A Rapid Determination of Oxidation Values of Non-Volatile Organic Compounds by the Iodic Acid Decomposition Method

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In the course of preparing organic compounds, on many occasions, it is only necessary to determine the percentages of carbon or other elements to serve as a check on the purity. For this purpose, however, it is not always necessary to determine the content of an element such as carbon, hydrogen, or nitrogen, but instead the "oxidation value" of the compound, named by the author, can also be useful. The oxidation value of a compound is defined as the number of oxygen atoms required to completely oxidize one molecule of the compound.

A survey of the literature reveals that Strebinger[1] and Christensen, Facer, and

1) R. Strebinger, *Z. analyt. Chem.*, 58, 97 (1919).

Wong[2,3] determined the "oxygen consumed" of an organic compound, which is defined as oxygen requirement in gram per hundred grams of the sample, by means of iodic acid in concentrated sulfuric acid. In spite of all these developments there is still need for wider applicability, simpler techniques, less expensive equipment, and methods by which the occasional determination can be made easily.

For the complete wet combustion of organic compounds a powerful oxidizing agent is required and, furthermore, to determine the oxidation values of the compounds, the reduced part of the oxidant must be measured readily and exactly after the oxidation reaction. Iodic acid in strong phosphoric acid is a very suitable reagent for this purpose. The strong oxidizing action of this reagent was already used by the author and his co-workers[4] for the determination of elementary carbon, such as charcoal, graphite, and others, which are completely oxidized by it to form carbon dioxide.

$$5C + 4HIO_3 = 5CO_2 + 2I_2 + 2H_2O$$

The amount of the reduced part of iodic acid can be known by means of a volumetric determination of the iodine produced.

Now one may suppose in general an organic compound composed of carbon, hydrogen, and oxygen, and indicate it as $C_kH_mO_n$. Then the oxidation of the organic compound with iodic acid is shown by the following equation (3), which is derived from equations (1) and (2).

$$C_kH_mO_n + (2k + m/2 - n)\,O = k\,CO_2 + m/2\,H_2O \quad (1)$$

$$2HIO_3 = H_2O + I_2 + 5O \quad (2)$$

$$5C_kH_mO_n + 2(2k + m/2 - n)HIO_3 = 5kCO_2 + (2k + 3m - n)H_2O + (2k + m/2 - n)I_2\,. \quad (3)$$

Namely, 5 mol. of the organic compound $C_kH_mO_n$ is oxidized completely with $2(2k+3m-n)$ mol. of iodic acid under the production of $(2k+m/2-n)$ mol. of iodine. Therefore, if the organic compound is completely oxidized with the reagent according to the above equation, its oxidation value may be obtained by the determination of the iodine produced.

In this study the method of determining the oxidation values based on the above-mentioned principle was investigated and the oxidation values were determined for several non-volatile organic compounds, which are composed of carbon, hydrogen, and oxygen.

Apparatus

The apparatus used in this study is illustrated in Fig. 1. It is mainly composed of two parts, a

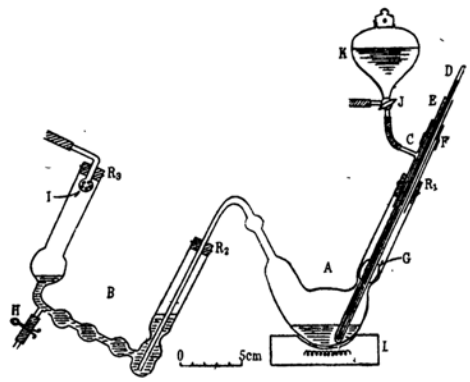

Fig. 1 Apparatus

A: Reaction vessel
B: Absorption vessel
C: Gas-introducing tube
D: Thermometer
E: Thermometer-protecting tube
F: Rubber tube
G: Glass lock
H: Pinch cock
I: Glass bulb
J: Three-way stopcock
K: Water-addition funnel
L: Electric heater
R_1-R_3: Rubber stopper

Fig. 2 Glass lock.

Fig. 3. Weighing tube.

reaction vessel A and an absorption vessel B. The right tube of the vessel A is closed at the top by means of a rubber stopper R_1, through which a gas-introducing tube and a thermometer are inserted. The thermometer is protected by a glass tube. If the thermometer-protecting tube is not used, the very thin bottom glass of the thermometer may easily be destroyed by heating with strong phosphoric acid. In the right arm of the vessel A, there is a constricted part above which a small glass lock shown in Fig. 2 is set for the sake of protecting it against the backward stream of gas. The left arm of the vessel A is inserted deeply into the absorption vessel B through a rubber stopper R_2. In order to prevent the liberated iodine from going upward to the rubber stopper R_2, the right arm of the vessel B is constricted at the position as shown in Fig. 1. On the left arm of the vessel B, there is an outlet, having a short rubber tube and a pinch cock, for convenience to pour out the solution in the vessel. The top of the left arm is closed by

2) B. E. Christensen and J. F. Facer, *J. Am. Chem. Soc.*, **61**, 3001 (1939).
3) B. E. Christensen and R. Wong, *Ind. Eng. Chem., Anal. Ed.*, **13**, 444 (1941).
4) T. Kiba, S. Ohashi, T. Takagi, and Y. Hirose, *Japan Analyst*, **2**, 446 (1953).

means of a rubber stopper R_3, through which a glass tube with a small glass bulb, having some pinholes, is inserted to prevent loss from a splash.

After passing through the solutions of sodium carbonate, potassium permanganate, and mercuric chloride in turn, the air is introduced by means of a suction pump into the vessel A through the three-way stopcock of a water-addition funnel, which is used to add water to the vessel A after the decomposition of a sample.

The vessel A is heated at the bottom with an electric heater, the temperature of which can be regulated with a transformer.

Reagents

Potassium Iodate.—Standard reagent grade (The Osaka Industrial Research Institute) or extra pure grade potassium iodate was used.

Strong Phosphoric Acid.—Commercial extra pure grade orthophosphoric acid (d=1.7) was dehydrated by heating until the temperature of the liquid reached 300°C. The very viscous liquid thus obtained is called strong phosphoric acid[5], which is a mixture of ortho-, pyro-, and triphosphoric acid.

Standard Solution of Sodium Arsenite.—A 0.1 N solution of sodium arsenite was used. Dissolve 4.95 g. of standard reagent grade (The Osaka Industrial Research Institute) arsenic trioxide in 150 ml. of 10% sodium carbonate solution, add 25 ml. of normal sulfuric acid, and dilute to 1000 ml.

Standard Solution of Iodine.—A 0.05 N solution of iodine was used. It was standardized with the above sodium arsenite solution.

Procedure

Weigh accurately a 15 to 100 mg. sample, depending upon its oxidation value, into a small weighing tube shown in Fig. 3; choose the sample weight so that the iodine formed will not consume more than 50% of the sodium arsenite used. From a buret, pour about 3 to 5 ml. of strong phosphoric acid into a reaction vessel A through its upper inlet, and add a suitable amount of powdered potassium iodate. The optimum amount of potassium iodate will be discussed later. Next, let fall the weighing tube containing the sample along the inside wall of the vessel carefully. Add 10 or 20 ml. of sodium arsenite solution into an absorption vessel B. If only 10 ml. of sodium arsenite solution is used, add further about 10 ml. of water. Then connect all of the vessel A, B and so on.

While a slow stream of washed air is flowing through the vessel A and B by a suction pump, gently heat the bottom of the vessel A on a small electric heater. With increase of temperature, viscosity of the reaction medium decreases and a decomposition reaction begins at the appearance of a violet vapor of iodine. During the decomposition reaction shake the vessel A in order to get a complete reaction.

The reaction temperatures are varied from 80° to 240°C in accordance with species of samples. However, the temperature of the reactants must be kept carefully under 260°C, because at any higher temperature than this limit iodic acid is decomposed with the evolution of iodine[6].

The end of the decomposition reaction is easily recognized by the ceasing of the production of iodine. After the end of the decomposition reaction, stand the vessel A aloof from the electric heater until the temperature of the reaction medium falls to about 140°C, while air is flowing through the vessel.

After the cooling, open the three-way stopcock and introduce 10 to 15 ml. of water into the vessel A. Then heat once more the aqueous solution in the vessel A on the electric heater, until all of the iodine dissolved in the reaction solution is removed and absorbed into the sodium arsenite solution.

Remove the absorption vessel B from the rubber stoppers, let the solution flow into a beaker, and wash out the vessel B and the small glass bulb with water. Add some sodium bicarbonate to the solution in the beaker and titrate the excess sodium arsenite with 0.05 N iodine solution using starch solution as indicator.

Results and Discussion

In order to estimate the indispensable quantity of potassium iodate for the complete oxidation of an organic compound, the following experiment was carried out in the case of oxalic acid as an example.

About 50 mg. of oxalic acid weighed accurately was oxidized with various amounts of potassium iodate and the iodine produced was measured by the procedure described above. Results obtained are given in Table I. Nos. 4 and 5 in this experiment have

Table I

Amount of potassium iodate required for complete oxidation of oxalic acid

No.	Sample Weight mg.	Potassium Iodate Used mg.	Potassium Iodate Ratio: mg. used to mg. equiv.	Iodine Produced Found mg.	Iodine Produced Ratio: mg. found to mg. calc.
1	51.5	20.5	0.58	11.6	0.56
2	50.0	30.5	0.98	18.7	0.92
3	50.7	32.7	0.95	17.9	0.88
4	49.2	34.0	1.02	18.2	0.92
5	50.6	40.0	1.16	19.8	0.90
6	51.1	52.2	1.50	20.4	0.99
7	50.0	65.3	1.91	20.1	0.99
8	49.8	100.5	2.97	20.1	1.00

indicated obviously that an amount of potassium iodate slightly in excess of that required theoretically can not oxidize the sample completely. For this purpose an excess of at least half as much again as the theoretical

5) L. F. Audrieth, "Inorganic Syntheses, Volume III", McGraw-Hill Book Company, Inc., New York, (1950), p. 89.

6) T. Kiba et al., loc. cit.

quantity should be used.

In the first course of this investigation the reactions were carried out in the stream of carbon dioxide, but if a sample and sodium arsenite solution can not be oxidized with air, air may be used instead of carbon dioxide. With regard to this presumption the following tests were performed.

At first in order to investigate the stability of sodium arsenite solution against aeration, the washed hot air accompanied with aqueous vapor was introduced into a certain amount of sodium arsenite solution at the rate of about 5 bubbles of air per second. After the aeration titrating the arsenite solution with the standard solution of iodine, the data shown in Table II were obtained. This result

TABLE II

EFFECT OF AERATION ON STABILITY OF SODIUM ARSENITE SOLUTION

Quantity of 0.05 N Iodine Solution Consumed	
Before Aeration ml.	After 1 hr. of Aeration ml.
34.43	34.44
34.43	34.44
8.89	8.88
8.89	8.88

shows that the sodium arsenite solution can not be oxidized by one hour's aeration. Since the period of aeration in the practical procedure is shorter than thirty minutes, the oxidation of the arsenite solution with air may be out of the question.

Next, for the determination of the oxidation value of sodium oxalate, for example, the air flowing method was compared with the carbon dioxide flowing method. As shown in Table III there is no difference between the two methods.

TABLE III

COMPARISON OF CARBON DIOXIDE FLOWING METHOD AND AIR FLOWING METHOD

Sample: Sodium Oxalate

Gas Used	Sample Weight mg.	Iodine Produced		Deviation mg.
		Calc. mg.	Found mg.	
CO_2	33.2	12.5_8	12.5_2	-0.0_6
〃	50.0	18.9_4	18.9_2	-0.0_2
〃	82.5	31.2_5	31.1_5	-0.1_0
〃	87.5	33.1_5	33.0_6	-0.0_9
Air	30.5	11.5_5	11.5_1	-0.0_4
〃	57.0	21.5_9	21.5_5	-0.0_4
〃	45.3	17.1_6	17.1_1	-0.0_5
〃	80.9	30.6_4	30.3_9	-0.2_5

Analyses of some known organic compounds were carried out by this method. These results are summarized in Table IV. Purest

TABLE IV

DETERMINATION OF OXIDATION VALUES OF SOME COMPOUNDS BY THIS METHOD

Substance	Oxidation Value Calc.	Reaction Temperature °C	Sample Weight mg.	Iodine Produced		Oxidation Value	
				Calc. mg.	Found mg.	Found	Deviation from Average
Oxalic acid	1	90–120	34.6	13.9_3	13.9_4	1.00_1	-0.00_1
$H_2C_2O_4 \cdot 2H_2O$			42.8	17.2_4	17.3_3	1.00_5	$+0.00_3$
			53.2	21.4_2	21.4_4	1.00_1	-0.00_1
			60.4	24.3_2	24.3_3	1.00_0	-0.00_2
			73.2	29.4_8	29.6_1	1.00_4	$+0.00_2$
					Av.	1.00_2	
Sodium oxalate	1	80–150	34.7	13.1_4	13.2_1	1.00_5	-0.00_1
$Na_2C_2O_4$			41.6	15.7_6	15.7_6	1.00_4	-0.00_2
			55.9	21.1_7	21.3_2	1.00_7	$+0.00_1$
			78.4	29.7_0	29.9_0	1.00_7	$+0.00_1$
					Av.	1.00_6	
Tartaric acid	5	80–150	25.4	42.9_5	42.9_7	5.00_5	$+0.01_1$
$C_4H_6O_6$			26.5	44.8_0	45.0_7	5.01_5	$+0.02_1$
			33.9	57.3_2	57.2_1	4.99_0	-0.00_4
			35.9	60.7_1	60.0_0	4.94_0	-0.05_4
			40.4	68.3_4	68.3_7	5.00_5	$+0.01_1$
			45.3	76.6_0	76.5_6	4.99_5	$+0.00_1$
			55.7	94.1_9	94.4_2	5.01_0	$+0.01_6$
			64.9	109.8	109.5	4.98_5	-0.00_9
			75.0	126.8	126.8	5.00_0	$+0.00_5$
					Av.	4.99_4	

TABLE IV (Contd.)

Substance	Oxidation Value Calc.	Reaction Temperature °C	Sample Weight mg.	Iodine Produced		Oxidation Value	
				Calc. mg.	Found mg.	Found	Deviation from Average
Sodium potassium tartrate	5	90–150	25.4	22.8_4	22.7_9	4.99_0	$+0.00_5$
$C_4H_4O_6NaK \cdot 4H_2O$			32.0	28.7_8	28.6_4	4.97_5	-0.01_0
			35.3	31.7_5	31.6_5	4.98_5	0.00_0
			47.1	42.3_6	42.1_9	4.98_0	-0.00_5
			50.4	45.3_2	45.2_6	4.99_5	$+0.01_0$
			65.3	58.7_2	58.5_4	4.98_5	0.00_0
					Av.	4.98_5	
Citric acid	9	80–150	23.5	41.0_9	41.4_9	9.08_1	$+0.00_3$
$C_6H_8O_7 \cdot H_2O$			26.8	58.2_6	58.5_8	9.05_4	-0.02_4
			39.5	85.8_7	86.7_1	9.09_0	$+0.01_2$
			39.8	86.2_3	86.9_3	9.07_2	-0.00_6
			40.7	88.4_8	89.2_8	9.08_1	$+0.00_3$
			48.1	104.6	105.6	9.09_0	$+0.01_2$
					Av.	9.07_8	
Sodium citrate	9	90–150	24.1	30.8_2	30.9_2	9.03_6	$+0.04_7$
$C_6H_5O_7Na_3 \cdot 5.5H_2O$			32.2	41.1_8	41.2_6	9.01_8	$+0.02_9$
			39.9	51.0_3	50.8_1	8.96_4	-0.02_5
			54.8	70.0_8	69.7_2	8.95_5	-0.03_4
			62.0	79.3_0	79.1_2	8.98_8	-0.00_1
			75.7	96.8_2	96.5_7	8.97_3	-0.01_6
					Av.	8.98_9	
Succinic acid	7	160–230	19.4	58.3_7	57.9_3	6.94_4	-0.01_4
$C_4H_6O_4$			20.9	62.8_9	62.4_5	6.95_1	-0.00_7
			22.0	66.2_0	65.9_9	6.97_9	$+0.02_1$
			29.1	87.5_6	87.0_1	6.95_8	0.00_0
			44.2	133.0	132.1	6.95_1	-0.00_7
			54.3	163.4	162.6	6.96_5	$+0.00_7$
					Av.	6.95_8	
Arabinose	10	90–230	19.8	66.1_9	66.3_5	10.0_2	$+0.0_2$
$C_5H_{10}O_5$			30.0	100.3	100.3	10.0_0	0.0_0
			33.4	111.7	111.2	9.9_5	-0.0_5
			47.1	157.5	156.7	9.9_5	-0.0_5
			50.5	168.8	169.8	10.0_6	$+0.0_6$
					Av.	10.0_0	
Glucose	12	80–250	26.6	88.9_2	88.9_1	12.0_0	$+0.0_6$
$C_6H_{12}O_6$			35.9	110.6	110.0	11.9_4	0.0_0
			36.6	122.4	121.2	11.8_8	-0.0_6
			41.1	134.2	133.8	11.9_6	$+0.0_2$
			44.4	136.9	136.3	11.9_5	$+0.0_1$
			62.8	193.4	192.5	11.9_4	0.0_0
					Av.	11.9_4	
Galactose	12	80–230	25.2	85.1_9	84.9_9	11.9_8	$+0.0_2$
$C_6H_{12}O_6$			26.5	89.5_8	88.9_8	11.9_2	-0.0_4
			35.9	121.4	120.9	11.9_5	-0.0_1
			46.3	156.5	156.4	11.9_9	$+0.0_3$
			50.6	171.1	170.7	11.9_8	$+0.0_2$
					Av.	11.9_6	
Dulcitol	13	90–200	25.6	92.7_4	92.3_0	12.9_3	-0.0_3
$C_6H_{14}C_6$			30.5	110.5	110.2	12.9_5	-0.0_1
			39.0	141.3	141.3	13.0_0	$+0.0_4$
			41.9	151.8	151.4	12.9_5	-0.0_1
			45.1	163.4	162.8	12.9_5	-0.0_1
			52.6	190.6	190.4	12.9_9	$+0.0_3$
					Av.	12.9_6	

TABLE IV (Contd.)

Substance	Oxidation Value Cale.	Reaction Temperature C°	Sample Weight mg.	Iodine Produced		Oxidation Value	
				Cale. mg.	Found mg.	Found	Deviation from Average
Saccharose	24	100–230	16.9	60.1_6	59.5_0	23.7_8	−0.0_3
$C_{12}H_{22}O_{11}$			20.7	73.6_9	73.0_7	23.8_1	0.0_0
			29.0	103.$_2$	102.$_4$	23.8_1	0.0_0
			33.8	120.$_3$	119.$_5$	23.8_3	+0.0_2
			37.1	132.$_1$	130.$_9$	23.7_8	−0.0_3
			40.0	142.$_4$	141.$_4$	23.8_3	+0.0_2
					Av.	23.8_1	
Treharose	24	90–230	12.4	44.1_3	44.0_3	23.9_5	+0.0_1
$C_{12}H_{22}O_{11}$			14.7	52.3_2	52.0_7	23.8_8	−0.0_5
			15.3	54.4_5	54.2_6	23.9_3	−0.0_1
			16.1	57.3_0	57.2_2	23.9_8	+0.0_4
					Av.	23.9_4	

grade organic compounds were selected or prepared and dried in the calcium chloride or sulfuric acid desiccator before analysis.

The results listed for the various organic compounds in Table IV indicate that the precision of the data is within ±1%.

The constantly high value obtained for citric acid might be due to the loss of a part of the crystallization water. The slightly low values for succinic acid and saccharose led to the belief that these substances had not been completely dried prior to analysis.

Most of the analyses reported in Table IV were conducted according to the procedure described above and required only twenty to thirty minutes for one estimation.

This method can not be applied to volatile samples such as benzoic acid. For the development of this method to the volatile compounds the apparatus would have to be improved. The investigation of this point is a future problem.

Summary

A new method has been developed to permit accurate and rapid determination of oxidation values of organic compounds. The oxidation value of a compound can be readily obtained by determining the iodine produced from the reaction of the organic compound and potassium iodate in strong phosphoric acid. The iodine produced is absorbed into the sodium arsenite solution and the excess arsenite is titrated with the standard solution of iodine.

The apparatus and procedures for this method have been investigated. According to the data obtained on some pure non-volatile organic compounds, utilizing sample weights of 10 to 80 mg., it is indicated that this method is very accurate and an analysis can be accomplished as rapidly as in twenty to thirty minutes.

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