LXXV.—*Combustion by Means of Chromic Anhydride.*

By C. F. CROSS and E. J. BEVAN.

SOME time since we published a preliminary note of results obtained on the combustion of carbohydrates with chromic anhydride and sulphuric acid as a method of ultimate analysis (*Chem. News*, October 23, 1885). Having observed that carbonic oxide was formed and evolved with the carbonic anhydride, we found it necessary to abandon gravimetric methods and to measure the volume of the evolved gas, the proportion of carbon per unit of *volume* being independent of the ratio $CO : CO_2$. We have employed mercury as the confining liquid, and an apparatus consisting of a U-tube graduated in the one limb which is in connection with the combustion flask, the other limb being open to the air, and connected with a reservoir of mercury, by means of which the levels are adjusted for reading (*Rep. Anal. Chem.*, 1887, 37). In some cases, we have employed a Lunge's nitrometer, but the particular form of apparatus to be employed for the purpose is rather a matter of detail.

Before proceeding to deal with the results obtained, we must briefly notice a well-known paper of Ladenburg's, published in 1865 (*Annalen*, **135**, 1), on the subject of ultimate analysis by the few methods other than incandescent combustion which are available. In this paper, we find chromic acid mentioned, but dismissed as unavailable by reason of its decomposition on heating with sulphuric acid, with evolution of oxygen. This decomposition was specially studied by one of us (Cross and Higgin, Trans., 1882, 113), with the result of showing that it took place only at high temperatures, the evolution of oxygen being imperceptible up to a temperature some degrees above 100°, and becoming brisk only as the boiling point of the acid was reached. At the same time it was noticed that the course of the decomposition differed somewhat when potassium dichromate was substituted for the chromic anhydride, taking place more readily, and yielding a sulphate of different character and composition. Ladenburg having dismissed chromic acid apparently as a result of a general impression of its instability, finally selected iodic acid, added in the form of silver iodate to the sulphuric acid used as the liquid auxiliary. His combustions were performed with this mixture in sealed tubes, and his estimations consisted in determining the loss of weight after completely removing the gaseous products, and the total oxygen consumed. The results he obtained leave nothing to be desired in point of accuracy, and we can only conclude that it is the trouble and risk attending operations with sealed tubes which have deterred chemists from adopting this method.

On the other hand, with an open combustion such as that we have employed, the operation is a very simple one, completed in a few minutes, and if proved to be accurate would be a useful addition to our laboratory methods, even if its applications were limited. But apart from any question of application, the results of such combustions, partial for certain groups of compounds, complete in others, cannot fail to throw some light on the problems of the molecular constitution of carbon compounds. We shall, therefore, in the meantime content ourselves with recording the results obtained, and leave it to the progress of research to determine their value.

The proportion of carbonic oxide formed in the combustion of the carbohydrates depends very much upon the conditions of the decomposition. We have found, under those which we have perhaps arbitrarily selected, that it is reduced to a minimum; this being so, and a strict uniformity in the conditions being observed, the "error of the apparatus" we find satisfactorily constant. The conditions we may note here are:—(1) A quantity of substance to be used yielding from 90 to 100 c.c. of gas; (2) the same volume of sulphuric acid, namely, 9 c.c., must be employed; (3) an excess of chromic acid of about 30 per cent. beyond that required for complete combustion.

The substance, cellulose for example, being dissolved in the acid, and the chromic anhydride introduced in a small tube into the neck of the flask, the latter is connected in the horizontal position with the U-tube, and after a suitable interval the level of the mercury is brought to zero. The thermometer having been read off, the tube containing the chromic anhydride is allowed to fall to the bottom of the flask, and is well shaken with the acid solution. The combustion proceeds rapidly, the temperature rising to 60—70°; after about two-thirds of the gas has been collected, it is necessary to apply heat, the remainder of the gas being rapidly expelled at 100°. The conclusion of the combustion is well marked by the cessation of the frothing which accompanies the evolution of the gas in the viscous medium. The flask is allowed to cool, and the gas volume read off with the usual precautions. If again heated, and a second reading taken after cooling, it will be found identical with the first. We may take this, together with the numerical results about to be described, as sufficient evidence of the stability of the chromic anhydride under the conditions of the combustion. But we shall revert subsequently and more specifically to this point.

In order to "standardise" the apparatus, and to determine the error due to the absorption of carbonic acid, we made several series of combustions of oxalic acid. We may cite the results of one of these, consisting of 16 experiments. The weight of substance taken varied from 0·05 gram to 0·25 gram. The mean percentage of carbon calculated from the gas volume obtained was 26·0 ($C_2H_2O_4$ = 26·6), with a probable error for a single observation of ± 0·2 per cent.

The absorption of CO_2 by H_2SO_4 is 0·75 vol. at ordinary temperatures. After reading off, and allowing an interval of some minutes before taking a second reading, we found that the latter showed no perceptible difference. But after half an hour a difference of level was manifest; in two hours the diminution of volume amounted to from 3—5 c.c. This is no doubt attributable to a gradual absorption of the gas by the acid. The absorption, therefore, under the conditions of observation adopted, is only a fraction of the theoretical maximum, and, as we find, about 2/7. Supposing this absorption constant, and the quantity of substance weighed for combustion to

	Weight taken.	Gas volume corrected to 0° and 760 mm.	Percentage carbon.	
			Found.*	Calculated.
Cellulose.				
Swedish filter-paper ..	0·1150	94·6 c.c.	44·0	44·4
	0·1157	94·1 „	43·6	—
	0·1165	94·5 „	43·4	—
	0·1141	93·5 „	43·9	—
	0·1143	94·0 „	44·0	—
	0·1147	94·9 „	44·3	—
	0·1280	104·3 „	43·6	—
Oxalic Acid	0·1344	66·1 „	26·3	26·6
	0·1305	64·0 „	26·2	—
	0·1750	86·2 „	26·3	—
	0·2080	102·2 „	26·2	—
	0·2020	98·0 „	26·0	—
Citric Acid	0·1625	108·9 „	35·9	37·5
Glycerin	0·1337	92·6 „	37·1	37·5
Phthalic Acid	0·0962	101·5 „	56·6	57·8
Salicylic Acid	0·0966	108·6 „	60·2	60·8
	0·0945	104·8 „	59·4	—
Phthalic Anhydride ..	0·0881	105·0 „	63·8	64·8
	0·0922	109·0 „	63·8	—
Benzoic Acid	0·0895	113·1 „	67·8	68·8
	0·0850	107·5 „	67·8	—

---

* The correction to be applied to these calculated numbers will be dealt with subsequently.

vary, the error, in defect, should vary in inverse proportion. We found the evidences of such a variation in our numbers, but the proportion was not sufficiently strict to be made the basis of a correction. We therefore found it necessary to eliminate the variation of the gas volume. Keeping this within the limits of 80—110 c.c., and comparing substances of varying carbon percentage, we find that the error is, with sufficient approximation, directly proportioned to the carbon percentage.

We give a selection of results (p. 891), obtained in series, showing the degree of approximation attainable in combustion according to this method.

A very large number of our earlier determinations were made with quantities of substance yielding gas volumes varying from 50—120 c.c. We do not think it necessary to reproduce these, since they merely serve to indicate the conditions necessary to secure a constant error. Under these conditions, already defined, the error may be empirically expressed by the following fraction:

$$\frac{\text{Carbon percentage of substance}}{25} \times 0{\cdot}4,$$

that is, the percentage calculated from the gas volume must be increased by this amount to give the true percentage. In order to investigate the process from the point of view of the oxidising substance, the following combustions of cellulose, purified bleached cotton, were carried out under the above conditions, but with a weighed quantity of potassium dichromate in excess. The residual chromic acid was determined by titration with ferrous sulphate in the usual way. The chromic acid used is expressed as the equivalent of oxygen; the quantity necessary for complete combustion to CO_2 is given side by side for comparison:—

Weight of cellulose.	Oxygen consumed.	Oxygen to burn to CO_2.	CO : CO_2.
0·1805	0·2010	0·2107	0·0169 : 0·2630
0·1803	0·2060	0·2106	0·0080 : 0·2770
0·1940	0·2126	0·2297	0·0294 : 0·2825
(*a.*) 0·1164	0·1350	0·1387	0·0065 : 0·1805
(*b.*) 0·1120	0·1300	0·1325	0·0044 : 0·1753

In the two latter the combustion was carried out in connection with the gas collecting apparatus; the following were the volumes estimated, corrected to 0° and 760 mm.

(*a.*) 94·5 = 43·5 C per cent.
(*b.*) 91·4 = 43·6 „

Taking the mean of these we may apply the correction as above described:—

$$43{\cdot}55 + \frac{43{\cdot}55}{25} \times 0{\cdot}4 = 44{\cdot}25 \text{ per cent. carbon.}$$

These numbers indicate a complete combustion to gaseous products, in which the proportion of carbonic oxide is very small. The formation of carbonic oxide we had verified at the time of publishing our first communication, by finding a combustible gas, burning with the characteristic blue flame, left after absorbing the carbonic acid by potash; the quantity of cellulose treated for the purpose being sufficient to yield 500 c.c. of gas. We have since made two observations on the gases evolved, (*a*) in the earlier stages, (*b*) in the latter stages of the combustion, under the conditions obtaining in our quantitative experiments:—

(*a*.) 40·5 c.c. treated with Cu_2Cl_2 in HCl gave a contraction of 2·5 c.c.

(*b*.) 30·8 c.c. treated with KOH gave a contraction of 30·4 c.c.

		CO.		CO_2.		CO.		CO_2.
The corresponding ratio by *weight* are	(*a*)	1	:	24	(*b*)	1	:	117.

The proportion of CO, therefore, varies with the conditions of the combustion.

We have now briefly to notice those cases in which our investigations have shown that the combustion is partial, these are more particularly acids of the fatty series and compounds containing nitrogen.

Combustions of palmitic and stearic acids with chromic anhydride yielded from 60—70 per cent. carbon in the form of gaseous products, and the results are variable. The partial nature of the combustion is referable to molecular structure rather than to the relatively large proportion of carbon, for we have obtained good results with aromatic compounds containing as much as 90 per cent. of carbon.

The second group of compounds which only partially burns is that of the organic bases. We propose to investigate this subject further: it is probable that useful information will be gained by a study of the residual products of combustion. It is worthy of note that under the conditions we have described, urea is not attacked.

In the course of this research we have made a number of observations on the behaviour of chromic anhydride and potassium dichromate when heated with sulphuric acid. We may cite the following:—

(*a*.) 0·010 gram CrO_3, heated at 100° with 9 c.c. sulphuric acid for three hours. No appreciable reduction.

(*b.*) 0·500 CrO_3, heated with 9 c.c. H_2SO_4 at 100° one hour, flask connected to gas apparatus. Increase of vol. at 16° (corr.) 0·75 c.c.

(*c.*) 0·300 $K_2Cr_2O_7$, heated with 9 c.c. H_2SO_4 two hours at 105°; residual $K_2Cr_2O_7$—estimated with $FeSO_4$—0·286; 0·014 decomposed in two hours. Eqt. of O evolved 0·0023.

(*d.*) 0·590 $K_2Cr_2O_7$, heated with 9 c.c. H_2SO_4 two hours at 105°. Residual $K_2Cr_2O_7$ determined 0·5700. 0·020 decomposed.

(*e.*) 1·574 $K_2Cr_2O_7$, heated with 9 c.c. H_2SO_4 two hours at 105°. Cr_2O_3 formed 0·101.

(*f.*) 1·904 CrO_2, heated with 9 c.c. H_2SO_4 two hours at 105°. Cr_2O_3 formed 0·085.

These results are sufficient to show that the instability* of the chromic anhydride begins to be manifest at 105°; the decomposition however, even at this temperature is extremely slow. It is more rapid with the dichromate than the anhydride, and, in both cases, increases with the mass.

The explanation of this we take to be that the portion remaining undissolved is more liable to decomposition than that dissolved in the acid. It is to be observed, however, that the conditions in the blank experiments above cited differ from those in the combustion process, by the absence of the sesquioxide and the presence of a large proportion of undissolved trioxide. The sesquioxide is peroxidised by the trioxide, as is well known, and its presence therefore is an additional element of stability. Finding no mention of investigations of the oxidation of the sesquioxide in presence of sulphuric acid, we made observations on this point. We find that it is rapidly oxidised to the trioxide by permanganate, under this condition; also, though less rapidly, by manganese dioxide.

The comparative stability of the trioxide under the conditions of the combustion is probably therefore due in part to the presence of the sesquioxide, as also to the relatively small mass of residual trioxide, and its being dissolved in the acid solution.

We made observations on the stability of the acid mixture which remained at the conclusion of a combustion of 0·14 gram of cellulose.

(*g.*) The combustion having been finished by raising the temperature to 90°, and agitating until no more frothing appeared, the acid solution (9 c.c.) was sealed in a tube of 20 c.c. capacity. This was heated at 104° for 1 hour. The tube, after cooling, was opened in gas-tight connection with a U-tube of mercury. A difference of level of 6 mm. was observed. The total volume

---

* The anhydride heated by itself begins to decompose at 250°.

between the sulphuric acid in the tube and the mercury in the U-tube being 30 c.c., the increase of gas in the tube is 0·3 c.c. at 15°.

(*h.*) The tube was again sealed and heated for two hours at 100° The difference of level in the U-tube on opening it, after cooling, was 40 mm.; the corresponding increase of volume in the tube 1·6 c.c.

(*i.*) Again sealed and heated for two hours at 190°, the gas evolved in the tube amounted to 2·3 c.c.

(*j.*) A similar mixture of sulphuric acid, chromic sulphate, and chromic anhydride was heated in a flask connected with a gas apparatus, as in a combustion, for 1½ hours at 105°. The increase of volume was 3 c.c.

These experiments are sufficient to show that the error due to decomposition of the chromic anhydride during the comparatively short period of heating necessary to complete the combustion, is so small that it may be neglected.

We wish to express our thanks to our friends, Mr. R. Merriman, for his assistance in the research, and to Mr. A. Green for kindly supplying pure preparations for analysis.