the acid is diluted with a small percentage of water seems to make no material difference in the results. The samples are heated in a sulfuric acid bath to 185° for twenty to forty minutes (see above) after which the mixture is transferred to an Erlenmeyer flask, diluted with 60 ml. of water and steamed for five minutes using a suitable source of clean steam. The inlet tube for the steam is then rinsed with 40 ml. of water and after cooling 0.75 g. of sodium bicarbonate is added to the flask to reduce acidity and give an atmosphere of carbon dioxide; 1.5 g. of powdered potassium iodide is added and the iodine which is freed is titrated with 0.1 *N* sodium thiosulfate. Most of the precautions which have to be observed are those involved in iodometric titrations in general and are not properly presented or discussed here. The purest available chemicals including "Kahlbaum" potassium iodate and sulfuric acid were used. When the samples were very small and 0.025 *N* thiosulfate was used, suitable corrections were applied for the "titration error."

Summary

Oxidation with iodate in concentrated sulfuric acid and back titration of the unused iodate constitutes a method (which, however, is not perfectly general) for determining the amount of oxygen necessary for the complete oxidation of organic compounds (see first article in this series). There is danger of oxidizing nitrogen, however, if the concentration of the sample is too high. Phthalates are oxidized with difficulty and nicotinic acid, for example, is oxidized very little. It can, however, be applied rather widely to compounds of various types and accurate analyses are possible with samples weighing a fraction of a milligram.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF OREGON STATE COLLEGE]

Organic Oxidation Equivalent Analysis. III. General Method Using Dichromate

BY BERT E. CHRISTENSEN, ROGER J. WILLIAMS AND ANNE E. KING

Dry combustion methods have been devised for determining the amount of oxygen consumed in the oxidation of organic compounds,[1-3] but either they are inaccurate or else involve a complicated apparatus and exacting technique in operation. Wet combustion, if applicable, should involve simpler apparatus and easy experimental methods.

Of the available agents for wet combustion which are obtainable in pure form, potassium iodate and potassium dichromate are outstanding. The use of iodate has been studied[4] and found to be of somewhat restricted value. Potassium dichromate has been used for the determination of oxygen consumed during combustion but if employed at relatively low temperatures[5] (100° or thereabout) is applicable to the oxidation of only a few types of compounds. If used at a sufficiently high temperature to bring about the complete oxidation of compounds generally, free oxygen is invariably produced in considerable quantity accompanied by the formation of carbon monoxide[6] in many cases (oftentimes even at low temperatures). This eliminates the possibility of determining the unused oxidizing agent directly by back titration.

This study was directed toward the perfection of a method using dichromate under conditions which would oxidize organic compounds generally, yet allow for an evaluation of the whole of the unused oxidizing agent (including oxygen gas) and eliminate or correct for the carbon monoxide produced.

It is obvious that many different media and conditions could be employed for the oxidation with dichromate. We have investigated the use of phosphoric acid, sulfuric acid and mixtures of the two. Phosphoric acid (85%) has certain advantages, particularly in that it prevents the formation of insoluble chromous oxide, but its use in connection with nitrogenous compounds is not feasible due to oxidation of ammonia. In this Laboratory it was found that ammonia is almost quantitatively converted to the nitrate in a phosphoric acid medium (a fact which as far as we know has not been previously recorded). Slightly diluted sulfuric acid seems to be most favorable[7]

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(1) Glockler and Roberts, THIS JOURNAL, **50**, 828 (1928).

(2) W. R. Kirner, *Ind. Eng. Chem., Anal. Ed.*, **6**, 358 (1934).

(3) W. R. Kirner, *ibid.*, **7**, 363 (1935).

(4) Williams, Rohrman and Christensen, THIS JOURNAL, **58**, 291 (1936).

(5) Simon and Guillaumin, *Compt. rend.*, **175**, 525 (1922).

(6) I. K. Phelps, *Am. J. Sci.*, **4**, 372 (1897).

(7) H. C. S. Snethlage, *Rec. trav. chim.*, **54**, 651 (1935).

and was used in the work here reported. If five volumes of sulfuric acid are diluted with one volume of water, chromous oxide is not precipitated enough to cause serious inconvenience.

Preliminary experiments indicated that for practically all compounds satisfactory oxidation takes place if the temperature is brought to the point where oxidation is vigorous for a few minutes and then raised and held at 165° for twenty minutes. In the case of a few compounds, when the vigorous oxidation (which is easily noted) fails to take place below 165°, it is necessary to modify the heating so that the ultimate temperature is perhaps 10° above the point where the reaction appears to be vigorous. Temperatures up to 200° were not sufficient to cause appreciable oxidation of ammonia.

Considering the danger of escape of volatile, difficultly oxidized compounds (particularly acetic acid) on the one hand and the size of the correction due to dissolved gases on the other, it was deemed advisable to use 12 ml. of medium per 1.5-g. charge of dichromate.

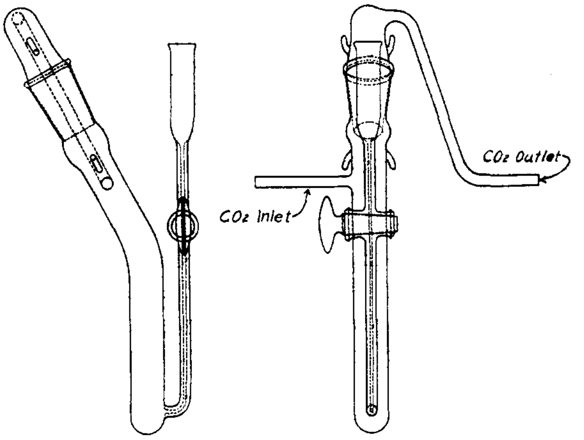

Fig. 1.

Two methods were available for the determination of the unreduced dichromate. The simplest procedure involves the thermal decomposition of the excess dichromate and the measurement of all the unused oxidizing agent as oxygen gas. However, in order to carry out the process in a reasonable length of time such high temperatures are required that ammonia if present, is oxidized. This makes the method inapplicable to nitrogenous compounds, and we were forced to determine the unreduced oxidizing agent by back titration. This was done iodometrically.

A cause of difficulty at this point is the fact that during the oxidation and partial decomposition of the dichromate small amounts of an intermediate product (perhaps perchromic acid or $Cr_2(SO_4)_5$[8]) are invariably formed which causes low results on titration. This was obviated by diluting the medium after oxidation with 12 ml. of 6 *N* sulfuric acid and boiling gently for five minutes. By this means complete recovery was consistently obtained when the oxygen gas collected and the unchanged dichromate were both taken into account.

We have found it impossible to prevent the formation of carbon monoxide while certain compounds (notably carbohydrates) are being oxidized. To avoid error due to this cause, the carbon monoxide may be oxidized to carbon dioxide with the oxygen which is evolved. This has been accomplished in this work by introducing a chamber containing a platinum spiral heated to dull red heat, into the train between the bubble counter and the oxygen buret, or by running the whole sample of gas after collection in the buret into a slow combustion pipet until all carbon monoxide has been oxidized.

Apparatus.—As some carbon monoxide is liable to be formed and large amounts of oxygen are always evolved during oxidation, it is necessary to utilize a closed system whereby these products can be retained. The apparatus used is simple and consists of (1) a Kipp generator for carbon dioxide production, (2) a reaction vessel of special design, (3) a bubble counter, (4) a gas buret (nitrometer), and (5) a slow combustion pipet.

The reaction vessel[9] is pictured in Fig. 1 and is made using a Pyrex No. 20 standard taper joint. The Kipp generator is charged with marble and air-free concentrated hydrochloric acid containing about 20% dissolved calcium chloride, in order that the carbon dioxide shall be as pure as possible; the bubble counter is one of the usual type but constructed so that there is no inverted pocket where gas may be retained; the gas buret is an ordinary Schiff nitrometer and the slow combustion pipet is of the type described by Engelder.[10]

The reaction vessel is heated by means of a special bath, which has been found very convenient, composed of 1 part of metaphosphoric acid and 4 parts of sirupy phosphoric acid.[11]

Procedure.—The reaction vessel is charged with a weighed quantity (about 1.5 g.) of potassium dichromate of known purity. The stopcock on the vessel is lubricated with phosphoric acid. Twelve ml. of a 5–1 (by volume) mixture of sulfuric acid and water is then introduced into

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(8) Ball and Crane, THIS JOURNAL, **55**, 4860 (1933).

(9) This unit can be purchased from the Corning Glass Works, Corning, New York.

(10) Engelder, "Gas, Oil and Fuel Analysis," John Wiley & Sons, Inc., New York, 1931, p. 30.

(11) Christensen and King, *Ind. Eng. Chem.*, *Anal. Ed.*, **9**, 194 (1936).

the reaction vessel through the capillary. The vessel is connected to the Kipp generator in such a position as to permit a porcelain boat to rest near the mouth of the vessel.

The porcelain boat containing a weighed sample to be analyzed (about 100 mg.[12]) is placed at the upper end of the reaction vessel. The seal is lubricated with sirupy phosphoric acid, closed and held together with small steel springs. The bubble counter is connected on the one hand to the outlet tube of the vessel and on the other to the gas buret. For connections sound heavy-walled rubber tubing (2 mm. internal diameter), well lubricated with water, is used.

In order to simplify the assembling of the apparatus the gas buret should be suspended from the top so that the position of the lower end can be adjusted easily.

The system is flushed with a moderate stream of carbon dioxide for about ten minutes; in the meantime the gas buret is charged with 30% potassium hydroxide solution which has been saturated previously with oxygen at room temperature. The flushing is complete when, as in the ordinary Dumas method for nitrogen, the bubbles are negligibly small (about 0.2 mm. in diameter).

The reaction vessel is now rotated to a position about 15° from vertical; this allows the boat and contents to slide into the reaction mixture, and the heating may be started. The bath is adjusted to surround the lower 5-cm. portion of the vessel and its temperature raised slowly (principally to avoid breaking the bath container since the bath mixture is viscous at first) until the oxidation proceeds vigorously. As indicated above, the bath mixture is in most cases held at approximately even temperature for two to five minutes and is then heated to about 165° for twenty minutes. The whole heating process as contrasted with that of carbon and hydrogen combustions is completed with a minimum of care since the bath temperature is regulated easily and, as a result of continuous evolution of gas, the reacting solution boils vigorously without any tendency to superheat or bump.

After the heating time has elapsed the bath is removed and 12 ml. of 6 *N* sulfuric acid is added through the capillary. The reaction mixture is boiled gently for five minutes using a free flame. The residual oxygen is flushed from the system for about four minutes or until the bubbles are negligibly small.

The gas buret is detached and connected to the slow combustion pipet where the carbon monoxide which may have been formed is oxidized by oxygen evolved during the oxidation. The gas is then transferred back to the nitrometer and allowed to stand in a room of even temperature until the volume remains constant.

In the meantime the contents of the reaction vessel are washed into a 500-ml. volumetric flask with boiled water. A 100-ml. aliquot is removed; to it are added 2 g. of sodium bicarbonate and 4 g. of potassium iodide. This is allowed to stand for a half hour in a stoppered bottle, diluted to about 300 ml. with boiled water, and titrated with 0.1 *N* sodium thiosulfate.[13]

The analysis is thus completed in less than two hours. A considerable part of this time (during the heating and waiting for the final titration) can be utilized for the preparation of samples for the next analysis, or completion of other analyses if more than one apparatus is available. It only remains to calculate the amount of oxygen (in milliequivalents) in the buret and the milliequivalents of residual oxidizing agent and subtract these from the milliequivalents of dichromate originally used. This gives the milliequivalents used by the sample. In calculating the milliequivalents of oxygen gas it is of course necessary to make the usual corrections for temperature, barometric pressure, vapor pressure of the potassium hydroxide solution[14] and calibration of the buret. In addition there is a small correction for the air which originates in the sulfuric acid solution or from the Kipp generator. This amounts to 0.3 to 0.4 ml. and as it is practically constant needs to be determined only occasionally. This is done by passing the gas into a Hempel pipet charged with alkaline sodium hydrosulfite, and measuring the unabsorbed gas. The air correction is calculated as five-fourths of the residual nitrogen.

Discussion and Results.—The results given in Table I are representative of those obtained under ordinary laboratory conditions. Partly through

TABLE I

RESULTS OF ANALYSES

The first nine analyses recorded were run with the platinum spiral combustion chamber in the combustion train behind the gas buret. This took the place of the slow combustion pipet.

Substance analyzed[a]	Percentage errors in milliequivalents of oxygen used. (Successive analyses)				
Succinic acid	+0.06[b]	+0.09	+0.30	+0.97	−0.11
Sucrose	.00	− .56[c]			
Potassium acid phthalate	− .17	− .31			
Sucrose	+ .10	+ .02			
Potassium acid phthalate	+ .47	+ .14			
Acetanilide	+ .45	− .51	−0.11	+0.22	
Benzoic acid	+ .22	+ .54	−2.06[d]		
	+ .03	−2.05[d]	+0.21	+0.19	
Leucine	+ .15	+0.06			
Quinoline	− .58[e]	− .92[e]			
Benzidine	+ .17	+ .68	+0.96		

[a] The samples used varied from about 0.15 g. for succinic acid down to 0.05 g. for benzidine. [b] The temperature of this combustion was 200° instead of 165°. [c] In this analysis, carbon monoxide was found to have escaped oxidation. The amount was determined and the value corrected accordingly. [d] The difficulty in these two benzoic acid determinations was found to be due to too rapid flushing and a consequent entrainment of some finely powdered benzoic acid which escaped oxidation. This defect was carefully guarded against in the last two analyses. [e] This compound was difficult to oxidize and the temperature was raised to 185° and held there for over thirty minutes. The indications are that even this may not have been entirely sufficient.

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(12) If the material is of a waxy or oily consistency or is known to be a compound of high oxygen requirement, the sample should be reduced somewhat (even to about half this size); whereas, if it is known to be a highly oxygenated compound such as a carbohydrate, the size of the sample may be increased by 50% or more.

(13) Willard and Furman, "Elementary Quantitative Analysis," D. Van Nostrand Co., New York, 1933, p. 187.

(14) "International Critical Tables," McGraw-Hill Book Co., Inc., New York.

intention and partly through necessity most of the analyses were run under conditions far from ideal. After the proper conditions had been established, the method, in the hands of a relatively inexperienced student using ordinary balances, weights, volumetric apparatus, and chemicals, gave results which are far from unsatisfactory.

All analyses made after the method was established in its present form are included in Table I except exploratory tests on materials known to be impure, such as paraffin, and tests on certain compounds (particularly asparagine) which were found later to be impure and variable in composition. It seems to be a significant fact that we have experienced no difficulty in obtaining *highly satisfactory results with every compound the standard of purity of which was unusually high* (succinic acid, potassium acid phthalate, sucrose, acetanilide, benzoic acid).

Duplicate analyses of nicotinic acid (which is almost untouched by the iodate method[7]) gave consistent results which were only slightly low. This sample upon further investigation was found to be impure. Subsequent work with quinoline indicates that the method apparently is applicable to compounds containing the pyridine nucleus.

Analyses of paraffin showed it to be difficult to oxidize, apparently not because of its stability toward the oxidizing agent but because of its insolubility. Using the ordinary procedure it is over 90% oxidized, but after the reaction mixture cools small flakes of unchanged paraffin are visible on the surface. The indications are that by modifying the procedure accurate analyses could be obtained even on paraffin.

On the basis of the above facts we are of the opinion that by using extra precautions and precision equipment it should be possible to obtain highly precise results in the analysis of organic compounds generally. Under ordinary conditions one can obtain results which are in error less than 5 parts per thousand, which is satisfactory for the purposes outlined in the first paper of this series.

Preliminary experiments indicate that compounds containing sulfur may require some special treatment to obtain accurate results, though values which are at least approximately correct are obtained using the method as here outlined. The adaptation of the method as outlined to a micro scale has led to irregularities presumably associated with the formation of intermediate reduction products of dichromate, which as yet we have been unable to eliminate.

Summary

A method for the accurate determination of the oxidizing agent required for the complete combustion of organic compounds, using potassium dichromate as the oxidizing agent, is described.

In accordance with equations developed in the first paper in this series, this determination can be substituted in the majority of cases for a combustion analysis.

Its advantages over combustion analyses are: (1) considering all preliminary preparations, it is quicker; (2) it uses a minimum of special equipment and none which cannot readily be made in the laboratory; (3) it requires no special catalysts or materials which are likely to introduce complications; (4) it involves the simplest technique and no careful control of heating or gas evolution; (5) it, when taken in conjunction with an accurate carbon determination, makes possible a more accurate determination of hydrogen than has hitherto been possible under ordinary analytical conditions.

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