



Evaluation of basis sets and theoretical methods for estimating rate constants of mercury oxidation reactions involving chlorine

Jennifer Wilcox, David C.J. Marsden, Paul Blowers *

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

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Abstract

The occurrence of elemental mercury in flue gases from coal combustion is a problem of current environmental concern. Oxidized mercury species can be effectively removed from the flue gases by chemical scrubbers. However, the detailed mechanism by which oxidation occurs remains unclear. Theoretical rate constants are calculated for mercury oxidation by atomic chlorine. The potential energy surface is determined using standard quantum chemical methods with relativistic effects included via the use of an effective core potential (ECP). Experimental thermodynamic and kinetic data are employed to assess the accuracy of these calculations. Results show that the QCISD method with the 1992 basis set of Stevens et al. gives good agreement with experiment, suggesting that this combination may be useful for other mercury–chlorine chemical systems.

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1. Introduction

The EPA reported that U.S. coal-fired electric utility boilers emitted 51.7 tons of mercury in 1994–1995 [1]. Once released into the atmosphere, mercury has the potential to bioaccumulate up to a factor of 10,000 within the aquatic food chain [2,3]. It is the chemistry of mercury in the gas phase that determines its ultimate fate in the environment.

Mercury released from coal combustion can exist in a variety of oxidation states. From an environmental viewpoint, oxidized mercury (Hg(I) and Hg(II)) species are preferred in flue gases because they are water-soluble and can be captured in wet scrubbers before

* Corresponding author. Tel.: +1-520-626-5319; fax: +1-520-621-6048.

E-mail address: blowers@enr.arizona.edu (P. Blowers).

release in the smoke stack gases [4]. Unfortunately, much of the mercury is not oxidized, but rather is released into the atmosphere as elemental mercury [5]. It has been determined that mercury can be oxidized by various chlorine species, but the mechanisms by which these reactions occur are still in question [6].

In order 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. However, there is currently a lack of rate constant data available for reactions involving mercury and chlorine. In this paper, the focus will be on the oxidation of mercury via chlorine atoms:



This is a reaction for which experimental data is available. Thus, with this relatively simple system, a comparison of the accuracy of various theoretical methods can be made. Given the discovery of a sufficiently accurate method, it may be employed to make theoretical predictions on related mercury–chlorine systems for which experimental data are currently absent.

2. Computational method

2.1. Basis sets and theoretical methods

Ab initio methods of quantum chemistry have in recent years proven to be effective in predicting the structure and thermodynamic properties of chemical systems. All such methods seek to derive a solution of the Schrödinger wave equation (SWE) for the molecular system, formulated as a stationary configuration of nuclei with an accompanying set of interacting electrons.

The nuclei can be considered stationary as, being approximately three orders of magnitude heavier than the electrons, their motion occurs on a much slower timescale than that of the electrons, and thus the nuclear and electronic motions are effectively decoupled. Therefore, the SWE can be separated for the two. This is commonly known as the Born–Oppenheimer approximation, and has the consequence that one need only seek solutions for the electronic SWE (stated here in the usual atomic system of units):

$$\left(\sum_{i=1}^n \Delta_i + \sum_{i>j=1}^n \frac{1}{r_{ij}} \right) \psi_{\text{el}} = E_{\text{el}} \psi_{\text{el}} \quad (2)$$

Eq. (2) may only be solved analytically for the single-electron problem, and so for larger systems of interest an approximate method must be employed. First it should be observed that Eq. (2) has an infinite dimensional solution space, and thus for computational purposes this must be approximated by a finite dimensional subspace, spanned by a chosen set of basis functions which hopefully offer a reasonable representation of the electronic motion. In the usual ab initio molecular orbital (MO) approach, one considers the molecular orbitals to be linear combinations of the atomic orbitals:

$$\psi_i = \sum c_{\mu i} \phi_{\mu} \quad (3)$$

ψ_i is the i th molecular orbital, $c_{\mu i}$ are the coefficients of the linear combination, ϕ_μ is the μ th atomic orbital, and n is the number of atomic orbitals [7]. The atomic orbitals are themselves expressible as linear combinations of the atomic basis functions. In general, the larger the basis set the closer to the “exact” solution one gets. However, larger basis sets require more computational resources, and so there are practical limits to the accuracy one can obtain.

Calculation methods can be divided into two categories: ab initio methods, which base themselves on the aforementioned MO ansatz, and density functional methods. The simplest ab initio method in common usage yielding at least semi-qualitative results is the Hartree–Fock self-consistent field (HF-SCF) approach [8]. In this method, Eq. (2) is reduced to a one-electron problem for each electron, coupled so that each electron interacts with the averaged field of its peers. These are the so-called Fock equations, and are solved iteratively until self-consistency is obtained. HF-SCF has the advantage of being a variational method—the energy obtained is an upper bound of the exact energy, and being reasonably cheap in terms of computational requirements. However, the “averaged field” assumption in the scheme means that short-range correlations between electrons are ignored, and this can be particularly important when heavy elements are part of the system under study.

Thus for the present system of interest, a post-SCF correlated method is greatly desirable. Møller–Plesset (MP) perturbation theory is the next step in sophistication, taking the HF wavefunction and energy as the zeroth order components and applying the standard ansatz of Rayleigh–Schrodinger (RS) perturbation theory [9]. Most commonly one takes the perturbation expansion to second order (MP2) or fourth order (MP4) depending on the computational resources available [10,11]. MP methods generally do a good job of including the correlation energy (the difference between the “exact” HF energy and the energy from the exact solution); however, it has been shown that the MP series expansion yields poor results for many heavy element systems [12].

Thus for systems such as the mercury reaction of present interest, an “infinite order” method such as the coupled cluster (CC) or quadratic configuration interaction (QCI) is preferred [13–16]. These methods use summation techniques to add certain terms in the MP expansion to infinite order, thus alleviating the problem of convergence. These approaches are also size-consistent—meaning that the method scales correctly with the number of particles in the system. This can be a problem when MP or truncated configuration–interaction methods are applied to systems with a large number of electrons (such as in the present case).

A final matter of concern with these calculations is consideration of special relativistic effects, which can have a marked effect on systems including heavy elements. These are most evident in the inner core electrons of heavy atoms where electron velocities can be a considerable fraction of the speed of light. We shall take account of such effects by employing an effective core potential (ECP) (often called a pseudopotential) which is an effective potential describing the inner core and at the same time semi-empirically accounting for relativistic effects [17,18].

The following relativistic effective core potentials are the most recent developed in the literature for mercury and are the ones compared in this research: Stuttgart 1997 [19], Stevens et al. [20], and Hay and Wadt [21]. 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 to calculate the energies and structures of the transition state, products and reactants using two different calculational methods: MP4 with single, double and quadruple excitations only (MP4SDQ) and QCI with single and double excitations (QCISD) [22].

In the study of the current reaction, MP4SDQ was used as one of the original method choices because MP4 energies are generally more accurate. As previously noted, MP convergence may be a concern for this system, so QCISD is another reasonable method of choice in the current work.

Density functional theory using the B3LYP method with the LANL2DZ basis set was also evaluated because it has been used to determine the activation energy and rate constants of bimolecular mercury oxidation reactions involving chlorine [6].

2.2. RRKM theory

Transition state theory is traditionally used to calculate rate constants for bimolecular reactions. However, the reaction of current focus is unimolecular, making Rice–Rampsberger–Kassel–Marcus (RRKM) theory a necessary tool. The overall unimolecular reaction is written in terms of two energies: E^+ and E^* . E^* is the energy of the reactant once it acquires the energy needed to react. The energy E^+ is the activation energy, E_0 , subtracted from the energy of the energized reactant (i.e. $E^+ = E^* - E_0$) [23]. The density of states, $\rho(E^*)$, and the sum of states, $W(E^+)$, were calculated using the Beyer–Swinehart algorithm [24]. The universal rate constant for a unimolecular reaction can then be calculated from:

$$k_{\text{uni}} = \frac{LQ_1^+ \exp(-E_0/kT)}{hQ_1Q_2} \int_{E^+=0}^{\infty} \frac{W(E^+) \exp(-E^+/kT) dE^+}{1 + k_a(E^*)/\beta_c Z_{LJ}[M]} \quad (4)$$

$$k_a(E^*) = \frac{LQ_1^+}{hQ_1\rho(E^*)} W(E^+)$$

E^*	total vibrational and rotational energy
E^+	total energy of a given transition state
E_0	activation energy
Q_1^+	partition function for the rotation of A +
Q_1	partition function for the rotation of A
Z_{LJ}	Lennard–Jones collision frequency
Q_2	partition function for nonrotational modes
L	statistical factor
k	Boltzmann's constant
β_c	collisional efficiency
$W(E^+)$	sum of states
$\rho(E^*)$	density of states
h	Plank's constant
$[M]$	concentration of bath gas

All of the parameters listed above can be obtained from theory with the exception of the collisional deactivation efficiency, β_c . This collisional efficiency is an empirical value that can be obtained through experimental knowledge of the reaction [25]. Many models have been determined for calculating the collision efficiency, but again experimental data is necessary [26,27]. Due to the lack of experimental data for the reaction studied in this paper, β_c is used as a fitting parameter that ranges between zero and one. It is important to note that the value of β_c does not change the rate constant by more than a factor of 6 (cf. Fig. 1).

2.3. Canonical variational transition state theory

Due to the shallow potential energy surface for reaction (1), the rate constants for each combination of method and basis set were calculated using canonical variational transition state theory (CVTST) given by:

$$k^{\text{CVT/G}}(T) = \kappa^{\text{G}}(T)k^{\text{CVT}}(T) \quad (5)$$

where T is the temperature, $\kappa^{\text{G}}(T)$ is a ground-state (G) transmission coefficient which primarily accounts for tunneling, and $k^{\text{CVT}}(T)$ is the hybrid canonical variational transition state theory (CVT) rate constant for which the intrinsic reaction coordinate is treated classically and the bound vibrations are quantized [28]. The hybrid CVT rate can be obtained by variationally minimizing the universal RRKM-theory rate constant, $k_{\text{uni}}(T)$ with respect to the position x of the generalized transition state along the reaction coordinate,

$$k^{\text{CVT}}(T) = \min_x k_{\text{uni}}(T, x) \quad (6)$$

where $k_{\text{uni}}(T, x)$ is expressed in Eq. (4).

3. Results and discussion

In the remainder of this work, zero point energies and thermal corrections were included in all calculated results and the frequency calculations were left unscaled due to the unavailability of proper scaling factors. The basis set for chlorine was chosen due to the agreement of the calculated theoretical rate constant with the experimental rate constant for the following reaction:



as shown by Fig. 2 [29]. Comparing the theoretical results to experiment, the decomposition reaction of chlorine has a collisional efficiency in the range of 0.1–0.2. Agreement between the theoretical and experimental rate constants showed that the 6-311++G(3df, 3pd) basis set was adequate for chlorine.

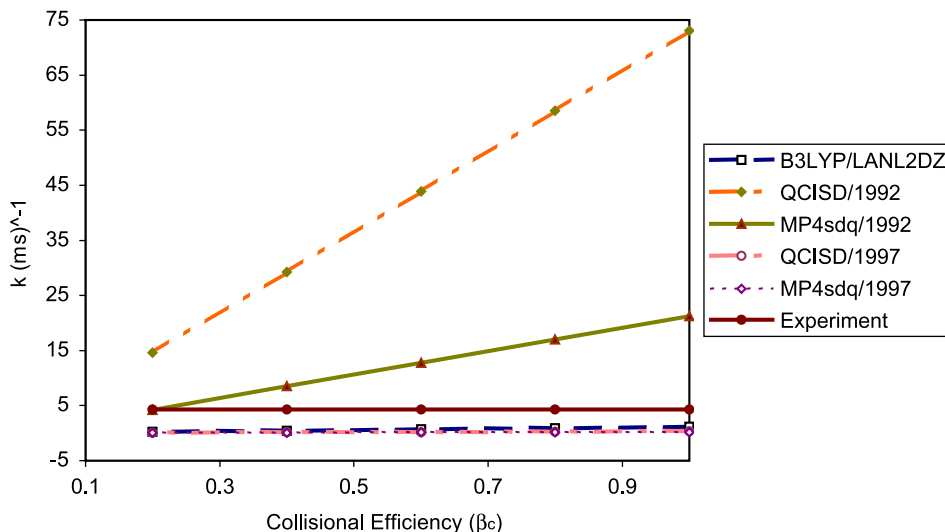


Fig. 1. Canonical variational transition state theory rate constant (k^{CVT}) at 393 K for each combination, compared to experimental rate constant, varying the collision efficiency, β_c . $\text{HgCl} + \text{M} \rightarrow \text{Hg} + \text{Cl} + \text{M}$.

The experimental rate constant reported for the reverse of reaction (1) is $1.95 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [30]. RRKM theory allows for the calculation of unimolecular decompositions in the forward direction only. Thus, the equilibrium constant was found to be $K_{\text{eq}} = 2.21 \times 10^{-10}$ with the Shomate equation and data from the NIST webbook [33] before the following relationship was used to calculate the equilibrium rate constant,

$$K_{\text{eq}} = \frac{k_1}{k_{-1}} \quad (8)$$

The experimental rate constant for the forward reaction is $4.309 \text{ M}^{-1} \text{ s}^{-1}$. Each of the mercury basis sets (1985, 1992, 1997) were combined with two chosen methods (MP4SDQ and QCISD) forming six different combinations. Density functional theory using B3LYP with the LANL2DZ basis set was also studied giving a total of seven theoretical combinations evaluated in this work. Experimental thermodynamic and kinetic data are compared to theory for each combination of method and basis set in Table 1.

The 1985 basis set was eliminated from consideration after comparing the calculated geometries with experiment with a minimum error of 25%. A reason for the inaccuracy of the 1985 basis set is due to the small number of basis functions outside the effective core. In general, the smaller the number of electrons represented as functions on their own, the less accurate the results will be. Unfortunately in the case of the 1985 basis set, a majority of the electrons are held ‘fixed’ in an effective core.

Similarly, density functional theory using the B3LYP/LANL2DZ combination yielded an inaccurate geometry value with an error of 11.6%. However, it is important to note that

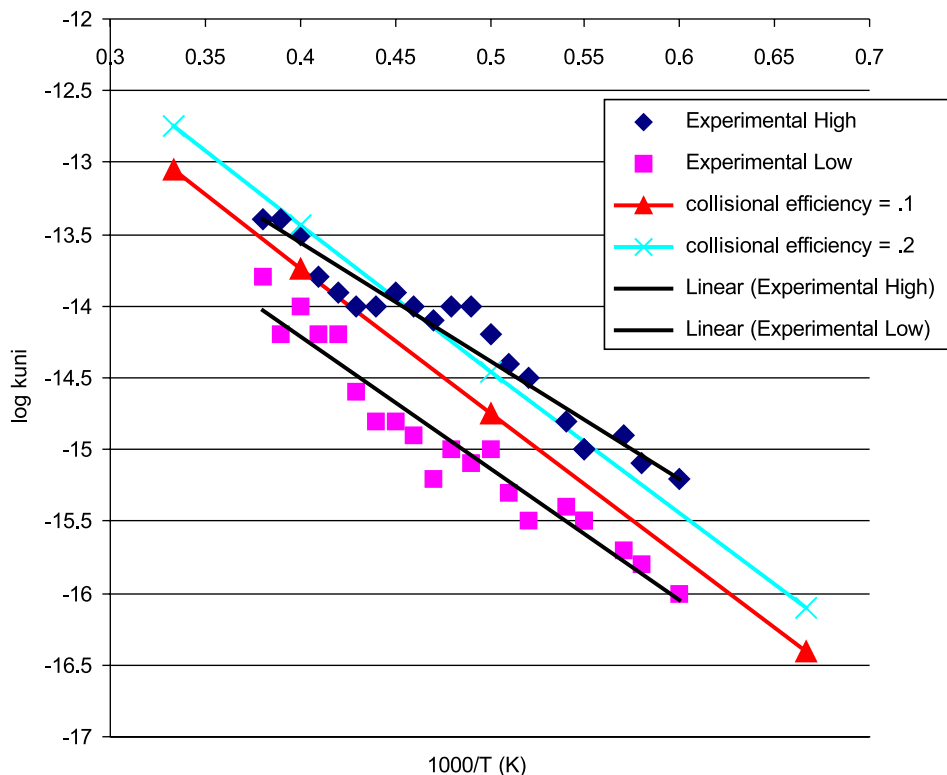


Fig. 2. Theoretical universal rate constant using 6-311++G(3df, 3pd), compared to experimental rate constant, varying $1000/T$. $\text{Cl}_2 + \text{M} \rightarrow 2\text{Cl} + \text{M}$.

the theoretical rate constant is within two orders of magnitude of the experimental value. Due to the large error of the estimated geometry by density functional theory, the accuracy of the rate constant calculation should be questioned and this method and basis set will not be considered further in this work. At this point, there are four combinations left for comparison.

Experimental frequency values for mercuric chloride could not be found, but the four theoretical combinations remaining give frequencies that range between 290 and 300 wave numbers. Comparing each combination of method and basis set to the experimental geometries, the errors are relatively equal, with 1997/MP4SDTQ having the lowest error of 2.7% and 1992/QCISD having the greatest error of 3.0%. A comparison of the heats of reaction shows that the 1992 basis set has a maximum error of 3.9% compared to the 1997 basis set which has a minimum error of 32.3%. This implies the energies using the 1997 basis set will not be accurate, leading to incorrect activation energies.

Comparing the theoretical rate constants to experiment, the most accurate combinations are 1992/QCISD and 1992/MP4SDQ. With $\beta_c = 0.2$ for the decomposition reaction of mercuric chloride, both rate constant estimates are within an order of magnitude of the

Table 1
Comparison of thermodynamic and kinetic data of the reaction, $\text{HgCl} + \text{M} \rightarrow \text{Hg} + \text{Cl} + \text{M}$

	Experimental	LANL2DZ B3LYP	1985 MP4SQ	1985 QCISD	1992 MP4SQ	1992 QCISD	1997 MP4SDQ	1997 QCISD
Geometry (Å)	2.28 ^a 2.34 ^b	2.612	1.689	1.689	2.406	2.412	2.404	2.407
ΔH_{rxn} (kJ/mol)	104.23 ^c	104.38	–	–	108.08	108.32	137.99	138.16
Frequency (1/cm)	–	228	1583	1582	292	290	300	292
Activation energy (kJ/mol) at 393 K	–	82.15	–	–	71.60	67.52	87.01	84.34
Rate constant ($\text{M}^{-1} \text{s}^{-1}$) at 393 K	$k_1 = 4.309$, $k_{-1} = 1.95 \times 10^{10\text{d}}$	$k_1 = 2.29 \times 10^{-1}$	–	–	$k_1 = 4.25$	$k_1 = 14.6$	2.98×10^{-2}	6.11×10^{-2}

^a Ref. [31].

^b Ref. [32].

^c Ref. [33].

^d Ref. [30].

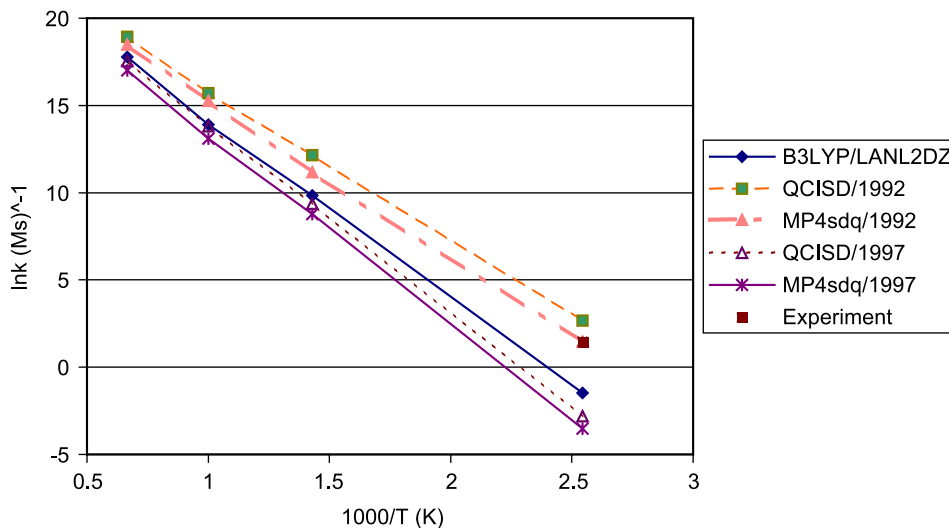


Fig. 3. Canonical variational transition state theory rate constant (k^{CVT}) for each combination, compared to experimental rate constant, varying temperature, $1/T$. Note: $\beta_e = 0.2$, $\text{HgCl} + \text{M} \rightarrow \text{Hg} + \text{Cl} + \text{M}$.

experimental rate constant value. These results lead to the conclusion that the 1992 basis set is the most accurate when compared to all available experimental data (Fig. 3).

This research strongly suggests that the 1992 basis set is a good basis set for representing mercury when calculating reaction phenomena. However, due to the lack of experimental data for reaction (1), it may be important to consider both the 1992 and 1997 basis sets for future oxidation reactions involving mercury and chlorine. Due to the convergence problems associated with large basis sets and Møller–Plesset perturbation theory, QCISD should be the method of choice for any mercury oxidation reactions involving chlorine.

From the calculations in this work, (Fig. 3) it was found that a good estimation of the rate constant for reaction (1) is:

$$k^{\text{CVT/G}} [\text{M}^{-1} \text{s}^{-1}] = 4.25 \times 10^{10} e^{-8588/T} \quad (9)$$

in the temperature range of 393–1500 K.

4. Conclusions

Theoretical rate constants were compared for a reaction involving mercury oxidation by chlorine atoms. Rate constants were calculated for seven different combinations of calculational methods and basis sets that include relativistic effective core potentials. Overall, the 1992/QCISD combination proved to be the most accurate when compared to experimental thermodynamic and kinetic data.

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