A very marked diminution of the induction period is brought about. The extent of the catalysis evidently depends, in large degree, upon the dispersity of the silver sulfide. Although there is, in consequence of the decomposition, immediate accretion of silver to the silver sulfide nuclei, yet it appears evident that the latter are quite capable of replacing silver nuclei as catalytic phase.

According to the Ostwald–Langmuir conception of these heterogeneous reactions, the reaction should proceed only at the three-phase boundary line, gas:solid I:solid II. G. Adhikari and J. Felman [*Z. physik. Chem.*, **131,** 347 (1928)] have demonstrated actual "adlineation" in the case of the reaction

$$\underset{\text{adsorption}}{Hg + I_2 \longrightarrow Hg : I_2 \longrightarrow HgI_2}$$

but they note that a physical theory which makes this result comprehensible is still lacking. The fact that silver sulfide can replace silver in the present reaction, as topochemically isomorphous, may give a clue to the mechanism, which will be discussed in a fuller report. Meanwhile, the replaceability of silver by silver sulfide in catalyzing the thermal decomposition of silver oxalate, where it can hardly act as an "acceptor" of carbon dioxide, makes less probable the "halogen acceptor" hypothesis proposed by K. C. D. Hickman [*Phot. J.*, **67,** 34 (1927)] for its photosensitizing effect with silver halides. Also it makes more doubtful the special photoelectrolytic theory of A. P. H. Trivelli [*J. Franklin Inst.*, **204,** 649 (1927); **205,** 111 (1928)]. The bearing of the present results on photosensitizing will be discussed in a fuller publication.

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RECEIVED JUNE 30, 1930
PUBLISHED AUGUST 5, 1930

ASSOCIATION POLYMERIZATION AND THE PROPERTIES OF ADIPIC ANHYDRIDE

Sir:

Faith in the existence of the once widely accepted hypothetical phenomenon, association polymerization, appears to have been revived (or strengthened) in the minds of some of its proponents by the discovery[1] of a spontaneously reversible relationship between a biosan (?) and a polysaccharide. No certain examples of this phenomenon have ever been adduced among materials of known structure, although its supposedly

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[1] Reilly and Donovan, *Sci. Proc. Roy. Dublin Soc.*, **19,** 409 (1930); Schlubach and Elsner, *Ber.*, **63,** 362 (1930); Vogel, *ibid.*, **62,** 2980 (1929); Pringsheim, Reilly and Donovan, *ibid.*, **62,** 2379 (1929). It now appears, however, that these observations may be capable of quite a different interpretation. See Berner, *ibid.*, **63,** 1356 (1930).

diagnostic features are clearly presented by certain six-membered cyclic esters.[2]

Adipic anhydride, recently studied by Dr. Julian W. Hill in this Laboratory, has already been described[3] as a solid melting at 97°, but the published evidence concerning its molecular weight is equivocal. It has now been found that adipic anhydride as prepared by the usual methods is polymeric. Its melting point varies considerably with accidental details of its preparation. It cannot be distilled as such, but on being heated in vacuo it is partially depolymerized, and the resulting (7-ring) monomer can be distilled. The latter is a colorless liquid that freezes at about 20°. It reverts spontaneously to the polymeric form. The reversion is catalyzed by traces of water: when it is poured into a not especially dried glass vessel, a scum of the polymer is formed at the walls within a few minutes.

The monomer and the polymer are sharply differentiated by their chemical behaviors. Both react practically instantaneously with aniline at room temperature; but the former yields only adipic acid monoanilide, whereas the latter yields a mixture of adipic acid, adipic acid monoanilide and adipic acid dianilide. The formation of dianilide (in 25% of the theoretical amount) constitutes a direct and decisive demonstration of the presence in the polymer of a series of adipyl residues united in a linear fashion by anhydride linkages

$$\mathrm{CO{-}(CH_2)_4{-}CO{-}O{-}CO{-}(CH_2)_4{-}CO{-}O{-}CO(CH_2)_4{-}CO{-}O{-}etc.}$$

Thus the existence of a very high degree of mobility in the relationship between a monomer and its polymer does not preclude the intervention of real primary valence forces in the process or the presence of a definite macro-molecular chemical structure in the polymer, even though the monomer may not be unsaturated in the usual sense.

A more detailed report of the study of adipic anhydrides will be submitted at an early date.

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WALLACE H. CAROTHERS

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THE PHOTOCHEMICAL OXYGEN-CARBON MONOXIDE REACTION

Sir:

We have been studying the photochemical oxygen–carbon monoxide reaction and wish to announce some of our results. At room temperature in a mixture of oxygen and carbon monoxide and with light-producing

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[2] Carothers and Van Natta, THIS JOURNAL, **52**, 318 (1929); Carothers, Dorough and Arvin, *ibid.*, **52**, 3292 (1930).

[3] Voermann, *Rec. trav. chim.*, [2] **23**, 265 (1904); Farmer and Kracovski, *J. Chem. Soc.*, 680 (1927).