

The phase transformations in sulphur are markedly accelerated when it is contaminated with carbon disulphide, and in films prepared from such material we have found that the temperature of the $\alpha\beta$ -transition point is not altered within the limits of accuracy (about 2°) of the hot stage used for our observations. This suggests that the carbon disulphide adds another phase as well as another component to the system, and this phase appears to be a liquid layer at the interface, since under the microscope bubbles can be seen moving about in this region as the reaction proceeds. If a $\gamma\beta$ -interface is established in such contaminated sulphur, observable movement at low temperatures now occurs; but at all temperatures down to -18° (the lowest attainable for microscopic observations with our present arrangements) the direction of the transformation is still γ to β . Thus the transition point, if it exists, is probably below this temperature.

Point *C* (Fig. 1) represents a somewhat similar case to that just discussed, for here the rates of transformation of γ to α and γ to β are equal, and the well-established transition point between the α - and β -forms exists at the not far distant temperature of 96° . The difference from the previous case is that the reactant phase (γ) is the same in the two transformations, whereas at point *A* it is the resultant phase (α) which is the same.

This work will be described and discussed in more detail in a further publication. It is also intended to attempt determinations of the vapour pressures of the β - and γ -forms down to low temperatures. This should provide conclusive evidence of the existence or otherwise of a transition point between these forms.

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² Elias, P. G., Hartshorne, N. H., and James, J. E. D., *J. Chem. Soc.*, 588 (1940).

³ Hartshorne, N. H., and Roberts, M. H., *J. Chem. Soc.*, 1097 (1951).

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A Rapid Gasometric Method of Analysis for 'Reducing' Sugars and Other Carbonyl Compounds

ANALYSIS for reducing sugars generally involves oxidation under highly disruptive conditions with an alkaline reagent. As a consequence of the oxidative fragmentation of the sugars, the stoichiometry of the reaction is not simple, and it is necessary to employ closely controlled concentration and temperature conditions¹. The interpretation of the results requires the use of extensive empirical tables. Since the reducing equivalence of the various mono- and di-saccharides is not the same, an additional dimension of uncertainty is introduced into the procedure for the analysis of mixtures of reducing sugars.

Employing aqueous solutions of sodium borohydride for the reduction of 'reducing' sugars to the corresponding polyols, we have been able to carry out the rapid determination of reducing sugars at acidities of pH 7 and higher. Sodium borohydride solution is standardized by measuring the volume

of hydrogen gas evolved when the solution is made acid. The sugar solution is treated with an aliquot of the sodium borohydride reagent, and after completion of the reduction, the excess of reagent is determined by acidification, etc., as in the standardization. The difference in volume of hydrogen evolved is equivalent to the amount of 'reducing' sugar. By collecting the hydrogen over water in a very simple apparatus, we have found that one mole of hydrogen is utilized for the reduction of one mole of glucose, fructose, galactose, lactose or glucosamine with an accuracy of better than 1 per cent. Complete reduction is achieved in 20–30 min. at room temperature, or in less than one minute at the boiling point. Although aqueous sodium borohydride solutions are stable at room temperature, aliquots are most conveniently pipetted at 0° C.

Since this analytical method has many obvious applications in organic, biochemical and clinical analyses, it was considered advisable to make a preliminary report. Detailed results relating to sugar analysis, and analysis for carbonyl compounds and derivatives in general will be published later.

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¹ Bates, F. J., and Associates, "Polarimetry, Saccharimetry, and the Sugars", 165 (U.S. Gov. Printing Office, Washington, D.C., 1942).

The Girard Reaction

Girard and Sandulesco¹ developed a method now known as the 'Girard reaction' for the isolation of small amounts of ketosteroids such as the sex hormones from natural products. Aldehydes and ketones in the mixture are converted into water-soluble hydrazone derivatives by treatment with the 'Girard P' or 'T' reagent, and the non-carbonyl compounds are removed by extraction with a non-polar solvent like ether. The ketone complexes are rapidly decomposed with mineral acid; but the aldehyde derivatives are claimed to be stable except in the presence of a large excess of acid and formaldehyde.

Recently, in an investigation of the compounds responsible for the so-called 'cardboard' flavour in skim milk, acetaldehyde was observed in 'ketonic fractions' isolated by these methods.

A study of the literature showed that Girard aldehyde complexes are not as stable as generally believed, for Lederer and Nachmias² were able to decompose some of them with hydrochloric acid after 12–14 hr. at room temperature giving 80–90 per cent yields of heptaldehyde, citral, *m*- and *p*-hydroxybenzaldehyde, 3,4-dihydroxybenzaldehyde and piperonal.

We were interested in saturated and unsaturated aliphatic aldehydes and ketones, and studied the stability of the 'Girard P' complexes of acetaldehyde, crotonaldehyde, propionaldehyde, butyraldehyde, *iso*-valeraldehyde and *n*-heptaldehyde and acetone, methyl ethyl ketone, mesityl oxide and methyl *n*-amyl ketone. In all cases the decomposition of the Girard complex with *N*/2 sulphuric acid was found to be almost instantaneous.

It seems that the Girard reaction, while it often fails to separate aldehydes and ketones, may be suitable for the separation of carbonyl from non-carbonyl