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Short communication

Some comments on ‘A study on the reaction mechanism and kinetic of mercury oxidation by chlorine species’ [J. Mol. Struct. (Theochem) 625 (2003) 277][☆]

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Abstract

In this paper, we comment on a recent article where mercury speciation reaction kinetics were reported. We examine certain difficulties and flaws in the theoretical treatment given in the recent article. In addition, we provide accurate geometries and heats of reaction results to validate a different quantum mechanical method and basis set combination which we encourage for use in theoretically calculating rate constants for mercury oxidation reactions involving chlorine.

Keywords: Transition state; Unimolecular reaction; Multichannel reaction

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1. Introduction

Mercury released from coal combustion can exist in a variety of oxidation states with Hg^{+} and Hg^{2+} being preferred because they are water-soluble and can be captured in wet scrubbers before being released in stack gases [1]. Unfortunately, much of the mercury is not oxidized, but is released into the atmosphere as elemental mercury [2]. Mercury can be oxidized by various chlorine species, but the mechanisms by which these reactions occur are still in question [3]. To optimize the capture of mercury from coal combustion, knowledge of the detailed chemistry and kinetics of reactions with oxidizing species such as chlorine and oxygen is essential.

2. Discussion

The reactions listed below may take place in the flue gases of coal combustion and have been studied theoretically by Li et al. [4] in a recent publication

$$Hg + HOCl \rightarrow HgCl + OH \tag{1}$$

$$Hg + HCl \rightarrow HgCl + H \tag{2}$$

$$HgCl + Cl_2 \rightarrow HgCl_2 + Cl \tag{3}$$

$$HgCl + HCl \rightarrow HgCl_2 + H \tag{4}$$

$$HgO + HCl \rightarrow HgCl + OH \tag{5}$$

$$HgO + HOCl \rightarrow HgCl + HO_2 \tag{6}$$

$$Hg + HgCl_2 \rightarrow Hg_2Cl_2 \tag{7}$$

To calculate a rate constant for a bimolecular reaction from theory, one traditionally uses transition state theory, which requires knowledge of an accurate transition state structure and activation energy. The following is a familiar equation for calculating the rate constant for a bimolecular reaction, originally derived from Eyring [5]

$$k_{\mathrm{bim}} = L^{*}\kappa \frac{\frac{Q^{\mathrm{TS}}}{V}}{\frac{Q_{\mathrm{A}}}{V}\frac{Q_{\mathrm{B}}}{V}} \frac{k_{\mathrm{B}}T}{h} \mathrm{e}^{-E_{\mathrm{a}}/k_{\mathrm{B}}T} \tag{8}$$

such that κ is the tunneling correction; L^{*} is the statistical factor; Q^{TS}, Q_{A}, and Q_{B} are the partition functions of the transition structure and reactant species, respectively; V is the volume; k_{B} is Boltzmann’s constant; h is Planck’s constant; and E_{a} is the activation energy. This specific formulation can work for reactions (3) and (4), but cannot be used for the other reactions as described next.

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2.1. Barrierless reactions

Examining reactions (1) and (2) with the QCISD method and high quality pseudopotentials for mercury [6,7] shows that the reactions take place on a barrierless $S = 0$ potential energy surface. Li et al. reported a distinct saddle point on the singlet potential energy surface of each of these reactions at the lower geometry optimization level. Intrinsic reaction coordinate calculations we have done based on their structure showed that there was indeed a transition state leading to the correct products and reactants with the SDD basis set, but higher level calculations do not confirm the existence of this structure. One method of calculating a rate constant for a barrierless reaction would involve the use of a variational method such as variational transition state theory developed by Truhlar [8].

2.2. Multichannel reactions and transition state theory

The use of transition state theory for reactions (5) and (6) would also be more difficult than implied in Li et al.'s previous work. Each of these reactions has two transition states linking the products and reactants. One would need to use an aggregated form of multichannel transition state theory to correctly estimate the reaction rates of these reactions and cannot simply use the activation energy they report in their work.

2.3. Unimolecular reactions and transition state theory

Li et al. used traditional transition state theory to calculate a rate constant for reaction (7), which is a unimolecular reaction in the reverse direction. Traditional transition state theory can be used to estimate reaction rates for unimolecular reactions at the high pressure limit, but the reactions here are at high temperatures and low pressures, placing them in the fall-off regime where RRKM theory or a Master Equation approach must be employed for the rate constant estimation [12].

2.4. Accuracy of theoretical results compared to experimental data

In general, the quantum mechanical method and basis set used for the transition structure optimizations should be examined carefully in terms of their accuracy relative to experimental data. Due to the lack of experimental rate constant data available for mercury oxidation reactions, validation of the method and basis set combination must be pursued through the comparison of theoretical geometries and heats of reaction to experiment.

The following relativistic effective core potentials were recently developed in the literature for mercury and are the ones compared in the current work: Stuttgart (1997) [6] and Stevens et al. (1992) [7], and will be referred to as the 1997 and 1992 basis sets, respectively [8]. The basis sets used for all other atoms such as chlorine, oxygen and hydrogen are standard Pople basis sets including both diffuse and polarization functions; 6-311++G(3df, 3pd). All pseudopotentials were used in GAUSSIAN 98 [9] for the geometry optimizations and energy calculations. Table 1 provides a list of optimized bond lengths for all basis set and method combinations, showing the QCISD/1992 combination to be the most accurate with an average absolute error of 0.03 Å. The 1992 and 1997 basis sets give low errors for all computational methods that have been examined.

Table 1
Bond lengths (Å) of species from theory compared to experimental values

Method Basis set	MP2 SDD	QCISD(T) SDD	QCISD 1992[a]	QCISD 1997[a]	B3LYP 1992[a]	B3LYP 1997[a]	B3LYP LANL2DZ	Experiment
HOCl:								
H–O:	0.997	0.9965	0.961	0.961	0.9666	0.9666	0.9576	0.975[b]
O–Cl:	1.856	1.889	1.6869	1.6869	1.6996	1.6996	1.7012	1.690
	∠103.4°	∠102.8°	∠103.5°	∠103.5°	∠103.6°	∠103.6°	∠103.2°	∠102.5°
OH	0.9973	1.0036	0.9684	0.9684	0.9739	0.9739	1.0017	0.9708
HCl	1.3144	1.3243	1.2833	1.2833	1.285	1.285	1.3149	1.2746[b]
HgCl	2.4705	2.4994[c]	2.412	2.4085	2.4896	2.4648	2.6122	2.23[d]
$HgCl_2$	2.3489	2.3612[c]	2.3003	2.3116	2.3195	2.3211	2.4423	2.28[e]
Cl_2	2.2455	2.2858	1.997	1.997	2.0106	2.0106	2.2244	1.9878[b]
H_2	0.7384	0.7473	0.7422	0.7422	0.7427	0.7427	0.7434	0.7414[b]
HgO	1.9075	2.0025	1.9413	1.9535	1.9497	1.9474	2.0444	–
Average absolute bond distance error	0.103	0.119	0.030	0.031	0.044	0.041	0.110	

[a] Pople: 6-311++G(3df,3pd) basis set used for atoms other than mercury.

[b] Ref. [16].

[c] Due to convergence problems these were run only to double excitations.

[d] Ref. [17].

[e] Ref. [18].

Table 2
Heats of reaction from theory compared to experiment (kcal/mol)

Method Basis set	MP2 SDD	QCISD SDD	QCISD 1992[a]	QCISD 1997[a]	B3LYP 1992[a]	B3LYP 1997[a]	B3LYP SDD	B3LYP LANL2DZ	Experiment NIST
$Hg + HOCl \rightarrow HgCl + OH$	15.54	12.11	22.71	14.94	29.99	22.61	17.20	11.19	31.199
$Hg + HCl \rightarrow HgCl + H$	55.85	59.47	77.06	69.28	85.65	78.27	67.44	62.53	78.243
$HgCl + Cl_2 \rightarrow HgCl_2 + Cl$	−45.49	−40.44	−30.07	−33.35	−18.04	−24.32	−31.51	−29.83	−24.723
$HgCl + HCl \rightarrow HgCl_2 + H$	5.23	9.95	23.78	20.5	35.81	29.53	21.38	25.77	20.449
$Hg + 2HCl \rightarrow HgCl_2 + H_2$	−25.93	−22.67	−3.67	−14.73	2.45	−11.21	−15.9	−16.42	−5.514
$Hg + Cl_2 \rightarrow HgCl_2$	−60.48	−54.88	−55.34	−66.4	−40.77	−54.44	−51.3	−54.43	−49.634
$Hg + Cl \rightarrow HgCl$	−15.13	−14.44	−25.27	−33.05	−22.73	−30.11	−19.79	−24.59	−24.911
$Hg + Cl_2 \rightarrow HgCl + Cl$	5.24	9.08	23.2	15.43	31.79	24.41	14.54	6.92	33.071
$HgCl + Cl \rightarrow HgCl_2$	−65.72	−63.96	−78.55	−81.84	−72.57	−78.85	−65.84	−61.35	−82.705
$HgCl + HOCl \rightarrow HgCl_2 + OH$	−35.04	−37.40	−30.56	−33.84	−19.84	−26.12	−28.85	−25.57	−26.595
Average absolute error	16.83	15.04	4.42	9.37	6.77	4.67	8.72	11.06	

[a] Pople: 6-311++G(3df,3pd) basis set used for atoms other than mercury.

In contrast, the research performed by Li et al. was based upon the SDD basis set and yielded an overall average error of 0.119 Å with the QCISD(T) method and 0.103 Å with the MP2 method. Inaccuracies in molecular geometries lead to incorrect vibrational analyses. The resulting shift in the partition functions implies an error in reaction rate which may be sizable in view of the size of the inaccuracies in their geometrical parameters.

Table 2 shows a summary of energy predictions for heats of reactions from theory compared to high quality experimental data from the National Institute of Standards and Technology database [10]. All geometries were fully optimized at the indicated level of theory and basis set. Vibrational frequency calculations were performed to obtain thermal corrections including zero point energies to the electronic energies reported by GAUSSIAN 98 [9]. The QCISD method with the 1992 basis set for mercury and the standard 6-311++G(3df,3pd) basis set for other atoms gives the best agreement with an average absolute error of 4.42 kcal/mol compared to experiment. On the other hand, the MP2 and QCISD results with the SDD basis sets lead to average errors that are between 16 and 15 kcal/mol.

We have calculated the activation energy for reaction (4) at the QCISD level of theory with both the 1992 and 1997 basis sets. We found that the activation energies are 30.27 and 27.10 kcal/mol for the 1992 and the 1997 basis sets, respectively. Li et al. calculated an activation energy of 13.64 kcal/mol using the SDD basis set at the QCISD(T) level of theory. Examination of Tables 1 and 2 reveals that this combination of method and basis set has greater error in both geometry and heats of reactions calculations when compared to the method and basis set combinations used in our work [8]. Recall that errors in activation energies of only a few kcal/mol lead to reaction rates that are orders of magnitude different from experimental values [11].

2.5. Referencing of experimental data

Some of the experimental values cited by Li et al. are estimates from previous kinetic models or from reactions that do not specifically involve mercury. The experimental data for reaction (2) was extracted from data by Widmer et al. in conference proceedings that predate their publication [13]. The publication, though, clearly shows that reaction (2) was not investigated as a fundamental reaction. Instead, they globally modeled the kinetics for the nonelementary reaction, $Hg + 2HCl \rightarrow HgCl_2 + H_2$.

In their research, Li et al. also referred to experimental data for reaction (4) by comparing the reaction to one where lithium replaced mercury. The authors failed to give justification of why the oxidation of lithium chloride via HCl would resemble the oxidation of mercuric chloride via HCl. Mercury and lithium are elements from different groups in the periodic table with substantially different electronic configurations. There has been no experimental rate constant data published on reaction (4) as far as we know, and theoretically this reaction has been studied by only two groups [3,11]. We calculated the following rate expressions for reaction (4)

$$k^{TST}\ (\mathrm{cm^3/mol\ s}) = 3.11 \times 10^{11}\ \mathrm{e}^{-15713/T}, \tag{9}$$

using QCISD/1992

$$k^{TST}\ (\mathrm{cm^3/mol\ s}) = 1.95 \times 10^{9}\ \mathrm{e}^{-12586/T}, \tag{10}$$

using QCISD/1997

in the temperature range of 298–2000 K [11]. As Li et al. did not specify units on their reported rate constant, our data cannot be compared directly with theirs.

While the rate constants calculated by Li et al. agree very well with the lithium reaction data they use for comparison, the lithium data should not be used to replace unmeasured mercury data. To demonstrate why this should not be done,

one only needs to consider similar literature from two homologous reactions. This work uses data for two reactions that are much more similar and still show large deviations from each other:

$$\mathrm{Na} + \mathrm{HCl} \rightarrow \mathrm{NaCl} + \mathrm{H} \tag{11}$$

$$\mathrm{Li} + \mathrm{HCl} \rightarrow \mathrm{LiCl} + \mathrm{H} \tag{12}$$

In this case, the activation energy for the sodium reaction is 9.99 kcal/mol [14], while the one for lithium is 1.75 kcal/mol [15]. This leads to a difference of about 2 orders in magnitude in the rate constant around 800 K. Even in this instance where lithium and sodium are in the same group in the periodic table, the rate constant values are not within an order of magnitude of each other. This example validates the necessity to estimate rate constants on a case by case basis instead of using data from homologous reactions.

2.6. Theoretically calculated results from previous work

The energy calculations from the work of Li et al. are also problematic for two reasons. First, their energy results were at the QCISD(T)/SDD//MP2/SDD level, while their vibrational analysis were done at the MP2/SDD level. However, they do not use the reported zero point energies. Neglecting thermal and zero point energy corrections changes their heats of reaction by as much as 3.5 kcal/mol for some of the reactions, and possibly more for their activation energies at 973 K where they do not report thermal corrections at that temperature. Secondly, much of the data for heats of reaction that are extracted from Table 1 and reported in Table 2 of their work are incorrectly computed from their own numbers.

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