[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS.]

A METHOD FOR THE DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS.

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The use of sodium peroxide for the determination of halogens in organic compounds is not new. S. W. Parr[1] and H. H. Pringsheim[2] have published a number of articles on the use of this reagent for the fusion of organic compounds containing halogens and they have shown that sodium peroxide has many advantages in both the qualitative and quantitative determinations.

The Carius method for determining halogens is at present most widely used and gives very good results. The method, however, has some serious disadvantages which are familiar to all. Delbridge[3] has obtained unsatisfactory results with the use of sodium peroxide. He recommends a modification of the lime method as giving the desired results in hundreds of determinations where it has been tried.

The work of Parr and that of Pringsheim has shown that sodium peroxide should have a very important place in organic quantitative analysis. The work to be described was carried out in an effort to perfect a method whereby a standard fusion cup[4] might be used in the determination of halogens in organic compounds. This led to a repetition of some of the work that had been done and to modifications in the method, particularly in the determination of iodine.

Experimental.

The first and most important detail of the method is the thorough mixture of the charge. Without a thorough mixture the fusion will be incomplete and the determination ruined. If all reagents are not free from halogens a blank must be run and the necessary corrections made. Approximately 10 g. of sodium peroxide and from 1 to 1.5 g. of very finely ground potassium nitrate are first thoroughly mixed in the fusion cup, a diagram of which is here given. From 0.4 to 0.45 g. of finely powdered benzoic acid or, better, cane sugar, is now added and the whole mass again thoroughly mixed. Finally add 0.2 to 0.25 g. of the finely ground compound with thorough mixing. In all cases care should be taken to guard against spontaneous ignition when the organic material comes in contact with the sodium peroxide. For volatile liquids the difficulty of securing an accurate sample is met by the following procedure: A light, round or egg-shaped bulb weighing 0.2 g. or less and

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[1] THIS JOURNAL, 30, 764–770 (1908).

[2] *Am. Chem. J.*, 41, 386 (1904).

[3] THIS JOURNAL, 31, 393–517 (1909).

[4] Manufactured by the Standard Calorimeter Co., East Moline, Illinois.

having a capillary tip is blown to an approximate diameter of 1 to 1.5 cm. Thin-walled glass tubing of about 4 mm. diameter is probably best suited to this purpose. After weighing the bulb, it is filled by alternate gentle warming and cooling, thereby drawing in the liquid. When about 0.2 g. is obtained, seal the capillary in the flame and weigh. The bulb is broken after sealing the bomb by gently tapping the bomb on the table. Unless a liquid is so volatile that it could not be kept in this kind of a bulb it should not present any further difficulty. The cup should always be tapped lightly after sealing to get the material in the bottom. The ignition is effected by heating in the hottest part of a Bunsen flame, the heating being continued until the cup is red for at least one-fourth its length. The bomb is immediately cooled under the water tap, opened, the top rinsed, and the cup placed in about 200 cc. hot water. Losses may be avoided by putting a watch glass over the beaker until the evolution of gas has ceased. After removing the cup, the solution is digested for a few minutes to decompose any sodium peroxide that may still remain. Acidify with concentrated nitric acid and boil for a few minutes, then cool the clarified solution and precipitate with a measured excess of 0.1 *N* silver nitrate. With a thorough breaking down of the larger particle and the coagulation of the precipitate by gentle boiling, it has been found unnecessary to filter the silver chlo-

Fig. 2

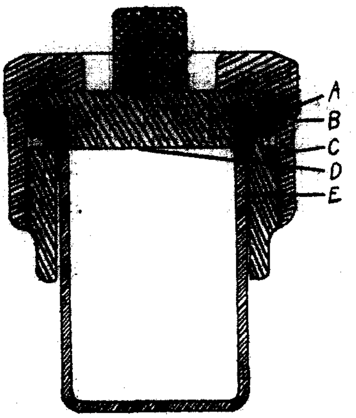

Fig. 1

The Parr Sulphur Bomb.

A— Rubber Gasket.
B— Screw Cap.
C— Screw Collar.
D— Cover.
E— Cup.

ride.[1] The solution is again cooled and the excess of silver nitrate determined by the Volhard method. The above procedure is almost identical with that used by E. R. Brunskill.[2]

Bromine and iodine were then determined in the same way but it was found that the results obtained did not even check with each other when run in duplicate, showing that the cause did not lie with the impurity of the sample. It is, of course, well known that hydriodic acid is easily oxidized by nitric acid giving free iodine. Upon boiling an acidified solution from an iodine fusion, free iodine could actually be seen coming off, showing that in both bromine and iodine determinations there might be a loss of halogens from this source. Pringsheim, however, does not mention this source of error. It may be that with only a slight excess of nitric acid and no boiling that such a reaction might not take place. Nevertheless, it would not be an easy matter to always determine with certainty that only the proper amount of nitric acid had been used. This difficulty was overcome by dissolving the fusion in water and by boiling this for several minutes to decompose all the sodium peroxide and to expel all of the hydrogen peroxide. Silver nitrate in excess is then added to the alkaline solution and this is digested for at least fifteen minutes in order to insure the complete precipitation of the iodide as silver iodide which is the most insoluble of the precipitated silver compounds. The solution may now be acidified with nitric acid without any loss of halogens.

The addition of compounds high in carbon and hydrogen, though necessary only with the more highly halogenated compounds, is advisable in all charges in order to insure thorough and uniform fusion. Due to the excess of sodium peroxide in the fusion cup some of the sodium iodide formed will be oxidized to the iodate or to other oxyacids. Silver iodate and the other oxyacids of iodine are somewhat soluble in hot water and in nitric acid and must first be reduced to silver iodide before the titration with ammonium thiocyanate. Alcohol, sodium sulfite, magnesium and zinc were all suggested. Alcohol where tried gave dark colorations and liberation of oxides of nitrogen, thus preventing good titrations. Sodium sulfite when used in quantities large enough to insure complete reduction invariably gave high results. When added only in small quantities the results were low. The high results may be due to the formation of some silver sulfate which may not all be dissolved. Metallic magnesium and zinc in acid solution were found to entirely reduce the iodate to free iodine but the reducing action was not strong enough to reduce the iodine further to the iodide, as is necessary. Silver bromate or the other oxyacids of bromine, however, can be reduced to the bromide by zinc or magnesium. Although silver bromate does not form in every

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[1] Treadwell-Hall, "Analytical Chemistry," 3rd Ed., 2, 708.

[2] Thesis for the B.S. Degree (1915), University of Illinois.

case, the addition of a reducing agent is recommended in order to be certain that no bromine is lost. Hydrazine sulfate was the next reducing agent tried. It is added slowly to the hot acidified solution containing the precipitated silver halide as indicated below:

$AgNO_3$	boil gently	AgI
AgI		$AgNO_3$
$AgIO_3$	$+ N_2H_4.H_2SO_4$	$NaNO_3$
$NaNO_3$		KNO_3
KNO_3		Na_2SO_4

If an oxyacid of either bromine or iodine is present there will be an immediate evolution of gas, which is nitrogen, and a precipitation of the silver salt, thus:

$$10N_2H_4.H_2SO_4 + 2AgIO_3 \longrightarrow 2AgI + 3N_2 + 3H_2SO_4 + 6H_2O$$

Compound.	Am't taken. Gram.	Per cent. halogen calculated.	Per cent. halogen formed.
Naphthalene sulfonyl chloride ($C_{10}H_7SO_2Cl$)	0.3804	15.65	14.27^{-}
	0.2919	15.65	14.45^{-}
Nitrobenzylchloride ($NO_2C_6H_4CH_2Cl$)	0.3809	20.67	20.47
	0.3804	20.67	20.08
p-Chlorobenzoic acid ($ClC_6H_4CO_2H$)	0.2500	22.65	22.32
	0.1848	22.65	21.86°
Phenylene-diaminehydrochloride ($C_6H_4(NH_2)_2.2HCl$).	0.2418	39.17	39.06
	0.2244	39.17	38.90
Chloronitrobenzene ($C_6H_4NO_2Cl$)	0.3010	22.95	22.41^{-}
	0.2778	22.95	22.41^{-}
p-Bromoacetanilide (C_8H_7NHOBr)	0.2862	36.34	37.30
	0.3200	37.34	37.02
p-Dibromobenzene ($C_6H_4Br_2$)	0.3896	67.76	67.61
	0.3859	67.76	60.01°
p-Bromobenzoic acid ($BrC_6H_4CO_2H$)	0.2791	39.76	39.63
	0.2761	39.76	39.98
Triphenylchloromethane ($(C_6H_5)_3C.Cl$)	0.2762	12.72	12.81
	0.2808	12.72	12.79
p-Bromosulfonyl derivative of arsanilic acid ($Br(C_6H_4)_2NHSO_2AsO_3H_2$)	0.2745	18.32	18.60
Tetrabromobenzoquinone ($C_6Br_4O_2$)	0.2000	75.45	74.28*
	0.2852	75.45	74.04*
Dinitrodibromobenzene ($C_6H_2(NO_2)_2Br_2$)	0.2801	49.04	50.14*
	0.2803	49.04	47.93*
Iodoform (CHI_3)	0.2000	96.65	96.50
	0.2000	96.65	96.90
p-Chlorotoluene ($ClC_6H_4CH_3$)	0.2380	28.02	27.71^{-}
	0.2378	28.02	27.70^{-}

Results obtained by E. R. Brunskill:

p-Chlorobenzoylacetic ester ($C_{11}H_{11}O_3Cl$)	15.67	15.79
p-Chlorobenzoylacetic acid ($C_9H_7O_3Cl$)	17.88	17.89
Phenacyl-*p*-chlorobenzoylacetic ethyl ester ($C_{19}H_{17}O_4Cl$)	10.33	10.36
4-Chlorodiphenacyl ($C_{16}H_{13}O_2Cl$)	13.02	13.28
p-Chlorophenacylbenzoylacetic ethyl ester ($C_{19}H_{17}O_4Cl$)	10.33	10.58

The hydrazine sulfate is added slowly with stirring until reaction ceases. No frothing indicates no more oxidation of the hydrazine sulfate. This was the only reliable reducing agent found for the iodates and its use is also recommended for bromates in preference to magnesium, zinc, or sodium sulfite. Results of the determinations made are given in the preceding table.

The errors in the above results probably did not originate from the method of titration, but from one or all of three other sources, namely, (1) poor fusions, (2) impure reagents, and (3) impure organic compounds. Small mechanical losses are, of course, unavoidable but in most cases these are negligible as compared with the other three. Results which vary and are most likely due to poor fusions are marked "°" in the above table. In the later part of the work good fusions were obtained and good checks, especially when sugar was used. All benzoic acid used in the fusions contained small amounts of halogens but this impurity was not uniformly distributed. This was partially overcome by a thorough mechanical mixing. Blank fusions run upon the acid gave the necessary corrections. Results where benzoic acid was used in the charge are marked "*" in the table. It is highly probable that in the results marked "–" the differences between the halogen found and the theoretical are due to slight impurities in the organic compounds. The results on the whole show the above procedure to be reliable when all details are closely followed. Upon studying the table it will be seen that a good fusion is absolutely essential in obtaining accurate results. Sugar is to be preferred to benzoic acid for getting a good fusion. An excess of silver nitrate is essential or some of the halogen will be liberated during the procedure to follow. A violet-colored solution which sometims appears during some part of the digestion should not be mistaken for escaping halogen. This color is sometimes caused by manganese which is in the steel alloy of the fusion cup, but it may be removed by the continued boiling of the acid solution or by the addition of a small amount of hydrogen peroxide. Although only one liquid was run the results obtained on the *p*-chlorotoluene show that this method is applicable alike to liquid and solid compounds. The variety of compounds used also seems to indicate that the method is reliable for all the halogen compounds regardless of the degree or type of halogenation.

Summary.

The chlorides, bromides, and iodides of a variety of organic compounds have been quantitatively determined by fusion with sodium peroxide in a Parr sulfur bomb. The essential points for obtaining correct results were found to be:

1. A thorough and uniform fusion.
2. The addition of an excess of silver nitrate to the alkaline solution

and the thorough coagulation by gentle boiling of any silver halide which may be formed at this point.

3. The addition of enough of some reducing agent to cause a rapid and total reduction of any oxyacids which may have been formed. Hydrazine sulfate was found to be far better than any other reducing agent which was tried.

4. This method is applicable to the highly halogenated and liquid compounds as well as to others.

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THE DETERMINATION OF SILVER IN ORGANIC COMPOUNDS.

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The determination of silver in those salts which are completely soluble in water, or in nitric acid, is easily accomplished by precipitating the silver as chloride, and weighing as such. If the salt is insoluble in water, and gives, when treated with acids, an insoluble organic compound, the chloride precipitation method cannot be used.

A very simple method is to heat the silver salt of the organic acid, whereby a residue of metallic silver remains. Compounds containing nitrogen or sulfur also give metallic silver upon ignition, but when sulfur is present, the heating must be continued until the silver fuses.[1] This method is not applicable to halogenated silver salts.

The method of Carius,[2] in which the substance is decomposed by heating with concentrated nitric acid in a sealed tube at a high temperature, is of general application, and gives good results. However, Pelzer[3] has shown that certain substances are not completely oxidized by this treatment.

In the determination of silver in halogenated silver salts, Rindl and Simonis[4] modify the method of Carius by adding a potassium halide.

Dupont and Freundler[5] employ aqua regia as an oxidizing agent, the silver remaining as silver chloride. Recently Datta and Chatterjee[6] have shown that a large number of compounds, including many hydroxy derivatives, give chloropicrin and chloroanil when treated with aqua regia.

In the method of Vanino[7] the silver salt is converted into metallic silver by the reducing action of formaldehyde in strong alkaline solution.

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[1] Salkowski, *Ber.*, **26**, 2497 (1893).

[2] *Ber.*, **3**, 697 (1870).

[3] *Ann.*, **146**, 301 (1868).

[4] *Ber.*, **41**, 838 (1908).

[5] "Manuel Operatoire de Chimie Organique," p. 80 (1898).

[6] THIS JOURNAL, **38**, 1813 (1916).

[7] *Ber.*, **31**, 1763, 3136 (1898).