

COMMUNICATIONS TO THE EDITOR

SIR JAMES IRVINE'S VIEW ON THE CONSTITUTION OF DI- AND POLYSACCHARIDES

Sir:

In a recent communication Irvine and McGlynn [THIS JOURNAL, 54, 358 (1932)] comment on the use of 2,3,6-trimethylglucose as a reference substance in structural investigations and urge that "much further work and the application of new methods are alike necessary before definite constitutions can be assigned to the disaccharides and polysaccharides which are convertible into 2,3,6-trimethylglucose." These conclusions are valid in so far as work initiated by Irvine is concerned, but they do not represent the present state of carbohydrate chemistry. No less than six years ago, and before the publication of Irvine and Black's paper on maltose [*J. Chem. Soc.*, 862 (1926)] an explicit statement of the ambiguity caused by the use of 2,3,6-trimethylglucose as a reference substance was given by Charlton, Haworth and Peat [*ibid.*, 98 (1926)] and in the same year (1926) Haworth and Peat [*ibid.*, 3094 (1926)] developed a new experimental method which solved completely the problem left undecided by the isolation of a trimethylhexose as a scission product of a fully methylated disaccharide. This method has been employed to determine the constitution of maltose, lactose, cellobiose, melibiose, 4-glucosido-mannose and 4-galactosido-mannose [*ibid.*, 544, 1527, 2809, 3146 (1927); 1349, 1354 (1931)]. Recently its use has been extended to problems connected with the polysaccharides, starch, glycogen and xylan [Haworth and Percival, *ibid.*, 1342, 2850 (1931)]. In addition to the full treatment given in the original papers, an ample discussion of the various problems has appeared in a monograph [Haworth, "Constitution of Sugars," Edward Arnold and Co., London, 1929] and on various occasions in summary form [see, for example, *Helv. Chim. Acta*, 534 (1928)]. No reference whatever to any of this work is made by Irvine and McGlynn.

In describing the conversion of 2,3,6-trimethylglucose, *via* its γ -methylglucoside into tetramethyl- γ -glucose, the latter authors have not observed that this series of transformations was carried out by Schlubach and Bomhard in 1926 [*Ber.*, 59, 845 (1926)]. Comment is necessary also on the conclusions drawn by Irvine and McGlynn from their experiments on the oxidation of 2,3,6-trimethylglucose. It is well known that in aqueous solution both γ - and δ -lactones enter into equilibrium with their parent acids. In those cases where both γ - and δ -lactones are obtainable from one acid (as with 2,3,6-trimethylgluconic acid) it is clear that no evidence of preferential oxidation to one particular lactone can be obtained by treatment of the sugar with bromine water, extraction of the aqueous solution with chloroform several hours after the commencement of the

reaction, and the mere isolation of that lactone on evaporation of the chloroform. Similar considerations apply when the oxidation is conducted in the presence of an excess of calcium carbonate, with the additional complication that under these conditions most of the product may pass through the stage of the calcium salt from which the organic acid, not the lactone, is liberated on acidification. The experimental procedure of these authors is ill-adapted to the problem they have in view and definite conclusions concerning the preferential formation of either lactone during the oxidation cannot be drawn from their present results.

CHEMISTRY DEPARTMENT
THE UNIVERSITY OF BIRMINGHAM
ENGLAND

E. L. HIRST

RECEIVED APRIL 13, 1932
PUBLISHED JUNE 6, 1932

THE EFFECT OF FOREIGN GASES ON UNIMOLECULAR REACTIONS

Sir:

The recent communication by Steacie [THIS JOURNAL, 54, 1695 (1932)] suggests a generalization that has apparently not been made hitherto, *viz.*, that foreign gases do not activate unimolecular reactions. The earliest experimental evidence on this subject is the work of Daniels [THIS JOURNAL, 47, 1602 (1925)], who showed that the rate of decomposition of nitrogen pentoxide in the presence of nitrogen falls off at about 0.01 mm. partial pressure. Later experiments show that the behavior is the same in the absence of nitrogen.

The conspicuous exception to this generalization is the action of hydrogen on certain organic compounds at elevated temperatures. The explanation of this exceptional behavior is to be sought in the fact that a reaction between the hydrogen and organic molecule would be predicted by an organic chemist.

While we do not know much about the conditions under which translational energy is converted into vibrational energy [see Kassel, Rice, *Chem. Rev.*, 10, 11 (1932)], the evidence is that this process does not take place readily. The early attempts to calculate the limiting pressure for the unimolecular decomposition of nitrogen pentoxide were without significance because only translational energy was considered.

On the other hand, vibrational energy is only transferred readily when there is a sharp resonance between the colliding molecules.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

W. H. RODEBUSH
M. J. COPLEY

RECEIVED APRIL 25, 1932
PUBLISHED JUNE 6, 1932