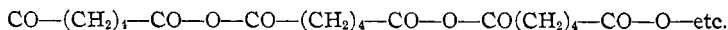


diagnostic features are clearly presented by certain six-membered cyclic esters.²

Adipic anhydride, recently studied by Dr. Julian W. Hill in this Laboratory, has already been described³ 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



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

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

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).

oxygen atoms, the reaction goes almost quantitatively with the formation of ozone. A comparison with equivalent mixtures of oxygen and nitrogen shows that of the two possible reactions of initially formed oxygen atoms, $O + O_2 + X = O_3 + X$ and $O + CO + X = CO_2 + X$, the first goes at least 100 times faster. As both reactions are exothermic and probably do not require activation energy the above result should be attributed to the necessity for the oxygen atom and the carbon monoxide molecule to be properly oriented at the moment of collision, while the oxygen atom and the oxygen molecule can react more independently of their relative orientation in a similar triple collision.

Some years ago Coehn and Tramm [*Ber.*, **54**, 1148 (1920)] reported that at room temperature water vapor has no influence on the rate of the photochemical oxygen-carbon monoxide reaction. We have repeated their experiments at 575° with the result that at this temperature water vapor has a very pronounced accelerating effect on the rate. This action is probably due to setting up of semi-thermal chains and may be linked with the well-known action of water in the thermal explosions of the carbon monoxide-oxygen mixtures. Further experiments on this subject are in progress and will be reported later in *THIS JOURNAL*.

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G. B. KISTIAKOWSKY

THE OXIDATION OF LACTAL

Sir:

M. Bergmann¹ states that when lactal is oxidized with perbenzoic acid 4-galactosido-mannose is produced in good yield. His experimental results indicate that solely this sugar is formed in the reaction. For the pure sugar he finds the value $[\alpha]_D^{23} + 23.04$ in water five minutes after solution, the rotation becoming constant at +30.0 after about eighty minutes. In the autumn of 1929 we undertook the preparation of a considerable quantity of 4-galactosido-mannose for the purpose of studying the rotations of the sugar and some of its derivatives. The beautifully crystalline lactal which was prepared showed $[\alpha]_D^{20} + 27.69$ in water, in full agreement with Bergmann's measurement (+27.70). The substance did not reduce Fehling's solution and was therefore free of sugar. Its oxidation by a solution of perbenzoic acid in ethyl acetate, following Bergmann's directions, gave a good yield of a crystalline sugar the initial and final rotations of which corresponded well with his data, previously quoted. When the product, which absorbed no bromine and therefore contained no residual

¹ M. Bergmann, *Ann.*, **434**, 79 (1923).