discharge produced by a radiofrequency-generated electromagnetic field is one which produces hexachloroethane, tetrachloroethylene, dichloroacetylene, hexachlorobenzene, chlorine, and chlorinated polymer. These same products plus a small amount of hexachlorobutadiene are formed from the thermal decomposition of carbon tetrachloride under reduced pressure over a carbon catalyst at 1200–1350°.[11] The fast-flow pyrolysis without a catalyst at 1000° gives hexachloroethane, tetrachloroethylene, hexachlorobenzene, and chlorine.[13] Any dichloroacetylene generated is possibly consumed

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[14] L. P. Blanchard and P. L. Goff, *Can. J. Chem.*, **35**, 89 (1957).

[15] F. Swift, Jr., *Sci. Am.*, **209**, No. 1, 146 (1963).

[16] The yields are percentages by weight.

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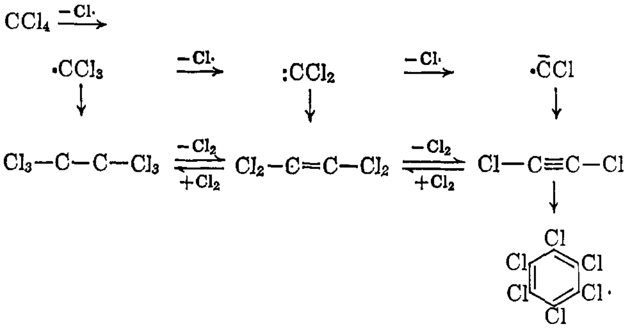
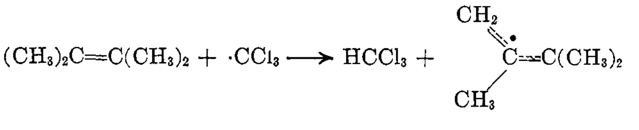
by the formation of hexachlorobenzene. By contrast, at 800° dichloroacetylene is observed but no tetrachloroethylene.[12] These products may be formed according to the following reaction scheme.



Any one of the three reactive species, the trichloromethyl radical, dichlorocarbene, or chloromethyne, could be the primary species responsible for the products. Coupling of the trichloromethyl radical would give hexachloroethane. It has been shown that thermal dechlorination of hexachloroethane to tetrachloroethylene takes place readily,[18] so that this path for the radiofrequency decomposition is not unreasonable. Dichlorocarbene, shown to be present in carbon tetrachloride pyrolysis by mass spectral analysis,[14] must be considered as another possible highly reactive intermediate.

An increase of the ratio of radiofrequency power per gaseous particle in the discharge zone produced a higher yield of tetrachloroethylene at the expense of hexachloroethane. This may be interpreted as either that the trichloromethyl radical was better able to eject another chlorine atom or that hexachloroethane was better able to lose chlorine.

It has been observed, however, that the generation of dichlorocarbene in the gas phase produces, among other products, some hexachlorocyclopropane.[19] We were not able to detect any hexachlorocyclopropane in our products. When tetramethylethylene was present in the gas phase immediately downstream from the discharge zone during the reaction, or when the products from the reaction were allowed to impinge on a liquid nitrogen cold finger immediately past the discharge zone and coated with tetramethylethylene, no dichlorotetramethylcyclopropane was obtained. Instead, chloroform was observed among the products. These



$$(CH_3)_2C{=}C(CH_3)_2 + \cdot CCl_3 \longrightarrow HCCl_3 + \overset{CH_2}{\underset{CH_3}{\dot{C}}}{=}C(CH_3)_2$$

results can only be interpreted to mean that the trichloromethyl radical is the primary reactive species responsible for the formation of the observed products and that if dichlorocarbene is produced, it is undetectable by these experiments.

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The Reaction of Benzene in a Radiofrequency Glow Discharge[1]

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The action of a glow discharge produced by radiofrequency energy on benzene in the gas phase at room temperature produces a complex mixture of products, the most prevalent of which are poly(*p*-phenylenes), biphenyl, fulvene, acetylene, allene, and methylacetylene. By employing deuterium as a trapping agent for the phenyl radical, deuterated benzene was formed in high yield. The emission spectrum of the phenyl radical was observed.

Extensive studies on the decomposition of inorganic and organic compounds in an electric discharge have been carried out.[2,3] There has been little or no work, however, on the decomposition of complex organic compounds in a microwave of radiofrequency glow discharge.[4]

The reaction of benzene under electron impact in an electrode discharge tube gives a variety of products, most of which are of higher molecular weight than benzene.[5] The reaction of benzene in an electrodeless system, a microwave discharge, has also been shown to afford higher molecular weight products as well as appreciable fragmentation products.[6] In this paper, we report some observations on the reaction of benzene in a glow discharge produced by a radiofrequency field.

Experimental

Apparatus.—The apparatus was made up of Pyrex glass, and its manipulation was effected as previously described.[7] The radiofrequency generator, which operates at 14 Mc. with an output up to 600 w. provided the energy for the discharge. The reaction tube was connected to a series of traps which were set at −20, −70, −80, and −196°.

Radiofrequency Decomposition Reaction of Benzene.—A sample tube containing 30 g. of thiophene-free benzene was frozen at −30°. In 7.5 hr., 19.63 g. of benzene was passed through the radiofrequency field. The approximate residence

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[1] Presented at the International Symposium on Organic Reaction Mechanisms, Cork, Ireland, July 20–25, 1964; Abstracts of Papers, p. 53.

[2] G. Glockler and S. C. Lind, "The Electrochemistry of Gases and Other Dielectrics," John Wiley and Sons, Inc., New York, N. Y., 1939.

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[7] For a more detailed description of the apparatus, see F. Swift, Jr., R. L. Sung, J. Doyle, and J. K. Stille, *J. Org. Chem.*, **30**, 3114 (1965).