

310. *The Formaldehyde Method of Detecting the Vinyl Group.*

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HARRIES (*Ber.*, 1903, **36**, 1933) postulated, and later (*Annalen*, 1905, **343**, 346) produced further evidence, that the formation of formaldehyde in the decomposition of an ozonide indicates the presence of a vinyl group in the original molecule. Such evidence has been utilised by Semmler and Meyer (*Ber.*, 1911, **44**, 3661), Ruzicka and Trebler (*Helv. Chim. Acta*, 1921, **4**, 566), Asahina (*J. Pharm. Soc., Japan*, 1927, No. 539, 1), and others. In many cases the yield of formaldehyde obtained is not stated.

Critical examinations of the process have been made by Blair and Wheeler (ethylene; *J. Soc. Chem. Ind.*, 1923, **42**, 343, 347T), Briner and co-workers (ethylene, acetylene, and several propylenes and butylenes; *Helv. Chim. Acta*, 1929, **12**, 154, 181, 529, 786), and Escourrou (several terpene-like unsaturated compounds; *Bull. Soc. chim.*, 1928, **43**, 1088). Under fairly drastic conditions, formaldehyde can be obtained by ozonisation of saturated compounds such as methane and *n*-hexane (Blair and Wheeler, *J. Soc. Chem. Ind.*, 1922,

41, 303T; 1924, 43, 289T), from amines (Strecker, *Ber.*, 1921, 54, 2695, 2704), and from aldehydes and ketones (Briner and Meier, *Helv. Chim. Acta*, 1929, 12, 529).

In the use of ozone for the elucidation of structural problems on certain of the terpenes, in these laboratories, curious results were obtained, and the present communication shows that, when various compounds, some of which do not contain the vinyl group, are ozonised in inert solvents, even at 0°, formaldehyde is isolable as its dimedon compound* (Ionescu and Bodea, *Bull. Soc. chim.*, 1930, 47, 1408).

In preliminary experiments with B.P. chloroform the alcohol present as anti-oxidant yielded considerable amounts of formaldehyde. It must be purified by shaking with concentrated sulphuric acid, washing with water, drying, and distillation.

The substances examined fall into two classes, those with a vinyl group yielding about ten times as much formaldehyde as those without. It is therefore clear that only quantitative estimation affords conclusive evidence for the presence of a vinyl residue.

Substance.	Wt. ozonised, g.	Wt. of formaldehyde dimedon compound, g.	Formaldehyde, %.
Vinylbenzene	0·2, 0·2	0·171, 0·170	30
Limonene.....	0·39	0·27	32
Cinchonine	0·1	0·02	20
1-Methylcyclohexene	0·5, 0·5	0·0151, 0·0150	1
Δ^3 - <i>p</i> -Menthene	0·5, 0·5	0·0280, 0·0280	2·6
α -Pinene	0·2, 0·2	0·010, 0·010	2·3
<i>p</i> -Cymene	0·5, 0·5	0·038, 0·040	2·7
Santonine	0·2	0·0025	1·1
A related compound	0·2	0·0050	2·3

The figure in the last column is calculated on the assumption that one mole of formaldehyde is derived from each mole of substance.

A solution of a weighed quantity of the substance (0·2—0·5 g.) in ice-cooled purified chloroform (10 g.) is ozonised in a stream of 8% ozone (about 33 c.c. per min.) for 4 hours. The chloroform is removed in a vacuum at room temperature, water (25 c.c.) added, and, after heating in the water-bath for 1 hour, the solution is distilled into 5 c.c. of ice-cooled water, leaving a residual 5 c.c. (approx.). The distillate, which contains any formaldehyde resulting from the ozonisation, is treated with 20% excess of dimedon dissolved in a few drops of alcohol, the solution heated on a water-bath for 10 minutes and kept over-night at room temperature, and the formaldehyde dimedon compound collected, dried, and weighed (m. p. 185—186°).

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