The yield was 93% of the theoretical. The percentage of bromine formed was 40.14; the theoretical percentage is 40.61.

Glycol.—Ten grams of the alcohol were heated 2 hours with 145 g. of constant-boiling hydrochloric acid (molecular ratio 1 : 5). The mixture was then fractionated; neither ethylene chloride nor the chlorohydrin were obtained. Twenty grams of glycol were boiled for 2 hours with 165 g. of hydrobromic acid (molecular ratio 1 : 3). The mixture was then fractionated, using a Glinsky tube. No bromohydrin was obtained, but there were formed 8 cc. of an insoluble oil which proved to be ethylene bromide, the yield being 36% of the theoretical. In another experiment when the mixture was heated for a shorter time, some of the bromohydrin was obtained. The exact conditions which determine replacement of one and two hydroxyl groups by bromine were not determined.

Glycerol.—A mixture of 10 g. of glycerol and 55 g. of hydrobromic acid (molecular ratio 1 : 3) was distilled slowly at ordinary pressure until the temperature of the vapor was 140°. The distillation was continued at 33 mm. pressure. The product obtained boiled at 146–175°. After three fractionations at 30 mm. pressure 6 g. of an oil which boiled at 145–147° (corrected) were obtained. The bromohydrins have not been carefully studied. It is probable that the compound obtained was identical with that described by Veley,[1] who prepared it by passing hydrogen bromide into glycerol. The boiling point recorded is 160° at 66 mm.

NASHVILLE, TENN.

HALOGENATION. X. CHLORIC ACID AS A REAGENT IN ORGANIC CHEMISTRY.

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The preparation of organic chlorates has not been attempted with the exception of a few isolated instances. It was thought desirable to study the chlorates of organic bases systematically, as also the action of chloric acid on organic compounds in general.

Chlorates have been prepared either by the direct action of chloric acid on the organic base or by means of double decomposition between the hydrochloride of the base and silver chlorate. They form readily with the aliphatic bases according to either of the above methods, but in the case of aromatic bases the action is quite different. Sometimes the chlorate could not be formed at all since the base undergoes oxidation rapidly. With an excess of chloric acid, the decomposing bases form brown to yellow oily substances which consist, generally, of the lower chloroquinones. With regulated amount of chloric acid, the decomposing substances form dyes. It has also been found that iodo derivatives of

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[1] *Jahresbericht d. Chemie*, 1883, 858.

aromatic hydrocarbons readily form iodoxy compounds when subjected to its prolonged action.

Chlorates are, as a rule, either explosives or highly unstable in the dry state, and special precautions must therefore be taken to determine their melting or decomposition point. Not all explode, however, some melting quite harmlessly and some with more or less decomposition. When held in a flame or touched with a drop of concentrated sulfuric acid, these chlorates burn off suddenly, in some cases with production of a sharp report. Chlorates of aromatic bases sometimes go off spontaneously, specially if the chlorate has been obtained by the direct action of chloric acid on the base, probably as the result of a little free chloric acid which might be present. Such spontaneous explosion does not take place if the chlorate be purified by recrystallization from alcohol.

The analysis of these chlorates is carried out by mixing with a large quantity of powdered copper oxide.

Experimental.

Action of Chloric Acid on Aniline.—Aniline chlorate has been prepared before by direct neutralization.[1] It has been found that when aniline is mixed with quite an excess of chloric acid, a vigorous reaction, with the evolution of a considerable amount of heat, takes place and as a result of the action a brown oil is formed which settles at the bottom. The oil consists of a mixture of the lower chloroquinones which is under examination. But if a little chloric acid is added to an excess of aniline and the mixture allowed to stand at the ordinary temperature, it undergoes gradual oxidation and finally a black substance is precipitated. This has been found on examination to be aniline black, giving all its reactions. (Found, N = 15.48; calc., N = 15.34.) The yield obtained is quantitative.

***o*-Toluidine Chlorate,** $C_7H_9N.HClO_3$.—To an excess of *o*-toluidine, chloric acid is added drop by drop, when crystals begin to make their appearance. Care is taken not to add an excess of chloric acid, as the presence of a little free acid will decompose the substance explosively at ordinary temperature, a slight excess of toluidine being maintained. The crystals are filtered with suction, washed thoroughly with ether and benzene, and finally recrystallized from alcohol when it is obtained in white plates.

0.1642 g. gave 0.2652 g. CO_2 and 0.0735 g. H_2O; 0.0594 g. gave 4.1 cc. N_2 at 28° and 763 mm.; 0.1435 g. gave 0.1068 g. AgCl.

Calc. for $C_7H_9N.HClO_3$: C, 43.86; H, 5.22; Cl, 18.5. Found: C, 43.77; H, 5.25; N, 7.6; C, 18.63%.

The crystals are not indefinitely stable in air, but turn gray and finally produce a black substance which, as will be shown later, is also formed

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[1] Beamer and Clarke, *Ber.*, **12**, 1066 (1879); Gerard, L'Hate, *Ann.*, [6] **22**, 404.

by the prolonged action of chloric acid on *o*-toluidine. *o*-Toluidine chlorate explodes at 88°. When a flame is applied to it, it burns explosively.

It has also been found that on adding an excess of chloric acid to a little *o*-toluidine, a blue-colored solution is produced and the mixture becomes hot. This is followed by a vigorous reaction, with boiling, and a brown-black viscous liquid separates at the bottom. This substance is under examination.

If an excess of *o*-toluidine is left in contact with chloric acid and the vessel cooled with water so as to avoid any vigorous reaction, the toluidine is slowly transformed into a black insoluble substance which gives some of the tests of *o*-toluidine black. The dye has been found to be quite distinct from *o*-toluidine black and is under systematic examination. The same dye is obtained by the gradual decomposition in air of *o*-toluidine chlorate, as has been already noticed.

***p*-Toluidine Chlorate,** $C_7H_9N.HClO_3$.—For the preparation of this compound *p*-toluidine is dissolved in ether and to it an aqueous solution of chloric acid is added drop by drop, taking care to keep the *p*-toluidine in slight excess. The ether is then allowed to evaporate at the ordinary temperature as rapidly as possible. As the ether evaporates, long, white crystals remain behind. The crystals are washed with ether and benzene and finally recrystallized from alcohol.

0.2110 g. gave 0.3405 g. CO_2 and 0.0993 g. H_2O; 0.0594 g. gave 3.85 cc. N_2 at 26° and 764 mm.; 0.1552 g. gave 0.1157 g. AgCl.

Calc. for $C_7H_9N.HClO_3$: C, 43.86; H, 5.22; N, 7.32; Cl, 18.54. Found: C, 43.22; H, 5.33; N, 7.33; Cl, 18.78.

p-Toluidine chlorate explodes at 125°, giving off a large amount of white fumes and takes fire suddenly when a flame is applied to it. The substance on exposure to air gradually turns gray owing to slow decomposition of the salt.

Similarly to *o*-toluidine, it has been found that on treating *p*-toluidine with an excess of concentrated chloric acid, a vigorous reaction begins in the course of an half-hour with considerable evolution of heat and as a result of the reaction a brown viscous oil, which is under examination, settles at the bottom. But if an excess of *p*-toluidine be kept with a little dilute solution of chloric acid in the cold, the mixture gradually turns black and the *p*-toluidine is ultimately converted into a black dye. The dye is under examination.

***p*-Phenylenediamine Chlorate.**—Chloric acid, when added directly to *p*-phenylenediamine, dissolves it and gives a deep blue solution which gradually assumes a brown color. If an ethereal solution of the diamine is mixed with chloric acid on a watch glass and the ether is allowed to evaporate rapidly, crystals are obtained. They could hardly be separated for purification as the material soon turns black. The same black dye is obtained when *p*-phenylenediamine is left in contact with chloric acid in the cold. The systematic investigation of the dye is in progress.

An attempt was made to obtain *m*-phenylenediamine chlorate by double decomposition between *m*-phenylenediamine hydrochloride and silver chlorate. The resulting solution began to turn dark as soon as double decomposition was complete. On allowing the solution to evaporate in a vacuum, instead of the chlorate, a gray-black dye is left behind. The further examination of this black substance is in progress.

Benzylamine Chlorate, $C_7H_9N.HClO_3$.—For the preparation of the chlorate an excess of benzylamine is mixed with an aqueous solution of chloric acid. The resulting solution is allowed to evaporate on the water bath and the product remains melted over it. On cooling, the liquid solidified in nice crystalline plates which are slightly yellow in color owing to the presence of benzylamine. To free it from benzylamine, it is washed thoroughly with ether and finally purified by recrystallization from alcohol.

0.1825 g. gave 0.2934 g. CO_2 and 0.0856 g. H_2O; 0.0730 g. gave 4.75 cc. N_2 at 23° and 765 mm.

Calc. for $C_7H_9N.HClO_3$: C, 43.86; H, 5.22; N, 7.32. Found: C, 43.83; H, 5.62; N, 7.6%.

Benzylamine chlorate melts at 110.5° to a yellow liquid. It is hygroscopic and dissolves in water and alcohol but not in ether and benzene.

Benzylmethylamine Chlorate, $C_6H_5CH_2NHCH_3.HClO_3$.—Equivalent quantities of benzylmethylamine and chloric acid are mixed with a slight excess of the former. The mixture is first heated on the water bath for about an hour and is then allowed to cool in a desiccator. The solid mass thus obtained is then washed thoroughly with ether and recrystallized from alcohol and dried.

0.1405 g. gave 0.2352 g. CO_2 and 0.0674 g. H_2O; 0.1038 g. gave 6.3 cc. N_2 at 23° and 762 mm.

Calc. for $C_8H_{11}N.HClO_3$: C, 46.7; H, 5.84; N, 6.81. Found: C, 45.52; H, 5.99; N, 7.02%.

The chlorate melts at 59.60°. It is soluble in water and alcohol but not in ether and benzene. It burns off suddenly when a flame is brought near to it.

Benzylethylamine Chlorate, $C_6H_5CH_2.NHC_2H_5.HClO_3$.—Equivalent amounts of benzylethylamine and chloric acid are mixed and heated on the water bath for some time. On cooling, crystals separate which are thoroughly washed with ether and recrystallized from dilute alcohol.

0.1010 g. gave 0.3626 g. CO_2 and 0.1052 g. H_2O; 0.1588 g. gave 8.85 cc. N_2 at 24° and 763 mm.

Calc. for C_9H_1 $N.HClO_3$: C, 49.2; H, 6.38; N, 6.38. Found: C, 49.19; H, 6.55; N, 6.33.

The chlorate melts at 81.5°. It takes fire suddenly when a flame is applied to it. It is very soluble in water and alcohol but insoluble in ether and benzene.

Piperazine Chlorate, $C_4H_{10}N_2.2HClO_3$.—Piperazine chlorate is prepared by double decomposition between silver chlorate and piperazine hydrochloride. On evaporation of the solution in a vacuum over sulfuric acid, the chlorate is obtained in nice, white, shining crystalline plates. On presenting a flame to it, it takes fire suddenly. It decomposed between 98 and 100°. In this case the decomposition was not explosive.

0.2215 g. gave 22.2 cc. N_2 at 24° and 760 mm.; 0.1234 g. gave 0.1378 g. AgCl.
Calc. for $C_4H_{10}N_2.2HClO_3$: N, 10.98; Cl, 27.8. Found: N, 11.22; Cl, 27.91.

Ethylenediamine Chlorate, $C_2H_4(NH_2)_2.2HClO_3$.—This chlorate is prepared by neutralizing ethylenediamine solution with chloric acid by the help of a litmus paper and evaporating the resulting solution on the water bath to crystallization where the substance is obtained in shining, white, flat crystals. As thus obtained, it is quite pure and a single recrystallization from water or alcohol gives a very pure product. It decomposes at 150°. Like the other chlorates, it burns off with a flash on presenting a flame to it.

0.1825 g. gave 19.85 cc. N_2 at 25° and 760 mm.; N, 12.34.
Calc. for $C_2H_4(NH_2)_2.2HClO_3$: N, 12.23.

Guanidine Chlorate, $CN_3H_5.HClO_3$.—This is obtained by the double decomposition between guanidine sulfate and barium chlorate and evaporating the resulting solution over a water bath, when white crystals are obtained. It decomposes at 148° and does not explode sharply at that temperature. However, it burns away on presenting a flame to it or touching with a drop of concentrated sulfuric acid.

0.1010 g. gave 26.3 cc. N_2 at 23° and 767 mm.
Calc. for $CN_3H_5.HClO_3$: N, 29.8. Found: 30.62.

Menthylamine Chlorate, $C_{10}H_{19}NH_2.HClO_3$.—This has been prepared by the double decomposition between menthylamine hydrochloride and silver chlorate and evaporating the solution in a vacuum over sulfuric acid. The chlorate is then left in beautiful, white, crystalline needles. It melts at 168°. This chlorate, unlike the previous ones, does not flash off when a burning stick is brought near it but it simply melts.

0.0828 g. gave 4.4 cc. N_2 at 24° and 762 mm.; N, 6.07.
Calc. for $C_{10}H_{19}NH_2.HClO_3$: N, 5.85.

Pyridine Chlorate, $C_5H_5N.HClO_3$.—When a slight excess of pyridine is mixed with concentrated chloric acid and the mixture is heated on the water bath, crystals of the chlorate are left. They are washed with water and recrystallized from alcohol, and then melt with decomposition at 147°.

0.1021 g. gave 7.6 cc. N_2 at 23° and 766 mm.; 0.1827 g. gave 0.1592 g. AgCl.
Calc. for $C_5H_5N.HClO_3$: N, 8.56; Cl, 21.7. Found: N, 8.58; Cl, 21.92.

Pyridine chlorate burns with a sudden flash. It also takes fire when concentrated sulfuric acid is allowed to come in contact with it. It is soluble in water and alcohol but does not dissolve in nondissociating organic solvents. The crystals are soft and soapy to the touch and give the odor of pyridine.

Quinoline Chlorate, $C_9H_7N.HClO_3$.—This has been prepared by mixing chloric acid with rather more than the theoretical amount of quinoline and evaporating on the water bath. The crystals obtained are washed with a mixture of alcohol and ether for purification. The compound melts at 66–67°.

0.1117 gave 6.65 cc. N_2 at 25° and 760 mm.
Calc. for $C_9H_7N.HClO_3$: N, 6.56. Found: N, 6.76.

The chlorate has a slightly yellowish tinge and is very hydroscopic. It is soluble in alcohol and water but cannot be successfully recrystallized from these solvents as the substance obtained on evaporating the solvents sets to a hard mass on drying. It decomposes with a flash and a large amount of smoke when a flame is applied to it or when touched with concentrated sulfuric acid, leaving a black residue behind.

Tetramethylammonium Chlorate, $N(CH_3)_4ClO_3$.—This is prepared by the double decomposition between tetramethylammonium iodide and silver chlorate and evaporating the resulting solution on the water bath to crystallization. As thus obtained, it consists of white crystals. It is freely soluble in alcohol and water. It explodes at 230°. It takes fire suddenly on presenting to a flame or touching with a drop of concentrated sulfuric acid.

0.0659 g. gave 5.25 cc. N_2 at 23° and 765 mm.; N, 9.02.
Calc. for $N(CH_3)_4ClO_3$: N, 8.89.

Tetraethylammonium Chlorate, $N(C_2H_5)_4ClO_3$.—This has been similarly prepared by the double decomposition between tetramethylammonium iodide and silver chlorate and evaporating the resulting solution on the water bath to crystallization when crystals are obtained on cooling. As thus obtained, the substance is quite pure. It can be recrystallized from water or alcohol. It melts with decomposition at 223°. It takes fire as usual when a flame is applied to it or when it is touched with a drop of concentrated sulfuric acid.

0.0895 g. gave 5 cc. N_2 at 24° and 766 mm.; N, 6.4.
Calc. for $N(C_2H_5)_4ClO_3$: N, 6.56.

Tetrapropylammonium Chlorate, $N(C_3H_5)_4ClO_3$.—This has been obtained as usual by the double decomposition between silver chlorate and tetrapropylammonium iodide and evaporating the resulting solution on the water bath to crystallization. The chlorate melts at 217° without decomposition. It dissolves freely in water and alcohol. It burns off as usual on the presentation of a flame or when touched with concentrated sulfuric acid.

0.1444 g. gave 3.9 cc. N_2 at 25° and 767 mm.; N, 5.52.
Calc. for $N(C_3H_5)_4ClO_3$: N, 5.2.

Dimethylphenylbenzylammonium Chlorate, $N(CH_3)_2(C_6H_5)C_7H_7ClO_3$.—This salt is prepared from dimethylphenylbenzylammonium bromide and silver chlorate by double decomposition and evaporating the solution in a vacuum over sulfuric acid. The chlorate obtained is white and crystalline in shape. It is hygroscopic and dissolves freely in water and alcohol. It decomposes without any sharp explosion at 137°, leaving a red mass as residue which does not melt on further heating. It, however, burns with a flash and decomposes explosively with concentrated sulfuric acid, and slowly decomposes to a gray mass on leaving it at the ordinary temperature for several days.

0.1527 g. gave 6.75 cc. N_2 at 24° and 763 mm.; N, 5.0.
Calc. for $N(CH_3)_2(C_6H_5)(C_7H_7)ClO_3$: N, 4.74.

Diethylphenylbenzylammonium Chlorate, $N(C_2H_5)_2C_6H_5C_7H_7ClO_3$.—This is prepared as usual by the double decomposition between the corresponding chloride and silver chlorate and evaporating the resulting solution in a vacuum over sulfuric acid. This is obtained in white crystals melting to a dark liquid at 77°. On further heating it becomes darker and darker until at 125° it decomposes with effervescence. It decomposes partly on leaving it for long periods in the air. It is soluble in water and alcohol and burns with a flash.

0.1623 g. gave 6.1 cc. N_2 at 765 mm.; N, 4.24.
Calc. for $N(C_2H_5)_2C_6H_5C_7H_7ClO_3$: N, 4.33.

Trimethylsulfine Chlorate, $S(CH_3)_3ClO_3$.—This salt is obtained by the double decomposition between silver chlorate and trimethylsulfine iodide and evaporating the resulting solution on the water bath. The salt could be recrystallized from water with difficulty since this salt is very soluble in cold water and the difference in solubility in hot and cold water is very small. It explodes at 170°. The salt explodes sharply on presenting a flame to it, the explosion being very rapid and sharp. It is hygroscopic and liquefies when exposed to air.

0.1474 g. gave 0.1212 CO_2 and 0.0666 g. H_2O; C, 22.32; H, 5.91.
Calc. for $S(CH_3)_3ClO_3$: C, 22.44; H, 5.61.

Oxidation of Organic Iodo-Compounds by Means of Chloric Acid.

Iodoxy-benzene, $C_6H_5IO_2$.—A little iodobenzene is taken in a crystallizing dish and to it is added an excess of concentrated chloric acid solution and kept aside for about two days. In the course of this period slightly yellow crystals appear. On washing with alcohol, in which it is insoluble, it is obtained in clear, white crystals. The substance explodes at 227–228°. An iodine estimation gave the following results:

0.1251 g. gave 0.1251 AgI; I, 54.03. Calc. for $C_6H_5IO_2$: I, 53.81.

o-Iodoxy-toluene, $CH_3.C_6H_4IO_2$.—This is obtained similarly to the above substance by allowing *o*-iodotoluene to remain in contact with chloric acid for several days. A crystalline product is obtained which is thoroughly washed with alcohol and separated by filtration. The product decomposes at 210°.

0.0855 g. gave 0.0854 AgI; I, 51.04. Calc. for $CH_3.C_6H_4IO_2$: I, 50.8.

p-Iodoxy-toluene, $CH_3.C_6H_4IO_2$.—This is obtained by exactly the same procedure as the previous compound. *p*-Iodtoluene is left for several days in contact with concentrated chloric acid. The crude product thus obtained is washed with alcohol. It decomposes at 229°.

0.1213 g. gave 0.1133 AgI; I, 50.73. Calc. for $CH_3.C_6H_4IO_2$: I, 50.8.

Iodoxy-m-xylene, $C_6H_3(CH_3)_2{}^{1,3}(IO_2)^4$.—This is obtained by keeping the iodocompound with a strong solution of chloric acid for two or three days at ordinary temperature. The resulting product is thoroughly washed with alcohol and is found to be iodoxy-*m*-xylene, exploding at 193°.

0.0709 g. gave 0.0627 g. AgI; I = 47.12. Calc. for $C_6H_3(CH_3)_2(IO_2)$: I = 48.11.

Iodoxy-o-xylene, $C_6H_3(CH_3)_2{}^{1,2}(IO_2)^4$.—This compound has been prepared for the first time, since it was not known before. Yellowish crystals were obtained by treating iodo-*o*-xylene with concentrated chloric acid in the cold for several days. On washing with alcohol the substance is obtained pure. It explodes at 192–193°. The salt was analyzed with the following result:

0.0989 g. gave 0.1310 CO_2 and 0.0817 g. gave 0.0729 g. AgI.

Calc. for $C_6H_3(CH_3)_2(IO_2)$: C, 36.36; H, 3.41; I, 48.11. Found: C, 36.18; H, 3.58; I, 48.9.

Iodoxy-mesitylene, $C_6H_2(CH_3)_3IO_2$.—This substance is obtained by keeping iodomesitylene for a few days in contact with strong chloric acid. The crystalline crude product thus obtained is washed with alcohol. It decomposes at 194°.

0.1415 g. gave 0.1191 g. AgI; I, 45.53. Calc. for $C_6H_2(CH_3)_3IO_2$: I, 45.68.

Investigations on similar lines are being continued.

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