THEORETICAL STUDY OF THE PRODUCTS OF ACETYLENE ADDITION TO HgCl₂

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The ab initio MP2 method is used with the LANL2DZ basis to calculate the mercury chloride π,π-complex with two acetylene molecules (1) and various isomeric forms of mercury di(β)-vinyl chloride σ-complexes (2): cis-cis (2A), cis-trans (2B), and trans-trans (2C). The π,π-complex is the most stable form of all those considered; the difference between 1 and 2A is 24.9 kcal/mole. A relation between the total energies (kcal/mole) for isomeric forms 2 is established to be 2A (0) < 2B (0.98) < 2C (1.58). Complex 1 is shown to be transformed into 2A via the intermediate formation of 3, which is a hybrid form of the complex (π,σ-complex of mercury chloride with two acetylene molecules). The structures of the transition states for the transformations of 1 into 3 (structure 4) and of 3 into 2A (structure 5) and the corresponding transition activation energies are determined. The interaction of 2A, 2B, and 2C with the Cl– anion as a model nucleophile is considered. It is shown that the resulting anions (6A, 6B, 6C) have a planar structure with the relative stability increasing in the series 6A < 6B < 6C.

Key words: ab initio MP2 calculations, interaction of two acetylene molecules with HgCl₂, π-complexes, mercury β-vinyl chloride derivatives.

INTRODUCTION

In our previous work [1], ab initio MP2 calculations have first revealed that the interaction between acetylene and mercury chloride easily forms a π-complex without activation energy (ΔH = −6.5 kcal/mole). The complex may be transformed into mercury cis-β-chlorovinyl chloride with an activation energy of about 30 kcal/mole. This agrees well with the results obtained by Freidlina and Nogina [2], where mercury cis-β-chlorovinyl chloride was prepared by direct interaction of mercury chloride vapors with gaseous acetylene. The reaction kinetics was studied in [3]; it was suggested that an acetylene π-complex with mercury chloride is preliminarily formed. According to Nesmeyanov et al. [4-11], mercury β-chlorovinyl chloride possesses dual reactivity, exhibiting properties of ordinary β-vinyl chloride compounds of nontransition metals with a σ-bond, on the one hand, and features of a mercury chloride π-complex with acetylene on the other. It was noted [12] that the reaction of ammonia with (asymmetric) mercury β-vinyl chloride compounds forms symmetric molecules of mercury di-(β-vinyl chloride).

The present work reports a theoretical study of symmetric mercury compounds with various isomeric structures. For this purpose, calculations were performed for mercury π,π-complexes with two acetylene molecules (1) and various isomeric forms of mercury di-(β-vinyl chloride) σ-complexes: cis-cis (2A), cis-trans (2B), and trans-trans (2C). The transformations of 1 into 2A were also studied.
DETAILS OF COMPUTATIONS

Second-order Möller–Plesset perturbation theory was used for the geometry and electronic structure calculations of the mercury chloride π,π-complex with two acetylene molecules 1; symmetric isomers 2A, 2B, and 2C; mixed σ,π-complex 3; the transition states of the transformations of 4 and 5; and the products of chloride anion addition to 2A, 2B, and 2C (structures 6A, 6B, 6C) [13]. The geometry optimization of the molecules and ions was performed using the Dunning–Hay double-zeta atomic basis sets [14] and the LANL2 pseudopotential for the mercury atom [14a]. A search for the transition states of the transformation of the π,π-complex into the σ,π-complex and of the σ,π-complex into symmetric cis-cis derivative 2A was accomplished in three steps. At a first step, an approximate structure of the transition state was determined by the QST2 synchronous transit method [15]. At a second step, the structure was refined by the quadratic synchronous transit (QST3) method [15]. At a third step, the structure of the transition state was precisely determined by the gradient method, the vibrational frequencies at the saddle point were analyzed, and the dependence of the total energy on the internal reaction coordinate was determined. The calculations were performed using the Gaussian-98 program (see [16]) on CRAY J-90 supercomputers (National Energy Research Scientific Computing Center, Berkeley, CA, USA).

RESULTS AND DISCUSSION

1. Structure of the Mercury Chloride π,π-Complex with Two Acetylene Molecules and Its Transformation into a σ,π-Complex and Further into Mercury cis-cis-di-(β-Vinyl Chloride)

Calculations on a system of interacting mercury chloride and two acetylene molecules have revealed a minimum on the potential energy surface, which corresponds to π,π-complex 1 with the following structure (Scheme 1):

Here x and y are the positions of the center of the triple CC bonds of the corresponding acetylene molecules.

The following peculiarities of structure 1 should be noted:

1) four carbon atoms of both acetylene molecules lie in the same plane;
2) both acetylene molecules and the CHgCl molecule comprising the complex are not strictly linear; the chlorine atoms of mercury chloride and the hydrogen atoms of the acetylene molecule tend to avoid each other; therefore, the Cl–Hg–Cl angle is 168.2° and the H–C=C angles are 178.4° (note that in the mercury chloride complex with one acetylene molecule, the Cl–Hg–Cl angle is larger, 172.1° [1]);
3) the distance between the acetylene carbon atoms is 1.248 Å, the Hg–Cl distances are 2.414 Å, the distance between the mercury atom and the middle of the C=C bond is 3.039 Å, and the C–H distances are 1.073 Å;
4) the x–Hg–y angle is 87.1°; the Cl1–Hg–x, Cl2–Hg–x, Cl1–Hg–y, and Cl2–Hg–y angles are 94.3°.

The calculated enthalpy of formation of this complex from the mercury chloride molecule and two acetylene molecules in the gas phase is –13 kcal/mole. The formation of the π,π-complex is an unactivated process. A vibrational frequency analysis for the π,π-complex shows that its IR spectrum is close to the spectrum of the π-complex formed by the mercury chloride molecule and an acetylene molecule, with the exception of minor red shifts of vibration frequencies corresponding to the mercury chloride molecule.