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Inhibition of hydrogen oxidation by HBr and Br_2

Graham Dixon-Lewis [a,1], Paul Marshall [b], Branko Ruscic [c], Alexander Burcat [d], Elke Goos [e], Alberto Cuoci [f], Alessio Frassoldati [f], Tiziano Faravelli [f], Peter Glarborg [g,*]

[a] Department of Fuel and Energy, University of Leeds, Leeds LS2 9JT, UK
[b] Department of Chemistry and Center for Advanced Scientific Computing and Modeling (CASCaM), University of North Texas, Denton, 1155 Union Circle #305070, TX 76203-5017, United States
[c] Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439, United States
[d] Faculty of Aerospace Engineering, Technion – Israel Institute of Technology, Haifa 32000, Israel
[e] Institute of Combustion Technology, DLR, Pfaffenwaldring 38-40, D-70569 Stuttgart, Germany
[f] Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta", Politecnico di Milano, P.zza Leonardo da Vinci 32, 20133 Milano, Italy
[g] DTU Chemical Engineering, Technical University of Denmark, 2800 Lyngby, Denmark

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ABSTRACT

The high-temperature bromine chemistry was updated and the inhibition mechanisms involving HBr and Br_2 were re-examined. The thermochemistry of the bromine species was obtained using the Active Thermochemical Tables (ATcT) approach, resulting in improved data for, among others, Br, HBr, HOBr and BrO. Ab initio calculations were used to obtain rate coefficients for selected reactions of HBr and HOBr, and the hydrogen/bromine/oxygen reaction mechanism was updated. The resulting model was validated against selected experimental data from the literature and used to analyze the effect of HBr and Br_2 on laminar, premixed hydrogen flames. Our work shows that hydrogen bromide and molecular bromine act differently as inhibitors in flames. For HBr, the reaction $HBr + H \rightleftharpoons H_2 + Br$ (R2) is rapidly equilibrated, depleting HBr in favor of atomic Br, which is the major bromine species throughout the reaction zone. The chain-breaking steps are then $H + Br + M \rightarrow HBr + M$ (R1), $Br + HO_2 \rightarrow HBr + O_2$ (R7), and $Br + Br + M \rightarrow Br_2 + M$ (R8). In Br_2-doped flames, the reaction $Br_2 + H \rightleftharpoons HBr + Br$ (R9) is far from equilibration and serves to deplete H in the reaction zone by competing with $H + O_2 \rightarrow O + OH$. The inhibition is augmented by recombination of Br (R8). If the inlet Br_2 mole fraction exceeds about 20%, reactions (R8) and (R2) are both reversed, now acting to promote chain branching and increase the flame speed. According to the present model, cycles involving HOBr are not important for generation or removal of chain carriers in these flames.

1. Introduction

Bromine reactions are important in stratospheric chemistry where, on a per atom basis, bromine is considerably more active in depleting ozone than chlorine [1]. Despite recent regulations, brominated flame retardants are still an ingredient in many materials, and bromine reactions continue to be a concern in relation to waste incineration processes [2,3]. Due to the interaction of bromine species with the combustion process and with other trace species, there is a renewed interest in the elementary reactions of bromine species, in particular at higher temperatures [4]. The presence of bromine species may enhance or inhibit fuel oxidation, depending on the reaction conditions [5]. This behavior is similar to that reported for trace elements naturally occurring in combustion, e.g., N, S, Cl, and K/Na [6]. In flames, bromine appears to be the most effective halogen inhibitor, and bromine species have been reported to narrow the composition limits of inflammability [7–11] and to decrease flame speeds [12–19]. The inhibiting effect of bromine species has also been observed at lower temperatures in batch reactor [20,21] and flow reactor [22] experiments. However, static reactor experiments have shown that hydrogen bromide acts to catalyze the slow oxidation of hydrocarbons [5,23–29].

Despite the considerable interest in high-temperature bromine reactions, details of the chemistry remain uncertain. Most bromine reactions have only been characterized experimentally at low temperatures, if at all, and bromine reaction mechanisms have not been validated over a wider range of conditions. The first computational studies of the inhibiting effect of bromine species in flames were conducted by Dixon-Lewis and coworkers [30–32] for premixed hydrogen–air flames and later by Westbrook for hydrocarbon flames [33,34]. These early studies dealt mainly with HBr and Br_2 as inhibitors. More recent chemical kinetic studies of the

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* Corresponding author. Fax: +45 4588 2258.
E-mail address: pgl@kt.dtu.dk (P. Glarborg).

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interaction of bromine species with combustion chemistry have emphasized CF_3Br and related halogens [19,22,34–39].

It is known that even for brominated hydrocarbons and commercial inhibitors such as CF_3Br (Halon 1301), the active species in the radical removal cycles are mainly HBr and Br, together with CH_3Br [14,16,22,35,40]. However, the earlier studies of the Br/H/O system and the effects of bromine on combustion were limited by incomplete data for thermodynamic properties of some of the potentially important bromine species, as well as uncertainties in the rate constants of many of the steps involved in the inhibition. The objective of the present work is to update our knowledge of the high-temperature bromine chemistry and re-examine the inhibition mechanisms involving HBr and Br_2. The thermochemistry of the bromine species is re-examined and the hydrogen/bromine/oxygen reaction mechanism is updated, partly based on ab initio calculations for key reactions. The resulting model is validated against selected experimental data from literature and used to analyze the effect of HBr and Br_2 on laminar, premixed hydrogen flames.

2. Thermochemistry

The thermochemistry of the bromine-containing species of interest, given in Table 1, was obtained using the Active Thermochemical Tables (ATcT) approach [41,42], which, in contrast to the traditional "sequential" approach, derives accurate, reliable, and internally consistent thermochemical values by analyzing and simultaneously solving [43–45] all the available thermochemical interdependencies defined in the underlying Thermochemical Network (TN) [46,47]. The most recent ATcT TN (ver. 1.110) [45,48], which contains more than 13,000 thermochemical determinations encompassing over 900 chemical species, has been expanded and updated (ver. 1.112) to accommodate the targeted bromine-containing species. The resulting ATcT values have been in turn used to update the database of Goos, Burcat, and Ruscic [49,50] with the appropriate polynomials.

Under the auspices of CODATA, Br_2, Br, and HBr, were established as "key" thermochemical species by Cox et al. [51], and the gas-phase enthalpies of formation that were derived by critical evaluation of data available up to (approx.) 1983, $\Delta_f H^0_{298}(Br_2) = 30.91 \pm 0.11$ kJ mol^{-1}, $\Delta_f H^0_{298}(Br) = 111.87 \pm 0.12$ kJ mol^{-1}, and $\Delta_f H^0_{298}(HBr) = -36.29 \pm 0.16$ kJ mol^{-1}, have been adopted without further scrutiny by virtually all subsequent thermochemical tabulations. For gaseous Br_2 (the formation enthalpy of which is equivalent to the vaporization enthalpy of condensed-phase bromine corrected for ideal vs. real behavior) there are indeed no relevant measurements since the evaluation of Cox et al. However, for Br and HBr, there are several newer determinations that can potentially improve and/or modify the thermochemistry of these two "key" species, such as, for example, the analysis of spectroscopic data by Gerstenkorn and Luc [52] leading to a refined value of $D_0(Br_2)$, or the spectroscopic determination of predissociation of HBr^+ [53] that allows access to $D_0(HBr)$ via a positive ion cycle. Thus, the current ATcT value for Br (unchanged from the value in the very recently given interim set of ATcT enthalpies of formation of several atoms [45]; enthalpy of formation at 298.15 K of 111.85 ± 0.06 kJ mol^{-1}, while confirming the original CODATA value [51]), is actually more accurate by a factor of two. The agreement for Br is not replicated in the case of HBr. The original CODATA value for HBr is essentially based on the assigned value for aqueous Br^- and the selected solvation enthalpy of HBr. In contrast to this, the ATcT TN – while also containing the relevant aqueous thermochemistry – takes advantage of newer thermochemical cycles that are entirely gas-phase. Consequently, ATcT currently produces an enthalpy of formation of HBr (-35.85 ± 0.15 kJ mol^{-1} at 298.15 K) that is higher (less negative) than the value assigned by CODATA by an amount that – while not large in absolute terms – exceeds substantially the combined uncertainties, leading to the conclusion that the aqueous thermochemical route selected by CODATA contains a hidden cumulative systematic bias that is larger than their declared uncertainty. It should be stressed here that while the current ATcT value for HBr relies heavily on spectroscopic data, it is, at the same time, still entirely consistent (within the respective uncertainties) with the relevant calorimetric [54,55] and aqueous [56–64] thermochemical measurements.

For BrO, the ATcT TN contains a number of experimental determinations that are relevant to defining its D_0 [65–71]. These are complemented by the results of several high-level electronic structure computations [72–78], which, if and when possible, were recast as congeneric reactions, adding within the TN relevant interdependences between various haloxyl radicals and/or their ion counterparts (halosyls and hypohalites). The resulting ATcT value for the enthalpy of formation of BrO (123.6 ± 0.3 kJ mol^{-1} at 298.15 K) is about 2 kJ mol^{-1} lower and nearly an order of magnitude more accurate than the value given by JANAF [79] and Gurvich et al. [80] (both report 125.8 ± 2.4 kJ mol^{-1}).

Good definition of the thermochemistry of the basic bromine-containing species discussed briefly above is a prerequisite for deriving with some confidence the thermochemistry of HOBr, which potentially plays a pivotal role in the chemical processes presented in this study. The often-cited lower limit for the enthalpy of formation of HOBr at 298.15 K of -56.2 ± 1.8 kJ mol^{-1} given by Ruscic and Berkowitz [81] is based on their determination of the photoionization onset for fragmentation into Br^+ and OH. However, two complications regularly seem to escape focus. Firstly, the limiting value derived from that particular photodissociative onset intrinsically depends, inter alia, on the choice for the enthalpy of formation of OH. Ruscic and Berkowitz have taken the latter from Gurvich et al. [80], which was the best datum available at that time. Ruscic et al. [82,83] have subsequently shown that $\Delta_f H^0(OH)$ needs to be revised downward by about 2 kJ mol^{-1}. The implication is that the limiting value of Ruscic and Berkowitz [81] should also be then revised accordingly. With auxiliary thermochemical data extracted from the current version of ATcT, the limit of Ruscic and Berkowitz, revised in light of the change for OH, would

Table 1
Thermodynamic properties for selected bromine species [49]. Units are kJ mol^{-1} and J mol^{-1} K^{-1}.

Species	$\Delta_f H^0_{298}$	S^0_{298}	$C_{p,300}$	$C_{p,400}$	$C_{p,500}$	$C_{p,600}$	$C_{p,800}$	$C_{p,1000}$	$C_{p,1500}$	$C_{p,2000}$
Br	111.85 ± 0.06	175.02	20.79	20.79	20.80	20.83	21.03	21.37	22.26	22.71
Br_2	30.88 ± 0.11	245.47	36.06	36.73	37.08	37.31	37.59	37.79	38.26	39.09
HBr	−35.85 ± 0.15	198.70	29.14	29.22	29.45	29.87	31.06	32.33	34.76	36.22
HOBr	−61.78 ± 0.54	247.78	38.36	41.13	43.23	44.82	47.14	48.92	52.16	54.15
BrO	123.61 ± 0.29	232.90	34.14	37.06	38.74	39.56	39.94	39.77	39.26	39.08
BrOO	110.17 ± 3.89	283.39	46.58	48.84	50.61	52.02	54.03	55.26	56.75	57.36
OBrO	158.18 ± 2.68	270.66	45.24	49.11	51.63	53.31	55.24	56.24	57.31	57.89
BrBrO	164.90 ± 2.14	302.17	51.30	53.48	54.83	55.72	56.97	58.56	67.20	76.09
BrOBr	104.61 ± 1.18	290.49	50.05	52.98	54.62	55.62	56.69	57.33	67.35	119.13