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Organic Oxidation Equivalent Analysis. II. By the Use of Iodate. (Micro and "Sub-micro" Methods)

By Roger J. Williams, Ewald Rohrman and Bert E. Christensen

The use of potassium iodate in slightly diluted sulfuric acid recommended itself to Strebinger[1] as a suitable process for determining the amount of oxygen used up in the oxidation of a compound because its use avoids the production of carbon monoxide, and allows for a simple back titration of the unused oxidizing agent. Stanek and Nemes[2] without cognizance of Strebinger's work used potassium iodate in concentrated sulfuric acid under similar conditions in a complicated system of micro organic analysis in which "oxygen consumed," carbon, nitrogen and halogens were determined.

We have investigated the quantitative oxidation of organic compounds by potassium iodate in concentrated sulfuric acid and have found the method to be applicable under suitable conditions to most carbon-hydrogen-oxygen compounds and to certain nitrogen compounds, but that it has definite restrictions other than those indicated by the work of the authors mentioned above. We shall, for economy of space, leave out data which fall in line with the observations of Strebinger and Stanek and Nemes and give in more detail the results which supplement or are contradictory to theirs.

Danger of Oxidizing Nitrogen.—While under the conditions used by Stanek and Nemes there is probably not a serious danger of oxidizing nitrogen, Strebinger's conditions are more unfavorable in this regard. On the basis of numerous duplicate analyses we find that when nitrogenous compounds are analyzed and the sample is increased up to the concentration used by Strebinger there is an extra "oxygen consumption" which must be due to the oxidation of ammonia.

That the danger lies in the accumulation of liberated iodine was shown by several experiments. For example three samples of acetanilide 4.02 mg. (pipetted in solution in test-tubes and evaporated in vacuum) were treated alike except that to the second and third were added 10 and 100 mg., respectively, of iodine. Oxidation was for thirty minutes at 185°. The oxygen consumptions in the three cases were, respectively, 0.15% low, 0.45% high and 8.0% high, indicating that iodine brings about additional oxygen consumption. In order to avoid this possibility we have used 3–4 mg. samples and 5 ml. of concentrated sulfuric acid, which reduces the concentration to about one-half that used by Stanek and Nemes and to about one-fifth that used by Strebinger.

Failure to Oxidize Nicotinic Acid.—Stanek and Nemes[2] pointed out that quantitative oxidation of nitrogen compounds with iodate is accomplished only when the nitrogen can be determined by the Kjeldahl method. Nitro compounds, hydrazones and heterocyclic nitrogen compounds fail to yield satisfactory results. When we applied the method to nicotinic acid (185° for twenty minutes) 3.8 and 4.1% oxidation resulted in duplicate analyses. Raising the temperature sufficiently to oxidize the ring without oxidizing nitrogen and introducing other complications does not seem feasible.

Acetates.—As a result of a rather extensive study we conclude that *generally speaking* acetic acid is the most difficultly oxidized organic compound with which we have been concerned. However, acetic acid is oxidized with iodate more easily than nicotinic acid, though when permanganate is the oxidizing agent the situation is distinctly reversed. Succinic acid is likewise difficult to oxidize (with iodate or dichromate) but not as difficult as acetic acid.

Many organic substances liberate iodine in the cold when the sulfuric acid-iodate reagent is used. Succinic acid required four minutes in a bath at 185° before appreciable iodine color appeared. Acetic acid required eight minutes at this temperature to bring about visible iodine liberation. The difficulty of oxidizing acetic acid is further shown by the fact that acetanilide cannot be oxidized completely with iodate at 185° in twenty minutes (Tables I and II). The aniline portion of the molecule is easily oxidized, however, and liberates iodine from iodate in the cold.

Phthalate Oxidations.—A further limitation of the method appeared when we attempted to apply it to potassium acid phthalate and phthalic anhydride. Strebinger reported one satisfactory analysis of phthalic acid and one of a naphthol. Stanek and Nemes reported no analyses of phthalates. Two determinations on potassium acid phthalate yielded results indicating an 80% and a 75% oxidation, respectively. In the second one of these analyses the sample was dissolved carefully before heating or introduction of iodate took place, but the result was even farther in error than the first. Oxidation of phthalic anhydride at the same temperature (185°) for thirty minutes instead of twenty minutes as used above, resulted in only 74% oxidation. Potassium acid phthalate appears, however, to be oxidized completely at higher temperatures. Thirty minutes at 200° brought the oxygen consumption to about 88% of the theoretical, while at 210° the oxidation appeared 99.3% complete in the same time. At 220° for thirty minutes nearly 2% too much iodate was used. This excess may have been due to thermal decomposition of iodic acid[2] or to oxygen consumption by the sulfuric acid used.

Use on a Micro Scale.—The data given in Table I were obtained as a result of a series of analyses none of which was

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(1) Strebinger, *Z. anal. Chem.*, **58**, 97–114 (1919).

(2) Stanek and Nemes, *ibid.*, **95**, 244 (1933).

TABLE I

MICRO ANALYSES

Substance	Wt. of sample, mg.	Time heated, min.	Wt. iodate used, mg. (plus 5 cc. H_2SO_4 and .2 cc. H_2O)	Iodate used up, mg.	Iodate used above blank	Theoretical	Error, %
Blank	...	40	59.005	0.556	....	....	.....
Blank	...	40	52.072	.582	....	....	.....
Blank	...	40	43.652	.514	....	....	.....
Sucrose	3.798	20	71.477	23.317	22.766	22.788	−0.096
Sucrose	3.536	20	86.026	21.801	21.250	21.216	+0.16
Acetanilide	3.095	20	96.028	34.582	34.031	35.314	−3.62
Acetanilide	2.953	20	92.350	32.690	32.141	33.694	−4.6
Sucrose	4.213	40	101.69	26.122	25.571	25.278	+1.16
Sucrose	3.905	40	91.283	24.263	23.712	23.430	+1.2
Acetanilide	2.982	40	96.892	34.259	33.708	34.025	−0.93
Acetanilide	3.297	40	100.73	38.228	37.677	37.619	+0.15

TABLE II

"SUB-MICRO" ANALYSES

Substance	Wt. of sample, mg.	Time heated, 185° min.	Wt. iodate used plus 1 cc. concd. sulfuric acid	Iodate used up, mg.	Iodate used above blank	Theoretical	Error, %
Blank	..	20	15.054	0.029	...	...	....
Blank	..	20	16.294	.018	...	...	....
Blank	..	40	15.248	.030	...	...	....
Acetanilide	0.438	20	17.849	4.790	4.764	4.99	−4.5
Acetanilide	.565	20	18.288	6.258	6.232	6.447	−3.3
Acetanilide	.536	20	18.726	5.851	5.825	6.116	−4.8
Valine	.459	20	16.521	4.000	3.974	4.030	−1.4
Valine	.608	20	16.003	5.258	5.232	5.338	−2.0
Acetanilide	.567	40	17.415	6.504	6.478	6.469	+0.14
Acetanilide	.539	40	18.236	6.150	6.124	6.150	−0.42
Acetanilide	.446	40	18.597	5.052	5.026	5.089	−1.2
Valine	.403	40	17.443	3.584	3.558	3.538	+0.56
Valine	.570	40	17.007	4.988	4.962	5.004	−0.84

discarded. It is given in some detail to show how closely duplicates may be expected to check and also to show that the method of analysis must be modified slightly for different types of compounds. A twenty-minute heating period gives remarkably accurate results with sucrose but with acetanilide (which is admittedly an extreme case due to acetic acid formation) large errors result using this length of time. A forty-minute period gives acceptable results with acetanilide but with sucrose this extra period throws the results off somewhat. Probably for general use thirty minutes gives the best results but it seems clear that modifications, dependent upon the character of the material analyzed, must be made to obtain the most accurate results. It seems likely from our experience that at least in the case of easily oxidized compounds (carbohydrates, for example) the iodate method *may* yield precise results. As a rapid micro method for obtaining results of moderate accuracy it should be useful and with materials of biological origin (with the exception of certain alkaloids) it should be applicable and useful.

Use on a "Sub-micro" Scale.—One of the reasons for being interested in the application of this method was the possibility that it might be used for analyzing samples weighing not more than a fraction of a milligram--or the order of one-tenth that used for ordinary micro combustions. That this is possible with certain types of compounds is indicated by the data presented in Table II. These constitute a consecutive series of determinations with no analysis excluded. The samples to be analyzed were each weighed into test-tubes in the form of a water solution, the weighed amount of iodate was added and the solution was evaporated overnight in a vacuum desiccator. For weighing the solutions (on an ordinary balance) bottles of the solution containing a ground glass medicine dropper were weighed before and after the samples were removed. The titrations were carried out with an ordinary buret using 0.025 *N* thiosulfate. The iodate can be weighed conveniently in solution with saving of time and as a result ten analyses can be completed within about one working day, with an overnight period allowed for evaporation.

Procedure.—The procedure which we recommend for "micro" work is exceedingly simple. The sample which weighs 3 or 4 mg. is introduced into a test-tube along with 5 ml. of sulfuric acid, 0.2 ml. of water, and sufficient potassium iodate to constitute at least 100% excess. Both the sample and iodate can be weighed in the form of water solution if desired and then evaporated. It is necessary that the sample and the iodate be well distributed throughout the medium before heating is begun. Whether or not 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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Organic Oxidation Equivalent Analysis. III. General Method Using Dichromate

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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).