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Theoretically Predicted Rate Constants for Mercury Oxidation by Hydrogen Chloride in Coal Combustion Flue Gases

JENNIFER WILCOX, JOE ROBLES,
DAVID C. J. MARSDEN, AND
PAUL BLOWERS*

*Department of Chemical and Environmental Engineering,
The University of Arizona, Tucson, Arizona 85721*

In this work, theoretical rate constants are estimated for mercury oxidation reactions by hydrogen chloride that may occur in the flue gases of coal combustion. Rate constants are calculated using transition state theory at the quadratic configuration interaction (QCI) level of theory with single and double excitations, and are compared to results obtained from density functional theory, both including high level pseudopotentials for mercury. Thermodynamic and kinetic data from the literature are used to assess the accuracy of the theoretical calculations when possible. Validation of the chosen methods and basis sets is based upon previous and current research on mercury reactions involving chlorine. The present research shows that the QCISD method with the 1992 Stevens et al. basis set leads to the most accurate kinetic and thermodynamic results for the oxidation of mercury via chlorine containing molecules. Also, a comparison of the heats of reaction data for a series of mercury oxidation reactions reveals that the density functional method, B3LYP, with the 1997 Stuttgart basis set provides reasonably accurate results for these large systems.

1. Introduction

Coal burning is the primary source of anthropogenic release of mercury, with about 72 tons per year being released in the United States alone (*1*). In 1998 U.S. EPA began discussion of mandatory mercury emission measurements from all coal burning plants to lay the groundwork for reducing these mercury emissions in the future (*2*). The EPA plans to issue final regulations on mercury emissions from coal- and oil-fired power plants by December 15, 2004, and is expected to require compliance by December 2007 (*3*). These steps are being taken because mercury can be found in many of the foods we eat, from fish (*4, 5*), to other foods we generally do not expect to contain mercury, like vegetables (*6, 7*). This would not be of concern except research has repeatedly shown that mercury may have many toxic effects on organisms, from reproductive effects (*8*), to developmental problems in children (*9*), and psychological or intellectual damage (*10, 11*).

To effectively capture mercury from the exhaust of coal combustion, it is necessary to understand the speciation of mercury in the exhaust environment. Mercury is in its elemental state when it is released from the coal combustion process, which makes it very difficult to capture (*1*). Elemental mercury is not soluble in water, the primary liquid media used for emissions control, and does not adsorb readily on most solid substrates with capture rates between 10 and 80% (*12*). Fortunately, elemental mercury reacts with oxidizing species that exist naturally in the coal exhaust and can be transformed into an oxidized form, $HgCl_2$, that can be captured more easily. However, the amount of oxidation is dependent on the concentration of oxidizing species available in the coal exhaust.

The major ways of determining possible mechanisms of oxidation are through extraction of kinetic data from simplifications of experimental flue gas oxidation conditions, calculation of kinetic and thermodynamic data for oxidation reactions using quantum mechanics, and kinetic modeling based upon partial data that is available through a combination of the above techniques.

There are many difficulties associated with experimentally determining mercury speciation kinetics. The current EPA methods (*13, 14*) that are being used to measure mercury can only differentiate Hg^0 and Hg^{2+}, leaving Hg^{1+} unmeasured; this form of oxidized mercury cannot be experimentally determined (*15*). Another difficulty with experimental measurements is due to the inability to measure mercury at low concentrations and high temperatures. Mercury is normally present in quantities around only 10 ppbv in flue gases, and simulated flue gases often use mercury concentrations that are orders of magnitude higher (*16*). In addition, temperatures below that of real flue gas conditions were used in many kinetic experiments so the reactions would be slower and could be measured (*17*).

Quantum chemical methods are capable of estimating reaction rates and kinetic parameters for mercury reactions and do not suffer from the difficulties in speciating mercury that the experimental methods do. However, few computational studies have been done so far to understand mercury reactions using quantum chemistry (*17−18*). Within the current research, a series of basis sets along with various quantum mechanical methods will be compared to determine which combination provides the most accurate results for the oxidation of mercury via hydrogen chloride.

2. Computational Methods

A. Basis Sets and Theoretical Methods. In this paper, the focus will be on using quantum chemical methods to investigate the oxidation of mercury via hydrogen chloride:

$$HgCl + HCl \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} HgCl_2 + H \qquad (1)$$

Because most computational methods scale with the number of electrons to the third, fourth, or higher power, mercury is a difficult element to study because it has 80 electrons. The large number of electrons makes the calculations computationally intensive, and to make the calculations tractable while obtaining accurate theoretical rate constants, the use of relativistic effective core potentials is necessary.

Theoretically determining the rate constants of mercury oxidation reactions will allow for an understanding of the chlorine transfer reaction mechanisms without the difficulties the experimental methods have. Fortunately, ab initio methods of quantum chemistry recently have proven to be effective in predicting the structure and thermodynamic properties of chemical systems (*19−22*).

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* Corresponding author telephone: 520-626-5319; fax: 520-621-6048; e-mail: blowers@engr.arizona.edu.

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TABLE 1. Comparison of Thermodynamic and Kinetic Data of the Reaction HgCl + M → Hg + Cl + M

	experimental	LANL2DZ B3LYP	1992 QCISD	1997 QCISD
geometry (Å)	2.23[a]	2.612	2.412	2.407
ΔH_{rxn} (kJ/mol) at 298 K	104.22[b]	102.89	105.7	138.27
frequency (1/cm)	292.61[c]	228	290	292
activation energy (kJ/mol) at 393 K	no experimental data available	82.15	67.52	84.34
rate constant ($M^{-1}\,s^{-1}$) at 393 K	$k_1 = 4.309$ $k_{-1} = 1.95 \times 10^{10}$ [d]	$k_1 = 2.29 \times 10^{-1}$	$k_1 = 14.6$	$k_1 = 6.11 \times 10^{-2}$

[a] Ref *41.* [b] Ref *34.* [c] Ref *42.* [d] Ref *32.*

In this work, the quadratic configuration interaction (QCI) with single and double excitations (QCISD) method was combined with existing basis sets for mercury and chlorine. Relativistic effects for mercury were included because of its size through the use of appropriate pseudopotentials. The following relativistic effective core potentials are the most recently developed in the literature for mercury and are the ones compared in this research: Stuttgart 1997 (*23*) and Stevens et al. 1992 (*24*); and these will be referred to as the 1997 and 1992 basis sets, respectively, throughout this work. The basis set used for chlorine is a standard Gaussian basis set including both diffuse and polarization functions; 6-311++G(3df, 3pd). All pseudopotentials were used in Gaussian 98 (*25*) to calculate the energies and structures of the transition state, products, and reactants using QCISD. The basis set used for hydrogen was obtained from the Handbook of Gaussian Basis Sets (*26*) and is labeled in the text as 1.37.1.

It is important to note that the basis sets mentioned above were used in this work to calculate the transition structures and rate constants for reaction 1 and also for the following unimolecular reactions:

$$\mathrm{HgCl} + \mathrm{M} \overset{k_1}{\underset{k_{-1}}{\leftrightarrow}} \mathrm{Hg} + \mathrm{Cl} + \mathrm{M} \qquad (2)$$

$$\mathrm{Cl_2} + \mathrm{M} \overset{k_1}{\underset{k_{-1}}{\leftrightarrow}} 2\mathrm{Cl} + \mathrm{M} \qquad (3)$$

These reactions, along with Rice−Ramsperger−Kassel−Marcus (RRKM) results for calculating the rate constants, have been studied in previous work so the details of the calculations will be omitted here (*27*).

B. Transition State Theory. The current reaction of focus, eq 1, is bimolecular so rate constants are calculated using traditional transition state theory with the following Arrhenius expression (*19*):

$$k = \frac{k_b T}{h} \kappa \frac{Q_{TS}}{Q_{HgCl} Q_{HCl}} \exp\left(\frac{-E_a}{RT}\right) \qquad (4)$$

such that $Q_{Total} = Q_{trans} Q_{rot} Q_{vib} Q_{elec}$ and κ accounts for tunneling.

3. Results and Discussion

In the remainder of this work, thermal corrections that include the zero point energies corrections were included in all calculated results and the frequency calculations were left unscaled because of the unavailability of proper scaling factors (*28*).

Because of the lack of experimental kinetic data for this reaction, the choice of method and basis set must be validated by analyzing reactions involving mercury and chlorine where experimental kinetic data are available. For this reason it is essential to first consider the results of reactions 2 and 3 from previous work. Because of the unimolecular nature of reactions 2 and 3, RRKM theory becomes essential and all of the parameters within RRKM can be calculated through theory with the exception of the collisional efficiency, β_c. The collisional efficiency is an empirical value that can be obtained through experimental knowledge of the reaction (*29*). Although many models have been determined for calculating the collision efficiency, experimental data are still necessary to estimate it (*30, 31*). Because of the lack of experimental data for reaction 2 in particular, β_c is used as a fitting parameter that ranges between zero and one. Comparing the theoretical results to those of experiment (*32*) as shown by Figure 1, the decomposition reaction of mercuric chloride has a collisional efficiency of 0.1. Both theoretically determined kinetic and thermodynamic data are compared to experimental data in Table 1. The results from Table 1 indicate that the 1992 basis set along with the QCISD method provide the most accurate heat of reaction with a deviation of 1.48 kJ/mol from experiment. This combination also yielded the most accurate rate constant, which is within a factor of 4 from the experimental value. However, because of the limited experimental data available on this reaction, it is important not to disregard the other computational methods and basis sets in this current work.

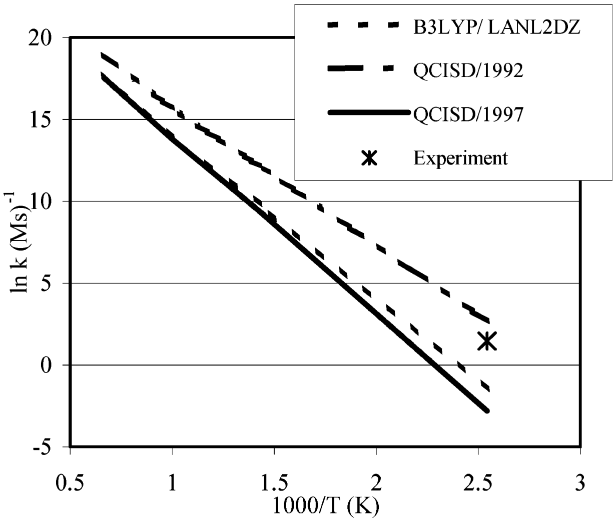

FIGURE 1. Canonical variational transition state theory rate constant (k^{CVT}) for each combination, compared to experimental rate constant (*32*), varying temperature, 1000/*T*. Note: β_c = 0.2, HgCl + M → Hg + Cl + M.

From the previous calculations (*27*) it was found that a good estimation of the rate constant for reaction 2 is

$$k\ [\mathrm{M^{-1}\,s^{-1}}] = 4.25 \times 10^{10}\ \mathrm{e}^{-8588/T} \text{ using QCISD/1992} \qquad (5)$$

$$k\ [\mathrm{M^{-1}\,s^{-1}}] = 5.43 \times 10^{10}\ \mathrm{e}^{-10801/T} \text{ using QCISD/1997} \qquad (6)$$

It was concluded from this previous research that although the 1992/QCISD combination provided the most accurate results, all combinations from Table 1 should be considered

TABLE 2. Comparison of Thermodynamic and Kinetic Data of the Reaction HgCl + HCl → $HgCl_2$ + H (T = 298 K)

	experimental	LANL2DZ B3LYP[a]	1992 QCISD	1997 QCISD
		Geometry (Å)		
HgCl	2.23[b]	2.6122	2.4121	2.4084
HCl	1.2746[c]	1.3149	1.2833	1.2833
HgC_2	2.28[d]	2.4417 ∠180°	2.3002 ∠180°	2.3116 ∠180°
transition structure	no experimental data available	HCl: 2.3335 HgCl (1): 2.4634 HgCl (2): 2.4517 ∠HHgCl: 179.89° ∠ClHgCl: 179.5°	HCl: 1.7781 HgCl (1): 2.3697 HgCl (2): 2.3576 ∠HHgCl: 180° ∠ClHgCl: 180°	HCl: 1.7598 HgCl (1): 2.3799 HgCl (2): 2.3383 ∠HHgCl: 180° ∠ClHgCl: 180°
		Frequencies (1/cm)		
HgCl[e]	292.61	228.92	290.69	297.81
HCl[e]	2989.74	2709.61	2947.12	2947.12
$HgCl_2$[f]	75, 363, 413	66, 66, 288, 345	97, 97, 340, 394	89, 89, 338, 388
transition structure	no experimental data available	61, 61, 103, 103, 283, 335, −247	81, 81, 250, 300, 508, 508, −1647	81, 81, 260, 305, 423, 423, −1584
		ΔH_{rxn} (kJ/mol)[g]		
	85.76	107.83	102.18	85.78
		Activation Energy (kJ/mol)		
forward	no experimental data available	108.34	126.66	113.42
reverse	no experimental data available	0.506	24.48	27.64
		Rate Constant (cm^3/mol s)		
forward	no experimental data available	3.57×10^{-5}	3.91×10^{-12}	8.86×10^{-10}
reverse	no experimental data available	4.11×10^{12}	1.62×10^{9}	3.91×10^{8}

[a] Ref *17*. [b] Ref *41*. [c] Ref *43*. [d] Ref *44*. [e] Ref *42*. [f] Ref *45*. [g] Ref *34*.

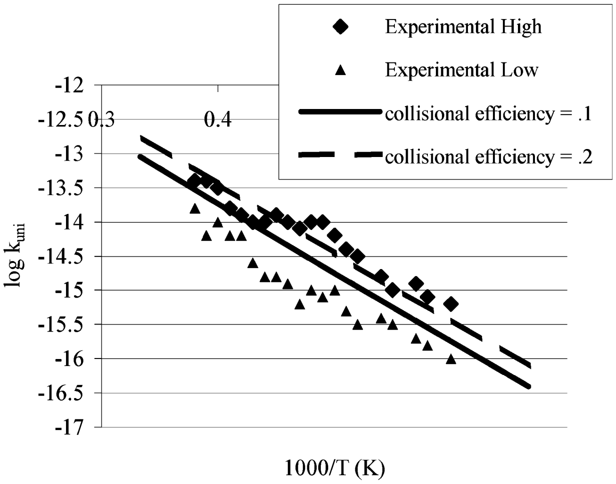

FIGURE 2. Theoretical universal rate constant using the 6-311++G-(3df, 3pd) basis set, compared to experimental rate constant (*33*), varying 1000/*T*. Note: β_c = 0.1−0.2, Cl_2 + M → 2Cl + M.

throughout this work because there was only one data point to use in verifying the previous research.

The basis set for chlorine was chosen due to the agreement of the calculated theoretical rate constant with the experimental rate constant for reaction 3, as shown by Figure 2 (*33*). Comparing the theoretical results to those of experiment, the decomposition reaction of chlorine has a collisional efficiency in the range of 0.1 to 0.2. Agreement between the theoretical and experimental rate constants showed that the 6-311G++(3df, 3pd) Pople basis set is an adequate choice for chlorine. Choice of the basis set for hydrogen was based upon the high accuracy of the theoretical heat of reaction compared to the experimental heat of reaction obtained from the NIST webbook (*34*). The theoretical heat of reaction for the decomposition of H_2 with the 1.37.1 basis set is 104.52 kcal/mol compared to the experimental value of 104.20 kcal/mol.

The experimental ΔH_{rxn} and the experimental geometries of the products and reactants for reaction 1 are compared to predictions from each combination of method and basis set in Table 2. For comparison, results from density functional theory using the LANL2DZ basis set are shown as this method was used in previous calculations for this reaction (*17*). Overall, density functional theory with the B3LYP method and the standard double-ζ LANL2DZ basis set provided the greatest errors with respect to the geometries and the frequencies of the products and reactants. Also, for the current reaction of focus, density functional theory exhibited the greatest error in terms of ΔH_{rxn} with a 22.07 kJ/mol deviation from experiment.

From Table 2, the QCISD method with either the 1992 or 1997 basis set provides reasonably accurate molecular geometries and frequencies. Due to the lack of experimental kinetic data, each method and basis set combination is considered in Figures 3 and 4. Although the 1997/QCISD combination provides the most accurate ΔH_{rxn} for reaction 1, this is not the trend for a larger series of mercury speciation reactions as can be seen from Table 3.

Heats of reaction predictions are compared to experimental results using a larger set of reactions involving mercury, chlorine, oxygen, and hydrogen atoms in Table 3 to further validate the choice of method and basis set. The SDD basis set with the QCISD calculational method was also considered in Table 3 because of its use in recent mercury speciation work (*18*). However, for the nine reactions in Table 3, the SDD basis set with the QCISD method provided the greatest errors with an average absolute error of 67.54 kJ/mol. Considering the importance of these reactions in the flue gases of coal combustion, this basis set and method

TABLE 3. Comparison of Theoretical and Experimental ΔH_{rxn} (kJ/mol) at 298 K

method:	B3LYP	QCISD	B3LYP	QCISD	B3LYP	QCISD	B3LYP	experiment
basis set for mercury:	LANL2DZ	1992	1992	1997	1997	SDD	SDD	NIST
basis set for all other atoms:	LANL2DZ	Pople[a]	Pople[a]	Pople[a]	Pople[a]	SDD	SDD	experiment
(1) $Hg + Cl + M \rightarrow HgCl + M$	−102.88	−105.73	−95.10	−138.28	−125.98	−1.86	−1.33	−104.23
(2) $HgCl + Cl_2 \rightarrow HgCl_2 + Cl$	−124.81	−125.81	−75.48	−139.53	−101.75	−227.73	−213.25	−103.44
(3) $HgCl + Cl + M \rightarrow HgCl_2 + M$	−256.68	−328.65	−303.63	−342.41	−329.90	−326.14	−356.88	−346.03
(4) $HgCl + HCl \rightarrow HgCl_2 + H$	107.82	90.54	122.05	76.82	95.77	−16.90	8.03	85.76
(5) $HgCl + HOCl \rightarrow HgCl_2 + OH$	−106.98	−129.83	−66.73	−143.55	−93.01	−215.01	−202.12	−111.27
(6) $Hg + 2HCl \rightarrow HgCl_2 + H_2$	−68.70	−24.77	16.94	−71.04	−40.21	−94.85	−66.52	−23.07
(7) $Hg + Cl_2 \rightarrow HgCl + Cl$	28.95	97.07	133.01	64.56	102.13	96.52	142.29	138.37
(8) $Hg + HOCl \rightarrow HgCl + OH$	46.82	93.05	124.10	60.50	93.18	109.24	153.42	130.53
(9) $Hg + HCl \rightarrow HgCl + H$	261.62	313.46	330.57	280.91	299.65	307.39	363.62	327.36
average absolute error	49.20	17.66	23.89	39.25	20.67	67.54	55.39	

[a] Pople: 6-311++G(3df,3pd).

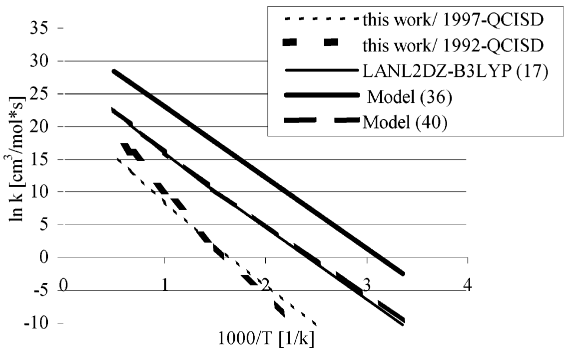

FIGURE 3. Comparison of rate constants calculated from both theory and a model available in the literature for the oxidation of mercury via hydrogen chloride. $HgCl + HCl \rightarrow HgCl_2 + H$.

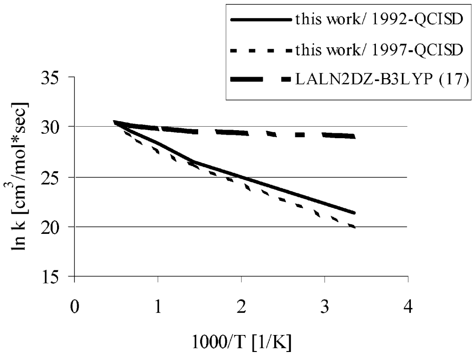

FIGURE 4. Comparison of rate constants calculated from theory for the reduction of mercuric chloride. $H + HgCl_2 \rightarrow HgCl + HCl$.

combination is not recommended for mercury speciation reactions. The incorporation of results with this computational combination into a kinetic model may lead to inaccurate predictions. Overall, the QCISD method with the 1992 basis set was the most accurate in terms of comparing the theoretical ΔH_{rxn} data to experiment, yielding an average absolute error of 17.66 kJ/mol for the nine reactions in Table 3. It is also important to note the accuracy of the 1997 basis set with the B3LYP density functional method. With an average absolute error of 20.67 kJ/mol, this combination of method and basis set should not be neglected. In fact, B3LYP requires significantly less computational time than QCISD so future work with this combination should be examined more closely to verify whether the accuracy seen here with enthalpies of reaction extends to kinetic estimations.

In an attempt to decrease the error of the theoretically calculated heats of reaction, the 1992 and 1997 basis sets were extended. In general, it is important for the basis sets of the atoms in a given reaction to be balanced in terms of polarization and diffuse functions (*35*). An imbalance can possibly result in superposition errors which may account for the errors in the theoretically calculated heats of reaction data from Table 3. Results of some basis set extensions were analyzed on only four of the nine reactions in Table 3 due to the computational expense of calculating the energies for $HgCl_2$. The extensions included the addition of a *d*-type diffuse function of 0.0837 and 0.01 to the 1992 and 1997 mercury basis sets, respectively, along with the addition of two *f*-type polarization functions with exponents of 0.4 and 0.9. These extensions were added to each of the basis sets in an attempt to gain a better balance. The results of this modification can be seen in Tables 4 and 5. This modification decreased the overall absolute error for the 1992/QCISD combination by 3.49 kJ/mol.

Also, the use of the correlation-consistent basis sets of Dunning instead of the Pople basis set used in the previous calculations decreased the error by an additional 0.29 kJ/mol. In fact, careful observation of the results in Tables 4 and 5 show that the use of Dunning or Pople basis sets for all other atoms aside from mercury provide similar results and either is a reasonable basis set choice for this system. Comparing the results of Tables 4 and 5 for the given set of reactions, it is clear that the extended 1992 basis set with the QCISD method provides the most accurate results in terms of $\Delta H_{rxn.}$ Further research should consider implementing this combination to reevaluate the results described in this work.

To possibly obtain further energetic accuracy compared to experiment, the quadratic configuration calculations were extended to include triple excitations. Using the 1992/QCISD(T) combination, the triple excitations increased the overall absolute error for $\Delta H_{rxn.}$ In the case of the 1997 basis set, however, the use of QCISD(T) decreased the error significantly. On the basis of results reported in Tables 4 and 5, the extended 1992 basis set for mercury with the QCISD method will be strongly considered for calculating transition structures for future rate constant calculations. When the 1997 basis set for mercury is used, QCISD(T) should be used in addition to the extensions to the basis sets.

It is important to emphasize that these thermodynamic results are based upon only four of the nine reactions studied in Table 3 because of the expense of computing the structure and frequencies of $HgCl_2$. To verify that the above-mentioned combination is indeed the most accurate, calculations will be carried out on all nine of the reactions in future work.

Using Figure 3, the rate expressions calculated for the oxidation of mercury chloride via hydrogen chloride are

$$k^{TST}\,[\mathrm{cm^3/mol{\cdot}s}] = 3.11 \times 10^{11}\,e^{-15713/T} \text{ using QCISD/1992} \quad (7)$$

TABLE 4. Comparison of Theoretical and Experimental ΔH_{rxn} (kJ/mol) with Extensions on the 1992 Basis Set

method: basis set for mercury: basis set for all other atoms:	QCISD 1992[a] Dunning[b]	QCISD 1992[a] Pople[c]	QCISD(T) 1992[a] Dunning[b]	QCISD(T) 1992[a] Pople[c]	QCISD 1992[a] Pople[c]	experiment NIST experiment
(1) Hg + Cl + M → HgCl + M	−92.09	−100.25	−127.78	−136.61	−105.73	−104.23
(2) Hg + HOCl → HgCl + OH	102.42	98.53	85.48	80.75	93.05	130.53
(3) Hg + HCl → HgCl + H	320.20	318.94	290.20	288.57	313.46	327.36
(4) Hg + Cl_2 → HgCl + Cl	106.69	102.55	87.74	83.01	97.07	138.37
average absolute error	19.77	20.06	39.10	44.08	23.55	

[a] 1992 refers to the modified 1992 basis set. [b] Dunning: cc-pVTZ. [c] Pople: 6-311++G(3df,3pd).

TABLE 5. Comparison of Theoretical and Experimental ΔH_{rxn} (kJ/mol) with Extensions on the 1997 Basis Set

method: basis set for mercury: basis set for all other atoms:	QCISD 1997[a] Dunning[b]	QCISD 1997[a] Pople[c]	QCISD(T) 1997[a] Dunning[b]	QCISD(T) 1997[a] Pople[c]	QCISD 1997[a] Pople[c]	experiment NIST experiment
(1) Hg + Cl + M → HgCl + M	−115.10	−119.87	−120.66	−125.98	−138.28	−104.23
(2) Hg + HOCl → HgCl + OH	79.41	78.95	92.63	91.38	60.50	130.53
(3) Hg + HCl → HgCl + H	297.18	299.36	297.35	299.19	280.91	327.36
(4) Hg + Cl_2 → HgCl + Cl	83.68	82.97	94.85	93.68	64.56	138.37
average absolute error	36.72	37.66	31.97	33.44	56.09	

[a] 1997 refers to the modified 1997 basis set. [b] Dunning: cc-pVTZ. [c] Pople: 6-311++G(3df,3pd).

$$k^{TST}\,[\mathrm{cm^3/mol{\cdot}s}] = 1.95 \times 10^{9}\ \mathrm{e}^{-12586/T} \text{ using QCISD/1997} \quad (8)$$

in the temperature range of 298−2000 K.

For the reverse of reaction 1, the calculated rate constant expressions are

$$k^{TST}\,[\mathrm{cm^3/mol{\cdot}s}] = 4.5 \times 10^{13}\ \mathrm{e}^{-3049.2} \text{ using QCISD/1992} \quad (9)$$

$$k^{TST}\,[\mathrm{cm^3/mol{\cdot}s}] = 3.8 \times 10^{13}\ \mathrm{e}^{-3420.3} \text{ using QCISD/1997} \quad (10)$$

These values are compared directly at 298 K in Table 2. Figure 3 shows a comparison of these theoretically determined rate constants compared to model-derived rate constants from previous work. Both models developed rate constants for reaction 1 of the form $k = A \times T^n \exp(-E/RT)$. The model developed by Widmer et al. (*36*) was developed from the chlorine chemistry of Senkin (*37*) and a general combustion chemistry mechanism adapted from the earlier work of Glarborg et al. (*38*). The preexponential factor was taken from corresponding reactions of lead presented by Cosic and Fontijn (*39*). The model developed by Niksa et al. (40) is in good agreement with the theoretical results of Sliger et al. (17) because Niksa et al. used a “frequency” factor in their model for reaction 1 in order to obtain this agreement. Niksa’s original value was based upon the hard sphere collision model, which was an order of magnitude lower than their new scaled value. However, in general, the hard sphere collision number derived from elementary gas-kinetic theory is calculated at the gas-kinetic limit and should be an overestimate of the rate constant (*19*). This highlights that fact that one of the difficulties of modeling is that one has to fit limited available data, which can lead to results that disagree with basic kinetic theory like in the case just described here.

Previous calculations for the reaction investigated in this work used the B3LYP method with the LANL2DZ basis set (*17*) to estimate the rate constant. However, the results from this work show that the reaction energetics using this basis set and density functional theory are highly inaccurate. The B3LYP method, even with larger basis sets, still does not lead to the same degree of accuracy that the QCISD results show with the 1992 basis set. In addition, the work here showed that use of the SDD basis sets even with high level methods leads to large errors.

Recalling the previous study of the unimolecular decomposition of mercury chloride (*27*), the QCISD method with either the 1992 or 1997 basis sets should be used for future study of mercury reactions involving chlorine species. The current research confirms these results. In general, for mercury oxidation reactions involving chlorine, either the 1992 or 1997 basis set combined with the QCISD method will provide reasonably accurate thermodynamic and kinetic results. However, a careful review of Table 3 reveals that the combination of the density functional method, B3LYP, with the 1997 basis set provides reasonably accurate heats of reaction. Because of the lower computational cost of B3LYP compared with that of the QCISD method, B3LYP is a direction of research that should be pursued for developing rate constants for mercury oxidation reactions involving chlorine. Also, Table 4 strongly suggests that the incorporation of the diffuse and polarization functions in the 1992 basis set in order to gain more balanced basis sets for each of the atoms within a given reaction will lead to improved energetics. In future work, these extensions will be studied for their validation with other mercury speciation reactions involving $HgCl_2$. Overall, the results from Tables 3 in combination with the present kinetic results suggest that the 1992 Stevens et al. basis set in conjunction with the QCISD calculational method can be used to accurately predict both thermodynamic and kinetic data for mercury oxidation reactions involving chlorine.

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