
Reactions of the Conjugated Dienes Butadiene and Isoprene Alone and with Methanol over Ion-Exchanged Montmorillonites

J. M. Adams and T. V. Clapp

Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth, Dyfed SY23 1NE, United Kingdom

Abstract: The reactions of simple conjugated dienes over divalent and trivalent transition metal-exchanged montmorillonites yield, in the absence of nucleophiles, a variety of products. Some of these products are a result of Diels-Alder cycloaddition reactions, whereas others are indicative of carbocation intermediates, i.e., other dimers, oligomers, and isomerization products of these intermediates. The reactions in sealed cells between 20° and 150° C show trends in the yields of the various product groups. Dimers of butadiene and isoprene formed by cycloaddition (i.e., 4-vinylcyclohexene and the monoterpene p-menthadiene (limonene)) were formed at low temperatures (20– 50° C). As the temperature was raised, the total yield of dimers increased and higher oligomers were formed along with isomerization products of the dimers and oligomers. The products of cycloaddition, however, did not increase markedly. The type of solvent used for the reaction was found to influence the reactivity, e.g., the use of 1,4-dioxan rather than chloroform led to a reduction in total conversion and also to a markedly higher degree of selectivity. In the presence of a suitable nucleophile (methanol), both dienes gave the 1,4-addition product predominantly, which suggests that an allylic carbocation intermediate was involved. The use of an interlayer-supported nickel complex, $[\text{HNi}(\text{P}(\text{OEt})_3)_4]^+$, produced the only large scale polymerization observed in this work.

Key Words: Butadiene • Catalysis • Diels-Alder reaction • Gas-liquid chromatography • Isoprene • Methanol • Montmorillonite • Transition metal

Clays and Clay Minerals; June 1986 v. 34; no. 3; p. 287-294; DOI: [10.1346/CCMN.1986.0340309](https://doi.org/10.1346/CCMN.1986.0340309)

© 1986, The Clay Minerals Society

Clay Minerals Society (www.clays.org)
