

V.—An Investigation of the Oxidation of Certain Aliphatic and Aromatic Carbon Compounds by Means of the Dichromate Reaction.

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GREY (J., 1914, **105**, 2204) devised a method for estimating the total carbon in organic compounds which depended upon (a) the gasometric estimation of carbon dioxide, and (b) the determination of the acetic acid content in the residual liquid. This method was simplified by Guyot and Simon (*Compt. rend.*, 1920, **170**, 514) and by Grey (*Biochem. J.*, 1923, **17**, 768). Assuming Grey's observations, confirmed by Simon (*Compt. rend.*, 1925, **180**, 1405), the author has carried out a systematic investigation of the oxidation, and has attempted to standardise the experimental conditions.

A solution of the substance in water (or acetic acid) is added to an excess of standard potassium dichromate solution, and concentrated sulphuric acid is added. Oxidation takes place almost immediately to carbon dioxide and water, and to acetic acid in addition when a $\text{CH}_3\cdot\text{CH}$ group is present with other carbon atoms.

The reaction mixture is poured into water, and the excess of dichromate determined by $N/2$ -ferrous sulphate. The reaction mixture selected was the following, being slightly modified as necessity demanded: 10 C.c. of 2*N*-potassium dichromate, 15 c.c. of water containing 0.1 g. of the compound, and 33 c.c. of concentrated sulphuric acid.

The "dichromate value" is the number of c.c. of *N*-potassium dichromate required for complete oxidation of 0.1 g. of substance. The results obtained are summarised below.

| | Dichromate value. | | | Dichromate value. | |
|--------------------------|-------------------|-------|----------------------------|-------------------|-------|
| | Found. | Calc. | | Found. | Calc. |
| <i>Alcohols.</i> | | | <i>Dibasic acids.</i> | | |
| Methyl | 18.74 | 18.74 | { Tartaric | 6.65 | 6.65 |
| Ethyl | 8.69 | 8.69 | { Racemic | 6.05 | 6.65 |
| Propyl | 16.20 | 16.65 | Malic | 9.02 | 8.95 |
| <i>n</i> -Butyl | 21.20 | 21.62 | Butylmalonic | 15.92 | 15.00 |
| <i>iso</i> Butyl | 21.80 | 21.62 | { Fumaric | 10.40 | 10.34 |
| Amyl* | 24.10 | 24.90 | { Maleic | 10.24 | 10.34 |
| Ethylene glycol ... | 16.04 | 16.10 | | | |
| | | | <i>Cyclic compounds.</i> | | |
| <i>Monobasic acids.</i> | | | Furfuryl alcohol ... | 22.41 | 22.45 |
| Formic | 4.35 | 4.34 | Amylene glycol | 19.18 | 19.23 |
| Acetic | No oxidation. | | <i>Aromatic compounds.</i> | | |
| Propionic | 8.37 | 8.10 | Benzoic acid | 23.08 | 24.60 |
| <i>n</i> -Butyric | 13.93 | 13.64 | Salicylic acid | 19.66 | 20.28 |
| <i>n</i> -Valeric | 17.30 | 17.50 | Protocatechuic acid | 15.72 | 16.88 |
| <i>iso</i> Valeric | 17.27 | 17.50 | <i>iso</i> Propoxybenzoic | | |
| Diethylacetic | 13.60 | 13.80 | acid | 20.40 | 20.73 |
| | | | Mandelic acid | 21.82 | 22.37 |

* Using 20 c.c. of 2*N*- $\text{K}_2\text{Cr}_2\text{O}_7$ and 40 c.c. of conc. H_2SO_4 .

Formic acid required only 16.0 c.c. of sulphuric acid, whilst with this concentration of acid, propionic acid was quite stable; it may thus be possible to estimate a mixture of formic, acetic, and propionic acids.

Exceptions.—Succinic acid is stable to the chromic acid unless the quantity of sulphuric acid exceeds 25 c.c., and succinamide, acetamide, urea, and α -aminoisobutyric acid are unaffected.

Aldehydes gave inaccurate dichromate values.

Halogen compounds gave free halogens which vitiated the subsequent titration.

The imino-group is oxidised and the method is therefore inapplicable to compounds containing it.

Summary.

(1) Aliphatic and aromatic substances can in general be oxidised to carbon dioxide and water, or to acetic acid in addition if a $\text{CH}_3\cdot\text{CH}$ group is present.

(2) This reaction can be used for the quantitative estimation of certain organic compounds, but others are either not oxidised or only partially so.

(3) Water or acetic acid must be used as solvent for the material to be analysed.

(4) Compounds containing hydroxyl groups are easily oxidised.

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