Computational Studies of the Thermochemistry of the Atmospheric Iodine Reservoirs HOI and IONO₂

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Contents		
	1. Introduction	160
	2. Methodology and Results	161
	3. Discussion	165
	3.1 Possible uncertainties	165
	3.2 Thermochemistry of HOI	167
	3.3 Thermochemistry of IONO ₂	168
	3.4 Comparison with halogen analogs	170
	3.5 IONO ₂ kinetics	171
	4. Conclusions	173
	Acknowledgements	173
	References	174

Abstract

CCSD(T) theory with aug-cc-pVTZ-PP and aug-cc-pVQZ-PP basis sets has been applied to hypoiodous acid and iodine nitrate, two potential reservoirs for atmospheric iodine. The results are employed in bond-conserving reactions and extrapolated to the complete basis set limit, to yield $\Delta_f H_{298}(\text{HOI}) = -59.2 \pm 3.3 \text{ kJ mol}^{-1}$ and $\Delta_f H_{298}(\text{IONO}_2) = 37.4 \pm 3.9 \text{ kJ mol}^{-1}$. For iodine nitrate the bond dissociation enthalpies $DH_0(\text{IO}-\text{NO}_2) = 113.6 \pm 3.1 \text{ kJ mol}^{-1}$ and $DH_0(\text{I}-\text{NO}_3) = 141.6 \pm 3.9 \text{ kJ mol}^{-1}$ are derived. $DH_0(\text{IO}-\text{NO}_2)$ is used in Troe's unimolecular formalism to yield the 298 K low-pressure limiting rate constant for $\text{IO} + \text{NO}_2$ addition as $(5.3\text{--}13.3) \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-1} \text{ s}^{-1}$ for N_2 bath gas, depending on the approach taken to define the rotational term F_{rot} . This

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range is in good accord with measured values. At 1 atm N₂ and 298 K, the lifetime for IONO₂ with respect to thermal dissociation is predicted to be of the order of 6 h, with an uncertainty of a factor of 3.5.

1. INTRODUCTION

Small quantities of iodine compounds, typically iodoalkanes and/or I₂ [1,2], are emitted from biomass combustion over land and by marine plankton and algae. Photolysis of these iodine compounds rapidly yields atomic iodine, which reacts with ozone:

Because a cycle can be closed by fast processes such as

even traces of iodine have been proposed to have a significant influence on stratospheric ozone concentrations [3,4]. The reaction

followed by photolysis of HOI back to I + OH has been suggested, together with (1), to form a significant ozone depletion cycle in the troposphere [5]. The efficiency of such cycles depends in part on how much active iodine (I and IO) is temporarily in the form of less reactive reservoirs such as HOI and iodine nitrate, formed via

The reverse of reaction (5) may be a nighttime source of IO. Iodine nitrate may be formed by the reaction

which, followed by reaction (1), may also act as an atmospheric source of IO at night [2]. Oxidation of IO may yield OIO, which has been detected in the marine boundary layer [6] and is implicated in the formation of aerosol particles by polymerization of iodine oxides in the marine boundary layer [7,8], which can act as cloud condensation nuclei. The broader significance of these studies concerns the influence of ozone and cloud cover on climate.

The aim of the present work is to derive the enthalpies of formation of HOI and IONO₂ via *ab initio* methods. The latter is used to investigate the kinetics of reaction (5). The NASA-JPL recommendation [9] for $\Delta_f H(\text{HOI})$ is based on calculations by Hassanzadeh and Irikura [10] and previous work from our laboratory on OH + CF₃I kinetics [11]. In the intervening decade there have been revisions to most of the ancillary thermochemical and kinetic data used in these calculations, and advances in computational technology and methodology make

it appropriate to revisit these molecules. In particular, the systematic extrapolation of coupled-cluster theory to the infinite basis set limit has proven to be of generally high accuracy [12], and the development of new basis sets by Peterson and coworkers has permitted sophisticated analysis of iodine-containing compounds [13,14]. The case of IO + NO₂ is one of several examples where Golden has noted difficulties in rationalizing the kinetics of halogen/nitrogen oxide systems with their thermochemistry [15] and found that an IO–NO₂ bond strength higher than values from most previous studies was needed to match RRKM theory with observation for reaction (5) [16]. A focus of the present study is to derive this bond strength independently and to explore the association and dissociation kinetics involving IONO₂.

2. METHODOLOGY AND RESULTS

We employed the aug-cc-pVTZ-PP and aug-cc-pVQZ-PP basis sets of Peterson *et al.* [14], which incorporate a relativistic pseudopotential (effective core potential) that largely accounts for scalar relativistic effects in iodine. For O and Cl we employed the aug-cc-pVTZ and aug-cc-pVQZ basis sets [17]. First, the optimized geometry, energy and harmonic frequencies for each molecule of interest were obtained with the triple zeta (TZ) basis sets and spin-unrestricted coupled-cluster theory with single and double excitations and quasiperturbative triples, CCSD(T), based on spin-restricted wavefunctions. Then the geometries were refined with the quadruple zeta (QZ) basis sets to obtain the QZ energy. All calculations were carried out with the Molpro series of programs [18]. The results are shown in Figure 9.1 and Table 9.1.

The thermochemistry of HOI was initially derived via the isodesmic process

which conserves the number and type of bonds. Experimental 0 K enthalpies of formation of the halogen monoxide anions were obtained from the enthalpies of the neutral oxides plus the energies of electron attachment (that is, minus the electron affinities). At 0 K the ion and electron conventions are equivalent. The closed-shell anions were chosen because first-order spin–orbit coupling (a vector relativistic effect) is eliminated, unlike for open-shell radicals with degenerate ground states, and second-order spin–orbit effects are negligible [19]. Bedjanian *et al.* [20] determined $\Delta_f H_{298}(\text{IO}) = 115.6 \pm 5.0 \text{ kJ mol}^{-1}$ from the ratio of forward and back rate constants for $\text{ClO} + \text{IO} = \text{I} + \text{OCIO}$, which equals the equilibrium constant K_{eq} and therefore yields ΔG_{298} , which in combination with a separately estimated ΔS_{298} leads to ΔH_{298} . As noted by Peterson *et al.* [14], a subsequent revision of $\Delta_f H_{298}(\text{OCIO})$ to $98.4 \pm 1.0 \text{ kJ mol}^{-1}$ by Davis and Lee [21] implies $\Delta_f H_{298}(\text{IO}) = 120.5 \pm 2.4 \text{ kJ mol}^{-1}$. This value is employed here. It is consistent with the estimate of $119.2 \text{ kJ mol}^{-1}$ by Kim *et al.* [22] who combined their new BrO thermochemistry with the $\text{Br} + \text{IO} = \text{BrO} + \text{I}$ equilibrium data of Bedjanian *et al.* [23,24]. For comparison, Hassanzadeh and Irikura computed

FIGURE 9.1 Structures of planar molecules computed with CCSD(T)/aug-cc-pVTZ-PP (upper numbers) and CCSD(T)/aug-cc-pVQZ-PP (lower numbers) theory. Distances are in 10^{-10} m and angles are in degrees. From top to bottom, HOI ${}^1A'$ and IONO $_2$ ${}^1A'$.

118.8 ± 7.6 kJ mol $^{-1}$, and Peterson *et al.* computed 125.1 ± 2.5 kJ mol $^{-1}$ [10,14]. $\Delta_f H_{298}(\text{IO}) = 120.5 \pm 2.4$ kJ mol $^{-1}$ in turn leads to $\Delta_f H_0(\text{IO}) = 122.6 \pm 2.4$ kJ mol $^{-1}$ [14]. Again for comparison, we note that Lee used similar arguments to reach $\Delta_f H_0(\text{IO}) = 120.4 \pm 2.6$ kJ mol $^{-1}$ [25], and that our chosen thermochemistry for IO lies midway between the recent calculations of Peterson and the re-evaluation of Lee. Addition of the electron affinity of 2.378 ± 0.006 eV (1 eV = 96.485 kJ mol $^{-1}$) measured by Gilles *et al.* [26] gives $\Delta_f H_0(\text{IO}^-) = -106.8 \pm 2.6$ kJ mol $^{-1}$. Coxon and Ramsay [27] measured the 0 K bond dissociation enthalpy of ClO to be 265.37 ± 0.03 kJ mol $^{-1}$. With enthalpy data for the atoms and elements, this yields $\Delta_f H_0(\text{ClO}) = 101.05 \pm 0.10$ kJ mol $^{-1}$ and $\Delta_f H_{298}(\text{ClO}) = 100.97 \pm 0.10$ kJ mol $^{-1}$. Using the electron affinity of 2.2775 ± 0.0013 eV measured by Distelrath and Boesl [28], we arrive at $\Delta_f H_0(\text{ClO}^-) = -118.69 \pm 0.16$ kJ mol $^{-1}$. Joens has reassessed $\Delta_f H_0(\text{HOCl})$ as -73.99 ± 0.12 kJ mol $^{-1}$, a value which takes account of recent revision in the thermochemistry of OH [29].

The CCSD(T) energy changes ΔE for reaction (7) are shown in Table 9.2. The energy changes were extrapolated to the complete basis limit using the relation of Halkier *et al.* [30]:

$$\Delta E_{\text{CBS}} = \frac{4^3 \Delta E_{\text{QZ}} - 3^3 \Delta E_{\text{TZ}}}{4^3 - 3^3}.$$

Further correction for changes in vibrational zero-point energy (ZPE) yields the reaction enthalpy at 0 K. Because of anharmonicity, the observed fundamental frequency for the transition $v = 0$ to $v = 1$, ν_0 , is less than ν_e , the harmonic frequency at the bottom of the well. The ZPE is between $\frac{1}{2}h\nu_0$ and $\frac{1}{2}h\nu_e$ for each mode, and

TABLE 9.1 Vibrational frequencies and *ab initio* energies

Species	TZ energy (au) ^a	QZ energy (au) ^b	Measured ν_0 (cm ⁻¹)					$\frac{1}{2}\Sigma h\nu_0$ (kJ mol ⁻¹)	Calculated TZ ν_e (cm ⁻¹)				$\frac{1}{2}\Sigma h\nu_e$ (kJ mol ⁻¹)
HOI	-370.529772	-370.567556	576	1070	3626			31.53	579	1095	3793		32.69
ClO ⁻	-534.830449	-534.872357	658					3.93	647				3.87
HOCl	-535.409072	-535.450074	724	1239	3609			33.32	726	1263	3779		34.49
IO ⁻	-369.953785	-369.992599	572					3.42	581				3.47
OH ⁻	-75.709425	-75.730336	3556					21.26	3723				22.26
H ₂ O	-76.342326	-76.363588	1595	3657	3756			53.87	1646	3810	3919		56.06
H	-0.499821	-0.499948	0					0.00	0				0.00
O	-74.978823	-74.995132	0					0.00	0				0.00
I	-294.799661	-294.815813	0					0.00	0				0.00
IONO ₂	-574.734656	-574.824148	(97) ^c (718) ^c	(185) ^c 815	(356) ^c 1276	580 1673	(711) ^c	–	101 746	192 822	370 1296	604 1706	739 16.46
ClONO ₂	-739.612951	-739.705569	124 780	273 809	434 1293	563 1737	711	17.25	122 794	260 814	443 1312	579 1767	724 17.47

^a CCSD(T)/aug-cc-pVTZ-PP.^b CCSD(T)/aug-cc-pVQZ-PP.^c Estimated from harmonic data (see text).

TABLE 9.2 Reaction energetics

Reaction	ΔE_{TZ} (kJ mol ⁻¹) ^a	ΔE_{QZ} (kJ mol ⁻¹) ^b	ΔE_{CBS} (kJ mol ⁻¹) ^c	ΔE_{ZPE} (kJ mol ⁻¹) ^d	ΔH_0 (kJ mol ⁻¹)
$\text{IO}^- + \text{HOCl} \rightarrow \text{ClO}^- + \text{HOI}$ (7)	6.9	7.2	7.5	-1.3	6.1
$\text{IO}^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{HOI}$ (8)	149.4	153.1	155.7	-4.5	151.1
$\text{HOI} \rightarrow \text{H} + \text{O} + \text{I}$ (9)	660.2	673.9	683.8	-32.1	620.5 ^e
$\text{IO}^- + \text{ClONO}_2 \rightarrow \text{ClO}^- + \text{IONO}_2$ (10)	4.3	4.4	4.4	-1.4	3.0

^a Energy change computed at CCSD(T)/aug-cc-pVTZ-PP level.

^b Energy change computed at CCSD(T)/aug-cc-pVQZ-PP level.

^c Energy change computed with molecular CCSD(T) energies extrapolated to the complete basis set limit.

^d Zero-point vibrational energy change (see text).

^e Includes atomic spin-orbit corrections.

we employ the mean of these two quantities, which should be a good estimate [31] (as discussed below, our results are rather insensitive to the extent of anharmonicity). We find that this estimate of ZPE is equal to $0.981 \frac{1}{2} \Sigma h\nu_e$ for the seven known molecules in Table 9.1. This relation is used to derive the ZPE for the molecule IONO_2 , for which a complete set of ν_0 has not been measured. The ν_0 data shown in Table 9.2 were taken from the NIST compilation [32].

The computed enthalpy change for reaction (7) is $\Delta_r H_0 = \Sigma \Delta_f H_0(\text{products}) - \Sigma \Delta_f H_0(\text{reactants})$, and with all $\Delta_f H_0$ except for HOI established above, $\Delta_f H_0(\text{HOI})$ is obtained. From Table 9.2, $\Delta_r H_0$ is 6.1 kJ mol⁻¹ and thus $\Delta_f H_0(\text{HOI}) = -53.8$ kJ mol⁻¹. The enthalpy correction $H_{298} - H_0$ was calculated via standard methods, with the JANAF [33] convention for polyatomic molecules of employing ν_0 for the frequencies. In the case of IONO_2 , where a complete set of observed ν_0 is unavailable, we use the relation observed $\nu_0 = (0.962 \times \text{calculated } \nu_e)$, derived from our TZ results in Table 9.1, to fill in the missing data. Together with $H_{298} - H_0$ for the elements in their reference state [33], the enthalpy of formation at 298 K is obtained as $\Delta_f H_{298} = \Delta_f H_0 + H_{298} - H_0(\text{HOI}) - \Sigma H_{298} - H_0(\text{elements})$.

As a check, the alternative isodesmic reaction

was employed, with $\Delta_f H_0(\text{OH}^-) = -139.2 \pm 0.1$ kJ mol⁻¹ derived from $\Delta_f H_0(\text{OH}) = 37.1 \pm 0.1$ kJ mol⁻¹ from Joens [29] and the electron affinity of 176.3 kJ mol⁻¹ from Smith *et al.* [34]. Reaction (8) yields $\Delta_f H_0(\text{HOI}) = -55.2$ kJ mol⁻¹. In principle, bond-conserving reactions of neutral IO, such as reaction (4), could also be analyzed. However there is some ambiguity in the spin-orbit splitting in IO, necessary for computation of reaction enthalpies, where the value of 25.0 ± 0.5 kJ mol⁻¹ measured by Gilles *et al.* [26] differs somewhat from the 21.2 kJ mol⁻¹ recently computed by Peterson *et al.* [14]. The atomization reaction

is also used for comparison, although the large changes in the electronic structure of the atoms eliminate the favorable error cancellation. There is a potential advantage that the enthalpies of formation of the atoms are very well defined. The

energies of the O and I atoms were corrected downwards by 0.9 and 30.3 kJ mol⁻¹, respectively, based on the measured spin-orbit splitting in these atoms. This atomization approach yields $\Delta_f H_0(\text{HOI}) = -50.5 \text{ kJ mol}^{-1}$.

Iodine nitrate was analyzed via the congeneric exchange reaction

in a similar manner. The NASA-JPL recommendation [9] for $\Delta_f H_{298}(\text{ClONO}_2) = 22.9 \pm 2.0 \text{ kJ mol}^{-1}$ is based on the work of Anderson and Fahey, who analyzed forward and reverse kinetics for $\text{ClO} + \text{NO}_2 = \text{ClONO}_2$ [35]. This is inconsistent with a prior determination of $26.4 \pm 0.8 \text{ kJ mol}^{-1}$ by Alqasmi *et al.* [36]. It is noted that the reaction enthalpy from Anderson and Fahey, combined with modern values for $\Delta_f H_{298}$ of ClO and NO₂ [9], yields $\Delta_f H_{298}(\text{ClONO}_2) = 24.3 \pm 2.0 \text{ kJ mol}^{-1}$ which appears to eliminate the disagreement. This value leads to $\Delta_f H_0(\text{ClONO}_2) = 30.9 \pm 2.0 \text{ kJ mol}^{-1}$, which is employed here. The computed $\Delta_r H_0$ of 3.0 kJ mol⁻¹ for reaction (10) (see Table 9.2) corresponds to $\Delta_f H_0(\text{IONO}_2) = 45.8 \text{ kJ mol}^{-1}$. The enthalpy change $H_{298} - H_0$ is calculated to be 15.6 kJ mol⁻¹ and, with similar data for the elements in their standard states [33], leads to $\Delta_f H_{298}(\text{IONO}_2) = 37.4 \text{ kJ mol}^{-1}$. The uncertainty in this result is discussed in Section 3.

The present values of $\Delta_f H_0(\text{IO})$ and $\Delta_f H_0(\text{IONO}_2)$, together with $\Delta_f H_0(\text{NO}_2) = 36.8 \pm 0.1 \text{ kJ mol}^{-1}$ from the Active Thermochemical Tables as quoted by Burcat and Ruscic [37], yield the bond dissociation enthalpy $DH_0(\text{IO}-\text{NO}_2) = 113.6 \pm 3.1 \text{ kJ mol}^{-1}$. It should be noted that because $\Delta_f H_0(\text{IO})$ is also used as the basis for the anion and thence $\Delta_f H_0(\text{IONO}_2)$, the bond dissociation enthalpy derived here is independent of the value chosen for $\Delta_f H_0(\text{IO})$, and there is no contribution from its uncertainty. NO₃ has a complex vibronic structure, that arises in part from Jahn-Teller distortion and coupling between the X²A₂' and A²E'' states [38]. $\Delta_f H_{298}(\text{NO}_3) = 74.6 \pm 0.7 \text{ kJ mol}^{-1}$ from the Active Thermochemical Tables as quoted by Burcat and Ruscic [37] plus data for atomic I [33] leads to $DH_{298}(\text{I}-\text{NO}_3) = 144.0 \pm 3.9 \text{ kJ mol}^{-1}$. The vibronic levels tabulated by Stanton [38] yield $H_{298} - H_0(\text{NO}_3) = 11.8 \text{ kJ mol}^{-1}$, and thus $DH_0(\text{I}-\text{NO}_3) = 141.6 \pm 3.9 \text{ kJ mol}^{-1}$.

3. DISCUSSION

3.1 Possible uncertainties

Neither the geometry of HOI nor that of IONO₂ has been determined experimentally. For comparison, the geometry of neutral OIO is also computed. At the TZ and QZ levels of theory r_{IO} and a_{OIO} equal $1.826 \times 10^{-10} \text{ m}$ and 111.0° , and $1.815 \times 10^{-10} \text{ m}$ and 110.5° , respectively. These parameters may be compared to the estimated equilibrium parameters of $1.800 \times 10^{-10} \text{ m}$ and 109.8° , from microwave spectroscopy by Miller and Cohen [39]. For neutral IO, r_{IO} is computed as 1.900×10^{-10} and $1.890 \times 10^{-10} \text{ m}$ at the TZ and QZ levels of theory, respectively, which may be compared to the state-resolved equilibrium values of

1.868×10^{-10} m ($^2\Pi_{3/2}$) and 1.885×10^{-10} m ($^2\Pi_{1/2}$) measured by Miller and Cohen [40]. This level of accord suggests the QZ geometries in Figure 9.1 may be reliable to around $\sim 0.02 \times 10^{-10}$ m and $\sim 1^\circ$. We note that for I–O stretching, such bond length errors correspond to energy errors of about 0.4 kJ mol^{-1} per bond.

The computed harmonic frequencies shown in Table 9.1 are, as expected, slightly higher than the observed fundamental frequencies. The scale factor of 0.962 given above corresponds to a root mean square deviation from the observed ν_0 values of 22 cm^{-1} . The observed fundamental frequency of ClO^- is atypically *above* the computed harmonic one, however, there is agreement when the $\pm 25 \text{ cm}^{-1}$ experimental uncertainty [26] is taken into account. The scale factor of 0.981 proposed for ZPE leads to a small root-mean-square deviation in ZPE for the data set in Table 9.1, of 0.06 kJ mol^{-1} .

The important consideration for the present analysis is uncertainty in the overall energy changes for the bond conserving reactions. The uncertainty from geometry errors is expected to cancel because of similar bonding in reactants and products, with residual errors perhaps as large as 0.5 kJ mol^{-1} . The greatest contribution of ZPE to the reactions used, (7), (8) and (10), is less than 5 kJ mol^{-1} . Thus the difference between the computed harmonic and observed fundamental contributions of $\Sigma \frac{1}{2} h\nu$ to $\Delta_r H_0$ is less than 0.2 kJ mol^{-1} . Therefore the impact of any uncertainty in the scaling of ZPE has a negligible impact.

Next the effect of basis set size is considered, i.e., potential uncertainty in the CBS extrapolation. For reaction (7) there is little difference (0.3 kJ mol^{-1}) between TZ and QZ reaction energies, while this difference is 3.6 kJ mol^{-1} for reaction (8). Because ΔE is already close to the convergence limit and is extrapolated by only 0.3 and 2.6 kJ mol^{-1} , respectively, the CBS extrapolation introduces little uncertainty, less than 0.2 kJ mol^{-1} . For reaction (10) the ΔE results are already converged before extrapolation (see Table 9.2).

The level of electron correlation employed influences the computed reaction energies. For reaction (7), at the HF/aug-cc-pVQZ-PP level of theory, i.e., with complete neglect of correlation, $\Delta E = -1.7 \text{ kJ mol}^{-1}$, indicating a fair degree of independence of ΔE from the level of correlation treatment. In other words, $\Delta E_{\text{QZ}}(\text{HF}) - \Delta E_{\text{QZ}}(\text{CCSD(T)}) = -8.9 \text{ kJ mol}^{-1}$. Comparison with CCSD results yields $\Delta E_{\text{QZ}}(\text{CCSD}) - \Delta E_{\text{QZ}}(\text{CCSD(T)}) = -1.8 \text{ kJ mol}^{-1}$, indicating that even before inclusion of the perturbative triples (T) contribution, ΔE is almost converged with respect to the level of correlation treatment. For reaction (8), the difference $\Delta E_{\text{QZ}}(\text{HF}) - \Delta E_{\text{QZ}}(\text{CCSD(T)})$ is 17.1 kJ mol^{-1} . The result from reaction (8), by the arguments of Hassanzadeh and Irikura [10], is therefore less reliable. CCSD data, i.e., with neglect of the triple excitation contribution, yield ΔE only 1.1 kJ mol^{-1} higher, so the result is insensitive to the level of correlation. For reaction (10) the impact is larger, where neglect of the (T) term reduces ΔE by 6.6 kJ mol^{-1} . The effect of extrapolation of electron correlation to the full configuration interaction limit was explored by Peterson *et al.*, who found for ClO^- and IO^- that the dissociation energies were increased by 1.5 and 1.8 kJ mol^{-1} , respectively [14]. Because these terms appear on opposite sides of the bond conserving reactions they largely cancel here. An estimated uncertainty of about 1 kJ mol^{-1} is allowed for here.

For the atomization reaction (9) the potential errors are much larger. The difference between ΔE at the TZ and QZ levels of theory, the size of the energy extrapolation, and the sensitivity to the correlation treatment as defined as the difference between CCSD(T) and HF results, are all much larger than for the other reactions at 13.7, 9.9 and $-319.8 \text{ kJ mol}^{-1}$, respectively, and there is no ZPE or geometry error cancellation. The thermochemistry obtained via reaction (9) is therefore the least reliable contribution towards $\Delta_f H_0(\text{HOI})$. The best estimate of $\Delta_f H_0(\text{HOI})$ is $-54.5 \text{ kJ mol}^{-1}$, which comes from averaging the results obtained via reactions (7) and (8) that differ by only 1.4 kJ mol^{-1} . The corresponding $\Delta_f H_{298}(\text{HOI})$ is $-59.2 \text{ kJ mol}^{-1}$. The propagated uncertainty of the ancillary thermochemistry, combined in quadrature, is 2.6 kJ mol^{-1} . An approximate estimate of the total uncertainty arising from the CBS extrapolation, ZPE difference, geometry errors and incomplete electron correlation is $\sim 2 \text{ kJ mol}^{-1}$. Combination in quadrature with the uncertainty of the ancillary thermochemistry leads to an overall uncertainty of $\sim 3.3 \text{ kJ mol}^{-1}$. Similar computational uncertainties are expected for the result obtained via reaction (10), where the propagated error limits in the auxiliary experimental data are 3.3 kJ mol^{-1} , with final error limits of around 3.9 kJ mol^{-1} .

3.2 Thermochemistry of HOI

The present result for $\Delta_f H(\text{HOI})$ is shown in Table 9.3, along with prior values of the thermochemistry. Early values based on extrapolated empirical trends in the series HOCl–HOBr–HOI [41,42] are seen to be too positive by 10–20 kJ mol^{-1} .

TABLE 9.3 Thermochemistry of HOI

$\Delta_f H_0$ (kJ mol^{-1})	$\Delta_f H_{298}$ (kJ mol^{-1})	Method
–33.5 to –37.7		Empirical trend ^a
–42.7		Empirical trend ^b
–44.7	–48.9	<i>Ab initio</i> ^c
-55.2 ± 6.9	-59.9 ± 6.9	<i>Ab initio</i> ^d
-64.9 ± 5.4	-69.6 ± 5.4	E_a difference ^e
-60 ± 12		<i>Ab initio</i> ^e
–68.4	–73.1	DFT ^f
-54.5 ± 3.3	-59.2 ± 3.3	This work

^a Ref. [42].

^b Ref. [41].

^c Ref. [43].

^d Ref. [10].

^e Ref. [11].

^f Ref. [44].

The result of Glukhovtsev *et al.* [43], who applied G2 theory to reaction (9), is also somewhat high, but there is particularly close accord with the results of Hassan-zadeh and Irikura [10]. Begović *et al.* [44] used density functional theory (DFT) to obtain values that are too negative by 14 kJ mol⁻¹. The value of Berry *et al.* [11], which is significantly below the present value, was derived from the difference between the measured forward activation energy E_a for

of 11.3 kJ mol⁻¹ and a predicted $E_a = 0 \pm 5$ kJ mol⁻¹ for the reverse process. This prediction was based on the absence of a barrier to the reverse process in a scan along the reaction coordinate at the G2(MP2) level of theory. E_a in the forward direction has since been redetermined as 16.6 ± 1.2 kJ mol⁻¹ [45] which, with the new thermochemistry plus data on CF₃, CF₃I [46] and OH [29] that yield $\Delta_r H_{298} = 23.9 \pm 4.4$ kJ mol⁻¹, implies $E_a = -7.3 \pm 4.6$ kJ mol⁻¹ for the back reaction. This is consistent with the earlier *ab initio* analysis of reaction (11), and is similar to the activation energy measured, for example, for the (CH₃)₃C + HI reaction where $E_a = -6.3 \pm 0.8$ kJ mol⁻¹ [47].

3.3 Thermochemistry of IONO₂

Table 9.4 summarizes prior data for IONO₂. Some of these have been reviewed recently by Golden [16], and are briefly discussed here. Complicating factors have included uncertainty in the heats of formation of IO and NO₃, where errors in these quantities will impact any IONO₂ thermochemistry derived via bond strengths. For this reason the 0 K bond strengths $DH_0(\text{IO}-\text{NO}_2)$ and $DH_0(\text{I}-\text{NO}_3)$, where

TABLE 9.4 Thermochemistry of IONO₂

$\Delta_f H_0$ (kJ mol ⁻¹)	$\Delta_f H_{298}$ (kJ mol ⁻¹)	$DH_0(\text{IO}-\text{NO}_2)$ (kJ mol ⁻¹)	$DH_0(\text{I}-\text{NO}_3)$ (kJ mol ⁻¹)	Method
		134 ± 13		Semi-empirical calculation ^a
70 ± 16		94.9	102.8	DFT ^b
		105		RRKM fit ^b
29.5 or 36.1 or 42.4		146.0 or 131.4	157.3	<i>Ab initio</i> ^c
		96	116	DFT ^d
		150		RRKM fit ^e
45.8 ± 3.9	37.4 ± 3.9	113.6 ± 3.1	141.6 ± 3.9	This work

^a Ref. [48].

^b Ref. [49].

^c Ref. [53].

^d Ref. [54].

^e Ref. [16].

derived previously, are also tabulated. These are fundamentally related to the kinetics of dissociation and recombination as well.

As seen in Table 9.4, the 1993 semiempirical (PM3) calculation of $DH_0(\text{IO}-\text{NO}_2)$ [48], which did not benefit from isodesmic reactions to minimize errors, is in the middle of the range of bond strengths which have subsequently appeared in the literature. Allan and Plane [49] applied DFT (B3LYP/6-311 + G(2d,p)) to the two bond strengths in IONO₂, which both led to the same heat of formation at 0 K, of 70 kJ mol⁻¹. This convergence is fortuitous because they used 0 K enthalpies of formation of IO and NO₃ of 132 and 68.8 kJ mol⁻¹, respectively, whereas the recommendations discussed above correspond to 122.6 and 80.2 kJ mol⁻¹, respectively. Allan and Plane carried out an RRKM fit to their measured rate constants k_5 for reaction (5) with $DH_0(\text{IO}-\text{NO}_2)$ as one of six adjustable parameters [49]. This is discussed in more detail in the next section. An important claim is that IONO₂ dissociation can be observed at 473 K. The ratio of their forward and reverse rate constants yields $K_{\text{eq},5} = k_5/k_{-5} = 1.8 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1}$, so that $\Delta G_{473} = -31.2 \text{ kJ mol}^{-1}$. With entropies at that temperature of 274.1 [10], 258.4 and 358.0 J K⁻¹ mol⁻¹ for IO, NO₂ and IONO₂, respectively, one derives $DH_{473}(\text{IO}-\text{NO}_2) = 114.2 \text{ kJ mol}^{-1}$ and hence $DH_0(\text{IO}-\text{NO}_2) = 107.9 \text{ kJ mol}^{-1}$. This approach has the advantage of independence from any details of an RRKM analysis, but in this case the k_{-5} information is highly uncertain. It corresponds to a small deviation from the observed decay of IO (see Figure 7 of Ref. [49]) with k_{-5} set to zero, comparable to the scatter in the IO fluorescence signal. If k_{-5} was smaller by, say, a factor of two, there would still be a match with the IO decay shown, and the corresponding $DH_0(\text{IO}-\text{NO}_2)$ would increase by 2.7 kJ mol⁻¹, to within the error limits of the present value. Similarly, Dillon *et al.* [50] set a lower limit $DH_0(\text{IO}-\text{NO}_2) > 107 \text{ kJ mol}^{-1}$ which is consistent with the above analysis and the present *ab initio* result. The present $DH_{298}(\text{I}-\text{NO}_3) = 144.0 \pm 3.9 \text{ kJ mol}^{-1}$ result given above, combined with $DH_{298}(\text{I}-\text{I}) = 151.1 \text{ kJ mol}^{-1}$ [33], implies that reaction (6) is endothermic by $7.1 \pm 3.9 \text{ kJ mol}^{-1}$ at room temperature. The lower end of this range is more consistent with the arguments of Chambers *et al.* [51], who observed a zero activation energy for this process and thereby deduced that reaction (6) is not endothermic. However, as emphasized recently, this is not strictly true [52]. In other words, the reverse of reaction (6) is predicted to show a negative activation energy. Such a measurement would be a good test of the thermochemistry proposed here.

Papayannis and Kosmas made single-point CCSD(T) calculations at B3LYP geometries, using a modest-sized LANL2DZ basis set augmented with two *d* and one *f* polarization function [53]. Some complications with their results have been discussed previously [16]: uncertainty in the spin-orbit splitting in IO gives alternative thermochemistry, and the bond strengths are not entirely consistent with each other when correct enthalpies for the fragments are employed. Their thermochemistry based on $DH_0(\text{I}-\text{NO}_3)$ appears to give the closest accord with the new values, but this was based on $\Delta_f H_0(\text{NO}_3) = 62.4 \text{ kJ mol}^{-1}$. The current Active Thermochemical Tables value of 80.2 kJ mol⁻¹ would increase their $\Delta_f H_0(\text{IONO}_2)$ to 60.2 kJ mol⁻¹.

Plane *et al.* made further DFT calculations on the OIO + NO system [54]. These included bond-additivity corrections for I₂ and IO, absorbed into “spin-orbit” corrections for I and IO. The bond strengths shown in Table 9.4 are derived from the differences between the computed reaction enthalpies reported by Plane *et al.* [54], as noted by Golden [55], and are reasonably close to the present values, both falling about 8 kJ mol⁻¹ smaller.

3.4 Comparison with halogen analogs

The thermochemistry of HOCl and ClONO₂ has been discussed above, and data for HOBr were reanalyzed by Joens [29]. Orlando and Tyndall studied the decomposition of BrONO₂ to BrO + NO₂, and from the equilibrium constant deduced the BrO–NO₂ bond strength. This is combined here with a new determination of $\Delta_f H_{298}(\text{BrO})$ by Kim *et al.* [22] to obtain $\Delta_f H_{298}(\text{BrONO}_2) = 39.4 \pm 6.3 \text{ kJ mol}^{-1}$. Alternatively, Hanson *et al.* studied the equilibrium $\text{BrONO}_2 + \text{H}_2\text{O} = \text{HOBr} + \text{HNO}_3$ and deduced $\Delta_r H_{298} = 5.4 \pm 2.9 \text{ kJ mol}^{-1}$ [56], which together with information about HOBr, H₂O and HNO₃ [29,37] implies $\Delta_f H_{298}(\text{BrONO}_2) = 44.1 \pm 3.4 \text{ kJ mol}^{-1}$. These two estimates are in accord, and are provisionally summarized here as $42 \pm 5 \text{ kJ mol}^{-1}$. These results are shown in Table 9.5. It may be seen that bond dissociation enthalpies are generally similar across the series, given the uncertainties. An exception is halogen–oxygen bonding, which is distinctly stronger for chlorine than bromine or iodine, in both the hypohalous acids and the halogen nitrates. The bonding to bromine and iodine is of similar strength in both systems. Differences between the behavior of halogen species depends significantly on differences in their reaction kinetics and also photochemistry: the typical photolysis of iodine compounds in the visible spectrum means that much of atmospheric iodine is in chemically active radical forms during daylight. An example where nighttime chemistry is impacted by the thermochemistry of iodine nitrate is discussed below.

TABLE 9.5 Comparison of HOX and XONO₂ thermochemistry (kJ mol⁻¹)

Halogen X	$\Delta_f H_{298}$ (HOX)	DH_0 (H–OX)	D_0 (HO–X)	$\Delta_f H_{298}$ (XONO ₂)	DH_0 (XO–NO ₂)	DH_0 (X–ONO ₂)
Cl	-76.9 ± 0.1^a	391.1 ± 0.2^a	230.75 ± 0.02^a	$24.3 \pm 2.0^{b,c}$	$168.8 \pm 2.1^{b,c}$	$107.0 \pm 2.0^{b,c}$
Br	-58.2 ± 1.8^a	$394.7 \pm 1.8^{a,b}$	202.7 ± 1.8^a	$42 \pm 5^{b,d,e}$	$142 \pm 5^{b,d,e}$	$111 \pm 5^{b,d,e}$
I	-59.2 ± 3.3^f	393.1 ± 2.3^f	198.8 ± 3.5^f	37.4 ± 3.9^f	141.6 ± 3.9^f	113.6 ± 3.1^f

a Ref. [29].

b See text.

c Ref. [35].

d Ref. [62].

e Ref. [56].

f This work.

3.5 IONO₂ kinetics

A particular application of $DH_0(\text{IO}-\text{NO}_2)$ is interpretation of the $\text{IO} + \text{NO}_2$ recombination reaction (5) at the low-pressure limit. Golden [16] has noted that the collisional energy transfer parameters employed previously [49] are unusually large. This will tend to increase the low-pressure limiting rate constant k_0 , while with smaller collisional parameters Golden needed $DH_0(\text{IO}-\text{NO}_2)$ to be as large as 150 kJ mol^{-1} . Golden also reported that Plane was subsequently able to fit the k_5 data with $DH_0(\text{IO}-\text{NO}_2) = 128 \text{ kJ mol}^{-1}$ and smaller collisional parameters than previously used [16]. Thus a lower bond strength offsets a higher collisional stabilization efficiency. Here, the new $DH_0(\text{IO}-\text{NO}_2)$ is kept fixed in RRKM calculations. Troe's unimolecular formalism [57] is employed, which for the addition reaction (5) at the low pressure limit may be cast in the form [58]:

$$k_0 = \beta_c Z_{\text{LJ}} \frac{\rho(E_0)RT}{Q_{\text{vib}}(\text{IONO}_2)} F_E F_{\text{anh}} F_{\text{rot}} \frac{Q(\text{IONO}_2)}{Q(\text{IO}) \cdot Q(\text{NO}_2)}, \quad (12)$$

where $\rho(E_0)$ is the vibrational density of states of IONO₂ at the threshold energy E_0 for dissociation to $\text{IO} + \text{NO}_2$, i.e., $E_0 = DH_0(\text{IO}-\text{NO}_2)$. The Q s are the partition functions, derived via the rigid rotor-harmonic oscillator approximation. F_E , F_{anh} and F_{rot} are factors to account for the energy dependence of $\rho(E_0)$, for the effects of vibrational anharmonicity, and for centrifugal barriers, respectively. $\beta_c Z_{\text{LJ}}$ is the weak-collision stabilization rate constant. The Lennard-Jones parameters chosen by Golden imply $Z_{\text{LJ}} = 7.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [16]. Here it is assumed that the efficiency of energy transfer between excited IONO₂ and N₂ bath gas is similar to that for excited INO₂, for which $\langle \Delta E \rangle = -4.1 \text{ kJ mol}^{-1}$ [57]. The corresponding β_c is 0.46, and so $\beta_c Z_{\text{LJ}} = 3.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. A difference from the various RRKM calculations reported to date (except the initial work of Rayez and Destriau [48] who also applied the Troe formalism) is the explicit inclusion of an anharmonicity correction via $F_{\text{anh}} = 1.38$. A crucial term is F_{rot} , which in essence is determined by the ratios of the moments of inertia of the structure at the dissociation transition state and of equilibrium IONO₂, I^+/I . For a loose transition state, as assumed here, with no potential energy barrier to association and located at the centrifugal maximum, F_{rot} depends sensitively upon the (unknown) long-range potential between IO and NO₂. Two different approaches are examined here. First, Troe's simplest treatment, based on a quasi-diatomic van der Waals potential [57], is employed here as Model A. This yields the inertia ratio via

$$\left(\frac{I^+}{I}\right)^2 = \frac{ABC}{\pi(RT)^3} \left(\frac{RT}{B_{\text{eff}}}\right) \left(\frac{24E_0}{B_{\text{eff}}}\right), \quad (13)$$

where A , B and C are the moments of inertia of IONO₂, expressed in J mol^{-1} , and B_{eff} is the mean of the two smallest values, B and C . Table 9.6 lists the input parameters for the Troe formalism, and these yield $I^+/I = 58.2$. There is an alternative choice [57] for the C_6 parameter that defines the $-C_6/r_6$ van der Waals potential, which replaces the 24 in Eq. (13) by 12. If this alternative is applied, then $I^+/I = 41.2$. This uncertainty in C_6 has little im-

TABLE 9.6 Parameters for Troe unimolecular analysis at 298 K^a

IONO ₂ frequencies 97, 185, 356, 580, 711, 718, 815, 1276, 1673 cm ⁻¹ ; $E_{\text{ZN}} = 38.3 \text{ kJ mol}^{-1}$
IO and NO ₂ frequencies 673 and 750, 1318, 1618 cm ⁻¹ ; $E_{\text{ZP}} = 26.1 \text{ kJ mol}^{-1}$
NO ₂ product of moments of inertia $15.36 \times 10^{-138} \text{ kg}^3 \text{ m}^6$
IO moment of inertia $8.230 \times 10^{-46} \text{ kg m}^2$
IONO ₂ rotational constants $A, B, C = 12.43, 1.346, 1.214 \text{ GHz}$; $B_{\text{eff}} = (B + C)/2 = 0.511 \text{ J mol}^{-1}$
Critical energy for dissociation $E_0 = 113.6 \text{ kJ mol}^{-1}$; $\Delta E_{\text{Z}} = 8.7 \text{ kJ mol}^{-1}$
Reaction coordinate stretch 580 cm ⁻¹ ; Morse $\beta = 4.06 \times 10^{10} \text{ m}^{-1}$ and $D = 125.8 \text{ kJ mol}^{-1}$
Looseness parameter $\alpha = 1 \times 10^{10} \text{ m}^{-1}$; $a_1 = 0.119$; $a_2 = 0.00666$
Centrifugal barriers $E_0(J) - E_0(J = 0) = 0.243 \text{ J mol}^{-1} [J(J + 1)]^{1.009}$
$F_{\text{E}} = 1.149$; $F_{\text{anh}} = 1.381$; $I^+/I = 8.16$; $F_{\text{rot max}} = 20.2$; $\rho(E_0) = 387 (\text{J mol}^{-1})^{-1}$; $Q_{\text{vib}}(\text{IONO}_2) = 6.40$; $Q_{\text{rot}}(\text{IONO}_2) = 1.92 \times 10^5$
$Q(\text{IONO}_2) = 3.10 \times 10^{39} \text{ m}^{-3}$; $Q(\text{NO}_2) = 1.37 \times 10^{36} \text{ m}^{-3}$; $Q(\text{IO}) = 2.09 \times 10^{36} \text{ m}^{-3}$

^a See Refs. [57,59].

pect on F_{rot} , which would drop from 15.2 to 13.8. Model B is a more sophisticated treatment of F_{rot} , derived by Troe via his statistical adiabatic channel model [59]. Centrifugal maxima are located in channel potentials of the form

$$V(z) = D[1 - \exp(-z)]^2 + \Delta E_{\text{Z}} \exp\left(-\frac{\alpha}{\beta} z\right) + E_{\text{ZP}} + J(J + 1) \frac{B_{\text{eff}}}{1 + a_1 z + a_2 z^2}, \quad (14)$$

with $z = \beta(q - q_e)$, where q is the IO–NO₂ separation, and D and β are Morse parameters (see Table 9.6). The second term describes the decay of zero-point energy in terms of a looseness parameter α , with a standard value of $\alpha = 1 \times 10^{-10} \text{ m}$ assumed here. The final term describes the rotational energy, with a_1 and a_2 derived in the standard manner [59]. The rotational barriers E_0 as a function of J are fitted to the form $E_0(J) - E_0(J = 0) = C_{\text{v}} J(J + 1)^{\text{v}}$, from which I^+/I may be deduced [57]. This second procedure leads to $F_{\text{rot}} = 6.02$, which is about a factor of 2.5 smaller than that derived via Model A. This difference emphasizes the inherent uncertainty in rotational effects.

Combining these data through the unimolecular formulation (12) yields $k_0 = 13.3 \times 10^{-31}$ (Model A) or 5.3×10^{-31} (Model B) cm⁶ molecule⁻¹ s⁻¹ for N₂ at 298 K.

These estimates bracket the NASA-JPL and IUPAC recommendations of 6.5×10^{-31} and $7.7 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-1} \text{ s}^{-1}$ [9,60]. It is therefore possible to reconcile the thermochemistry proposed here with the observed IO + NO₂ recombination kinetics while employing reasonable input parameters for the unimolecular model. Nevertheless it must be stressed, as emphasized earlier [16], that there is considerable uncertainty in some of the input parameters to an RRKM analysis, especially the F_{rot} term. It is of interest to compare the present kinetic calculations with the Multiwell [61] Master Equation calculations on this system by Golden [16]. He used a Morse potential to locate the centrifugal maximum, and from the bond extension $F_{\text{rot}} \sim 2.1$ is derived, about 1/7 of that used here. On the other hand, the higher E_0 value yields a density of states larger by a factor of ~ 6 , and these two factors largely cancel.

The present computed equilibrium constant for reaction (5) at 298 K is $8.9 \times 10^{-8} \text{ cm}^3 \text{ molecule}^{-1}$. For 1 atm of N₂, the effective second-order $k_5 \sim 4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [49]. Thus the corresponding first-order dissociation rate constant is $k_{-5} \sim 4.5 \times 10^{-5} \text{ s}^{-1}$ at these conditions, i.e., the lifetime is ~ 6 h. This estimate of k_{-5} is about two orders of magnitude smaller than that of Allan and Plane [49], but still high enough for appreciable IONO₂ dissociation to take place overnight. The dissociation rate is very sensitive to $DH_0(\text{IO}-\text{NO}_2)$: the present error limits correspond to an uncertainty of a factor of 3.5, and so a reliable measurement of k_{-5} would allow reliable experimental determination of the thermochemistry.

4. CONCLUSIONS

Hypiodious acid and iodine nitrate have been investigated with coupled cluster theory and the results extrapolated to the complete basis set limit. Together with revised thermochemistry for several ancillary molecules, the enthalpy changes of working reactions yields new thermochemistry for HOI and IONO₂. The latter data, employed in unimolecular rate theory, appear to be consistent with kinetic measurements on the IO + NO₂ reaction to within the uncertainties of the kinetic analysis.

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