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Ab initio MP2 calculations of the products of acetylene addition to $HgCl_2$

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Gas-phase reaction of acetylene with $HgCl_2$ resulting in β-chlorovinylmercury derivatives and their interaction with Cl^- and I^- anions and KI molecule was studied by the *ab initio* MP2 method with the Dunning—Hay double zeta basis set and LanL pseudopotential for Hg, K, and I atoms. The reaction was shown to proceed *via* a π-complex of acetylene and $HgCl_2$ (the calculated enthalpy of formation is −6.5 kcal mol^{-1}). According to calculations, the activation energy of formation of *cis*-β-chlorovinylmercury chloride from acetylene and $HgCl_2$ is 31 kcal mol^{-1}. Chloride and iodide anions and KI molecule are readily added to both *cis*- and *trans*-isomer of β-chlorovinylmercury chloride to give stable species.

Key words: *ab initio* quantum-chemical calculations, MP2 method; acetylene—$HgCl_2$ interaction, π-complex; *cis*-β-chlorovinylmercury chloride, *trans*-β-chlorovinylmercury chloride, complexes with Cl^- and I^- anions and KI molecule.

cis-β-Chlorovinylmercury chloride was synthesized[1] in the reaction of $HgCl_2$ vapors with acetylene gas. Based on the results of the reaction kinetics studies, it was suggested[2] that the synthesis of *cis*-β-chlorovinylmercury chloride involves the formation of a π-complex of acetylene with $HgCl_2$ as precursor. However, this complex has not been isolated as individual substance so far. β-Chlorovinylmercury chloride is known to possess dual reactivity.[3—9] It exhibits the properties of both σ-bonded β-chlorovinyl derivatives of non-transition metals and a π-complex of $HgCl_2$ with acetylene. β-Chlorovinylmercury chloride readily eliminates $HgCl_2$ under the action of nucleophilic reagents (KI, Ph_3P, KCN, *etc.*), the *cis*-isomer being less reactive than the *trans*-isomer. This distinction is thought to be due to the intramolecular coordination between the Hg atom and the Cl atom of the chlorovinyl group. The NMR spectra of *cis*- and *trans*-β-chlorovinylmercury chloride were also interpreted[10,11] from this standpoint. Theoretical studies[12—14] revealed additional stabilization of the *cis*-isomer owing to the Coulomb interaction between the Hg atom and the Cl atom of the chlorovinyl group.

In this work,* we report the results of *ab initio* MP2 study of the potential energy surface (PES) fragments of the reaction between $HgCl_2$ and acetylene molecules. Transformation of the acetylene—$HgCl_2$ π-complex into *cis*-β-chlorovinylmercury chloride and the gas-phase reactions of both *cis*- and *trans*-β-chlorovinylmercury chloride with Cl^- and I^- anions and KI molecule were studied. The relative stabilities of the intermediates formed were also estimated.

Calculation Procedure

The geometries and electronic structures of the acetylene—$HgCl_2$ π-complex (**1**), *cis*-β-chlorovinylmercury chloride (**2**), *trans*-β-chlorovinylmercury chloride (**3**), transition state (TS) (**4**) of the transformation of complex **1** into **2**, and of the addition products of Cl^-, I^-, and KI to **2** and **3** (structures **5** and **6** for chloride anion, **7** and **8** for iodide anion, and **9** and **10** for KI molecule, respectively) were calculated at the second-order level of Møller—Plesset perturbation theory (MP2)[15] using the Dunning—Hay double zeta basis set[16] and LanL pseudopotential (Los Alamos) for Hg, K, and I atoms.[17,18] The basis sets employed are rather simple since they were first of all developed to obtain qualitative results. However, the results of studies of heavy-metal (including Hg) complexes with these basis sets were found to be realistic.[19—21] This is also supported by comparison of the calculated (see this work) and experimental interatomic distances and normal frequencies of *cis*- and *trans*-β-chlorovinylmercury chloride.

The procedure for location and identification of the TS of the transformation of the π-complex into *cis*-β-chlorovinylmercury chloride involved three steps. First, we calculated an approximate geometry of TS **4** by the method of linear synchronous transit (QST2)[22] along the line connecting the points corresponding to structures **1** and **2**. Then, structure refinement was performed by the quadratic synchronous transit (QST3) method.[22] Finally, we refined the geometry of TS **4** by the gradient method, analyzed the vibrational frequencies at the saddle point of the PES, and proved the correspondence between the results obtained and the reaction under study by the intrinsic reaction coordinate (IRC) method. Calculations were carried out using the GAUSSIAN-98 program package[23] on a CRAY J-90 supercomputer (National Energy Research Supercomputer Center, Berkeley, California, USA).

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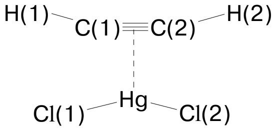
Results and Discussion

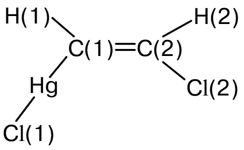
Geometry of π-complex (1) of acetylene with $HgCl_2$ and its transformation into *cis*-β-chlorovinylmercury chloride (2). A minimum corresponding to complex **1** was located on the PES of the reaction between the acetylene and $HgCl_2$ molecules.



1

Table 1 lists selected geometric parameters (interatomic distances and bond angles) of complex **1** and the free acetylene and $HgCl_2$ molecules as well as their total energies calculated without and with inclusion of zero-point vibrational energy (*ZPE*) correction (*E* and *E* + *ZPE*, respectively). The experimental[24] geometric parameters of the reactants are given in Table 1 in parentheses. Complex **1** has a planar geometry; both constituent molecules are somewhat nonlinear owing to mutual repulsion between Cl atoms of the $HgCl_2$ molecule and H atoms of acetylene molecule (the Cl—Hg—Cl angle is 172.05° and the H(1)—C(1)—C(2) and H(2)—C(2)—C(1) angles are 178.3°). The complex has a C_{2v} symmetry. The distance between the midpoint of the C≡C bond and the Hg atom is 3.018 Å. The calculated energy of formation of the π-complex is −6.5 kcal mol^{-1} (−5.0 kcal mol^{-1} with inclusion of *ZPE* correction). The activation barrier to rotation of the acetylene molecule in complex **1** about the axis passing through the Hg atom and the midpoint of the C≡C bond is 2.5 kcal mol^{-1}. The calculated and experimental frequencies for free acetylene and $HgCl_2$ as well as the calculated frequencies and intensities of normal vibrations of complex **1** are listed in Table 2.

The results of calculations of the PES fragments for the acetylene—$HgCl_2$ system suggest that complex **1** is coupled by a reaction channel to *cis*-β-chlorovinylmercury chloride **2** whose molecular geometry is shown below. Table 1 lists the calculated geometric parameters and total energies of molecule **2** and the experimental bond lengths and bond angles obtained in gas-phase electron diffraction study[25] (figures in parentheses). The calculated geometric parameters of *trans*-β-chlorovinylmercury chloride **3** are also listed in Table 1.



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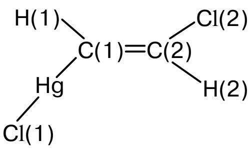

3

According to calculations, the *cis*-isomer, **2**, is energetically more favorable than the *trans*-isomer, **3**. The energy difference between the isomers is 0.69 kcal mol^{-1} (0.63 kcal mol^{-1} with inclusion of *ZPE* correction). The bond lengths in structures **2** and **3** differ only slightly; however, the bond angles differ appreciably. For instance, the H(1)—C(1)—C(2) and H(2)—C(2)—C(1) angles increase by ~2° while the Hg—C(1)—C(2) and Cl(2)—C(2)—C(1) angles decrease by ~2° on going from **2** to **3**. The geometry of the TS (**4**) of the transformation of complex **1** into **2** is shown below. The calculated geometric parameters and total energies of TS **4** are listed in Table 1. The activation energy of formation of the *cis*-isomer **2** from

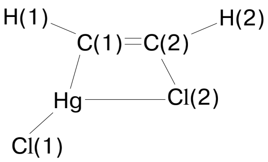

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Table 1. Geometric parameters, total energies, and dipole moments of free acetylene and $HgCl_2$ molecules and structures **1**—**4** calculated by the MP2/LanL2DZ method

Parameter	C_2H_2 + $HgCl_2$	**1**	**2**	**3**	**4**
Bond/Å					
H(1)—C(1)	1.072	1.073	1.097	1.096	1.088
C(1)=C(2)	1.246 (1.203)[a]	1.248	1.362 (1.33)[b]	1.363	1.285
C(2)—H(2)	1.072	1.073	1.093	1.091	1.079
C(1)—Hg	—	3.111	2.115 (2.14)[b]	2.114	2.314
C(2)—Cl(2)	—	3.671	1.834 (1.69)[b]	1.840	2.423
Hg—Cl(1)	2.381 (2.29)[a]	2.397	2.396 (2.27)[b]	2.396	2.410
Hg—Cl(2)	2.381 (2.29)[a]	2.397	3.524 (3.24)[b]	—	2.688
Bond angle/deg					
Hg—C(1)—C(2)	—	78.73	122.68	119.99	104.45
Cl(2)—C(2)—C(1)	—	118.46	123.45 (123)[b]	122.09	109.91
H(1)—C(1)—C(2)	180.00	178.26	116.11	119.63	137.53
H(2)—C(2)—C(1)	180.00	178.26	125.08 (123)[b]	126.89	161.34
−*E*/au	147.9985	148.0089	147.9946	147.9935	147.9485
−(*E* − *ZPE*)/au	147.9717	147.9797	147.9608	147.9598	147.9187
μ/D	0.00	1.97	4.99	1.15	7.33

Note. The experimental values[a,b] given in parentheses were taken from Refs. 24 and 25.

Table 2. Frequencies and intensities of normal vibrations in the IR spectra calculated by the MP2/LanL2DZ method

System	ν/cm^{-1}	Intensity (rel. unit)	Vibration
Free molecules C_2H_2 and $HgCl_2$	84 (75)^a	9	Cl—Hg—Cl b
	330 (363)^a	0	Cl—Hg—Cl s
	393 (413)^a	49	Cl—Hg—Cl as
	621 (612)^a	0	HCCH s
	724	116	HCCH as
	728 (729)^a	121	HCCH as
	1888 (1974)^a	0	C=C
	3426 (3373)^a	58	C—H
π-Complex C_2H_2 and $HgCl_2$ (**1**)	322	1	Cl—Hg—Cl as
	381	149	Cl—Hg—Cl s
	747	117	HCCH
	758	151	HCCH
	1878	4	C=C
	3413	80	C—H
	3501	3	C—H
cis-β-Chlorovinylmercury chloride (**2**)	347	29	Hg—Cl
	556	7	C—Cl
	744 (772)^b	89	HCCH out-of-plane
	976 (918)^b	2	CCH out-of-plane
	1182 (1135)^b	7	HCCH p
	1334 (1275)^b	29	CCH p
	1555 (1520; 1580)^b	81	C=C
	3168	8	C—H
	3231	10	C—H
trans-β-Chlorovinylmercury chloride (**3**)	357	50	Hg—Cl
	644	6	C—Cl
	720 (773)^b	58	HCCH out-of-plane
	1033 (940)^b	70	CCH out-of-plane
	1222 (1154)^b	30	HCCH p
	1352 (1280)^b	3	CCH p
	1544 (1580; 1680)^b	122	C=C
	3168	6	C—H
	3231	5	C—H
TS (**4**)	i454	263	Reaction coordinate
	348	41	Hg—Cl
	739	202	HCCH
	934	45	HCCH
	1694	330	C=C
	3277	69	C—H
	3405	9	C—H

Note. The experimental values^{a,b} given in parentheses were taken from Refs. 27 and 10, respectively. Notations of vibrations: b is bending, s is symmetric, as is asymmetric, and p is planar vibration.

acetylene gas and $HgCl_2$ vapor was found to be 31.4 kcal mol^{-1} (33.3 kcal mol^{-1} with inclusion of *ZPE* correction).

Transition state **4** has a planar geometry.

Previously,[26] it was experimentally found that *trans*-β-chlorovinylmercury chloride cannot be formed in the gas-phase reaction of acetylene with $HgCl_2$ and that *cis*-*trans*-isomerization can occur only in the presence of peroxides. Presumably, it proceeds by a radical mechanism.

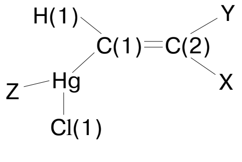
The calculated dipole moments of all intermediates are listed in Table 1. The dipole moment of *cis*-β-chlorovinylmercury chloride is nearly four times larger than that of *trans*-β-chlorovinylmercury chloride. A rather large dipole moment of π-complex **1** (1.97 D) is due to the electron density transfer from acetylene to $HgCl_2$ molecule.

The calculated normal vibrational frequencies and intensities in the IR spectra of isolated C_2H_2 and $HgCl_2$ molecules and structures **1**—**4** are listed in Table 2. The experimental vibrational frequencies of $HgCl_2$, acetylene,[24] and molecules **2** and **3** (see Ref. 10) are given in parentheses. The difference between the calculated and experimental vibrational frequencies is ~5%.

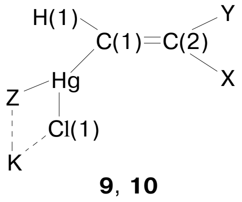
Similarly to free acetylene molecule, the C=C vibration in the IR spectrum of π-complex **1** was also found to be of low intensity. For TS **4**, the ν(C=C) frequency is shifted by 184 cm^{-1} toward the long-wavelength region and the vibration intensity increases substantially. For *cis*-β-chlorovinylmercury chloride, the ν(C=C) frequency is additionally shifted by 139 cm^{-1} toward the long-wavelength region as compared to TS **4**.

As mentioned above, π-complex **1** was not isolated as individual substance. This was assumed to be due to the low binding energy of the complex upon its formation from acetylene and $HgCl_2$ and to rather high temperature of the gas-phase synthesis of *cis*-β-chlorovinylmercury chloride[1,2] (the vaporization temperature of $HgCl_2$ exceeds 300 °C).[28]

Addition of Cl$^-$ and I$^-$ anions and KI molecule to *cis*- and *trans*-isomers of β-chlorovinylmercury chloride. Experimental studies of the reactivity of *cis*-β-chlorovinylmercury chloride (**2**) and *trans*-β-chlorovinylmercury chloride (**3**) have shown that the latter readily eliminates acetylene under the action of nucleophiles.[3—9] Compound **2** was found to be less prone to this transformation. In this work, we attempted to rationalize these distinctions based on the results of quantum-chemical calculations for the gas-phase systems resulted from compounds **2** and **3** upon addition of Cl$^-$ and I$^-$ anions and KI molecule. The geometries of intermediates **5**—**10** obtained from our calculations are presented below.



5—8



9, **10**

	5	**6**	**7**	**8**	**9**	**10**
X	Cl	H	Cl	H	Cl	H
Y	H	Cl	H	Cl	H	Cl
Z	Cl$^-$	Cl$^-$	I$^-$	I$^-$	I	I

Table 3. Geometric parameters, total and relative energies of *cis*- and *trans*-isomers of intermediates **5**—**10**

Parameter	**5**	**6**	**7**	**8**	**9**	**10**
Bond/Å						
C(2)—X	1.856	1.090	1.855	1.090	1.839	1.091
C(1)=C(2)	1.359	1.356	1.359	1.355	1.361	1.361
C(2)—Y	1.095	1.901	1.095	1.903	1.094	1.860
C(1)—H(1)	1.105	1.099	1.105	1.099	1.101	1.097
C(1)—Hg	2.180	2.195	2.187	2.204	2.161	2.159
Hg—Cl(1)	2.505	2.563	2.510	2.567	2.587	2.714
Hg—Z	2.598	2.525	2.890	2.797	2.914	2.787
Cl(1)—K	—	—	—	—	3.011	2.967
Z—K	—	—	—	—	3.499	3.592
Bond angle/deg						
X—C(2)—C(1)	124.4	127.9	124.4	127.9	124.2	126.7
Y—C(2)—C(1)	126.5	123.2	126.4	123.3	125.3	122.5
C(2)—C(1)—H(1)	113.2	119.6	113.2	119.8	115.4	120.8
C(2)—C(1)—Hg	129.9	116.8	129.6	116.5	126.1	116.6
C(1)—Hg—Cl(1)	142.7	117.4	139.4	114.6	139.7	108.0
C(1)—Hg—Z	109.7	132.0	111.5	131.9	123.1	152.9
Cl(1)—Hg—Z	107.6	110.6	109.2	113.5	97.2	99.1
$-E$/au	162.8485	162.8566	159.2951	158.3038	187.1570	187.1618
ΔE/kcal mol^{-1}	5.09	—	5.49	—	2.97	—

Table 3 lists the geometric parameters and total energies of structures **5**—**10** and Table 4 lists their Mulliken effective atomic charges.

The total energies of isolated I^- and Cl^- anions and KI molecule calculated by the MP2/LanL2DZ method are −11.2479, −14.7784, and −39.1152 au, respectively. According to calculations, the addition of these species to molecule **2** (**3**) proceeds exothermically and the energy gained is 47.3 (53.1) kcal mol^{-1} for Cl^- anion, 33.0 (39.2) kcal mol^{-1} for I^- anion, and 29.6 (33.2) kcal mol^{-1} KI molecule. Thus, the gas-phase addition of all the three species (Cl^-, I^-, and KI) to *trans*-β-chlorovinylmercury chloride is energetically more favorable than their addition to *cis*-β-chlorovinylmercury chloride.

Addition of chloride anion to molecules **2** and **3**, respectively, results in anions **5** and **6** with strongly different C—Cl bond lengths (see Table 3), namely, this bond in the latter intermediate is much longer than in the former. This also holds for the C—Hg bonds in **5** and **6**, though free isomers **2** and **3** are characterized by the same C—Hg bond length. The Cl—Hg—Cl angle in molecule **6** is larger than in **5**. A similar pattern of structural changes is observed when comparing pairs of species **7** and **8** and **9** and **10**. Thus, the geometry of the intermediates formed from *trans*-β-chlorovinylmercury chloride is closer to that of acetylene elimination products than the geometry of the species formed from *cis*-β-chlorovinylmercury chloride.

Table 4 lists the results of calculations of Mulliken atomic charges in intermediates **5**—**10**. In species **6**, the effective atomic charge (q) of Cl in the chlorovinyl group is much larger than in **5** (−0.256 e *vs.* −0.196 e, respectively). A similar picture is observed when comparing pairs of intermediates **7** and **8** and **9** and **10**.

Table 4. Mulliken effective atomic charges (q/e) in structures **5**—**10**

Atom	**5**	**6**	**7**	**8**	**9**	**10**
X	−0.196	0.242	−0.191	0.244	−0.144	0.257
C(2)	−0.283	−0.256	−0.279	−0.253	−0.252	−0.249
C(1)	−0.381	−0.416	−0.383	−0.422	−0.407	−0.402
Y	0.196	−0.256	0.198	−0.257	0.224	−0.176
H(1)	0.161	0.180	0.161	0.180	0.191	0.207
Hg	0.677	0.670	0.609	0.585	0.657	0.585
Cl(1)	−0.544	−0.600	−0.540	−0.596	−0.595	−0.670
Z	−0.630	−0.564	−0.575	−0.481	−0.528	−0.417
K	—	—	—	—	0.854	0.864

Peculiarities of the geometry of and the electron density distribution in these species represent an indirect evidence that intermediates formed from *trans*-isomer **3** can eliminate acetylene more readily than derivatives of **2**.

The relative energies of the *cis*- and *trans*-structures of the intermediates formed by addition of halide anions or KI to the *cis*- and *trans*-isomers of β-chlorovinylmercury chloride (**2** and **3**, respectively) are listed in Table 3. In all cases, *trans*-structures appeared to be more energetically favorable. This is rather unexpected since the reverse holds for free isomers **2** and **3**.

In actual practice, reactions of *cis*- and *trans*-isomers of β-chlorovinylmercury chloride with nucleophiles (*e.g.*, halide anions or KI) followed by elimination of acetylene proceed in aqueous alcohol solutions. Since we performed gas-phase calculations without considering solvent effects, it is difficult to estimate the energetics of reactions in solutions. According to our calculations, intermediates **5**—**10** are stable, so that only endothermic elimination of acetylene is possible. The energy preferableness of the *trans*-configurations of the intermediates as compared to their *cis*-configurations suggests that compounds **6**, **8**, and **10** can be more readily formed in solutions than compounds **5**, **7**, and **9** and, hence, a nucleophilic attack on the *trans*-isomer **3** results in easier elimination of acetylene.

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