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Critical Review of Mercury Chemistry in Flue Gas

Energy Systems Division

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1 INTRODUCTION

Mercury (Hg) and its compounds have long been recognized as potentially hazardous to human health and the environment. Many man-made sources of mercury have been reduced in recent years through process changes and control measures. However, emissions of mercury from coal-fired power plants, while exceedingly dilute by the usual pollution standards, still constitute a major source when considered in the aggregate. Concerns over those emissions and the prospect of impending emissions regulations have led to a wide range of research projects dealing with the measurement and control of mercury in flue gas. This work has made considerable progress in improving the understanding of mercury emissions and their behavior, but inconsistencies and unexpected results have also shown that a better understanding of mercury chemistry is needed.

To develop a more complete understanding of where additional research on mercury chemistry is needed, the U.S. Department of Energy (DOE) asked Argonne National Laboratory (Argonne) to conduct a critical review of the available information as reported in the technical literature. The objectives were to summarize the current state of the art of chemistry knowledge, identify significant knowledge gaps, and recommend future research to resolve those gaps. An initial evaluation of potential review topics indicated that the scope of the review would need to be limited and focused on the most important topics relative to mercury control. To aid in this process, Argonne developed a brief survey that was circulated to researchers in the field who could help identify and prioritize the many aspects of the problem. The results of the survey were then used to design and guide a highly focused literature search that identified key papers for analysis. Each paper was reviewed, summarized, and evaluated for the relevance and quality of the information presented. The results of that work provided the basis for conclusions regarding the state of knowledge of mercury chemistry and recommendations for further research.

This report begins by summarizing the survey process and describing how the results were used to shape the critical review. Analyses of information obtained from the various publications are presented chronologically, beginning with the earliest relevant publication found and concluding with the end of the review in early 2003. Finally, the conclusions and recommendations for future research are presented. The survey instrument is included in Appendix A, while detailed information on each of the publications reviewed is given in Appendix B.

2 SURVEY OF EXPERTS

2.1 OVERVIEW OF SURVEY

The survey instrument was kept relatively brief to encourage the maximum number of responses. We developed an initial structure for the survey on the basis of our previous research experience in mercury control technology.[1,2,3] Opinions were solicited in four key areas:

1. Which reaction types (e.g., gas-phase, gas-solid, gas-liquid, liquid-phase) are most important for Hg control technology development?
2. Which mercury reactant species are most important?
3. Which non-mercury reactant species are most important?
4. What aspect of reaction chemistry is most important (e.g., mechanisms, kinetics)?

The survey was distributed to about 45 individuals known to be active in various aspects of mercury research within government agencies, industry, universities, and research organizations. Responses were obtained from 16 members of the survey group and were supplemented by direct discussions with a number of the experts. The results were as diverse as the target group, but several clear priorities did emerge.

2.2 SURVEY RESPONSES

The 16 survey respondents included eight from industry, three from research organizations, three from universities, and two from other organizations. Of the 16 replies, 13 respondents answered all four questions, while one person responded to only one of the questions. The majority of respondents included some comments with their replies to provide justification or elaboration. One person provided information via telephone without giving specific responses to the survey.

In the responses,

- 85% listed gas-solid reactions as most important, while 62% listed gas-phase reactions (some respondents selected more than one type of reaction);

- 100% saw elemental mercury (Hg^0) as the most important mercury reactant species;

- Hydrochloric acid (HCl) and chlorine (Cl_2) were cited as the most important non-mercury reactants; and

- 100% listed mechanisms as the most important aspect of reaction chemistry.

In the following sections, we will review the responses and comments in more detail.

2.2.1 Reaction Type

The first survey question addressed the reaction type (gas-phase, gas-liquid, gas-solid, etc.) that would be the most important to understand. The responses were:

- Gas-solid reactions — 11 out of 13 responses (85%),
- Gas-phase reactions (homogeneous and/or heterogeneous) — 8 out of 13 (62%),
- Liquid-phase reactions — 3 out of 13 (23%),
- Gas-liquid reactions — 2 out of 13 (15%), and
- All reaction types are important — 1 out of 13 (8%).

It is noteworthy that while five individuals gave gas-solid reactions as their only response, only two gave gas-phase reactions as their sole response. This result is a secondary indicator of the importance attached to gas-solid reactions by the respondents.

In the comments received for this question, four persons cited the importance of gas-solid reactions with regard to the interaction of Hg with fly ash. Most of these individuals were concerned with the adsorption of Hg on the surface of fly-ash particles in the flue-gas stream. One person commented on the importance of chlorine chemistry because of the probable mechanism of Hg oxidation by either chlorine atoms (Cl) or Cl_2. Indirectly, the importance of HCl was inferred because of its role in the formation of both Cl and Cl_2 in the gas phase. Another person suggested that gas-phase reactions were most important "in terms of what is coming to the control device." However, gas-liquid, gas-solid, and liquid-phase reactions were most important "in the reactions of control." This statement implies that he considered those to be the reactions actually occurring in the control devices and that they need to be understood in order to improve and maximize the efficiency of the control technologies. An individual who felt that all reaction types were important asked the question, "Can we rule any of these processes out given the present dearth of knowledge and the apparent complexity of flue-gas components/Hg species/sorption processes?"

2.2.2 Mercury Reactant Species

The second survey question asked which mercury species were most important in terms of understanding the reaction chemistry. In this case, there was strong agreement on Hg^0 as shown by:

- 13 of 13 responses (100%) indicated gaseous Hg^0,
- 5 of 13 (38%) included mercuric chloride ($HgCl_2$), and

- 4 of 13 (31%) mentioned mercurous chloride ($HgCl$, Hg_2Cl_2).

The majority of the respondents (7 of 13) gave Hg^0 as their only response. Of the four individuals who mentioned mercurous chloride, only one specifically identified HgCl as the species of interest, while the others did not distinguish between HgCl and Hg_2Cl_2. One respondent mentioned mercuric oxide (HgO), while another included all mercurous and mercuric halides.

Very few comments were received in response to this question. Two people ventured to say that Hg^0 is the most important because "on an industry average basis, more Hg is in the elemental state." One respondent qualified their answer by saying that Hg^0 and HgCl were most important "with respect to control technologies" and noted that "the possible role of Hg_2Cl_2 has intrigued me." Another person stated that even though gaseous Hg^0 "is usually the Hg species of highest concentration in the gas phase and most difficult to capture, there is little evidence that Hg is present in that form on sorbents." The respondent continued by asking "So how and where does it oxidize?. . .As it is captured by the sorbent?…Or prior to capture in the gas-phase?"

2.2.3 Non-Mercury Reactant Species

Question three asked which gaseous reactants other than mercury were most important. This topic produced the widest range of responses:

- 8 of 13 (62%) gave HCl,
- 7 of 13 (54%) mentioned Cl_2,
- 5 of 13 (38%) said nitrogen dioxide (NO_2),
- 4 of 13 (31%) gave sulfur dioxide (SO_2), and
- 3 of 13 (23%) mentioned nitric oxide (NO).

None of the potential reactants provided in the survey went unmentioned — two persons said that all reactants were important (one of these ranked the reactants in order of their importance). Seven respondents mentioned other reactants that included molecular fluorine (F_2), hydrofluoric acid (HF), ammonia (NH_3), Cl, sulfur trioxide (SO_3), hydrocarbon radicals, and hydroxyl radicals (OH). It is interesting to note that SO_3 was the only one of these to be mentioned more than once — three respondents listed it.

Several respondents also mentioned fly ash as an important factor in reactions. For example, one individual said, "I think the fly ash reactions – both catalyzing Hg + Cl as well as possible adsorption – are the key 'practical' reactions in regards to form of Hg for power plants." Another person gave "various metals and their oxides as catalysts" as important reactants. This probably refers to the components of fly ash. Finally, two respondents said (identically) that "It is becoming more obvious that understanding the interplay between fly ash and the other gaseous components in flue gas and their impact on Hg speciation is critical to our understanding of what it will take to construct cost-effective control strategies for Hg in coal-fired boiler flue gases."

One respondent felt that all of the possible reactants are important and stated that "Although a. (Cl_2) and b. (HCl) are the most important in terms of direct reaction with Hg species, all of the indicated compounds, as well as hydrocarbon species and radicals such as OH, play a role in the oxidation chemistry of mercury. Their interrelationship is poorly understood."

2.2.4 Reaction Dynamics

Question four asked about the importance of thermodynamics, kinetics, and reaction mechanisms. The responses clearly supported an emphasis on understanding the basic mechanisms:

- 14 of 14 (100%) said reaction mechanisms,
- 7 of 14 (50%) listed reaction kinetics, and
- 3 of 14 (21%) mentioned thermodynamics.

Six respondents gave reaction mechanisms as their only answer. Three persons mentioned equilibrium thermodynamics, but two of those ranked it last in importance. One person specifically mentioned "interface reaction mechanisms of gas-solid" as important, while another mentioned the "interaction of Hg compounds with fly ash" as important.

One respondent included the following comments for this question: "Both the capacity and reactivity of a solid sorbent are key, as well as the mechanism. Stability of the adsorbed waste is also important." Another respondent said, "Although we do not have an accurate measure of the rates of several key steps in the reaction pathway, I believe there are several key steps that are missing in the mechanisms themselves that we are using."

2.2.5 Additional Comments

The survey elicited a few comments that were not associated with the answer to any particular question. For example, one respondent wrote the following at the end of the survey: "There are three important aspects of Hg chemistry in combustion flue gas. They include: 1. Reactions of Hg compounds in the combustion zone 2. Reactions of Hg compounds in the post-combustion zone 3. Absorption of Hg compounds on fly ash. For units equipped with scrubbers, interaction of Hg with scrubber liquor could be of interest."

Another respondent, who in effect only answered question 4, stated "In my opinion the answer to all of the questions above is 4c" (reaction mechanisms). He went on to state, in part, that "The study of mercury chemistry must be done holistically. Let's say that everyone who took this survey agreed that the reaction between Hg and HCl was the 'most important'. Does that mean that the mercury community would focus only on that reaction? …I think that a far more useful endeavor would be to solicit different researchers' opinions or perhaps 'hypotheses' regarding the mechanisms governing the behavior of mercury in combustion and boiler backend equipment. That might then be used to design appropriate experiments."

A few respondents expressed general support for the idea of a review of mercury chemistry. For example, one person stated that "I'm glad to see people looking at the fundamental chemistry."

Finally, there was one individual who did not respond directly to the survey but who provided information in a telephone interview. This information was primarily related to efforts to model Hg oxidation chemistry in coal-fired utility boilers. In a recent conference paper, the individual outlined a specific reaction model containing eight reaction equations involving Hg^0, HgCl, HCl, Cl, Cl_2, and hypochlorous acid (HOCl). One point that this individual stressed was that it would be important to include gas-solid interactions in any overall model. While this was not a formal response to the survey, it has been factored into the analysis of the results.

2.3 DISCUSSION OF SURVEY RESULTS

2.3.1 Physical State of Reactants

A majority of the respondents indicated that gas-solid reactions were of the greatest importance, but a significant number also mentioned gas-phase reactions. In our opinion, both reaction types are important and both should be investigated in any thorough review of Hg chemistry that is relevant to the emission and control of Hg from coal-fired boilers.

As noted in one comment, one should consider where in the system the reactions involving Hg species might be occurring. For instance, in regions of high temperature (the combustion zone), the predominant reactions involving Hg species are likely to include only gas-phase species. As the gas cools, reactions/interactions with particulate matter (fly ash) can begin to play a role. Of course, gas-phase reactions with other flue-gas species can continue to be important in this regime as well. Finally, the type of control technology one is considering will determine if and when gas-solid, gas-liquid, liquid-phase, and/or other reactions may be of importance. For solid-sorbent-based control technologies, gas-solid reactions will be of primary importance. For liquid-based control technologies (scrubbers), it is obvious that gas-liquid and liquid-phase reactions will be of importance. However, if the scrubber contains solids, then it is likely that solid-liquid interactions will also be important. Similarly, solid-liquid reactions may need to be understood if one is to deal with possible reactions of the by-products with groundwater.

Therefore, to narrow the focus of the chemistry review with respect to the physical state of the reactants, it will be important to focus attention on the likely temperature regime, which is related to the location in the system where the important reactions with Hg species are happening. In other words, one could focus on reactions occurring in or near the boiler (highest temperature zones), downstream of the boiler but upstream of the control device (intermediate temperature regime), or in the control device/exhaust stack (lowest temperature zones). Furthermore, if reactions in the control device are deemed important, specifying the type of control device of interest is important because solid sorbents and aqueous scrubbers have important differences in the physical states of the reactants.

2.3.2 Mercury Reactant Species

In the second survey question, we sought input on which Hg-containing reactants are the most significant. The unanimous suggestion was gaseous elemental Hg. It is certainly true that Hg^0 is the primary building block from which other species are derived and that relatively recent market shifts from high-sulfur eastern and midwestern coals to low-sulfur, low-chlorine western coals have tended to promote emissions of Hg^0. However, it is also important to recognize that actual flue-gas streams have been shown to span the gamut of very little to almost all Hg^0, depending mainly on the type of coal and combustion conditions. Furthermore, a significant number of respondents suggested that $HgCl_2$ should also be considered. Although (to the best of our knowledge) a specific oxidized Hg species has not been positively identified, most workers in this field have presumed that $HgCl_2$ is the most abundant oxidized species existing in the flue-gas stream. Recently, some workers have suggested that HgCl might be an important intermediate species in the gas phase. Note that while Hg_2Cl_2 has also been suggested as a possible species, the likelihood that it will be present in any significant concentration in the gas phase is problematic. This reactant, if considered, would most likely be of importance mainly in the liquid phase.

Thus, we believe that while Hg^0 is clearly the most important Hg-containing reactant species, information on other gas-phase species should not be ignored. For example, once $HgCl_2$ has formed, will it react further with other gas-phase species to be reduced back to Hg^0 or to other compounds? Also, what about the fate of whatever Hg species is formed on the surface of a sorbent and what about the reactions of Hg species in the aqueous or solid phases of a wet-scrubber solution? These questions are just a few examples of where the chemistry of species other than gaseous Hg^0 might be important. However, until the roles and importance of other species become more evident from either modeling or experimental studies, a focused effort on Hg chemistry should be directed initially to reactions of gaseous Hg^0.

2.3.3 Non-Mercury Reactant Species

The topic of non-Hg-containing reactants generated the greatest variety of responses. Nevertheless, a consensus was evident in that either Cl_2 or HCl was mentioned by 11 of the 13 respondents (85%). This finding indicated the importance that most of the workers attached to at least one of the chlorine species suspected to be present in a flue-gas stream.

The next most popular choice of an important reactant was NO_2. At the other end of the spectrum, carbon monoxide/carbon dioxide (CO/CO_2) were consistently seen as the least important of all the choices given. To further complicate the issue, many other reactants were mentioned under the choice of "others." These included SO_3 most frequently (three times), F_2, HF, NH_3, fly ash, Cl, hydroperoxy radical, OH, hydrocarbon radical, and "various metals and their oxides as catalysts." Except for SO_3, all other species were mentioned only once by six different respondents.

The obvious variety of responses makes it challenging to determine a focal point for non-Hg reactants. Clearly, Cl_2 and HCl need to be the primary focus in an initial study. However, one should not overlook the importance of other reactants that workers in this field have mentioned. In particular, we feel that it is important to look at reactants that could serve as oxidizing agents for Hg^0. These would include atomic species, such as Cl, all radical species, and potential oxidizing agents, such as NO_2, SO_3, and even oxygen (O_2).

2.3.4 Reaction Dynamics

The question of what type of reaction dynamic was the most important to study yielded the second unanimous response in the survey. All respondents named "reaction mechanisms" as the most important aspect of reaction chemistry to investigate either by itself or with reaction kinetics as co-equal in importance. Only three respondents mentioned thermodynamics at all, two listed it last in importance, and the other listed it as co-equal with the other two choices.

While equilibrium thermodynamics certainly plays an important part in the overall understanding of a chemical reaction, apparently almost all workers in this field either consider this information to be well known or believe that its importance is minimal in the dynamic conditions found in a flue-gas stream. Once the important chemical reactions are identified, the real lack of data appears to be in the areas of kinetics and detailed reaction mechanisms. Note that detailed reaction mechanisms include not only product identification, but also pre-equilibria, intermediates of all types (primary, secondary, etc.), and potential competing or side reactions. A detailed mechanistic understanding would also include the answers to such questions as where does the oxidation of Hg take place when a solid sorbent is involved? Does oxidation occur near the surface but prior to adsorption or does it occur on the surface after adsorption?

2.4 CONCLUSIONS

The results of the survey were very helpful in identifying and prioritizing the issues to be considered in a critical review of Hg chemistry. Guidelines for conducting the critical review were developed by combining this information with our existing knowledge of the available literature gained through an earlier review of Hg emissions[1] and recent research on Hg oxidation[3].

- Search the literature initially for information on gas-phase reactions with a secondary emphasis on gas-solid reactions. Information on the latter was expected to be relatively sparse compared to gas-phase reactions.

- Focus on gaseous Hg^0 as the most important mercury-containing reaction species. However, also consider $HgCl_2$ and HgCl.

- Emphasize Hg^0 reactions with Cl_2 and HCl.

- Identify and review available information on detailed Hg reaction mechanisms as the single most important issue. However, reaction kinetics are also important and available information should be collected and reviewed as well.

3 LITERATURE REVIEW

3.1 APPROACH

Information for this review was obtained in several ways. We performed a literature search of ISI's Web of Science database[4] using the terms "mercury and chlorine" and "mercury and hydrochloric acid." This produced a thorough search of the journal literature back to 1986. In addition, a search of *Chemical Abstracts* (CA) was performed both manually and by computer. Keywords used in the computer search included "reaction, mercury, chlorine, and gas-phase." The CA were searched as far back as 1907. In addition to these traditional search methods, we used other less well-defined and/or ad-hoc methods to obtain some of the information used in this review. These methods included manually searching the proceedings of recent scientific conferences that presented topics on mercury research, using the list of references contained in several relevant papers, and reviewing papers referred by other workers in the field. Because of the schedule of the project, the most recent literature reviewed was published early in 2003.

As each paper was read, a summary review report was prepared. These summaries are included in Appendix B of this report. Each summary contains a bibliographic citation, including title, author(s), and source information. A summary of the relevant work is presented, followed by a recitation of important data contained in the paper. For reports of experimental research, a brief assessment of the approach taken in the work is given to help identify any issues that could affect the relevance of the results for this review. Forty-two of these summaries are included in Appendix B, as well as two additional references that were not reviewed in detail. Because the initial purpose of the summaries was to note comments and/or thoughts on the papers as they were being read, they should not be taken as complete descriptions of the publications. In addition, they may occasionally contain observations and opinions based on our previous research experiences. Nevertheless, they are included in this report as a record of the materials that were reviewed and to serve as an indication of the type of information that we regarded as significant.

The evolution of knowledge relevant to the behavior of mercury in flue-gas streams has not followed a consistent path, but rather has reflected changing priorities within the technical community. These priorities include such diverse topics as waste incineration, lasers, atmospheric chemistry, and coal-fired power generation. In the following sections of this report, we will review the relevant literature in approximately chronological order, beginning with a paper on the reaction of gaseous mercury with molecular chlorine from 1949. Particular attention is given to the years beginning in 1998, when detailed mercury oxidation mechanisms began to appear in the literature.

3.2 Hg – Cl_2, HCl CHEMISTRY: 1907–1967

Only one paper was found in this time period that was judged to be directly relevant to our search.[5] Although the title of this paper is *Kinetics of the Reaction between Mercury Vapor* *and Ozone*, some information was presented on the reaction of Hg with Cl_2. In particular, data were presented on the distribution of the products formed from this reaction as a function of the ratio of chlorine to mercury atoms (Cl:Hg). The primary reaction product was reported to be Hg_2Cl_2, with only gradually larger fractions of $HgCl_2$ found when the initial Cl:Hg ratio was increased. With regard to the kinetics of this reaction, the article from CA states that "The reaction is too fast for kinetic measurements." This is the first of an interesting series of reports appearing up to 2002 that seem to document a dichotomy in the results for this reaction, which will be a continuing thread of the story in the sections that follow. Also, the appearance of both Hg_2Cl_2 and $HgCl_2$ as products is of interest regarding the oxidation mechanism. However, no specific reaction mechanisms were given in this paper.

3.3 Hg – HCl CHEMISTRY: 1968–1988

Between 1968 and 1986, several papers were published that dealt with the reaction of Cl_2 with excited-state Hg atoms[6,7,8,9] and the reaction of Cl with Hg.[10] The appearance of these papers was related to interest at that time in the development of lasers using gaseous Hg and halogen-containing gases. Although the applicability of these data to reactions with ground-state Hg^0 atoms (the expected species in ordinary flue-gas streams) is questionable, a relatively fast rate constant of 3.2×10^{-10} cm^3 $molecule^{-1}s^{-1}$ was found for the reaction of excited-state Hg with Cl_2 molecules.[6] The rate constant for the reaction of excited Hg^0 atoms with Cl was found by Horne et al.[10] to be from 1.5 to 5×10^{-14} $molecule^{-1}s^{-1}$ in gas mixtures of chlorotrifluoromethane (CF_3Cl) alone or CF_3Cl plus argon (Ar) at temperatures from 110 to 170°C. Mercury was shown to react with Cl to yield HgCl,[10] which is then able to dimerize to form Hg_2Cl_2 as the final product in this system. In the work with Cl_2, the following mechanism was proposed:[7,8,9]

$$Hg^0(g) + Cl_2(g) \rightarrow HgCl(g) + Cl(g).$$

A consequence of this information is that Hg^0 should not react directly with Cl_2 to yield $HgCl_2$. This product should only form upon further reaction of HgCl with either Cl or Cl_2. These mechanistic steps would appear much later as part of an overall Hg/Cl oxidation mechanism. No further references to laboratory work on the reaction of Hg^0 with Cl were found until 2002.

In 1979 and 1980, two other papers were published that are significant for this review. The work by Medhekar et al.[11] was the first to actually obtain kinetic information on a surface-catalyzed reaction of Hg^0 with Cl_2. The original intent of this research was to investigate the reaction of Hg^0 with Cl_2 in a container at elevated temperature. The authors quickly determined that a reaction was occurring on the walls of the container. Although this study proved *not* to be of the homogeneous gas-phase reaction, this work is important because the surface-catalyzed fast reaction may explain the results obtained by P'yankov.[5] In addition, while the heterogeneous reaction of Hg^0 was not considered in mechanistic models until recently, it may be an important pathway for oxidation of this species in real-world flue-gas streams that contain particulate matter (which can provide surfaces on which fast, heterogeneous reactions may occur).

The authors of this paper gave the following reaction mechanism for the surface-catalyzed reaction:

$$nHg^0 + nCl_2 \xrightarrow{\text{walls}} (HgCl_2)_n$$

Note that the product, given as polymeric $HgCl_2$, was not actually characterized but rather was assumed from the reaction stoichiometry that was observed (i.e., about 1 mole of Cl_2 was consumed for each mole of Hg^0 that disappeared). Note also that four different wall materials were tested, and each gave a different reaction rate. In particular, the fastest rate was observed with a Teflon-coated stainless-steel surface, followed by uncoated stainless steel, quartz, and Inconel. This may be important when considering the effects of different surfaces on the rate of a heterogeneous oxidation mechanism.

From the data provided in this paper, we calculated a rate constant for the proposed reaction at 250°C and at 0.95 atm pressure by assuming a first-order reaction. The rate constant we calculated is 2.0×10^{-10} mole cm^{-3} s^{-1}. This value is much larger (meaning a faster reaction) than a rate constant obtained from data presented in the next paper, which is presumably more reflective of the true homogeneous gas-phase rate constant.

The 1980 paper by Menke and Wallis[12] focused on the measurement by industrial hygienists of mercury in the presence of Cl_2 and water vapor. Thus, the primary thrust of this paper was *not* a basic measurement of the kinetics of the reaction of Hg^0 with Cl_2. Nevertheless, the data in this paper have been subsequently used (either directly or indirectly) by other investigators as the main source for the rate constant for this reaction. In retrospect, the use of these data is somewhat unfortunate as a recent determination of the rate constant for this reaction found a value more than two orders of magnitude lower than that calculated from this paper.

The authors did not specifically characterize the chemical reaction(s) in their system beyond noting that the product is "possibly $HgCl_2$." Hence, the only work that appears to have been performed up to 1980 on characterization of the product of the reaction of Hg^0 with Cl_2 is that of Ref. 5 and Ref. 11. The latter paper indicates that the product is $HgCl_2$ since the apparent stoichiometry of the reaction is about 1:1.

3.4 Hg – Cl_2, HCl CHEMISTRY: 1989–1992

During the period 1989–1992, proposed mechanisms for Hg^0 oxidation in a flue-gas stream began to appear. The paper by Hall et al.,[13] published in 1990, is the earliest paper we have found that proposed such a mechanism. These workers proposed that Hg^0 will react with O_2 at temperatures from 300 to 500°C to form HgO. This mechanism is depicted below.

$$Hg^0(g) + 1/2\ O_2(g) \leftrightarrow HgO(g)$$

They further conjectured that in the presence of HCl, other reactions might occur. These possible reactions are given as follows:

$HgO(g,s) + 2HCl(g) \leftrightarrow HgCl_2(g) + H_2O(g)$

$2HCl(g) + 1/2\ O_2(g) \leftrightarrow Cl_2(g) + H_2O(g)$

$Hg^0(g) + Cl_2(g) \leftrightarrow HgCl_2(g)$

$2Hg^0(g) + Cl_2(g) \leftrightarrow Hg_2Cl_2(s)$

$Hg_2Cl_2(s) \leftrightarrow Hg^0(g) + HgCl_2(g)$

The first reaction presupposes formation of HgO, but conditions for this reaction were not well defined. The third and fourth reactions are overall reactions for the two most likely products from the reaction of Hg^0 with Cl_2. These products were already found in 1949 by P'yankov.[5] The last reaction represents the thermal decomposition of the solid Hg_2Cl_2 obtained from the previous equation. Despite its overall simplicity, this mechanistic proposal was important in that it was the first to recognize the possible importance of HCl in an overall oxidation mechanism because of the possibility for formation of Cl_2 from HCl. Further development of these ideas would wait until the late 1990s.

Note that the reaction of HCl with O_2 to give Cl_2 and water is similar (i.e., the same reactants and products) to the commercial, metal-catalyzed Deacon process for production of Cl_2.[14] As will be noted later, other workers have also described this reaction as “Deacon-like” in their discussions of this possible Cl_2 formation mechanism.

A second important paper was published by Hall et al. in 1991.[15] This paper presented some kinetic data for the reaction of Hg^0 with both HCl and Cl_2. Further mechanistic ideas were also discussed in this paper. For the reaction of Hg^0 with HCl, these workers found that at 900°C, more than 90% of the Hg^0 was oxidized in less than 1 s. At temperatures from 20 to 300°C, the reaction was found to be very slow, with only about 20% of the Hg^0 being oxidized in 2.8 s. They suggested that the most likely overall reaction is given by the following equation:

$2Hg^0(g) + 4HCl(g) + O_2(g) \leftrightarrow 2HgCl_2(s,g) + 2H_2O(g).$

A second possible oxidation mechanism to produce Hg_2Cl_2 was also suggested:

$4Hg^0(g) + 4HCl(g) + O_2(g) \leftrightarrow 2Hg_2Cl_2(s,g) + 2H_2O(g).$

Note that the first reaction (forming $HgCl_2$) can be obtained by summation of the equations for the reaction of Hg^0 with O_2 and the reaction of HgO with HCl from the 1990 paper of Hall et al.[13] This may be important because it illustrates a potential for forming HgO as an intermediate in the oxidation of Hg^0. This possible pathway appears to have been lost in most recent formulations of an overall Hg oxidation mechanism.

For the reaction of Hg^0 with Cl_2, a fast reaction was reported. At 700°C, Hall et al. found that the reaction went to greater than 90% completion in 0.8 s. At 20°C, the time was 2.8 s. However, the authors recognized that the reaction they measured was likely influenced by heterogeneous reactions that probably formed a product on the surface of the reaction cell. They even noted that this was in agreement with the results of Medhekar et al.[11] Nevertheless, these are the first laboratory experiments that attempted to measure the rate constant for the reaction of Hg^0 with Cl_2 at higher temperatures of up to 700°C. Again, a simple mechanism is proposed for the reaction of Hg^0 with Cl_2. This is reflected in the two equations below that were proposed in this paper (similar to two of the reactions from their earlier paper[13] discussed above):

$Hg^0(g) + Cl_2(g) \rightarrow HgCl_2(s,g)$ and

$2Hg^0(g) + Cl_2(g) \rightarrow Hg_2Cl_2(s)$.

Again, further development of this mechanism awaited work in the late 1990s.

Finally, a paper by Skare and Johansson on the reaction of Hg^0 with Cl_2 was published in 1992[16] and provides further insights into reaction kinetics. The intent of this study was to investigate whether reactions between Hg^0 vapor and Cl_2 gas should be considered, from a hygienic point of view, at concentrations that are relevant in a chlor-alkali plant. This work was performed near room temperature (25°C) and showed that the reaction was very slow. After 24 h, the Hg^0 concentration was found to have decreased by only about 40% from its initial value. This indicates that the homogeneous gas-phase reaction is *at least* 10^5 times slower than the surface-catalyzed heterogeneous reaction.

3.5 ATMOSPHERIC CHEMISTRY OF MERCURY: 1991–1998

Several papers dealing with atmospheric Hg chemistry published between 1991 and 1998 have been widely cited and were judged to be relevant to this review. Four of these are summarized in this section.

A paper published by Schroeder et al. in 1991 appears to be the first paper to bring together and discuss gas-phase Hg chemistry with a view toward development of atmospheric models for the transformation and transportation of Hg.[17] According to the ISI Web of Science database,[4] this paper had been cited 69 times up to July 2003. The authors derived a rate constant of 4×10^{-16} cm^3 $molecule^{-1}s^{-1}$for the reaction of $Hg^0(g)$ with $Cl_2(g)$ by using the data of Menke and Wallis[12] discussed earlier. The authors noted that this value is likely to be an upper limit at the conditions specified (Cl_2 concentrations of 4.4 and 10.3 mg/m^3 and a relative humidity of 13%). The authors also recognized that there may be a “significant contribution to the total reaction rate from heterogeneous reactions” that could be facilitated by the presence of moisture. This connection was not explained further, and the reader is left to presume that moisture can enhance a surface-catalyzed reaction between these two gaseous components. This was not alluded to previously in the literature, and a plausible mechanism for this phenomenon is not apparent to us.

Another atmospheric chemistry model was published by Seigneur et al. in 1994.[18] Again, a rate constant for the reaction of $Hg^0(g)$ with $Cl_2(g)$ was given and is reported as $\leq 4.1 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}. The references for this value are the previous paper by Schroeder et al.[17] and the Ph.D. dissertation of Bjorn Hall.[19] This paper was cited 49 times up to July 2003, according to ISI's Web of Science database. The authors presented several mechanisms for gas-phase reactions of Hg^0 and two other Hg compounds, as well as aqueous-phase reactions of Hg^0 and other Hg compounds. Some information was also given for heterogeneous reactions of solid Hg compounds, gas/liquid equilibria of Hg^0 and four Hg compounds, and water solubility data for four solid Hg compounds. All of these data were then incorporated into an atmospheric chemical kinetic model. Interestingly, the authors stated that "large uncertainties exist in the gas-phase reaction rates of Hg^0 with Cl_2, O_3 and H_2O_2 and the overall half-life of Hg^0 due to chemical reactions in the atmosphere cannot be assessed with certainty without further laboratory kinetic data."[*] This is the earliest documented evidence we have seen of the need for more laboratory kinetic data on gaseous Hg reactions.

A paper published by Carpi in 1997 discussed emission and transport of Hg from combustion sources, including coal-combustion facilities and municipal solid-waste incinerators.[20] Although the paper included a figure showing various hypothesized Hg transport and deposition processes, there was very little reference to specific Hg/Cl chemistry. At one point, however, the author noted that "The partitioning of mercury between Hg^0 and Hg(II) (possibly $HgCl_2$) is likely dependent on the concentration of HCl and other pollutants in the feed stocks and stack emissions." However, no explanation for this comment was offered.

The most frequently cited paper on this topic that we have discovered was published in 1998 and is entitled "Atmospheric Chemistry - An Overview".[21] This paper is important because it contains a large number of references (103). Thus, it can be viewed as a key introduction to this field, as well as a thorough summary of the current knowledge (up to early 1997) on the behavior of mercury in the atmosphere. The presentation discusses many different atmospheric pathways and processes, including "anthropogenic and natural sources of Hg emissions to the atmosphere, aerial transport and dispersion (including spatial and temporal variability), atmospheric transformations (both physical and chemical types), wet and dry removal/deposition processes to Earth's surface." Numeric models that deal with atmospheric transport and processes are also reviewed. However, there is no specific discussion of Hg/Cl chemistry in this paper, and it is included in this report mainly because of its importance in the field of atmospheric Hg.

Atmospheric mercury modeling has not been a major factor in the detailed mechanistic study of the reactions of Hg with chlorine-containing reactants, but it has possibly influenced workers in the laboratory to make measurements of the rate constants of various reactants with gaseous Hg. Several papers of this type have appeared subsequent to the reviews discussed above. For example, an important paper on the reaction of Hg with ozone by Hall[22] was published in 1995 and may have been at least partly inspired by concerns about the lifetime of Hg^0 in the atmosphere. In addition, measurements of the rate constants for reactions of Hg^0 with

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[*] O_3 – ozone; H_2O_2 – hydrogen peroxide

Cl_2, Cl, bromine (Br_2), and atomic bromine (Br) were published in 2002 with atmospheric Hg chemistry implications in mind.[23]

3.6 Hg – Cl_2, HCl CHEMISTRY AND MODELING: 1998–2003

3.6.1 1998–1999

The degree to which the preceding work influenced the development of a detailed chemical mechanism for oxidation of Hg in chlorine-containing flue-gas streams may not be obvious, but one point is clear: the lack of precise experimental data on rate constants for most gas-phase reactions of Hg^0 has hampered the validation a detailed kinetic model. Although workers at McGill University in Canada have recently made available some data for rate constants,[23] we have not as yet noted their use.

Many workers attribute the beginning of the development of a detailed Hg oxidation model to the work of Widmer et al. in 1998.[24] The experimental work in this paper showed the dependence of Hg oxidation (identified as $HgCl_2$ formation by analysis with a Method 29 sampling train) on both temperature and HCl concentration. In fact, at high temperatures (greater than about 700°C), these workers showed that the extent of Hg oxidation was similar to the amount of $HgCl_2$ that could be predicted from thermodynamic equilibrium data. At lower temperatures, they found that the extent of Hg oxidation was considerably below what would be projected from equilibrium thermodynamics. This was particularly true at the lowest HCl concentration used (300 ppmv). A kinetic limitation at the lower temperatures was suggested because those data fit a plot of ln k vs. 1/T (where T is absolute temperature) when k (rate constant) was calculated using the equation

$$\ln P_{Hg}/P^0_{Hg} = -k \bullet P_{HCl} \bullet t,$$

where P^0_{Hg} is the initial Hg concentration, P_{HCl} is the HCl concentration, and t is the time.

The rate constant for the reaction of Hg^0 and HCl can also be expressed in the standard Arrhenius form

$$k = C \bullet \exp(-E_a/RT),$$

where C is called the pre-exponential factor, T is temperature, R is the universal gas constant, and E_a is the activation energy. From their plot of ln k vs. 1/T, the authors determined a pre-exponential factor of 2.2×10^7 L/mol-s and an activation energy of 45.4 kJ/mol. Although the rate equation used to calculate these data is merely an empirical expression, it can still be used to provide information on the mechanism. The important point is that the oxidation of Hg^0 in the presence of HCl appears to be first order with respect to both the HCl and Hg^0 concentrations. Their data also suggest that the maximum extent of oxidation is strongly temperature dependent, especially at lower temperatures.

In 1999, Ghorishi et al. published a paper on Hg oxidation using simulated flue gases and "model" fly ashes.[25] These workers noted a negative effect on Hg oxidation from the gaseous components SO_2 and water vapor (H_2O). This negative effect was attributed to destruction of the chlorinating/oxidizing agent Cl_2 via the following mechanism:

$Cl_2 + SO_2 + 2H_2O \rightarrow 2HCl + H_2SO_4$.

The effect of fly ash on Hg oxidation was also an important part of this investigation. Model fly ashes were prepared by mixing various ratios of aluminum oxide, silicon dioxide, ferric oxide (Fe_2O_3), cupric oxide (CuO), and calcium oxide (CaO). As mentioned earlier in the paper of Hall et al.,[13] Ghorishi and co-workers once again brought up the possibility of forming Cl_2 in these systems via a "Deacon process reaction" of HCl with O_2. This reaction can presumably be accelerated on some particle surfaces. Their data suggested that Fe_2O_3 may be an important catalytic phase because greater Hg oxidation was obtained with increasing concentrations of Fe_2O_3 in the fly ash. The authors also suggested that Cl_2 may be produced at a higher rate in the presence of CuO as compared to Fe_2O_3, on the basis of the observed greater extent of Hg oxidation in the presence of fly ashes with CuO compared with those containing Fe_2O_3.

Another possible oxidation mechanism they suggested involved NO on catalytic surfaces, such as CuO and Fe_2O_3. This would presumably produce HgO as the primary product rather than the $HgCl_2$ produced from Cl_2. The fact that HgO could be a possible oxidation product is an important hypothesis that needs some attention because HgO could have a significantly different pathway for a downstream removal process when compared with the much more water-soluble product $HgCl_2$.

3.6.2 2000

In 2000, Widmer et al. presented a paper wherein an eight-step reaction mechanism for the formation of $HgCl_2$ from Hg^0 and chlorine-containing species was detailed for the first time.[26] Mercurous chloride is an intermediate in this reaction scheme as it presumably reacts rapidly with several available reactants to form the final product, $HgCl_2$. This detailed mechanism is shown below where M indicates a non-changing, participant molecule.

1. $Hg^0 + Cl + M \leftrightarrow HgCl + M$

2. $Hg^0 + Cl_2 \leftrightarrow HgCl + Cl$

3. $Hg^0 + HCl \leftrightarrow HgCl + H$

4. $Hg^0 + HOCl \leftrightarrow HgCl + OH$

5. $HgCl + Cl_2 \leftrightarrow HgCl_2 + Cl$

6. $HgCl + Cl + M \leftrightarrow HgCl_2 + M$

7. $HgCl + HCl \leftrightarrow HgCl_2 + H$

8. $HgCl + HOCl \leftrightarrow HgCl_2 + OH$

The authors used various assumptions to derive rate constants for all of these reactions. However, their study found only reactions 1, 5, 6, and 8 to be of significance. They tested their model by comparing results from an earlier experiment[24] with their model calculations. We characterize the agreement between the model calculations and the experimental data as good up to about 1,000 K. At higher temperatures, the model greatly under-predicts the extent of Hg oxidation. The authors offered an explanation for this under-prediction that is plausible, but certainly not proven.

Also in 2000, Sliger et al. published papers[27,28] in which data were presented for the reaction of Hg^0 with HCl at various concentrations and at various temperatures from 860°C to either 1,071 or 1,171°C. There is a bit of confusion on the upper end of their temperature range because the abstract gives 1,171°C as the maximum, while the data shown in the paper gave 1,071°C as the highest temperature. In either case, the authors proposed that the fast oxidation of Hg^0 is via reaction with Cl atoms to give HgCl (reaction 1 in the eight-step mechanism shown above). The authors stated that this reaction is fast at room temperature and reference the work of Horne et al.[10] They additionally stated that the intermediate HgCl produced from this first reaction can then react further (via reactions like 5, 6, and 7 above) to produce $HgCl_2$. They also noted that an abstraction reaction to produce Hg^0 should be considered as well. This is the reverse of Reaction 2 above:

$HgCl + Cl \rightarrow Hg^0 + Cl_2$.

Because of the high concentration of HCl in their system, they considered Reaction 7 in some detail. Sophisticated methods were used to calculate both forward and reverse rate constants for this reaction. Sliger et al. then proceeded to develop a model that incorporated a reaction set using H_2, O_2, CO, CO_2 and another reaction set with 18 equations involving Cl, Cl_2, HCl, ClO (chlorine monoxide), and HOCl. Using this model, they compared their laboratory results and the results of Hall et al.[15] with their calculations. We characterize the agreement as very good.

A paper by Mamani-Paco and Helble discussed some aspects of the Hg^0 oxidation mechanism involving Cl-containing species.[29] The authors presented data from a bench-scale study of the oxidation of Hg^0 in the presence of various reactant species, including HCl and Cl_2. As mentioned in some previous papers, Mamani-Paco and Helble noted that they observed no reaction of Hg with Cl_2 at temperatures below 773 K. They stated that “literature reports of rapid room temperature homogeneous gas phase mercury oxidation by molecular chlorine may have been influenced by surface reactions.” This same observation was noted as far back as 1979.

Finally, work reported by Senior et al.[30] demonstrated that they were able to achieve calculated oxidation results, using a model identical to that of Widmer, that were of “comparable magnitude to field observations” but were still considerably below the 40–80% observed in some field measurements. They also recognized the key role that the concentration of both Cl atoms and Cl_2 molecules are likely to play in the overall mechanism of Hg^0 oxidation. Both this and the preceding paper were not reviewed in further detail because later papers by both groups provided more insights into the proposed oxidation mechanism.

3.6.3 2001

A paper published by Edwards et al.[31] addressed the development of a detailed chemical mechanism that was used to fit Hg oxidation results from the laboratory work of Widmer[24] and Ghorishi.[32] This model used four reactions involving Hg^0 and HgCl. Three of these reactions were the same as reactions 1, 2, and 6 above. The fourth reaction was between Hg^0 and oxygen atoms to yield HgO. In addition to these reactions, 14 equations that allowed for production of Cl or Cl_2 from chlorine-containing species, such as Cl, Cl_2, HCl, ClO, and HOCl, were included. An additional 17 reactions involving the formyl radical (CHO) and carbonyl chloride (COCl), as well as a hydrocarbon mechanism for H_2-O_2-CO having 25 reactions involving 11 species, were also added. The complete reaction mechanism these authors used consisted of 60 reactions involving 21 species. The authors found good agreement with experiments only for higher temperatures where a high Hg oxidation conversion was observed. For temperatures below about 770°C where Hg^0 conversion/oxidation was low, agreement with the model predictions was poor (the model greatly underpredicted Hg^0 conversion). In two of their calculations, the authors added a trace of Cl_2 (1 ppmv) to their initial conditions, and this greatly improved the agreement with experiments. The authors indicated that this significant change is an indication of how the precise concentration of Cl_2 (or Cl) can have a large effect on the final level of Hg oxidation. Because Cl_2 was not specifically added in the experiments, the authors speculated on how Cl or Cl_2 might be formed. One suggested possibility was production of Cl_2 via a "Deacon-type process." This is something we have noted in two previous papers. The authors also stated that "The results described above, although inconclusive, do suggest that another, probably heterogeneous mechanism is dominant at low temperatures." Thus, we have another voice that suggests that homogeneous gas-phase reactions, although possibly important at high temperatures, are probably not the most important Hg oxidation mechanism at low temperatures. This matter should be kept in mind when we discuss a paper from 2002 that appears to be the first to include heterogeneous reactions as part of an overall Hg oxidation mechanism.[33]

The Edwards paper appears to be the first since the work of Hall et al.[13] to recognize the possible importance of O_2 or O atoms. The authors included a reaction of Hg^0 with O atoms in their overall mechanism, but they noted that the mechanism for reaction with O atoms appears to be unimportant, probably because the concentration of this species is so low. Despite this conclusion, we think that it is important for kinetic models to include this possible pathway for oxidation of Hg. As a final comment on this paper, we note that the rate constant used for the reaction of Hg^0 with Cl_2 is similar to that suggested by the data of Menke and Wallis[12] and used by many others (about 5.6×10^{-15} $cm^3 molecule^{-1} s^{-1}$).

A journal paper published by Niksa et al.[34] duplicated the eight-step reaction mechanism proposed in the earlier conference paper by Widmer et al.[26] The rate constant for the Hg^0+Cl_2 reaction used in this paper was the same as that estimated by Widmer from the analogous reaction involving lead. We note that this rate constant does have a temperature dependence associated with it. This is in contrast with the rate constant used by Edwards et al.[31] in the paper described above. We calculate that this temperature dependence would lead to an increase in the reaction rate by more than three orders of magnitude when going from 20°C to 700°C.

In addition to the eight-step reaction set, Niksa's model used a sub-mechanism that coupled chlorine chemistry with nitrogen oxides (NO_x) chemistry. A moist CO oxidation sub-mechanism and an H/N/O sub-mechanism were included as well. In total, 102 elementary chemical reactions were included in the homogeneous Hg^0 oxidation mechanism. Calculations using this mechanism were compared with the laboratory data of Sliger et al.[27], Widmer et al.[24], Hall et al.[15], and Mamani-Paco et al.[29] This model gave the best fit to Hall's data that we have seen to date. However, the shapes of the curves do not fit well for tests that were performed at temperatures below 700°C. By comparing the results of Sliger with those of Hall, the authors concluded that Hg^0 oxidation is inhibited by the presence of moisture and NO. Their model was able to predict these differences. The authors suggested that the inhibition caused by the presence of NO is due to the following reaction:

$$NO + OH + M \rightarrow HONO + M.$$

Although it is not stated, we presume that the importance of this reaction is the destruction of the OH radical, which is an important source of Cl atoms via the reaction with HCl. However, the authors went on to point out that low levels of NO (25 ppm was used in their calculations) can actually greatly *increase* the extent of Hg^0 oxidation when quench rates above 1,000°C/s are applicable. Hence, the effect of NO is quite complex and could not have been predicted before the development of this model. This appears to be the first example of how a species other than HCl or Cl_2 can greatly affect model predictions for Hg oxidation.

3.6.4 2002

A paper published in 2002 by a group of workers from McGill University (Ariya et al.[23]) in Canada is particularly important because it was the first laboratory measurement of the rate constant for the homogeneous gas-phase reaction between Hg^0 and Cl_2 since the work of Menke and Wallis.[12] In addition, this paper gave data on the rate constants for reactions of Hg^0 with Cl, Br_2, and Br. We regard the kinetic data in this paper to be superior to the data in Menke and Wallis (used by Schroeder et al.[17] to estimate a rate constant for Hg^0 plus Cl_2) for several reasons. The authors were aware of the severe wall effects that could influence the determination of the rate constant for this reaction pair. Because of this constraint, they took great care to both reduce wall effects to a minimum and to account for any residual wall effects in their rate-constant calculation. There were no indications that wall effects were either excluded or minimized in the experiments of Menke and Wallis. Menke and Wallis also omitted some important experimental details in the description of their tests, such as the temperature at which their measurements were made. In this paper, very detailed descriptions of the experimental apparatus, procedures, and conditions were given. Menke and Wallis had only one data point for each of their test conditions, and thus a rate constant can only be approximated by assuming first-order behavior. On the other hand, Ariya et al. performed true kinetic measurements and presented kinetic runs with at least 15 data points (as a function of time) for each test. Finally, although Menke and Wallis used multiple measurement methods to determine their Hg concentrations, Ariya et al. used two modern spectroscopic techniques (cold vapor atomic absorption spectroscopy [CVAAS] and gas chromatography–mass spectroscopy [GC-MS]) to measure their reactant/product concentrations. The accuracy of these measurements was partially reflected in the overall error range given for their measured rate constants. These error limits ranged from less than 10% for the reaction with Cl_2 or Br to about 20% for the reaction with Cl or Br_2. We recommend using the values obtained in this work for all future modeling work that requires a rate constant for any of these reactions. The rate constants are given in Table 1.

TABLE 1 Recommended Values for Rate Constants after Aryia et al.[23]

Reactant	Temperature (K)	Rate Constant (cm^3 $molecule^{-1}s^{-1}$)
Cl_2	298 ± 1	$(2.6 \pm 0.2) \times 10^{-18}$
Cl	298 ± 1	$(1.0 \pm 0.2) \times 10^{-11}$
Br_2	298 ± 1	$<(0.9 \pm 0.2) \times 10^{-16}$
Br	298 ± 1	$(3.2 \pm 0.3) \times 10^{-12}$

None of the experiments, which used two different sampling methods, showed the presence of gaseous Hg oxidation products. The only major products identified were the solid products $HgCl_2$ and $HgBr_2$ absorbed on the reactor wall. The authors postulated that no HgCl or HgBr (via decomposition of Hg_2Cl_2 or Hg_2Br_2) was found in their experiments because of the relatively high concentrations of Cl or Br that were produced, leading to the following reaction as the dominant pathway for HgX:

$$HgX + X \rightarrow HgX_2.$$

This work was also one of the few where the actual reaction products were analyzed. The absence of Hg_2Cl_2 in these tests suggests that, perhaps, $HgCl_2$ is the primary product of homogeneous gas-phase oxidation, while Hg_2Cl_2 (observed by P'yankov) may be the primary product produced from heterogeneous oxidation. This hypothesis requires further testing. The oxidation product could be important in downstream removal technologies as the solubility difference between these two species is great ($HgCl_2$ is about 30,000 times more soluble than Hg_2Cl_2 at room temperature[18]).

The paper noted previously by Niksa et al.[33] was the first paper we found that included a *heterogeneous* mechanism as part of an overall Hg oxidation mechanism. This first attempt to model oxidation of Hg^0 with a gas/solid mechanism was fairly simple and involved only the following three equations:

$$StSA(s) + HCl \rightarrow StCl(s) + H,$$

$$StCl(s) + Cl \rightarrow Cl_2 + StSA(s), \text{ and}$$

$StCl(s) + Hg^0 \rightarrow StSA(s) + HgCl$.

In these equations, StSA(s) denotes an unoccupied carbon site and StCl(s) denotes a chlorinated carbon site on the solid surface. The solid was assumed to be unburned carbon particles that were incorporated into various ash fractions. This heterogeneous mechanism was in addition to a 102-step homogeneous reaction mechanism that was identical to that described above.[34]

The authors compared the results of calculations made by using the homogeneous model alone and the combined homogeneous/heterogeneous model with experimental results obtained from a laboratory-scale furnace. The combined homogeneous/heterogeneous mechanism gave improved agreement with experimental results over the homogeneous model alone in all 16 cases where the calculations were made. The most important factor in determining the extent of Hg oxidation using the heterogeneous mechanism was the level of unburned carbon in the particles as measured by the loss-on-ignition (LOI) or the size of the unburned carbon particles. One important implication of this paper is that to accurately model Hg oxidation for a real-world flue gas that contains particulates (especially unburned carbon), one must consider and include heterogeneous mechanisms as part of an overall oxidation mechanism. We consider the heterogeneous oxidation mechanism shown above to be the first attempt to develop a detailed understanding of interactions between Hg and other gaseous flue-gas components with the solid surfaces present in typical flue-gas streams.

A paper presented by Senior et al.[35] used the same eight-step reaction set discussed previously. All of the rate constants appear to have been estimated in one manner or another, except for Reaction 1 (Hg^0+Cl+M), which was altered to match experimental data of Sliger et al.[27] The authors first tested the sensitivity of their model to the initial composition of the gas and to the cooling rate. For “dry” conditions, the model generally under-predicted the laboratory results of several groups.[15,36,32] However, the model gave moderately good agreement with laboratory data from Sliger at high temperature and with 10–14 vol% water.[36] In comparing model results with data from Gaspar et al.,[37] there was poor agreement at temperatures below about 1,200 K, but there was moderately good agreement with data obtained at 1,200 K. Finally, model calculations were compared with data of Fujiwara et al.[38] obtained from a pulverized coal furnace. For one coal, the agreement was fair, while for two other coals, the agreement was poor (more than a factor of two off when comparing observed Hg^0 conversion with the calculated value). The largest discrepancies between the model calculations and experimental results appeared to occur for tests performed at lower temperatures. The authors suggested that these differences might be due to catalytic effects on Cl production. The authors further noted that from dioxin research it is known that “catalysis plays a major role in modifying the chlorine chemistry at low temperatures.” We take these comments to imply that Cl_2 may be produced from catalytic processes (like the Deacon-type process discussed earlier) that are not accounted for in their homogeneous gas-phase model.

The final paper reviewed from 2002 was by Lee et al.[39] These workers reported laboratory kinetic experiments for the reaction of Hg^0 with HCl. A series of experiments was performed involving temperatures from 24°C to 190°C. They also studied variations in both the initial Hg^0 concentration and the initial HCl concentration. The authors did not attempt to fit their data to a precise mechanism, but instead they calculated an overall rate constant and activation energy. These overall values were based on the pathway given below:

$Hg^0 + HCl \rightarrow$ oxidized products (HgCl and/or $HgCl_2$).

In other words, the authors obtained their kinetic values for the overall reaction by measuring the disappearance of one of their reactants (in this case, Hg^0 concentration was monitored). Although data were not given for individual kinetic runs, a graph was shown in which the value of the reaction order with respect to Hg^0 concentration was determined. This value was -1.55. Once this value was determined, the authors were able to plot a complex expression for the overall rate constant versus the reciprocal temperature to obtain values for the activation energy and overall rate constant. They found a value of 16.13 kJ/mol for the overall activation energy and a value of $5.07 \times 10^{-2} \exp(-1939.68/T)\ [\mu g/m^3]^{-0.55} s^{-1}$ for the overall rate constant. The authors recognized that these rate data were only applicable to the specific conditions used during these tests.

In addition, the authors briefly discussed two more detailed reaction pathways. The first pathway was the direct reaction with Cl_2 to yield $HgCl_2$. They suggested that formation of Cl_2 in the gas phase may be kinetically limited. Presumably, this was not an important pathway at the low temperatures used in these experiments. The second pathway involved the reaction of Hg^0 with atomic Cl to form HgCl. This is similar to reaction No. 1 from the eight-step mechanism presented above. They also added reactions Nos. 6 and 7 to their mechanism. The authors suggested that the mechanism to produce atomic Cl could be the reaction of HCl with an hydroxyl radical, which is thermodynamically favored at higher temperatures. This is interesting in view of the effect of NO discussed previously. If NO reacts with OH radicals, then this reaction could affect the formation of Cl, a potentially critical species in the oxidation of Hg^0.

This paper also presented data on experiments with particulate matter consisting primarily of titanium dioxide. The goal of the tests was to study the removal of Hg^0 via heterogeneous gas-solid reactions and by direct gas-phase oxidation. Results from these tests will not be described in this review. However, we note that the authors suggested that in three of their tests, there was formation of sub-micrometer particles from chlorinated Hg in the gas phase. This is the first experiment that we are aware of that indicates that oxidized Hg may exist in a solid form (albeit very small particulates). The presence or absence of Hg-containing particulates could be an important consideration in different control technologies.

3.6.5 2003

Three papers that were published early in 2003 were selected for review. Two of these papers contained some additions to the basic eight-step Hg/Cl mechanism discussed above. To the best of our knowledge, these are the first two papers since 2000 that proposed modifications to the homogeneous gas-phase mechanism previously developed. The first of these papers was by Qiu et al.[40] and added two reactions that included a sulfur monoxide (SO) species and a sulfur mono-chloride (SCl) species. The rate constants for these reactions were calculated by the authors. These two reactions are:

$SO + OCl \rightarrow SO_2 + Cl$ and

$SCl + O \rightarrow SO + Cl$.

The importance of these reactions appears to be that they provide additional pathways for the formation of Cl atoms, which were not considered in the past. Also, five reactions for conversion of Cl-containing species (HCl, Cl_2, and ClO) were specifically listed for the first time, along with their rate constants (obtained from data published by Senkan[41]). The authors also used sophisticated methods to calculate rate constants for three of the reactions in the eight-step Hg/Cl mechanism.

Using this model, the authors obtained very good agreement between the calculated results and their experimental data. The experimental data showed that SO_2 had a significant effect in reducing the level of Hg^0 oxidation compared with tests in which no SO_2 was present. For example, under stoichiometric conditions and with 250 ppm Cl_2 present, Hg^0 oxidation was reduced from 61% with no SO_2 in the simulated flue gas to about 10% with 500 ppm of SO_2 present. The authors presented a complex argument to indicate how the presence of SO_2 can reduce the oxidation of Hg^0. They argued that HOCl is an important species in the oxidation mechanism because HOCl can react with HgCl (a primary intermediate in Hg oxidation) to yield $HgCl_2$ (the primary final oxidation product) and an OH radical. However, the presence of SO_2 consumes OH radicals via the reactions

$SO_2 + OH \rightarrow SO_3 + H$ and

$SO_2 + OH + M \rightarrow HSO_3 + M$.

Finally, the reduction of OH radicals leads to reduction of HOCl produced via the reactions

$Cl_2 + OH \rightarrow Cl + HOCl$ and

$Cl + OH \rightarrow HOCl$.

As proof that other reaction mechanisms were not responsible for this effect (such as direct reaction of SO_2 with Cl and/or Cl_2), the authors stated that “Simulations corresponding to our experimental conditions indicate that reaction pathways involving S-Cl-O species do not significantly affect mercury oxidation.” We also note that OH radicals are important because they provide an important pathway to formation of Cl (as shown above in the reaction of Cl_2 with OH). As has been mentioned several times, the reaction of Hg^0 with Cl is thought to be the main initial pathway for oxidation of Hg^0.

Next, we reviewed a paper from China by Xu et al.[42] This was the first paper we found in which the authors listed all of the reactions along with the rate constants used in their model. Their homogeneous oxidation model consisted of 107 reactions and 30 species. In addition to the eight reactions with Hg/Cl chemistry described above, these authors included six additional reactions that contain the species HgO. Other than that described in the paper of Edwards et al.,[31] this is the only homogeneous oxidation model we are aware of that specifically includes reactions with HgO. These six additional reactions are:

1. $Hg^0 + ClO \rightarrow HgO + Cl$,
2. $Hg^0 + ClO_2 \rightarrow HgO + ClO$,
3. $Hg^0 + O_3 \rightarrow HgO + O_2$,
4. $Hg^0 + N_2O \rightarrow HgO + N_2$,
5. $HgO + HCl \rightarrow HgCl + OH$, and
6. $HgO + HOCl \rightarrow HgCl + HO_2$.

An interesting result of this model was that in all of the cases studied, 1.5–6.0% of the Hg in the product was predicted to be present as HgO. This prediction remains to be verified by experimental data. The authors suggested that the two most important reactions involving HgO were the formation of HgO from Hg^0 plus ClO and the reaction of HgO with HCl to yield HgCl. This mechanism can explain how the production of $HgCl_2$ increases while that of HgO declines because an additional pathway is available for the oxidation of Hg^0 into $HgCl_2$ that is not present in the other mechanisms discussed above. That pathway begins with Hg^0 reacting with ClO to yield HgO. The HgO can then react with HCl to yield HgCl, which finally reacts with any of the four chlorine species in the eight-step model to yield $HgCl_2$.

The validity of the model was tested by comparing calculated results and various experimental data. Reasonable agreement was obtained with data of Mamani-Paco et al.[29] When 10 v/v% O_2 was added to the flue-gas composition, the level of Hg^0 oxidation appeared to increase. It also appeared to increase in terms of absolute percentage with increasing Cl_2 concentration. On the other hand, poor agreement was obtained when their calculations were compared to results of Widmer et al.,[26] particularly at lower temperatures. Good agreement with the work of Sliger, et al.[43] was obtained for four of their six data points. The other two model calculations were low by an average of about 36%. Thus, the agreement with four of Sliger's data points was very impressive (calculations within 2% for two of the data points and within 10% for the other two). However, the most specific predictions that could be tested with this model were their calculations that show production of 1.5–6% HgO as a product in all the cases studied.

A paper by Niksa and Fujiwara[44] was the last to be reviewed and was similar in content to their earlier paper.[33] As in the previous paper, both a homogeneous and a heterogeneous oxidation mechanism were included. There is some uncertainty as to the number of steps included in the homogeneous mechanism since the abstract states that "a 104-step mechanism" is used, while in the body of the paper the authors state: "In total, 102 elementary chemical reactions are included in the homogeneous Hg^0 oxidation mechanism." In any case, the same eight-step Hg/Cl oxidation mechanism was used, and a three-step heterogeneous oxidation mechanism also appears to be identical to that proposed in their earlier paper. The principal difference from the previous paper appears to be in some of the data presented in the figures. One of these shows two excellent fits for the homogeneous mechanism alone with two different experiments — one without water and NO and the other in the presence of these two gases.

4 SUMMARY AND CONCLUSIONS

The focus of this review was on reactions of gaseous Hg^0 with chlorine-containing reactants. Particular emphasis was placed on Cl_2 and HCl. In this concluding section, we summarize our findings, draw conclusions on the current state of knowledge, identify significant gaps in that knowledge, and make recommendations for further research.

The earliest paper that we were able to identify that addressed the question of the reaction of gaseous Hg^0 with Cl_2 was a Russian publication from 1949.[5] Although no specific kinetic data were presented in this paper, the author found this reaction to be "too fast" for the type of kinetic measurements that he was prepared to perform. As to the mechanism of this reaction, the author found both Hg_2Cl_2 and $HgCl_2$ as products, with Hg_2Cl_2 appearing to be the dominant species. This finding provides a baseline for comparing the advances made in understanding the mechanism and kinetics of this reaction that followed over the next 54 years.

The next significant experiments with these reactants were not reported until 1979, and it quickly became obvious that the results reported in 1949 were most likely due to a surface-catalyzed reaction (after the work of Medhekar et al.[11]). When work in this area was renewed in the late 1980s and early 1990s, this fact appears to have been recognized in the papers by Hall et al.[15] and by Skare and Johansson.[16] The work by Menke and Wallis[12], despite its inherent shortcomings from a detailed kinetics point of view, was nonetheless important simply because it was the first published study to indicate that the gas-phase homogeneous reaction was indeed very slow, at least at room temperature. A rate constant was derived by Schroeder et al.[17] from the data in the paper by Menke and Wallis. This calculated rate constant was cited (either directly or indirectly) in later papers. More recently, models for Hg/Cl reaction chemistry have used rate constants proposed by Widmer et al.[26] or by Sliger et al.[27] Both of these values have their limitations, as the one proposed by Widmer is based on a similar reaction for lead, while the number proposed by Sliger is based upon limited data of Hall et al. A more recent determination of the rate constants for the reaction of Hg^0 with Cl_2 and with Cl was published in 2002 by Ariya et al.[23] We recommend that all subsequent work that requires a rate constant for either of these reactions (i.e., Hg^0+Cl_2 or Hg^0+Cl) use the data provided in that paper and noted in Table 1 in this report. However, since these values were measured at room temperature only, we suggest that the temperature dependence used either by Widmer et al. or by Sliger et al. be incorporated when performing calculations at higher temperatures.

As the work on this review progressed, it became evident that the reaction of Hg^0 with HCl was probably more important in flue-gas streams from a mechanistic point of view than that with Cl_2. Hall et al.[15] found that this reaction (in the presence of O_2) occurred from room temperature (about 20% oxidized Hg) up to 900°C (>90% oxidized Hg). The extent of Hg oxidation was roughly the same from 20°C to 300°C. However, the direct reaction of Hg^0 with HCl is judged to be unlikely because tri-molecular reactions ($Hg+2HCl \rightarrow HgCl_2+H_2$) are not common in general and are usually quite slow. Furthermore, this direct oxidation of Hg^0 by HCl is not thermodynamically favored at temperatures above 300°C. Therefore, Hall et al. suggested the participation of O_2 in their mechanism for the reaction of Hg^0 with HCl.

Another pathway for the reaction with HCl is via a metal-catalyzed Deacon-type reaction:

$$2HCl + 1/2O_2 \overset{M}{\leftrightarrow} Cl_2 + H_2O,$$

where M is a catalyst. In this scheme, HCl does not react directly with Hg^0 but rather is a source of Cl_2, which can react either homogeneously or heterogeneously with Hg^0. The importance of this reaction in flue-gas streams is difficult to assess because of uncertainties in reaction dynamics (i.e., effect of different catalysts on the kinetics of this reaction).

More recent work by Sliger et al.[27,28] has suggested that the fast reaction of Hg^0 with Cl is the most important pathway for Hg oxidation. To assess the likelihood of this mechanism, a larger set of reactions must be considered that involves H/Cl/O chemistry and such species as Cl, Cl_2, HCl, ClO, and HOCl, as well as H, O, OH, HO_2, H_2O_2, and H_2O. Sliger et al. have done this in their work from 2000. Of the possible reactions that yield Cl atoms, two involve HCl, as shown below. This again suggests the possible importance of HCl in an overall mechanistic model for the oxidation of Hg.

$$HCl + O \rightarrow Cl + OH$$

$$HCl + OH \rightarrow Cl + H_2O$$

Despite the apparent need for HCl, Widmer et al.[26] suggested that the rate-determining step in the oxidation of Hg^0 is the reaction of Hg^0 with the radical species Cl. Also, the mechanism of Sliger et al.[27] suggests that the primary pathway for Hg^0 oxidation is the reaction of Hg^0 with Cl to yield first HgCl, followed by reaction with another chlorine atom to yield $HgCl_2$ as the final product. To help assess the extent of the various possible pathways, obtaining measurements of Cl_2 and/or Cl concentrations in either "real-world" or simulated flue gas streams is very important. The practicality of this suggestion remains to be determined.

In the mechanistic model presented in 2000 by Widmer et al.,[26] an eight-step Hg/Cl reaction set was proposed. This model consisted of a four-part first step that involved reactions between Hg^0 and the reactants Cl, Cl_2, HOCl, and HCl. The Hg product in all four reactions was HgCl. The remaining four steps described how HgCl can react with the same four Cl-containing reactants to yield the final product $HgCl_2$. Sliger et al.[27] and others thereafter have tried to prove the validity of this and other models by comparing calculations of Hg oxidation with laboratory experimental data. These attempts at validation have met with varying levels of success. One problem with using the laboratory results that have been available to the modelers is that these data were obtained by using flue-gas streams that did *not* contain any particulate matter. Particulate matter would, of course, be present in real-world flue-gas streams and could be an important component of any overall mechanism for the oxidation of Hg^0. This leads us to consider possible heterogeneous mechanisms as part of an overall oxidation mechanism.

A recent attempt to address the effects of particulate matter (in the form of unburned carbon particles) has been discussed by Niksa et al.[33] These workers suggested a model that included a heterogeneous reaction mechanism, in addition to a fairly complex and extensive homogeneous reaction mechanism. The success of this model in predicting laboratory results is encouraging. While not by any means a complete model, we believe that this work points in a direction that future work should continue. More specifically, both homogeneous and heterogeneous mechanisms should be incorporated into an overall mechanism for the oxidation of Hg^0 in real-world flue-gas streams.

With regard to the product(s) of oxidation, most workers in this field appear to have assumed that $HgCl_2$ is the only or dominant product. Assessing the literature, we have found very few studies that actually try to characterize the product(s) obtained from oxidation of Hg^0 with either Cl_2 or HCl. As mentioned earlier, P'yankov[5] claimed to have found both chlorides in his product mixture, with Hg_2Cl_2 being dominant. Medhekar et al.[11] suggested $HgCl_2$ as the main product, primarily from their observation of the stoichiometry for the reaction (i.e., 1:1). Ariya et al.[23] recently found $HgCl_2$ as the primary product in their experiments. Many other workers have inferred that $HgCl_2$ is the primary product of Hg^0 oxidation on the basis of measurements of Hg captured in aqueous solutions. This conclusion is based on the relatively high solubility of $HgCl_2$, as compared to Hg^0. However, $HgCl_2$ is also much more soluble than other oxidized species, such as Hg_2Cl_2 or HgO. As a result, the analytical methods will tend to exclude any Hg_2Cl_2 or HgO that might be formed in the experiments. The actual product distribution is of more than academic interest in that the product species that are formed from the oxidation of Hg^0 can affect their downstream removal. Aqueous removal, in particular, will not be as effective in removing Hg_2Cl_2 or HgO as it will be for removing $HgCl_2$. Conditions that promote formation of HgO might be important if the removal of particulates is envisioned downstream of the oxidation zone. This leads us to discuss possible mechanisms involving oxygen-containing species as a concluding point of interest.

In our opinion, recent research has not focused enough attention on the possible reaction of Hg^0 with oxygen-containing species. Reactions of Hg^0 with oxygen-containing species (such as O_2, O, and OH) are plausible, and reactions that have pathways for Hg^0 to react with these (and perhaps other) oxygen-containing species should be included in an overall oxidation mechanism. Other than the discussion mentioned above by Hall et al.[13] on possible pathways that would include HgO as a product, only two other papers that we are aware of have discussed this possibility. Edwards et al.[31] included the reaction of Hg^0 with O in their model. However, they concluded that this reaction was unimportant for all the cases that they investigated. This conclusion was probably based on the fact that O is only present in trace amounts. The only other paper that discusses a possible role for HgO (both as a product and a reactant) is the very recent work of Xu et al.[42] Their model showed HgO as a minor product in all their calculations. Although the predicted amount of HgO product was low (1.5–6%), this provides some incentive for actually trying to measure the product distribution in either laboratory or field experiments with more precision than has been done in the past. If more detailed analyses were performed, measurable amounts of HgO might be discovered (probably in the "particulate" portion).

In conclusion, considerable progress has been made in recent years toward achieving an understanding of the mechanisms and kinetics of Hg oxidation in flue gas. Ongoing work, particularly in the area of modeling, is continuing to expand and enhance that understanding. Nevertheless, there is still a pressing need to conduct experimental investigations that will identify/verify the reaction pathways and products, measure the key kinetic parameters that are required for meaningful calculations, and investigate measures to tailor the reactions to maximize the efficacy of control.

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APPENDIX A:

SURVEY INSTRUMENT

APPENDIX A: SURVEY INSTRUMENT

Dear Colleague,

Many of us in the flue-gas cleanup community have devoted considerable effort to the topics of mercury measurement and control over the last decade (or more). Nevertheless, it seems that there is much yet to learn about the chemistry of mercury in combustors and flue-gas cleanup systems. A better understanding of that chemistry should enable us to develop improved control strategies for the future. With that in mind, DOE has asked Argonne to conduct a critical review of the available knowledge about mercury chemistry and to identify the most significant gaps in that knowledge.

We hope that you will be able to assist us in developing an initial focus for the review by responding to the brief survey below. In addition to the listed options, please feel free to add options and comments based upon your experience. We would also welcome suggestions about relevant literature or copies of publications that you may be able to provide.

1. Which of the following reaction types do you consider to be the most important in terms of Hg control technologies applied to coal-fired boiler plants?
   a. Gas phase reactions (homogeneous and/or heterogeneous)
   b. Gas-liquid reactions (both absorption and dissolution)
   c. Gas-solid reactions (adsorption and absorption)
   d. Liquid phase reactions (including reactions with liquid elemental Hg)
   e. Liquid-solid reactions (mainly adsorption or absorption of aqueous Hg by a solid sorbent)

2. Which of the following gaseous Hg species do you consider to be most important with respect to understanding their reaction chemistry?
   a. Elemental Hg
   b. $HgCl_2$
   c. HgCl (Hg_2Cl_2)
   d. Others (please specify)

3. Which of the following gaseous reactants do you consider to be most important with respect to understanding their reaction chemistry with elemental Hg or other Hg species?
   a. Cl_2
   b. HCl
   c. SO_2
   d. NO
   e. NO_2
   f. CO/CO_2
   g. O_2
   h. Others (please specify)

4. Which aspects of reaction chemistry do you consider most important to understanding and developing Hg control technologies for flue gas from coal-fired boilers?
    a. Equilibrium thermodynamics
    b. Reaction kinetics
    c. Reaction mechanisms (including reaction pathways and products)

5. Comments:

If possible, return your response to us via e-mail at mendelsohn@anl.gov. You may also fax it to C.D. Livengood at 630-252-3443. Thank you for your help in this endeavor.

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APPENDIX B:

LITERATURE SUMMARIES

APPENDIX B: LITERATURE SUMMARIES

Title: Predicting the Levels and Speciation of Mercury in Coal-Derived Utility Exhaust Streams
Author(s): S. Niksa and N. Fujiwara
Reference: Proceedings of the 28th International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, Florida, March 9–13, 2003.

Summary

A model is used to predict Hg speciation in coal-fired flue-gas streams. The model consists of 104 chemical mechanisms, including a heterogeneous oxidation mechanism on unburned carbon particles. Chemical mechanisms are similar to those developed in earlier papers. While homogeneous reaction mechanisms can accurately model much of the data reported in laboratory experiments without particulate matter, these models fail to accurately predict Hg oxidation in experiments performed on "real" coals with particulate matter being present (see paper by Fujiwara et al. 2002). For this reason, the authors have developed a heterogeneous reaction subset that can be combined with the homogeneous mechanism developed previously. Three reactions are included in the heterogeneous mechanism subset.

Important Data

The authors state "All the mercury leaving a furnace is elemental." Therefore, "the extent of Hg oxidation from the economizer outlet through the stack inlet is determined by chemical kinetics." "Oxidation and adsorption are not independent, because unburned carbon and high levels of Ca and Fe in flyash promote Hg oxidation, as apparent in the significant surge in the extent of oxidation across baghouse filter cakes." The most important factor in determining the extent of Hg oxidation is the amount of unburned carbon in the flyash. They found that as the amount of unburned carbon was increased from 0.1 to 7 wt.%, the predicted extents of Hg oxidation increased from 5 to 90%. The least important factors were found to be the concentrations of oxygen and nitric oxide. Quench rate was also found to have a substantial effect on the calculated extent of Hg oxidation. For example, the fastest quench rate tested gave the extent of Hg oxidation as 59%, the baseline quench rate gave 74.8%, and the slowest quench rate used gave a Hg oxidation of 93.5%. One conclusion these authors reach is that "We can find no basis in the reaction mechanisms to reliably estimate extents of Hg oxidation from coal-Cl contents as the primary independent variable."

Quality of Data

No independent kinetic data are reported in this paper. This paper represents the current "state of the art" (in our opinion) with regard to modeling the mechanism for Hg oxidation under realistic conditions that include particulate material represented as unburned carbon.

Title: Heterogeneous Oxidation of Mercury in Simulated Post Combustion Conditions
Author(s): G.A. Norton, H. Yang, R.C. Brown, D.L. Laudal, G.E. Dunham, and J. Erjavec
Reference: Fuel 82(2):107–116 (2003).

Summary

Heterogeneous Hg oxidation was studied by using fly ash samples from either Powder River Basin (sub-bituminous) or bituminous coal. These authors found that "The presence of NO_2, HCl, and SO_2 resulted in greater levels of mercury oxidation, while NO inhibited mercury oxidation." NO_2 plus HCl and NO_2 plus SO_2 produced higher levels of oxidation than either of those components alone. The highest level of Hg oxidation, however, was observed when all three gases were present.

Important Data

Significant Hg oxidation was found *only* in the presence of fly ash. Fly ash higher in iron (magnetic fly ash) appeared to be not as effective as non-magnetic fly ash in oxidizing Hg. However, the non-magnetic fly ash also had a higher surface area than the magnetic fly ash, thus making it difficult to draw any definitive conclusions regarding the effect of the presence of iron on Hg oxidation. Some contradictory evidence on the effect of particle size for gas blends with NO_2 plus HCl indicate that the synergistic effect of these two gases on heterogeneous Hg oxidation requires further study. There appears to be a correlation between Hg oxidation and the surface area of the fly ashes used in their study. However, the data also suggest that there is also a correlation with the amount of calcium in the lime. The level of Hg oxidation decreased as the amount of calcium decreased.

Quality of Data

No kinetic data are presented in this paper.

Title: Development of an Improved Model for Determining the Effects of SO_2 on Homogeneous Mercury Oxidation
Author(s): J. Qiu, R.O. Sterling, and J.J. Helble
Reference: Proceedings of the 28th International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, Florida, March 9–13, 2003.

Summary

This paper gives results of Hg oxidation experiments performed with four different levels of SO_2, ranging from 0 ppm to 500 ppm. Two different levels of chlorine and HCl were also tested. The results of these tests were compared with calculations of Hg oxidation by using a model detailed in the paper. The model is similar to that developed and used by others in recent papers. However, SO_x conversion reactions are included in this paper, along with 2 S-Cl-O reactions that appear not to have been considered previously. Eight Hg/HgCl and 5 Cl-containing species reactions are included and listed in two tables in the paper.

The calculations using their model indicated that "SO_2 strongly reduces Hg oxidation by either Cl_2 or HCl by scavenging of OH and O radicals." The agreement between their experimental results and the model calculations was excellent and was generally within 10%. Good agreement was also obtained with laboratory results of Ghorishi et al. (1998).

Important Data

Their calculated results show that Hg oxidation was reduced from 56% to 8% in the presence of 250 ppm Cl_2 when the concentration of SO_2 is increased from 0 to 500 ppm (lab results for these conditions were 61% with 0 ppm SO_2 and 10% with 500 ppm SO_2). Similarly, Hg oxidation decreased from 14% to 2% in the presence of 300 ppm HCl with the addition of just 100 ppm SO_2. No laboratory results are given for these conditions with HCl.

Quality of Data

No experimental details are given in this paper. The reader is referred to another conference paper published in 2000.

Title: Modeling of Homogeneous Mercury Speciation Using Detailed Chemical Kinetics
Author(s): M. Xu, Y. Qiao, C. Zheng, L. Li, and J. Liu
Reference: Combustion and Flame 132(1/2):208–218, 2003.

Summary

These authors used a chemical kinetic model for Hg oxidation that uses 107 reactions and 30 species. *All* of their reactions and species are given in an Appendix at the end of their paper. Besides the eight Hg/HgCl reactions used by others, these authors include six additional reactions that involve HgO. The rate constants for these HgO reactions were all calculated directly from transition state theory. These authors propose new Hg oxidation mechanisms not previously recognized. They suggest that the importance of HgO derives from an oxidation reaction of Hg with chlorine monoxide (ClO) that yields HgO and Cl atoms. All of their calculations predict the presence of 1.5–6.0% HgO in the final product mix.

Important Data

Rate constants (in Arrhenius form) are given for all 107 reactions in their model in an Appendix. Reasonable agreement with data of Mamani-Paco et al. (2000) was obtained. Addition of 10% v/v oxygen to the initial flue gas composition increases the percentage of Hg oxidized (according to their calculations) by about 5% on average. The two most important reactions involving HgO are suggested to be the reactions listed below:

$$Hg^0 + ClO \rightarrow HgO + Cl$$

$$HgO + HCl \rightarrow HgCl + OH$$

with the former reaction being the most important. This mechanism explains why production of $HgCl_2$ increases while HgO decreases. That is because of the possible pathway for elemental Hg into first HgO then HgCl and then finally $HgCl_2$.

Poor agreement using this model was obtained by using data from experiments by Widmer et al. (2000). On the other hand, good agreement was obtained with four of six data points from Sliger et al. (1998) (i.e., within 10%), while two model calculations were low by an average of 36% (32% and 40%).

Quality of Data

The rate constants for six reactions involving HgO appear to be new. These constants were all calculated by using transition state theory. Without understanding all of the details of these calculations, we cannot assess the quality of these data.

Conclusions

Although this model is probably superseded by the newer model of Niksa and Fujiwara (2003), it is of interest to note the effects that were discovered when reactions that included HgO were added to the original model developed by various authors in the 1998–2001 time period.

Title: Reactions of Gaseous Mercury with Atomic and Molecular Halogens: Kinetics, Product Studies, and Atmospheric Implications
Author(s): P.A. Ariya, A. Khalizov, and A. Gidas
Reference: Journal of Physical Chemistry A 106(32):7310–7320, 2002.

Summary

This paper presents experimental results for the rate constants of reactions of gaseous Hg^0 with Cl_2, Cl, Br_2, and Br. Reaction products were also analyzed in the gas phase, from suspended aerosols, and from the wall of the reactor.

The authors make the following conclusions: Reactions of gaseous Hg^0 with molecular halogens "are too slow to be important in atmospheric mercury transformation. Reactions of mercury with atomic halogens are considerably faster . ." However, they believe that Br is the only likely candidate to explain the rapid depletions of Hg^0 in the Arctic because of the much higher inferred concentration for Br compared with Cl atoms in this environment.

Important Data

Measured rate constants with gaseous Hg^0 at 298 K in N_2 were as follows.

Reactant	k (pseudo-first-order) ($cm^3 molecule^{-1} s^{-1}$)
Cl_2	$(2.6 \pm 0.2) \times 10^{-18}$
Cl	$(1.0 \pm 0.2) \times 10^{-11}$
Br_2	$<(0.9 \pm 0.2) \times 10^{-16}$
Br	$(3.2 \pm 0.3) \times 10^{-12}$

"The major products identified were $HgCl_2$ and $HgBr_2$ adsorbed on the wall. Suspended aerosols contributed less than 0.5% of the reaction products under their experimental conditions." Also, the authors note that "the amount of Hg_2X_2 and HgO in particulate form on the walls seems to be negligible."

Quality of Data

The data in this paper would appear to be of very high quality. The experimental equipment was described in detail, and the procedures used were explained in-depth.

Title: Hg Reactions in the Presence of Chlorine Species: Homogeneous Gas Phase and Heterogeneous Gas-Solid Phase
Author(s): T.G. Lee, E. Hedrick, and P. Biswas
Reference: Journal of the Air & Waste Management Association 52:1316–1323, 2002.

Summary

The kinetics of Hg chlorination with HCl were studied. The kinetic parameters for reaction order, overall rate constant, and activation energy were estimated. The effects of chlorine species (HCl, CH_2Cl_2) on a previously developed in-situ Hg-capture method were also investigated. This method involves production of UV-irradiated titanium dioxide (TiO_2) sorbent particles.

Important Data

The reaction order (with respect to the Hg concentration) was 1.55. The overall rate constant was $5.07 \times 10^{-2} \exp(-1939.68/T)\ [(\mu g/m^3)^{-0.55}(s^{-1})]$. Finally, the activation energy was determined to be 16.13 kJ/mol.

The rate of Hg oxidation in these experiments was *highly* dependent on the reaction temperature. Reaction temperatures ranged from 24°C to 190°C. Over that range, the overall rate constant increased from $7.4 \times 10^{-5}\ (\mu g/m^3)^{-0.55}\ s^{-1}$ to $7.7 \times 10^{-4}\ (\mu g/m^3)^{-0.55}\ s^{-1}$, or about one order of magnitude.

Quality of Data

The quality of the data appears to be good. There are two figures of the experimental setup and detailed descriptions of the equipment and procedures used.

Title: The Fate and Behavior of Mercury in Coal-Fired Power Plants
Author(s): R. Meij, L.H.J. Vredenbregt, and H. te Winkel
Reference: Journal of the Air & Waste Management Association 52:912–917, 2002.

Summary

This paper presents data showing that about 49% of the Hg was found in the ash material collected in the electrostatic precipitator (ESP), about 25.7% was found in various portions of the wet scrubber system, and about 25% was emitted into the air as gaseous Hg in the flue gases.

The authors suggest that coals with higher amounts of chlorine will emit more Hg in the oxidized form than those with lower chlorine contents. They also found that lower operating temperatures for the ESP result in higher Hg removal. In the flue-gas desulfurization (FGD) system, the authors found that the Hg ends up mainly in the sludge and gypsum components (i.e., associated with the solids).

Important Data

Data supporting the assertions above are given in the paper.

Quality of Data

In general, the data presented in this paper appear to be of good to excellent quality. One measure of the quality of the data is the mass balance obtained for various parts of the system. For example, an average mass balance of 96 ± 23% was obtained on the total Hg around a boiler and an ESP for eight different cases.

Title: A Mechanism for Mercury Oxidation in Coal-Derived Exhausts
Author(s): S. Niksa, N. Fujiwara, Y. Fujita, K. Tomura, H. Moritomi, T. Tuji, and S. Takasu
Reference: Journal of the Air & Waste Management Association 52:894–901, 2002.

Summary

This paper presents a Hg oxidation mechanism consisting of a homogeneous subset with 102 reactions and a three-step heterogeneous mechanism that includes unburned carbon (UBC) particles. The role of Cl atoms in the homogeneous mechanism is supplanted with carbon sites that have been chlorinated by HCl. Carbon is presumed to have a large storage capacity for Cl atoms over a broad temperature range. Therefore, Hg oxidation initiation is not problematic and super-equilibrium levels of Cl atoms are not required. These properties enabled Hg oxidation to occur with realistic quench rates.

Important Data

Agreement between the combined homogeneous/heterogeneous (HO-HE) model predictions and the experimental data, while not exceptional, was better than the results predicted from using the homogeneous model alone. Also, the HO-HE model was far superior in predicting the behavior of one particular coal with a high Cl content that had consistently high Hg oxidation performance.

Hg oxidation was found to depend most strongly on the surface area of the UBC downstream of the cyclone and on the LOI (loss-on-ignition) of the filter ash material.

Quality of Data

This paper is the first presentation of a model that includes effects of particulate matter, which is modeled in this case as UBC. This model is updated in the more recent paper of Niksa and Fujiwara in 2003 (summarized on page 35).

Title: Effect of NO_x Control Processes on Mercury Speciation in Utility Flue Gas
Author(s): C. Richardson, T. Machalek, S. Miller, C. Dene, and R. Chang
Reference: Journal of the Air & Waste Management Association 52:941–947, 2002.

Summary
This paper addresses the effects of various selective catalytic reduction (SCR) catalysts on the amount of Hg oxidation observed in several commercial utility power plant locations. One particular catalyst that was titanium/vanadium-based appeared to be superior to the others tested with regard to its ability to oxidize elemental Hg under various flue gas conditions.

Important Data
Intrinsic information is difficult to discern from the tests described in this paper because of the variability in test parameters.

Quality of Data
Good descriptive material is given for test methods, and a detailed discussion of the flue-gas Hg measurements is given.

Title: Mercury Oxidation in Coal-Fired Utility Boilers: Validation of Gas-Phase Kinetic Models
Author(s): C. Senior, Z. Chen, and A. Sarofim
Reference: Proceedings of the 95th Annual Conference and Exhibition of the Air & Waste Management Association, Baltimore, Maryland, June 23–27, 2002.

Summary

This is another paper that presents a mechanism for Hg oxidation chemistry. The Hg chemistry is identical to that proposed by Niksa (2001). These authors, however, make some changes in the chlorine chemistry that was used previously. Again, the rate constant for reactions of Hg with Cl_2 and HCl is estimated from analogous reactions with lead.

The model developed is tested against experimental data from several different studies.

Important Data

Not applicable.

Quality of Data

No independent rate data are reported in this paper.

Title: A Study of Gas-Phase Mercury Speciation Using Detailed Chemical Kinetics
Author(s): J.R. Edwards, R.K. Srivastava, and J.D. Kilgroe
Reference: Journal of the Air & Waste Management Association 51:869–877, 2001.

Summary

Although this article gives no new laboratory data, it does present a detailed chemical model that contains 60 reactions and 21 species. This model is used to explain experimental results published by two different authors that explore the effect of HCl on the oxidation of Hg^0 at elevated temperatures. For one set of laboratory data (B. Ghorishi, 1998), the model fit the experimental data extremely well at the highest temperature studied (754°C) for three different HCl concentrations (200, 100, and 50 ppmv). The model greatly *underpredicted* Hg oxidation at the two lower temperatures studied (515°C and 634°C). The fit at lower temperatures could be improved significantly by the addition of a trace amount of chlorine (1 ppmv) to the gas mixture.

A second set of experimental data obtained by Widmer et al. in 1998 was also modeled. Again, at the highest temperatures studied (771, 869, and 876°C), the model gave good results at two different HCl concentrations (300 and 3000 ppmv). However, at lower temperatures (from 424 to 649°C), the model once again significantly underpredicted the amount of Hg^0 oxidation.

In the conclusions, the authors give the following reasons for the underprediction of Hg^0 oxidation at lower temperatures: "These deviations may in the future be explained by the presence of trace Cl or Cl_2, significant errors in published reaction rates for lower temperatures, the need for additional chlorination and Hg oxidation pathways, or surface-induced catalysis effects."

Important data

Reaction rates were modeled using the Arrhenius equation:

$$K_f = C\, T^a \exp(-E_a/(RT))$$

with C in units of cm^3/mol-s and E_a in kJ/mol. A table is given in their appendix that lists values of C, a, and E_a for 18 different chemical reactions. For this part of our review, I will include only those for reactions with Hg or HgCl with Cl or Cl_2.

Reaction	C	a	E_a
$Hg^0 + Cl = HgCl$	1.95×10^{13}	0	0
$HgCl + Cl = HgCl_2$	1.95×10^{13}	0	0
$Hg^0 + Cl_2 = HgCl_2$	3.4×10^{9}	0	0

Although the authors do not state specifically where these rate constants came from, it appears to us that these are merely estimates or guesses. We say this because, as can be seen in the table above, the rates used for the first two reactions are identical, and both are simple first order rate constants with no temperature dependence. Also, the rate for the third reaction is the same as that for Hg plus O (oxygen atom) and is a first order rate constant and independent of temperature.

Quality of data

Because no independent data are presented, an assessment of quality does not apply. The authors did not indicate specifically where the rate constants in their appendix came from.

Title: Kinetic Modeling of Homogeneous Mercury Oxidation: The Importance of NO and H_2O in Predicting Oxidation in Coal-Derived Systems
Author(s): S. Niksa, J.J. Helble, and N. Fujiwara
Reference: Environmental Science & Technology 35(18):3701–3706, 2001.

Summary

This paper presents the development and evaluation of a reaction mechanism for homogeneous Hg oxidation. The authors begin their work by using the model developed by Widmer (2000). To these reactions are added a Cl oxidation submechanism, including the coupling of Cl and NO_x chemistry. Moist CO oxidation and H/N/O submechanisms are also added. A total of 102 elementary chemical reactions are included in their homogeneous Hg^0 oxidation mechanism. Four laboratory studies using HCl as the primary Cl-containing species were used to analyze their kinetic model. These studies each had different conditions, including test-gas composition. Besides Hg^0 and HCl, other gaseous components included O_2, CO_2, H_2O, and NO. Only one of the experiments included all of these components.

Nitric oxide was found to be an inhibitor of Hg oxidation, primarily through elimination of OH radicals. The authors state, "The impact of NO on homogeneous Hg oxidation is surprisingly strong." Moisture was also found to inhibit Hg^0 oxidation. On the other hand, model calculations showed that oxygen appears to be a weak promoter of homogeneous Hg^0 oxidation. Quench rate appears to be even more important than oxygen, however.

These authors propose that the dominant reaction channel for oxidation of Hg^0 is first an attack by Cl radicals to form HgCl and then reaction of HgCl with Cl_2 to form $HgCl_2$. This is similar to what was proposed in the paper by Widmer et al. (summarized on p. 56).

Important Data

Model calculations show that the effect of NO is complex. At low NO concentrations, it appears to promote Hg^0 oxidation, with a maximum effect observed with 25 ppm NO. At higher NO concentrations, it clearly inhibits Hg^0 oxidation until at a concentration of 100 ppm NO Hg^0 oxidation goes to zero (see Figure 5 in paper). A complex interaction between the absence or presence of NO and quench rate was also discovered. These behaviors are illustrated in Figure 6 of their paper.

Quality of Data

No independent rate data are reported in this paper.

Title: Mercury Transformations in Coal Combustion Flue Gas
Author(s): K. C. Galbreath and C. J. Zygarlicke
Reference: Fuel Processing Technology 65–66:289–310, 2000.

Summary

This paper primarily reviews information on mercury/fly-ash interactions in order to identify fundamental mechanisms involved in Hg combustion transformations. Some results of Hg transformations found for a laboratory-scale (42-MJ/h) coal combustion system are also presented. The importance of particulate-surface interactions with gaseous Hg species is corroborated by these experimental observations, especially for temperatures greater than 250°C.

Experimental results are limited to those obtained with one particular coal, known as Absaloka, a Powder River Basin subbituminous coal. Absaloka coal is low in both sulfur and chorine.

Important Data

The only relevant kinetic observation was that gaseous Hg in a gas mixture containing 8.5 vol% O_2 and 30 ppmv NO_x was transformed rapidly (<0.1 s) to oxidized Hg in a refractory-lined section of a combustor where the gas temperatures decreased from 620°C to 250°C. A Hg/O_2 reaction “catalyzed by $Al_2O_3(s)$ and/or $TiO_2(s)$ components of the refractory is postulated.” The “suspected reaction product” is $HgO(g)$.

Quality of Data

No new kinetic data are presented, other than the observation noted above.

Title: Effects of Flue Gas Constituents on Mercury Speciation
Author(s): D. L. Laudal, T. D. Brown, and B. R. Nott
Reference: Fuel Processing Technology 65–66:157–165, 2000.

Summary

Results in this paper were from a project to validate the Ontario Hydro method for Hg speciation. Authors tested several constituents, including SO_2, HCl, NO/NO_2, Cl_2, Hg^0, and $HgCl_2$, in a simulated flue gas. These variable constituents were in addition to fixed concentrations of oxygen (4%), carbon dioxide (15%), water vapor (10%), and nitrogen (N_2) for the balance. They found that addition of NO/NO_2 with fly ash resulted in significant conversion of Hg^0 to Hg^{+2}. However, without fly ash, there was little conversion. Chlorine, even without fly ash present, had a profound effect on Hg speciation (yielding over 80% oxidized Hg). Fly ash, NO_x, and SO_2 were also found to have significant effects. Sulfur dioxide was found to greatly reduce the Hg oxidation effect of chlorine and other combinations that contained chlorine. In contrast, HCl appeared to have little significance for Hg oxidation.

Important Data

No kinetic data are presented in this paper.

Quality of Data

The quality of the data presented in this paper was not assessed.

Title: Bench-Scale Examination of Mercury Oxidation Under Non-Isothermal Conditions
Author(s): R.M. Mamani-Paco and J. J. Helble
Reference: Proceedings of the Air & Waste Management Association 93rd Annual Conference and Exhibition, Salt Lake City, Utah, June 2000.

Summary

No reaction was observed between HCl and Hg at temperatures of from 750 to 1,150 K and a cooling rate of 400 K s^{-1}. Reaction with Cl_2 ranged from 10% conversion (oxidation) with 500 ppm Cl_2 to 92% conversion with 500 ppm Cl_2. An overall rate constant of $4.8 \pm 1.7 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} was obtained. No additional oxidation was observed at temperatures below 773 K and cooling rates less than 100 K s^{-1}. The authors suggested that reports in the literature of a rapid room-temperature homogeneous gas phase Hg oxidation by Cl_2 may have been influenced by surface reactions.

Important Data

Only very limited reaction of Hg^0 with HCl was observed (about 2%) at temperatures below 1,000 K and temperature gradients (cooling rates) of 100–500 K/s. Oxidation of Hg^0 with Cl_2 was dependent on Cl_2 concentration. Four different concentrations, from 50 to 500 ppm Cl_2, were studied. With 50 ppm Cl_2, the average Hg^0 oxidation found was about 9%, while with 500 ppm Cl_2, about 92% of the Hg^0 was oxidized (despite the lower temperature profile with this higher concentration). One test with both HCl and Cl_2 present gave the same result as with Cl_2 alone. The authors calculated a rate constant from Hall's (1991) data of 1.07×10^{-15} cm^3 $molecule^{-1}$ s^{-1}. They also calculated an activation energy from these data plus room temperature data of Seigneur (1994). The activation energy was calculated to be 3.7 kJ mol^{-1}.

Because the authors found no difference in the amount of Hg^0 oxidized between two of their sampling ports, they suggested that this indicated a "lack of reaction at 600 K." This implies that "fast reaction at ambient temperatures is unlikely." Finally, they concluded that "Reports of ambient and low temperature reaction in the literature are therefore likely reports of heterogeneous reaction and are not indicative of a room temperature gas phase pathway."

They calculated a rate constant for the global reaction by modeling a plug-flow reactor under non-isothermal conditions. Two values were obtained for two of their sampling ports. The higher-temperature port yielded a value of $4.8 \pm 1.7 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}, while the lower-temperature port gave a value of $2.4 \pm 1.0 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}.

Quality of Data

There is a fairly detailed description of the experimental apparatus and a schematic drawing of their experimental system. Two additional figures show the temperatures and physical placement of their sampling ports. In their conclusions, they provide a value for the global rate constant that appears to be inconsistent with other values given in the text and in the abstract. Other than this inconsistency, the quality of the data appears to be good.

Title: Effects of Fly Ash on Mercury Oxidation in Simulated Flue Gas Environments
Author(s): G.A. Norton, H. Yang, R.C. Brown, D.L. Laudal, G.E. Dunham, and J.M. Okoh
Reference: Proceedings of the Air & Waste Management Association 93rd Annual Conference and Exhibition, Salt Lake City, Utah, June 2000.

Summary

Hg oxidation was studied by using two different fly ashes. Results indicated that substantial amounts of Hg oxidation did not occur with either fly ash. The authors then say, "These results suggest that the gas matrix may be more important than the ash components with respect to the distribution of Hg species observed in gaseous effluents at coal-fired power plants." Tests with one of the fly ashes indicated that HCl, NO_2, and SO_2 were the critical gas components that dictated the degree of Hg oxidation. Also, NO appeared to suppress oxidation and "may also play an important role in Hg chemistry."

This paper appears to contain data reported in a more recent paper (see Norton et al. 2003) that was also reviewed for this report. That paper is summarized on page 36.

Important Data

See paper by Norton et al. 2003.

Quality of Data

Not assessed.

Title: Gas-Phase Transformations of Mercury in Coal-Fired Power Plants
Author(s): C.L. Senior, A.F. Sarofim, T. Zeng, J.J. Helble, R. Mamani-Paco
Reference: Fuel Processing Technology 63:197–213, 2000.

Summary

The authors' objective in this paper appears to have been to predict the rate of oxidation of Hg^0 from the furnace exit to the convective air heater (i.e., to predict Hg speciation at the inlet to the air pollution control device). An equilibrium model predicted complete oxidation of Hg^0 to $HgCl_2$ at temperatures below about 725 K (450°C). The chlorine content of the coal determines the temperature below which $HgCl_2$ is thermodynamically stable. For example, the 50:50 point for Hg^0:$HgCl_2$ decreases from about 900 K with 4,000 ppm Cl in the coal to about 830 K with 1,000 ppm Cl in the coal (see Figure 2 in paper). On the basis of the limited data available, the authors concluded "that the assumption of equilibrium for mercury species in coal combustion flue gas is not valid."

Their kinetic model showed that conversion of HCl to Cl_2 in the flue gas of a coal-fired power plant is kinetically limited. Therefore, at lower temperatures (lower than about 500 K), less than 1% of the chlorine is converted to Cl_2. To use their model, detailed knowledge of the super-equilibrium chlorine atom concentration as a function of temperature and cooling rate is required. That is because their primary reaction pathway is the reaction of Hg^0 with a chlorine atom to form HgCl.

Important Data

No independent rate data are given in this paper.

Quality of Data

Not applicable.

Title: Towards the Development of a Chemical Kinetic Model for the Homogeneous Oxidation of Mercury by Chlorine Species
Author(s): R.N. Sliger, J.C. Kramlich, and N.M. Marinov
Reference: Fuel Processing Technology 65–66:423–438, 2000.

Summary

Mercury oxidation was measured at temperatures from 860°C to 1171°C. A chemical kinetic model was proposed. The model suggested that "atomic chlorine is the key oxidizing species." Further, the authors suggested that "oxidation is limited to a temperature window between 700°C and 400°C." Their data suggested that the three most important factors affecting mercury concentration were as follows: "(1) HCl concentration, (2) quench rate, and (3) background gas composition."

Important Data

From the data of Hall et al. (1991), the second order rate constant for the reaction of Hg^0 with Cl_2 was found to be 3.4×10^9 cm^3/mol-s. This rate was substantially reduced in the presence of flue gas components, such as CO_2, H_2O, and O_2. The direct reaction of Hg^0 with HCl is "hindered by a very high energy barrier and cannot be considered as an important path under practical conditions."

Quality of Data

The quality of the data cannot be completely assessed because part of the experimental system has been described in another paper that was not a part of this review. Otherwise, there appears to be a minor contradiction in the paper as to the highest temperature for which data were taken. The abstract quotes a maximum temperature of 1171°C, while the graph in Figure 4 shows data up to a maximum temperature of 1071°C. Perhaps the 1171°C is a maximum possible temperature and not that at which data were actually observed.

Title: Development of an Elementary Homogeneous Mercury Oxidation Mechanism
Author(s): R.N. Sliger, J.C. Kramlich, and N.M. Marinov
Reference: Proceedings of the Air & Waste Management Association 93rd Annual Conference and Exhibition, Salt Lake City, Utah, June 2000.

Summary

From a review of the abstract, this paper appears to be similar to one from Fuel Processing Technology that is reviewed on page 53, and so the reader is referred to that review.

Important Data

See the review on page 53.

Quality of Data

See the review on page 53.

Title: Distribution Equilibrium of Mercury (II) Chloride between Water and Air Applied to Flue Gas Scrubbing
Author(s): J. Sommar, O. Lindqvist, and D. Stromberg
Reference: Journal of the Air & Waste Management Association 50:1663–1666, 2000.

Summary
This paper provides fundamental information on the gas/liquid equilibrium constant for mercuric chloride ($HgCl_2$). Because of these data, it is possible to conclude that waste incinerator scrubbers will probably not be saturated by $HgCl_2$.

Important Data
The equilibrium constant (Henry's law constant) for the distribution of $HgCl_2$ between water and air at 293 K was found to be 5×10^{-7} atm dm^3/mole. The temperature dependence for this constant between 283–323 K is 5.5×10^5 x $\exp[-(8060 \pm 2200)/T]$.

Quality of Data
The quality of the data determined in these laboratory tests was not assessed.

Title: Thermochemical Study of Mercury Oxidation in Utility Boiler Flue Gases
Author(s): N.C. Widmer, J. West, and J.A. Cole
Reference: Proceedings of the Air & Waste Management Association 93rd Annual Conference and Exhibition, Salt Lake City, Utah, June 2000.

Summary

This paper presented a study of the rate of mercury oxidation by chlorine species under municipal waste combustor exhaust conditions. The effect of thermal quench rates on these reactions was examined. A global reaction rate constant was developed, as was a kinetic mechanism. The predicted rate constant for the initial attack of Cl radicals on elemental Hg was about 10^{16} $cm^6mol^{-2}s^{-1}$.

Because of the much lower concentration of HCl under coal-fired utility conditions, observed rates of Hg oxidation are much slower.

The dearth of available experimental kinetic data is once again emphasized by a quote from the last line of their results and discussion section. They stated, "To date, very few reliable kinetic rate data have been measured for mercury species in combustion systems and a need for these data is evident."

Important Data:

The mechanism for Hg chemistry was described by using a series of eight reactions involving either Hg^0 or the radical molecular species HgCl as primary reactants. Chlorine reactants were Cl, Cl_2, HCl, or HOCl. Rate equations of the following form were used:

$$k_f = A \bullet T^{-B} \bullet \exp(-E_a/RT).$$

As the authors stated, "In the absence of actual rate data for the gas phase reactions of mercury, Arrhenius constant were estimated from a variety of sources." A table in their paper lists values for A, B, E_a, and ΔH_{rxn} for all 8 reactions.

Reactants	A (cm^3-mole-s)	B	E_a (kcal/mol)
Hg^0 (g) + Cl_2 (g)	1.39×10^{14}	0	34.0
Hg^0 (g) + HCl (g)	4.94×10^{14}	0	79.3

The rate they chose for the reaction with Cl_2 was about three orders of magnitude slower than the global rate derived by Sliger (1999) from the data of Hall (1991). For both reactions above, the pre-exponential factors were taken as those presented by Cosic and Fontijn (1999) for the corresponding reactions of lead. The activation energies were set equal to the reaction enthalpies.

Quality of Data

No independent rate data were reported in this paper.

Title: Mercury Speciation in Combustion Systems: Studies with Simulated Flue Gases and Model Fly Ashes
Author(s): S.B. Ghorishi, C.W. Lee, and J.D. Kilgroe
Reference: Proceedings of the Air & Waste Management Association 92nd Annual Meeting and Exhibition, St. Louis, Missouri, June 20–24, 1999.

Summary
Bench-scale experiments were performed to study the effects of various flue-gas and fly-ash parameters on the oxidation of Hg^0 in simulated flue gases containing HCl, NO, NO_2, SO_2, and water vapor. Oxidation was very slow at temperatures below 350°C. With HCl, Hg^0 oxidation occurred at measurable rates only at high temperatures (>700°C) and high HCl concentrations (>200 ppm). The presence of SO_2 and H_2O in the flue gas significantly inhibited the gas phase oxidation of Hg^0 by HCl.

Alumina and silica model fly ashes were inactive for the oxidation of Hg^0 in the presence of HCl, but they were active in the presence of NO. Cupric oxide (CuO) and Fe_2O_3 exhibited significant catalytic activity in the oxidation of Hg^0 when either HCl or NO was present. It was hypothesized that these oxide surfaces could convert HCl to Cl_2, thus significantly affecting Hg^0 oxidation. The Deacon process, which converts HCl to chlorine via the reaction below, was hypothesized to be the reason for the improved oxidation of Hg^0 in the presence of certain fly ashes.

$$2\,HCl + 1/2\,O_2 \rightarrow Cl_2 + H_2O \text{ (Deacon process reaction)}$$

CuO was much more effective than Fe_2O_3 for Hg^0 oxidation and was less sensitive to the negative effects of SO_2 and H_2O. As little as 0.1 wt% CuO in the model fly ash yielded a Hg^0 oxidation result of 95% in the temperature range of 150–250°C. A similar performance was obtained with 14 wt% Fe_2O_3. “The mechanism for the heterogeneous oxidation of Hg in the presence of NO is unknown at this time.”

Important Data
Graphical data were presented on the extent of Hg^0 oxidation in simulated flue gas streams with and without SO_2 and H_2O, at different HCl concentrations and at different temperatures. Graphical data were also presented on the effect of different model fly ashes on the extent of Hg^0 oxidation at different temperatures and with or without SO_2.

Quality of Data
The quality of the data could not be completely assessed as a detailed description of the experimental setup was given in another paper not reviewed as a part of this work.

Title: Mercury Control Research: Effects of Fly Ash and Flue Gas Parameters on Mercury Speciation
Author(s): S.B. Ghorishi, C.W. Lee, and J.D. Kilgroe
Reference: Proceedings of the 6th Annual Waste-to-Energy Conference, Miami Beach, Florida, May 11–13, 1998.

Summary

This paper is similar to the more recent paper by the same authors published in the Proceedings of the 92nd Air & Waste Management Association Annual Meeting, which was reviewed on page B-25. (One of the authors [Ghorishi] has communicated this information to us.)

Important Data

See the preceding review on page B-25.

Quality of Data

See the preceding review on page B-25.

Title: Atmospheric Mercury — An Overview
Author(s): W.H. Schroeder and J. Munthe
Reference: Atmospheric Environment 32(5):809–822, 1998.

Summary

This paper has been cited 97 times according to ISI's Web of Science database. The importance of this paper, as viewed by others, is likely due to the large number of references that it contains. This paper referenced 103 other works and can, therefore, be viewed as an important introduction to this field, as well as a thorough summary of the current knowledge (up to early 1997) in the field of mercury in the atmosphere. However, rather than emphasizing Hg chemistry, this review discusses many different atmospheric pathways and processes, including "anthropogenic and natural sources of Hg emissions to the atmosphere, aerial transport and dispersion (including spatial and temporal variability), atmospheric transformations (both physical and chemical types), wet and dry removal/deposition processes to Earth's surface." Also reviewed were numeric models that dealt with atmospheric transport models and process-oriented models. However, there is no specific review or discussion of Hg/Cl chemistry in this paper.

Important Data

Not applicable.

Quality of data

Not applicable.

Title: Kinetic Investigation of the High-Temperature Oxidation of Mercury by Chlorine Species
Author(s): N.R. Sliger, J.D. Going, and J.C. Kramlich
Reference: Western State Section/The Combustion Institute, Fall Meeting, Seattle, Washington, 1998.

Summary

This paper is referenced by Xu et al. 2003 regarding data that are taken from this paper and used to compare to model calculations. The data given in the paper of Xu et al. appear identical to data given in the Sliger et al. paper of 2000 (see previous review). We did not obtain a copy of this specific publication for our review.

Important Data

Not applicable.

Quality of data

Not applicable.

Title: Practical Limitation of Mercury Speciation in Simulated Municipal Waste Incinerator Flue Gas
Author(s): N.C. Widmer, J.A. Cole, W.R. Seeker, and J.A. Gaspar
Reference: Combustion Science and Technology, 13:315–326, 1998.

Summary

The fate of gaseous Hg was studied at different temperatures by using a simulated municipal solid waste incinerator exhaust gas. Two different concentrations of HCl were used: 300 and 3000 ppmv. The initial Hg concentration was 3000 $\mu g/m^3$. The authors found that Hg speciation approaches equilibrium at 800°C when sufficient residence time is provided. The abstract does not say how much time this is. At temperatures below 800°C, conversion to HgO is kinetically limited, and the data are fit by an Arrhenius correlation with an activation energy of 45.4 kJ/mol. The impact of HCl concentration on Hg conversion to the chloride is at least as strong as the effect of temperature. At lower HCl concentrations, conversion is limited by thermodynamics at higher temperatures and by kinetics at lower temperatures.

Important Data

Oxidized Hg (assumed to be $HgCl_2$) levels appeared to attain equilibrium values when the reactor temperature was above about 700°C. They were considerably below equilibrium levels at lower temperatures, especially at the lower HCl concentration (300 ppmv). A kinetic limitation at the lower temperatures was suggested because those data fit a plot of ln k vs. 1/T when k was calculated by using the equation below.

$$\ln P_{Hg}/P^0_{Hg} = -k*P_{HCl}*t$$

This analysis yielded a pre-exponential factor of 2.2×10^7 L/mol-s and an activation energy of 45.4 kJ/mol. Finally, plots are given that show that temperature, as well as HCl concentration, is an important factor in determining the time constant for conversion of Hg^0 to $HgCl_2$.

Quality of Data:

The data in this paper appear to be of reasonably good quality in that their apparatus and procedure are illustrated and described in fair detail. However, a Method 29 sampling train was used to speciate the Hg at the outlet of their reactor, and possible inaccuracies in this method have recently been discussed by Laudal et al.

Title: Mercury from Combustion Sources: A Review of the Chemical Species Emitted and their Transport in the Atmosphere
Author(s): A. Carpi
Reference: Water, Air, and Soil Pollution 98:241–254, 1997.

Summary

This article was intended to be a review of the knowledge at that time "about emissions of mercury species from coal and municipal solid waste facilities, and the fate and transport of these species in the atmosphere." In the first part of this paper, mercury emissions and their control are reviewed. One of the author's conclusions is that "The partitioning of mercury between Hg^0 and Hg(II) (possibly $HgCl_2$) is likely dependent on the concentration of HCl and other pollutants in the feed stocks and stack emissions."

The second part of this paper reviews work related to the transport and reaction of mercury in the atmosphere. The only reference to chlorine in this section is a paper by Seigneur et al. that is reviewed later in this section.

In the conclusions, the author states, "Although of increasing regulatory concern, the speciation and transport of mercury in the atmosphere are not well understood."

Important data

No independently determined data were presented in this paper.

Quality of data

Because no independent data are presented, an assessment of quality does not apply. Regarding the data that are reviewed, this paper does not assess the quality of that data.

Title: Modelling the Atmospheric Mercury Cycle — Chemistry in Fog Droplets
Author(s): K. Pleijel and J. Munthe
Reference: Atmospheric Environment 29(12):1441–1457, 1995.

Summary

This paper presents a detailed model that describes the mass transport and chemistry of different forms of mercury in the atmosphere. The primary focus is on the behavior of mercury dissolved in fog droplets. Although 80 reactions describing gas-phase chemistry are included in this model, none of them include Hg or Hg-containing species. The only gas-phase reaction containing Hg that is discussed in this paper is the reaction of gaseous Hg^0 with ozone. Two references are given (P'yankov 1949; Yarwood and Niki 1990) for this reaction. A value of 4.9×10^{-18} molecule cm^{-3} s^{-1} is given as a calculated value from Yarwood and Niki's paper, on the basis of P'yankov's data. However, the authors note, on the basis of a then-recent paper by Hall (1995), that this value is likely greatly overestimated and, therefore, the lifetime of Hg^0 in the atmosphere is likely much greater than what this rate constant would imply. The authors state that an atmospheric chemical lifetime of 6–12 months is indicated with the newer results.

Important Data

Not applicable.

Quality of Data

Not applicable.

Title: A Chemical Kinetic Mechanism for Atmospheric Inorganic Mercury
Author(s): C. Seigneur, J. Wrobel, and E. Constantinou
Reference: Environmental Science & Technology 28(9):1589–1597, 1994.

Summary

This is a fairly comprehensive paper that attempts to develop a chemical model for the atmospheric chemistry of Hg and its compounds. Tables of equilibrium constants and rate parameters are presented for gas-phase reactions, as well as aqueous-phase and gas-solid reactions. Gas-liquid and water-solid equilibria data are also given.

One of the important results in this paper is the effect that the presence of HCl has on the ratio of Hg^0 to Hg(II) in the liquid phase, either with or without dissolved SO_2. HCl also affected this ratio when the effect of pH was examined.

In several places in this paper, the authors state the uncertainties in the data that they were using. For example, in the abstract they state, "However, large uncertainties exist in the gas-phase reaction rates of Hg(0) with Cl_2, O_3, and H_2O_2, and the overall half-life of Hg(0) due to chemical reactions in the atmosphere cannot be assessed with certainty without further laboratory kinetic data." Other gaps in the data are mentioned in their conclusions when they state, "It should be noted that several processes are not presently included in the chemical kinetic model because of a lack of data. Such processes include the mass transfer kinetics of Hg between the gas phase and aerosol/droplets and the atmospheric chemistry of organic mercury species."

Important data

The following literature data for reaction of Hg^0 with Cl_2 and HCl in the gas phase are presented in their Table 2.

Reactants	Rate parameter (cm^3 $molecule^{-1}$ s^{-1})	Reference
Hg^0 (g) + Cl_2 (g)	$\leq 4.1 \times 10^{-16}$	W.H. Schroeder 1991; B. Hall, Ph.D. Thesis, 1992
Hg^0 (g) + HCl (g)	1.0×10^{-19}	B. Hall, EPRI Report, 1993

Quality of data

Because no independent data are given, an assessment of quality does not apply. Regarding the data that are presented, this paper does not assess the quality of those data.

Title: Transformation Processes Involving Mercury Species in the Atmosphere — Results from a Literature Survey (vol. 56, p. 653, 1991)
Author(s): W.H. Schroeder, G. Yarwood, and H. Niki
Reference: Water, Air, and Soil Pollution 66:203–203, 1993.

Summary
An Erratum gives a correction to one value published in Table I of the original paper.

Important Data
The water solubility of Hg^0 at 20°C was incorrectly published as 63.9 µg/L. This is actually the value at 25°C. The correct solubility at 20°C is 45.0 µg/L.

Quality of data
This correction appears to be appropriate.

Title: Reactions Between Mercury Vapor and Chlorine Gas at Occupational Exposure Levels
Author(s): I. Skare and R. Johansson
Reference: Chemosphere 24(11):1633–1644, 1992.

Summary

This study was intended to look at the reaction of gaseous Hg^0 at a concentration of about 10 ppb with gaseous Cl_2 at a concentration of about 1 ppm. This situation results in about a 1,000-fold stoichiometric excess of Cl_2. An important difference in this experiment from previous work is that the authors were able to show that their Tedlar container did *not* absorb any appreciable amounts of Hg^0-vapor in the absence of Cl_2 gas. Therefore, when the mixture was studied, the authors were able to attribute the disappearance of Hg^0 to the homogeneous gas-phase reaction of these two components.

The authors also studied the reaction of Hg^0 and gaseous Cl_2 when bubbled through various aqueous solutions. Mercury transfer in the range of 60–70% to the liquid phase was observed for 0.1 M HCl, 0.1 M NaCl, and 0.1 M NaOH solutions. However, mucin and natural saliva solutions showed almost no transfer of Hg^0.

In addition to the gas-phase and gas-liquid experiments mentioned above, the authors also briefly looked at the reaction of Hg^0 and Cl_2 in contact with a glass surface. In agreement with two other reviewed papers (Medhekar 1979; Hall 1991), these workers also observed an important surface-catalyzed reaction. They stated the following: "After a prolonged exposure of the cell from air mixtures containing Hg^0-vapor and chlorine gas, however, the overall reaction rate was getting much faster, thus indicating that mercury-chloride deposits previously formed on the walls should play an important role in catalyzing these surface reactions."

Finally, the authors disputed the conclusions of a toxicological study performed by Viola and Cassano in 1968 concerning the effect of chlorine on Hg vapor intoxication. They maintained that the earlier work (1) used too high a Hg concentration to be relevant and (2) did not recognize the importance that the formation of solid $HgCl_x$ products could play both in the experimental design and in the analyses.

Important data

When Hg^0 and Cl_2 were stored together at 25°C for 24 h, there was a significant reduction in gas phase Hg^0 concentration both with and without moisture added to the gas mixture. This reduction amounted to about 40% of the original Hg^0. However, their data indicated that the majority (if not all) of the $HgCl_x$ product produced in this reaction was *not* gaseous, but most likely a solid product that forms on the walls of their Tedlar container. The authors also stated that their slow observed reaction of Hg^0 with Cl_2 (~2% per hour at 25°C) is "not inconsistent with results from Iverfeldt and Lindqvist 1984 and 1986, stating that the homogeneous gas phase oxidation of Hg^0-vapor, even with ozone, is very slow."

Quality of data

These data appear to be of high quality for two main reasons. First, well-designed baseline tests have been performed to confirm that Hg^0 does not disappear or react with the reaction container over a period of 24 h when Cl_2 is not present. Second, a detailed description of the experimental apparatus and procedures is given in the paper.

Title: Chemical Reactions of Mercury in Combustion Flue Gases
Author(s): B. Hall, P. Schager, and O. Lindqvist
Reference: Water, Air, and Soil Pollution 56:3–14, 1991.

Summary

This paper talks about the reaction of gaseous Hg^0 with several components of flue gas, including NH_3, N_2O, SO_2, H_2S, O_2, and NO_2. However, for this part of our review, we have concentrated only their data for reactions with HCl and Cl_2.

Interestingly, the authors mentioned that they had to perform several trials before obtaining reproducible results. They further stated that "This is probably due to formation of a product on the surface of the reaction cell, which influences the rate of the overall reaction." They cite this result as being in agreement with that reported by Medhekar (1979).

Important data

The data relevant to chemical mechanisms are presented in graphical form in this paper. One graph for the reaction with HCl visually depicts a decline in Hg^0 concentration as the HCl concentration increases from 0 to a maximum of 150 µL/L at 500°C. In words, they state that "The reaction rate increases with increasing temperature, and at 900°C more than 90% of the gaseous Hg is oxidized in less than 1 sec." This yields a minimum calculated rate constant of 0.9 s^{-1}, assuming simple first-order kinetics. They postulated two possible reaction mechanisms that involve molecular oxygen:

$$2\ Hg^0\ (g) + 4\ HCl\ (g) + O_2\ (g) \rightarrow 2\ HgCl_2\ (s,g) + 2\ H_2O\ (g)$$

$$4\ Hg^0\ (g) + 4\ HCl\ (g) + O_2\ (g) \rightarrow 2\ Hg_2Cl_2\ (s) + 2\ H_2O\ (g)$$

Similarly, the graph for reaction with Cl_2 shows that the Hg^0 concentration declines as a function of the Cl_2 concentration at temperatures from 20°C to 700°C. At 500°C, they found that 70% of the Hg^0 was oxidized in 1.5 s. From these data, we can estimate a simple first-order rate constant of 0.47 s^{-1}. They state that at 700°C, the reaction time is 0.8 s, while at 20°C, it was 2.8 s. (It is not clear if these data are for the same 70% reaction condition as noted above for 500°C.) From these data, one could attempt to estimate an activation energy for this reaction. As in the case of HCl, two possible mechanisms are proposed for these reactants:

$$Hg^0\ (g) + Cl_2\ (g) \rightarrow HgCl_2\ (s,g)$$

$$2\ Hg^0\ (g) + Cl_2\ (g) \rightarrow Hg_2Cl_2\ (s)$$

Quality of data

We would describe the experimental descriptions given in this paper as being of moderate detail. Although most system components appear to be identified in a figure, no dimensional details are given. We would therefore rate the overall quality of the data as moderate to high.

Title: Transformation Processes Involving Mercury Species in the Atmosphere — Results from a Literature Survey
Author(s): W.H. Schroeder, G. Yarwood, and H. Niki
Reference: Water, Air, and Soil Pollution 56:653–666, 1991.

Summary

This paper likely represents the most comprehensive review of the literature relevant to mercury chemistry in the atmosphere published up to the time (the most recent references in this report are from 1990). This paper references two other literature reviews that were available as reports to the organization Environment Canada. The current availability of these two referenced reports is not known. However, the authors stated that "selected results from these reports are presented here." With regard to the gas-phase chemistry of Hg^0 with Cl_2, the authors referenced the work of P'yankov (1949) and Menke and Wallis (1980). No other references related to Hg/Cl chemistry are given in this paper.

Important Data

These authors calculated a rate constant for the reaction of gaseous Hg^0 with gaseous Cl_2 on the basis of the data of Menke and Wallis. The value given in their paper is described as "an upper limit." The value reported was calculated from "the lowest values observed, viz., 4×10^{-16} cm^3 $molecule^{-1}$ s^{-1} (at $[Cl_2(g)] = 4.4$ and 10.3 mg m^{-3}; R.H. = 13%)."

Quality of data

The value given for the rate constant appears to be an accurate estimate based on the data of Menke and Wallis (1980). However, there are questions regarding the data of Menke and Wallis, as noted in the review of that paper presented later in this section.

Title: Mercury Chemistry in Simulated Flue Gases Related to Waste Incineration Conditions
Author(s): B. Hall, O. Lindqvist, and E. Ljungstrom
Reference: Environmental Science & Technology 24(1):108–111, 1990.

Summary

These authors studied the reaction of gaseous Hg^0 with HCl in a simulated flue gas produced from a propane burner. Without HCl present, about 20–30% of the Hg^0 was oxidized, presumably by O_2 to mercuric oxide (HgO). When HCl was added to the gas mixture, roughly 60–70% of the Hg^0 was oxidized. When HCl is present, several reactions are possible, including direct reaction with HgO and indirect reaction (via formation of Cl_2) with Hg^0. The authors postulated that HCl can react with HgO (g,s) to produce mercuric chloride and water vapor. They also suggested that Cl_2 produced via reaction of HCl with O_2 can produce gaseous mercuric chloride and/or solid mercurous chloride (Hg_2Cl_2). While these may be viewed as overall reactions, the authors clearly stated that “the mechanisms for oxidation and chloride formation are not known in detail.”

Evidence in this paper suggests that the most likely reaction product is gaseous mercuric chloride. “This conclusion is in agreement with previous reports on solid waste incineration, where it has been proposed that nearly all mercury exists as mercury chlorides, predominantly mercury (II) chloride.” Two literature references are given to support this statement.

At lower temperatures (around 150–200°C), reduction of oxidized Hg occurred in many of their experiments. This is attributed to reaction of oxidized Hg with an activated iron surface on their steel duct. The type of steel used in their apparatus was not given.

Some observations not related to reaction with HCl are also made in this paper. Among the most important was the statement that while reaction of gaseous Hg^0 with oxygen can occur in the temperature range of 300–500°C, “at temperatures lower than 300°C, the reaction rate is probably too slow.” Also, some tests with activated carbon were performed (without HCl present). The results showed a significant amount of the Hg^0 was oxidized (around 60–70%). This is attributed to the activated carbon behaving as a catalyst for the reaction of Hg^0 with oxygen. In this case, about 13–20% of the total Hg was recovered as a solid product.

Important data

Most important was the conclusion that the most likely product of the reaction of Hg^0 with HCl was mercuric chloride. As for the kinetics, the vast majority of the reaction of Hg^0 with oxygen appears to occur in 0.8 s or less. A similar conclusion can be reached for the reaction of Hg^0 with HCl. However, these are *not* constant temperature experiments, and therefore these kinetic data are only of limited usefulness.

Quality of data:

The quality of the data in this paper appears to be above average. Baseline tests were performed, and the data appear to be internally consistent. Diagrams of the experimental apparatus and the analytical system are given. Some details of the apparatus appear to be missing, such as the type of steel used for the duct.

Title: A Critical Review of Available Information on Transformation Pathways for Mercury Species in the Atmospheric Environment
Author(s): G. Yarwood and H. Niki
Reference: Report prepared for Atmospheric Environment Service, Environment Canada, Downsview, Ontario, Canada, 1990.

Summary
This report is referred to in both the paper of Schroeder et al. (1991) and the paper of Pleijel and Munthe (1995). Selected results from this report are presented by Schroeder et al. A copy of this report was not obtained for this review.

Important Data
Not known.

Quality of Data
Not known.

Title: A Flowing-Afterglow Study of the Quenching Reactions of Hg($^3P_2$) and Hg($^3P_0$) Atoms by Halogens, Interhalogens, and Polyatomic Halide Molecules
Author(s): F.M. Zhang, D. Oba, and D.W. Setser
Reference: Journal of Physical Chemistry 91(5):1099–1114, 1987.

Important data
Relative rate constants are calculated for the formation of HgX from excited Hg atoms and molecular halogens. Part of their Table II is reproduced below.

Reagent	k (HgX, B) (cm^3 molecule^{-1}sec^{-1})
Cl_2	32×10^{-11}
Br_2	50×10^{-11}
I_2	40×10^{-11}

Comments
In this paper, the authors specifically mentioned that the flow reactor was maintained at a temperature of ~50°C. Unlike the next two papers, a rate constant for the reaction of Hg with I_2 is included.

Quality of data
Same comments as for Dreiling and Setser (1982) (see the summary on page 74).

Title: Interpretations of the Mercury Halide ($B^2\Sigma^+$ -$X^2\Sigma^+$) Chemiluminescence from Reactive Quenching of Hg($^3P_2$) by Halogen Containing Molecules
Author(s): T.D. Dreiling and D.W. Setser
Reference: Journal of Chemical Physics 79(11):5423–5438, 1983.

Important data
Relative rate constants are calculated for the formation of HgX from excited Hg atoms and molecular halogens. Results are the same as those given in the table from Dreiling and Setser (1982) in the review on page 74.

Comments
See the summary on page 74.

Quality of data
See the summary on page 74.

Title: A Flowing Afterglow Source of Hg($^3P_0$) and Hg($^3P_2$) Atoms: Application to HgX(B), X = F, Cl, Br and I, Formation Kinetics
Author(s): T.D. Dreiling and D.W. Setser
Reference: Journal of Physical Chemistry 86(13):2276–2279, 1982.

Important data

Relative rate constants are calculated for the formation of HgX from excited Hg atoms and molecular halogens. Part of their Table I is reproduced below.

Reagent	k (HgX, B) (cm^3 molecule^{-1}sec^{-1})
F_2	99×10^{-11}
Cl_2	32×10^{-11}
Br_2	50×10^{-11}

Comments

Even though this work examines the reaction of gaseous Hg atoms with Cl_2 molecules, the results are not readily comparable to the results of the study by Krause et al. described on page 79. This is primarily because this study uses excited-state Hg atoms produced in a dc discharge device. The primary product in this reaction is HgX, whereas in the other experiments, the primary product was assumed to be $HgCl_2$. The units for the rate constant in this study appear to be the inverse of those evaluated in the previous paper.

The temperature of the reactor in these tests is not explicitly given. However, in a later paper with the same senior author, the reactor temperature was given as ~50°C.

Quality of data

The experimental techniques used are outside our general area of experience, and so we will not assess the quality of the data obtained in these tests. However, we can note that their result for the Cl_2 reaction agrees well with that reported in another paper in the literature (Krause 1975).

Title: Homogeneous and Heterogeneous Reactions of Mercury and Some of its Compounds in the Atmosphere
Author(s): Concord Scientific Corporation
Reference: Report prepared for Atmospheric Environment Service, Environment Canada, Downsview, Ontario, Canada, 1981.

Summary
This report is referred to in the paper by Schroeder et al. (1991), and selected results from this report are presented. A copy of this report was not obtained for this review.

Important Data
Not known.

Quality of Data
Not known.

Title: Detection of Mercury in Air in the Presence of Chlorine and Water Vapor
Author(s): R. Menke and G. Wallis
Reference: American Industrial Hygiene Association Journal 41(2):120–124, 1980.

Summary

The interaction of mercury with chlorine vapor at two levels of relative humidity was studied. Other authors have used these data to calculate a rate constant for the reaction of gaseous Hg^0 with molecular Cl_2. These authors have likely assumed a reaction time of 8 s, as this is the residence time given in this paper.

Important Data

Authors have assumed that the reaction product ("possibly $HgCl_2$") is absorbed in polyurethane. Both tabular and graphical data for the amount of Hg absorbed in polyurethane are presented for four different chlorine concentrations (0, 0.5, 1.5, and 3.8 ppm) and at two different relative humidities (13% and 80%).

Quality of Data

A diagram of the experimental setup is given. However, the temperature of the final gas mixture is not given. It can be assumed to be at room temperature, but this is not explicitly stated. Each set of experimental conditions was tested at least four times. The residence time is given as "about" 8 s at a flow rate of 1.4 L/min. Possible variations in flow rate are not discussed.

In our opinion, use of this data to calculate a rate constant is severely limited by the fact that essentially only one point is used on a rate curve that was obtained for a residence time of 8 s. Therefore, these data should be used only with caution and may very well represent only an upper limit for the overall rate constant.

Title: Surface Catalyzed Reaction of Hg + Cl_2
Author(s): A.K. Medhekar, M. Rokni, D.W. Trainor, and J.H. Jacob
Reference: Chemical Physics Letters 65(3):600–604, 1979.

Summary

This paper asserts and provides evidence that the gas-phase reaction of Hg^0 atoms and Cl_2 occurs via a surface-catalyzed mechanism. The authors further asserted that a surface coating of $HgCl_2$ or $(HgCl_2)_n$ that is formed quickly dominates and makes the initially different surface materials behave in a similar manner. Surface materials tested included Inconel (least reactive) < quartz < stainless steel < Teflon-coated stainless steel.

The authors state on page 603 that the reaction mechanism is consistent with a "diffusion dominated heterogeneous surface reaction."

Important data

Regardless of the wall material used, the reaction rate became faster until it was the same for all materials tested after a few runs. The authors conclude that "the reaction products formed on the surface eventually dominate the surface chemistry."

By assuming a simple first-order rate model, we calculate a rate constant for the reaction of gaseous Hg^0 with Cl_2 to be the following from the data presented in two graphical figures (3b and 4b) in their paper.

Temperature (°C)	Total Pressure (atm)	k (mole cm-3 s-1)
250	0.95	2.0×10^{-10}
250	2.0	1.05×10^{-10}

Quality of data

These experiments appear to have been done in a well-controlled environment. Several different variables were tested to validate the above assertions, including wall materials, total gas pressure, and reaction cell diameter.

Title: Kinetics of the Reaction between Mercury Vapor and Ozone
Author(s): V.A. P'yankov
Reference: Zhur. Obshchei Khim. 19:224–229, 1949; Journal of General Chemistry USSR (Engl. Transl.) **19**:187–192, 1949.

Summary

Although the original paper is written in Russian, an English translation exists and can be obtained. An alternative to this is an English review of this paper in Chemical Abstracts. For this review, we have used the English review as the source of information.

Although the primary topic of this paper is the reaction of Hg vapor with ozone, the author also reports on some experiments that were performed on the reaction of Hg with Cl_2 in an air stream. For this reaction, a product mixture of mercurous and mercuric chlorides is reported with the majority of the product being Hg_2Cl_2. The percentage of mercuric chloride in the product increases as the ratio of Cl/Hg increases, but only slowly. Kinetic measurements could not be made because the reaction was "too fast." Although not specifically stated in the review, the reaction was likely studied at 20°C, as this is the temperature at which the Hg vapor was produced.

Important data

The table below shows results for the percentage of Hg(II) species (assumed to be mercuric chloride) in the product as a function of the ratio of Cl/Hg in the reactant mixture.

Cl/Hg	Hg (II) (%)
2	7.3
4	12.3
8	19.0
16	28.6

The statement, "The reaction is too fast for kinetic measurements," is from the abstract and was presumably extracted directly from the Russian text.

Quality of data

The quality of the data from this paper cannot be fairly assessed unless a complete English translation of the original Russian paper could be obtained and reviewed. However, we can note that in the original Russian paper there is a diagram of the experimental apparatus. Also, there are four figures and six tables of data presented.

Related References Not Reviewed in Detail

Title: *Reactions of Metal Atoms. I. The Combination of Mercury and Chlorine Atoms and the Dimerization of HgCl*
Author(s): D.G. Horne, R. Gosavi, and O.P. Strausz
Reference: Journal of Chemical Physics 48(10):4758–4764, 1968.

Title: *Crossed Molecular Beam Study of Excited Atom Reactions: Hg(6 $^3P_2^0$) with Cl_2 and Chlorinated Methane Molecules*
Author(s): H.F. Krause, S.G. Johnson, S. Datz, and F.K. Schmidt-Bleek
Reference: Chemical Physics Letters 31(3):577–581, 1975.

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