DCC-23 (Univ. Zagreb)

Croat. Chem. Acta **38** *(1966)*

Study of Partial Reactions of Dehydration and Oxydation of Methanol in the Presence of Combined Silver-molybdenum Catalyzers under Conditions Encountered in the Commercial Process

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The effect of molybdenum oxide as a promoter upon the catalytic activity of electrolytic silver in the production of formaldehyde from methanol has been investigated. To this end, ammonium molybdate has been introduced in varying concn. into granules of a detd. size by impregnating them with solns. of that salt. The promoting effect of the molybdenum oxide upon the dehydration of methanol was established by gases leaving the reactor was measured, and both gases and liquor analyzed detg. the space-time yield of the reaction. Simultaneously, the temp. of the gases leaving the reactor was measured, and both gases and liquor analyzed after absorption of the former in the latter. The test app. used for the expts. simulated the industrial equipment used in the works of the »Kemijski kombinat Zagreb« for the com. production of formaldehyde. The gas mixt. subjected to the reaction contained methanol and air in the ratio 1:1, and the contact time was 0.018 sec.

The results of the run of expts., in which only the proportion of promotor added to the silver catalyzer was varied, all other factors remaining unaltered, lead to the conclusion that molybdenum oxide in the granules favorably affects the space-time yield if present in a concn. exceeding $1.4.10^{-4}$ g./g. Below this concn. the favorable effect of the molybdenum oxide on the reaction rate was found to cease, and when the concn. was decreased below a detd. limit, a stifling action of the molybdenum oxyde on the reaction has been established. The molybdenum oxide acts as an electronic promoter and does not affect the surface of the silver granules. The surface area of the granules was measured by the BET method. The molybdenum content in the silver was checked by means of the isotope ^{99}Mo. The overall activity and the gamma-spectrum was detd. It was established by these expts. that with this type of catalyzers the dehydration of methanol occurs under adsorption of the methanol on the silver.

Examiners: Prof. M. Karšulin, Dr. P. Fuderer, and prof. I. Lovreček.

Oral examination: October 8, 1965.

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V. FIOLIĆ

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1. Study of Partial Reactions of Dehydration and Oxydation of Methanol in the Presence of Combined Silver-molybdenum Catalyzers under Conditions Encountered in the Commercial Process

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Catalyst
Formaldehyde, production of
Molybdenum oxide
Silver catalyst

MCC-24

Master of Science Thesis

Croat. Chem. Acta **38** *(1966)*

Method of Maximum Overlap and its Application on Calculation of Several Methyl-substituted Cyclopropanes

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The hybridisation in various methyl-substituted cyclopropanes is detd. by the method of max. overlap. This method is discussed in detail and it is proposed to modify it by introducing weighting factors (k_{ij}). The systematic variations of the hybrids, in the procedure of maximisation of the overlap, were performed by changing the angles (Θ_{ij}) between the hybrids on the same atom in 1/4° steps. The atomic overlap integrals are calcd. using the Slater orbitals and assuming the standard C-C and C-H bond lengths (1.53 Å and 1.07 Å). We have investigated the hybridisation in the following methyl substituted cyclopropanes: 1-methyl; 1,1-dimethyl; 1,1,2-trimethyl; and 1,1,2,2-tetramethyl.

The main results are summarised as follows:

1. The hybridisation within the methyl-group is unaffected by substitution of another methyl-group on the same carbon or on the other carbon atom in the ring.

2. The re-hybridisation of one carbon atom of the cyclopropyl ring causes only slight change in the hybridisation at the other positions.

3. The optimum values for a no. of variational parameters are independent of the choice of other parameters. Because of that it is possible to transfer bond overlaps between related parts of the molecules.

4. Successive methyl substitution results in stabilisation of the cyclopropyl ring. The corresponding bond overlaps are: 0.5762, 0.5816, 0.5853, 0.5906 and 0.5943.

5. The substitution of a hydrogen atom by the CH_3 group removes some s-character from the substituted bond, and this is then redistributed amongst the other bonds.

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Examiners: Prof. B. Težak, Prof. M. Randić, and Dr. S. Borčić.

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I. Method of Maximum Overlap and its Application on Calculation of Several Methyl-substituted Cyclopropanes

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Cyclopropane
— , methyl-substituted
Hybrids
Hybridisation
Overlap
— , atomic integrals
— , maximum
Ring compounds, small
— , strain