

Letters to the Editor

The Editor does not hold himself responsible for opinions expressed by his correspondents. He cannot undertake to return, or to correspond with the writers of, rejected manuscripts intended for this or any other part of NATURE. No notice is taken of anonymous communications.

NOTES ON POINTS IN SOME OF THIS WEEK'S LETTERS APPEAR ON P. 897.

CORRESPONDENTS ARE INVITED TO ATTACH SIMILAR SUMMARIES TO THEIR COMMUNICATIONS.

The Kinetics of Polymerization

A RECENT paper¹ on the kinetics of gaseous polymerization reactions appears to lead to some doubts concerning the interpretation of experiments in the liquid phase. It is now found that gaseous styrene is stable at temperatures up to 400° C., a result which seems inconsistent with the published data on the rate of polymerization of liquid styrene. The results of Schulz and Husemann² can be expressed by means of a unimolecular constant, given by

$$k_1 = 1.1 \times 10^7 e^{-21,000/RT} \text{ sec.}^{-1},$$

while Suess, Pilch and Rudorfer³ find a bimolecular constant,

$$k_2 = 2.5 \times 10^9 e^{-21,500/RT} \text{ mol./l./sec.}$$

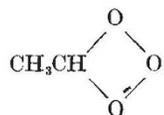
Further, Wassermann⁴ has shown that the rates of a number of diene additions are the same in the gas phase and in solution, so that we can with some confidence employ the expressions above to calculate the rate of the gaseous polymerization.

At sufficiently high temperatures, the reverse process of depolymerization will become sufficiently important to mask the forward reaction. According to Blyth and Hofmann⁵, polystyrene is depolymerized on heating above 300° C., and up to this temperature the above formulae should therefore hold. The calculated half-lives for the reaction at 300° C. and atmospheric pressure are 6 sec. and 46 min., and it is clear that there is a very large discrepancy between these figures and the results of Kistiakowsky. It is suggested in explanation that the liquid phase results refer to a catalysed reaction, the catalyst being in all probability a peroxide which may initiate chains by the formation of a complex⁶.

Definite evidence has been obtained that this is the case for vinyl acetate, which Kistiakowsky also found to be stable up to 360° C. in the gas phase. Starkweather and Taylor⁷ found that the polymerization of liquid vinyl acetate at 101° C. could be represented by a first order constant, $k = 5.0 \times 10^{-3} \text{ min.}^{-1}$. Breitenbach and Raff⁸ were unable to obtain consistent results in glass vessels, and Breitenbach⁹ has attributed this difficulty to the presence of traces of moisture which react with the alkali of the glass to give sodium hydroxide. When the ester was dry, Breitenbach found that its rate of polymerization at 98° C. was only one hundredth of that found by Starkweather and Taylor. We have found that pure vinyl acetate does not polymerize measurably at 100° C., and believe the rates measured by the former authors to be due to the presence of peroxides.

Commercial vinyl acetate may contain a small amount of acetaldehyde¹⁰ which in the presence of air

forms a peroxide, probably of the formula



Samples of vinyl acetate capable of polymerizing at 100° C. always gave a peroxide test, and the rate and extent of polymerization were found to be associated with the amount of peroxide present. It is perhaps significant that this substance can be eliminated by distillation with an efficient fractionating column but is by no means completely removed by careful vacuum distillation. It is probable that the role of the sodium hydroxide produced when the ester is moist is to saponify some of the vinyl acetate yielding vinyl alcohol, which is tautomeric with acetaldehyde. We may note further that aldehyde-free vinyl acetate does not polymerize at 100° C. even in the presence of oxygen: samples were shaken with air or oxygen for two weeks but remained stable when afterwards heated to 100° C. Identical results were obtained from supplies of vinyl acetate from two sources.

The study of the initiation of polymerization by aldehydes and oxygen is being continued and fuller details will be published in due course.

A. C. CUTHBERTSON.

Dept. of Chemistry,
Mount Allison University,
Canada.

GEOFFREY GEE.
E. K. RIDEAL.

Laboratory of Colloid Science,
Cambridge.

- ¹ Harkness, Kistiakowsky and Mears, *J. Chem. Phys.*, **5**, 632 (1937).
- ² Schulz and Husemann, *Z. phys. Chem.*, **36**, B, 194 (1937).
- ³ Suess, Pilch and Rudorfer, *Z. phys. Chem.*, **179**, A, 361 (1937).
- ⁴ Wassermann, *Farad. Soc.*, General Discussion, September, 1937.
- ⁵ Blyth and Hofmann, *Ann.*, **53**, 315 (1845).
- ⁶ Gee and Rideal, *Trans. Farad. Soc.*, **32**, 666 (1936).
- ⁷ Starkweather and Taylor, *J. Amer. Chem. Soc.*, **52**, 4708 (1930).
- ⁸ Breitenbach and Raff, *Ber.*, **69**, 1107 (1936).
- ⁹ Breitenbach, *Z. Elektrochem.*, **43**, 323 (1937).
- ¹⁰ Blaikie and Crozier, *Ind. Eng. Chem.*, **28**, 1155 (1936).

Phase Transformation in Locusts in the Field

IN 1921 Uvarov¹ enunciated the 'phase theory' to account for the swarming of locusts, a theory which postulated post-embryonic divergences in the pigmentation, structure and behaviour of members of the same species. This theory has since been proved by field observations and by experiment to be correct in a number of locust species, and in breeding experiments the changes were found to be due to the density of population of locusts².