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Activation and reaction volumes for [4 + 2] and [3 + 2] additions involving maleic anhydride

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Abstract

The partial molar volumes of reactants and products of the [3 + 2] addition of C-(p-nitropheny-)-N-phenylnitrone to maleic anhydride and of the [4 + 2] addition of 9,10-dimethylanthracene to the same dienophile were determined, and the reaction volumes were calculated. A new method was suggested for determining the reaction volume. The activation volumes of both reactions were calculated from the dependences of the reaction rates on the external pressure. The volume parameters of the reactions involving the reagents of close size are close. The ratios of the activation volumes to the reaction volumes are unity, which suggests a common concerted mechanism of the reactions. Factors that could be responsible for significant changes in the absolute values of the reaction volume parameters are discussed.

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