after hydrolysis 433 mg. of dihydrostreptosonic acid lactone.

Determination of Periodate Consumption by Dihydrostreptosonic Acid Lactone.—A 5-ml. aqueous solution of 12.0 mg. of the lactone and 78.0 mg. of sodium metaperiodate was allowed to stand at room temperature. The periodate consumption was determined by the standard arsenite method.[13] A 1-ml. aliquot required 7.975 ml. of sodium arsenite solution (1 ml. $\cong$ 1.09 mg. of sodium meta periodate) corresponding to 2.1 moles after fifteen minutes. No further consumption was observed after one hour.

Oxidation of Dihydrostreptosonic Acid Lactone (VII).—A 36.6-mg. quantity of dihydrostreptosonic acid lactone was dissolved in 11.7 ml. of water containing 98 mg. of paraperiodic acid (determined by titration with standard sodium arsenite solution). After two hours, a 1-ml. aliquot was removed and treated with strontium carbonate. The excess strontium carbonate and strontium iodide was removed by filtration. The aqueous filtrate was adjusted to a volume of 1.5 ml. and then treated with 1.5 ml. of an alcoholic solution containing 50 mg. of dimedone. After two hours at 5°, the crystalline product was removed by filtration; yield, 5.5 mg. (97% theory), m. p. 193–194°. After recrystallization of the product from alcohol–water, the melting point did not change. When this derivative was mixed with the dimedone derivative of formaldehyde, no depression of melting point was observed; m. p. 193–194°.

Hydrazide of Dihydrostreptosonic Acid (IX).—A solution of 183 mg. of dihydrostreptosonic acid lactone in 10 ml. of ethanol and 0.5 ml. of hydrazine hydrate was allowed to stand for two hours at room temperature. Fifteen milliliters of chloroform was then added and the solution was allowed to stand for one and one-half hours at 5°. The crystalline hydrazide was removed by filtration; yield, 204 mg., m. p. 135–136°. After several recrystallizations from methanol–water, it melted at 137–139°, $[\alpha]^{25}\text{D}$ + 23° (*c*, 0.9 in water).

Anal. Calcd. for $C_6H_{14}N_2O_5$: C, 37.09; H, 7.26; N, 14.4. Found: C, 36.91; H, 6.96; N, 14.8.

Acknowledgment.—The authors are indebted to Dr. Nelson Trenner and his associates for potentiometric titrations and infrared absorption data, and to Mr. Richard Boos and his associates for microanalytical data.

Summary

Methyl pentaacetyldihydrostreptobiosaminide was converted into amorphous pentaacetyldihydrostreptobiosamine, through the intermediate ethyl thioglycoside, which gave a crystalline hexaacetyldihydrostreptobiosamine. Oxidation of pentaacetyldihydrostreptobiosamine with bromine gave amorphous hexaacetyldihydrostreptobiosamic acid lactone which was hydrolyzed to N-methyl-L-glucosamine and the new dihydrosteptosonic acid lactone.

Tetraacetylstreptobiosamine was hydrogenated selectively with Raney nickel catalyst to the new crystalline tetraacetyldihydrostreptobiosamine. Oxidation and hydrolysis of the tetraacetyldihydro derivative gave also dihydrostreptosonic acid lactone. The lactone gave a hydrazide.

Application of rules of rotation to streptosonic acid diamide and dihydrostreptosonic acid hydrazide indicates that the configuration at C_2 is D. The configuration of streptose and streptobiosamine are now known.

RAHWAY, NEW JERSEY RECEIVED SEPTEMBER 27, 1948

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[13] Jackson, "Organic Reactions," Vol. II, p. 361.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Reactions of Free Hydroxyl Radicals with Organic Compounds

BY NICHOLAS A. MILAS, LOUIS E. STAHL[1] AND BENJAMIN B. DAYTON[2]

In previous publications on hydroxylation of organic compounds in solution with hydrogen peroxide in the presence of catalysts[3] or ultraviolet light[4] we postulated the formation and subsequent reaction of free hydroxyl radicals with organic compounds.[5,6] Hydroxylations of this type have not been attempted previously in the gaseous phase in spite of the fact that numerous reactions have been studied with free hydroxyl radicals usually obtained by the dissociation of water or mixtures of water and oxygen in glow discharges.[7–10]

The present investigation describes some experiments in which free hydroxyl radicals were allowed to react in the gaseous phase with saturated and unsaturated hydrocarbons. It has been found that free hydroxyl radicals are much more reactive in the gaseous phase than in solution. For example, in solution hydroxyl radicals are not known to react with saturated aliphatic hydrocarbons, while in the gaseous phase they react readily with methane to form chiefly carbon dioxide and formic acid, small amounts of methanol, and traces of ethanol. With ethylene and a large excess of hydroxyl radicals, formaldehyde, formic acid and carbon dioxide were the chief products with possible traces of ethylene glycol. When ethylene was used in large excess so that it entered the discharge tube, besides formaldehyde, acetylene and ethane were found among the condensa-

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[2] B.S. Thesis, M. I. T. 1937. Present address: Distillation Products, Inc., Rochester, N. Y.

[3] Milas and Sussman, THIS JOURNAL, **58**, 1302 (1936); **59**, 2345 (1937); Milas, *ibid.*, **59**, 2352 (1937); Milas, Sussman and Mason, *ibid.*, **61**, 1844 (1939); Milas and Maloney, *ibid.*, **62**, 1841 (1940).

[4] Milas, Kurz and Anslow, Jr., *ibid.*, **59**, 543 (1937).

[5] Weiss, *Trans. Faraday Soc.*, **36**, 856 (1940).

[6] Waters, *Ann. Reports*, **42**, 131 (1946).

[7] Rodebush and Campbell, *J. Chem. Phys.*, **4**, 293 (1936); Rodebush, Keizer, McKee and Quagliano, THIS JOURNAL, **69**, 538 (1947).

[8] Frost and Oldenberg, *J. Chem. Phys.*, **4**, 642 (1936); Oldenberg and Rieke, *ibid.*, **6**, 169, 439 (1938); **7**, 485 (1939).

[9] Kondrat'ev and Ziskin, *Acta Physicochim. U. S. S. R.*, **5**, 301 (1936); Kondrat'ev, *ibid.*, **8**, 315 (1938); **10**, 791 (1939).

[10] Smith, *J. Chem. Phys.*, **11**, 110 (1943).

tion products, while a considerable amount of a white solid polymer of aromatic odor was formed in the inner surface of the discharge tube. With isobutylene, acetone and formaldehyde were the chief products isolated. In all cases hydrogen peroxide and organic peroxides were also detected among the condensation products when liquid nitrogen was used as the cooling bath while no hydrogen peroxide or organic peroxides were detected when solid carbon dioxide–acetone mixture was the cooling bath.

Discussion

Perhaps the high reactivity of hydroxyl radicals in the gaseous phase is due to the fact that as they emerge from the discharge tube they are associated with considerably more energy than those which are formed in solution. Furthermore, the hydroxyl radicals in solution may be associated with other groups while those in the gaseous phase are free. Besides, it is quite possible that under the conditions of our experiments other reactive groups, such as atomic hydrogen, may be present in the gaseous phase which, together with the hydroxyl radicals, may initiate reaction outside the glow discharge to produce other radicals. Although a number of possibilities have occurred to us regarding the interpretation of these reactions, we do not wish to propose them at present, since we have not carried out detailed kinetic studies.

Experimental

Arrangement of Apparatus.—A high frequency oscillator[11] similar to that used[12] for the conversion of ergosterol to vitamin D was used in these experiments. It had a frequency range of 4,000 to 22,000 kilocycles. When the oscillator was operating at 19,000 kilocycles with a tank current of 21 amperes, plate current of 340 milliamperes, plate voltage of 1800 volts and filament voltage of 10 volts and maintaining the water vapor at a pressure of 0.1 to 0.2 mm., ample hydroxyl radicals were obtained as judged by the light red or pink color of the glow.[13] The apparatus and traps were arranged as shown in Fig. 1. A Cenco Hyvac oil pump was connected to tube A which was loosely packed with anhydrous calcium chloride. The two-way stopcock B served to draw air into the oil pump when the latter was stopped for purposes of withdrawing samples for analysis. The dibutyl phthalate manometer C was connected to a dibutyl phthalate pump[14] and calibrated to read directly in millimeters of mercury. This was used with the precautions recommended by von Brandenstein and Klumb.[15] The large trap D was immersed in liquid nitrogen during runs to condense all gases with the exception of hydrogen. The organic gases were slowly fed in at E passing through the capillary F and into the reaction or mixing chamber G (4 × 4 cm.). The visible glow in the discharge chamber H (6 × 25 cm.) extended only to the mouth of the reaction chamber.

The water was fed in from I through the capillary J. To prevent condensation of moisture which turned into ice and clogged the mouth of the capillary, the long arm between I and J was wrapped with asbestos tape. The rate of flow of water vapor was controlled by the temperature of I.

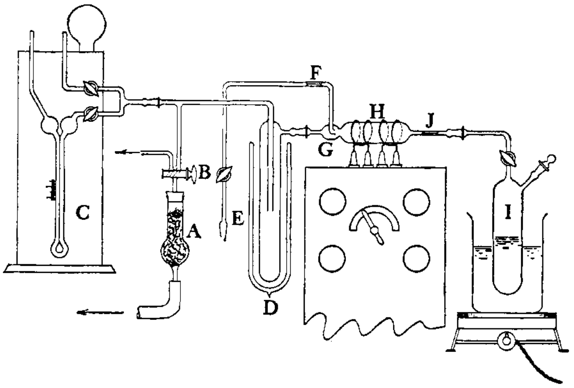

Fig. 1.—Diagram of apparatus for hydroxylation of organic compounds in the gaseous phase.

The pure organic gases were stored over brine and were introduced at E by means of an auxiliary apparatus consisting of a calibrated buret and the usual leveling bottles. The rate of flow was so adjusted as to prevent the organic gases from entering the discharge chamber thereby causing a discoloration of the glow and a deposit of a white solid in the inner surface of the discharge tube.

Before any run was made, the glass apparatus was treated with hot chromic–sulfuric acid solution and thoroughly washed with tap water followed by distilled water and baked in an oven. Since the recombination and destruction of free radicals is known to be a surface reaction, water vapor was passed through the system before the discharge was turned on to poison the glass surface thereby inhibiting this reaction.

Reaction of Free Hydroxyl Radicals with Ethylene.—When 1090 cc. (N. T. P.) of ethylene was allowed to react with excess hydroxyl radicals (from water vapor at 0.1–0.2 mm.) in the course of twelve hours, 500 cc. of gaseous and 9 cc. of liquid products were obtained. An analysis of the gaseous products showed the presence of 70% carbon dioxide, 4% ethylene and 26% ethane. The liquid was strongly peroxidic, the peroxide being mainly hydrogen peroxide, since it was largely destroyed by a clean platinum gauze. A weak test for the presence of organic peroxides was noted after the hydrogen peroxide was thoroughly destroyed. When the liquid was distilled, all but about 0.2 cc. of a yellowish oil distilled at 99°, indicating that most of it was water. However, the distillate gave a strong fuchsin–aldehyde reaction and a positive reaction for formic acid. The formaldimethone was prepared,[16] m. p. 188° (cor.), showing that the aldehyde was chiefly formaldehyde. The residual oil boiled above 110° and was suspected of being ethylene glycol. Attempts to prepare a dibenzoate or a di-*p*-nitrobenzoate yielded fine colloidal suspensions which were difficult to purify. In view of small quantities obtained in each experiment it was not found possible to establish definitely the presence of ethylene glycol.

When the experiment was run in such a manner that excess ethylene was allowed to enter the discharge tube, the glow of the discharge changed from pink to purple. After a run of nine hours, the gas analysis showed no carbon dioxide but considerable acetylene and much ethylene. A white deposit which was probably a polymer of ethylene covered the inner surface of the discharge tube. About 1 cc. of a yellow oil condensed in the liquid air trap which gave the usual tests of peroxides, aldehydes and formic acid. In addition, the liquid gave a positive iodoform reaction indicating the presence of small amounts of either ethyl alcohol or acetaldehyde. The formaldimethone prepared from this liquid melted at 185–188° (cor.).

Reaction of Free Hydroxyl Radicals with Methane.—In the first experiment 860 cc. (N. T. P.) of methane was

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[11] Built by Harvey Electric Co., of Brookline, Massachusetts.

[12] Milas, U. S. Patent, 2,117,100, May 10, 1938.

[13] Rodebush and Wahl, *J. Chem. Phys.*, **1**, 699 (1933).

[14] Hickman and Sanford, *Rev. Sci. Instr.*, **1**, 140 (1940).

[15] von Brandenstein and Klumb, *Physik. Z.*, **33**, 88 (1932).

[16] Huntress and Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 155.

introduced into the reaction chamber very slowly in the course of twelve hours. At the end of the run the gases were analyzed and found to contain 80% carbon dioxide, no unsaturated hydrocarbons, small amounts of oxygen and saturated hydrocarbons (assumed to be methane). About 10 cc. of water-like liquid having an ethereal odor was collected in the liquid air trap. A test for hydrogen peroxide was negative, although a positive test for organic peroxides was obtained. A clean platinum gauze failed to destroy the peroxides. Both the fuchsin–aldehyde test and the "dimedon" reaction were negative. Both the resoninol–sulfuric acid and the U. S. P. tests[17] for methyl alcohol were strongly positive. Formic acid was also found to be present.

In a second run an excess of methane was used and it was allowed to enter the discharge chamber giving a blue-white glow at one end with the pink (water) glow limited to the end of the tube at which the water vapor entered. A volume of 3 liters of methane was used in this run. The gases were not analyzed. About 16 cc. of a liquid was obtained in the liquid air trap, and was found to give the same positive tests as that of the previous run, but in addition it gave a positive iodoform reaction indicating the presence of small amounts of ethanol.

Reaction of Free Hydroxyl Radicals with Isobutylene.—Isobutylene was prepared by the dehydration of *t*-butyl alcohol (80 g.) with oxalic acid (27 g.) and the vapors collected in a trap immersed in acetone–carbon dioxide ice. It was then distilled from the trap by allowing the vapors to pass through a 2-foot vertical column packed with calcium chloride and condensed in another trap to which was attached a stopcock and a ground glass female joint. The isobutylene (10 g.) was introduced into the reaction chamber through the connection E (Fig. 1) by allowing it to evaporate slowly. During the run some isobutylene entered the discharge tube thereby forming purple rings nearer to the reaction chamber while the pink glow (water) persisted in the left half of the discharge tube. At the end of four hours the reaction was stopped and the products condensed in the liquid air trap examined. A liquid (4 cc.) was obtained having a strong odor of formaldehyde. It gave a positive fuchsin–aldehyde test and the formaldimethone prepared from it melted at 188° (cor.). After the removal of formaldehyde the remaining solution gave a strong test for acetone using the sodium nitroprusside reaction.[18] The original liquid also gave a positive test for organic peroxides showing that hydrogen peroxide was probably bound either to formaldehyde or to acetone. The gases were not analyzed.

Summary

1. The reaction between free hydroxyl radicals formed in a glow discharge and methane, ethylene and isobutylene was studied in the gaseous phase.
2. It has been found that free hydroxyl radicals are much more reactive in the gaseous phase than in solution.
3. Methane was mainly converted to carbon dioxide. Other products found were small amounts of peroxides, methanol, ethanol and formic acid.
4. Ethylene was converted mainly to carbon dioxide, small amounts of peroxides, formaldehyde, formic acid and possibly ethylene glycol. With a large excess of ethylene no carbon dioxide was formed, but formaldehyde, formic acid, traces of ethanol and possibly ethylene glycol, acetylene and a solid polymer were noted.
5. With isobutylene, peroxides, formaldehyde and acetone were the chief products detected.

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[17] Reference 16, p. 427.

[18] Reference 16, p. 357.

CAMBRIDGE, MASSACHUSETTS RECEIVED OCTOBER 25, 1948

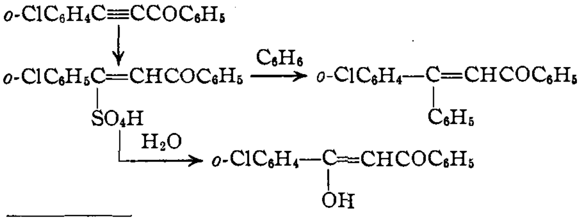
[CONTRIBUTION FROM THE THOMPSON LABORATORY OF THE PHILLIPS EXETER ACADEMY]

The Addition of Benzene to an Acetylenic Ketone

BY CHARLES L. BICKEL AND AUGUSTUS J. FABENS[1]

The literature contains several reports on the reaction of benzene and some of its simple substitution products with α,β-unsaturated ketones. Vorländer and Friedberg,[2] as well as Fuson and co-workers,[3] used a mixture of aluminum chloride and hydrogen halide as the condensing agent, Fuson reporting that these reactions are reversible. Kohler[4] found that benzene adds to chalcone in the presence of sulfuric acid, giving β,β-diphenylpropiophenone as the only identified product. This reaction is also assumed to be reversible,[5] although the nature of the aromatic residues does not permit a study of reversibility in this case.

The reaction of aromatic compounds with the more highly unsaturated acetylenic ketones has not been reported. The present investigation is a study of the reaction of *o*-chlorophenylbenzoyl acetylene with benzene in the presence of sulfuric acid. Two products have been isolated from this reaction, *o*-chlorodibenzoylmethane and β-(*o*-chlorophenyl)-chalcone. The diketone is the sole product when a sulfuric acid solution of the acetylenic ketone is treated with water[6]; thus, the isolation of the diketone in this instance indicates either incomplete reaction with benzene or a reversible reaction. β-(*o*-Chlorophenyl)-chalcone is the product of the net addition of benzene to the acetylenic ketone. A mechanism which is consistent with the known facts is formulated as follows



$$o\text{-ClC}_6\text{H}_4\text{C}{\equiv}\text{CCOC}_6\text{H}_5$$
$$\downarrow$$
$$o\text{-ClC}_6\text{H}_5\underset{\text{SO}_4\text{H}}{\text{C}}{=}\text{CHCOC}_6\text{H}_5 \xrightarrow{\text{C}_6\text{H}_6} o\text{-ClC}_6\text{H}_4\text{—}\underset{\text{C}_6\text{H}_5}{\text{C}}{=}\text{CHCOC}_6\text{H}_5$$
$$\xrightarrow{\text{H}_2\text{O}} o\text{-ClC}_6\text{H}_4\text{—}\underset{\text{OH}}{\text{C}}{=}\text{CHCOC}_6\text{H}_5$$

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[1] A senior in the Phillips Exeter Academy during the school year, 1948–1949.

[2] Vorländer and Friedberg, *Ber.*, **56**, 1144 (1923).

[3] Fuson, Eaton and Black, THIS JOURNAL, **56**, 687 (1934).

[4] Kohler, *Am. Chem. J.*, **31**, 650 (1904).

[5] Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, 1938, p. 585.

[6] Bickel, THIS JOURNAL, **69**, 74 (1947).