

The Iodide-Catalyzed Decomposition of Hydrogen Peroxide: Mechanistic Details of an Old Reaction as Revealed by Electrospray Ionization Mass Spectrometry Monitoring

Ilza Dalmázio,^a Flávia C. C. Moura,^a Maria H. Araújo,^a Tânia M. A. Alves,^b Rochel M. Lago,^a Guilherme F. de Lima,^a Hélio A. Duarte^a and Rodinei Augusti^{*a}

^aDepartamento de Química, Universidade Federal de Minas Gerais, Av. Antônio Carlos, 6627, 31270-901 Belo Horizonte-MG, Brazil

^bCentro de Pesquisas René Rachou, Fundação Osvaldo Cruz, 30190-002 Belo Horizonte-MG Brazil

A espectrometria de massas com ionização electrospray no modo negativo, ESI(-)-MS, foi usada para investigar a decomposição da água oxigenada catalisada por iodeto em meio aquoso. O monitoramento por ESI(-)-MS revelou a presença de um ânion intenso de m/z 287, o qual foi sugerido possuir a estrutura $[I\text{-IOOH}]^-$ em solução aquosa, através de uma interação entre o íon iodeto e a espécie neutra e instável IOOH. Evidências da estrutura proposta para tal ânion foram obtidas através de sua fragmentação por colisão com hélio, a qual forneceu, exclusivamente, um íon-produto de m/z 254 (I_2^-), através de uma perda de radical peroxila (HOO^\bullet , 33 Da). Cálculos teóricos *ab initio* revelaram que a formação do ânion $[I\text{-IOOH}]^-$, a partir da interação entre IOOH e I^- , é um processo termodinamicamente favorável, enquanto que sua fragmentação levando a I_2^- e HOO^\bullet , é o canal de dissociação mais provável. Deste modo, foi proposto um novo mecanismo para a decomposição da H_2O_2 catalisada por iodeto para gerar H_2O e O_2 tendo como base a participação do intermediário-chave IOOH.

Electrospray ionization mass spectrometry in the negative ion mode, ESI(-)-MS, was used to investigate the iodide-catalyzed decomposition of H_2O_2 in aqueous medium. ESI(-)-MS monitoring revealed the presence of an intense anion of m/z 287, suggested to be the $[I\text{-IOOH}]^-$ anion, which was proposed to be formed in solution (and then transferred to the gas phase by the ESI process) via an interaction between iodide and the neutral and short-lived species IOOH. Evidences for the proposed structure were obtained by CID (collision-induced dissociation) experiments, which yielded exclusively a product ion of m/z 254 (I_2^-) via a peroxide radical (HOO^\bullet , 33 Da) loss. High level *ab initio* calculations revealed that the formation of the $[I\text{-IOOH}]^-$ anion from IOOH and I^- is a thermodynamically-favored process whereas its fragmentation leading to I_2^- and HOO^\bullet is the most favorable dissociation channel. Hence, an unprecedented mechanism for the iodide-catalyzed decomposition of H_2O_2 to H_2O and O_2 based on the assumption of the participation of the key intermediate IOOH was proposed.

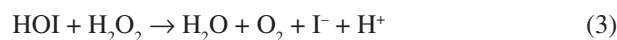
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Introduction

The iodide-catalyzed disproportionation of H_2O_2 to H_2O and O_2 in aqueous solution (equation 1) at neutral pH has been extensively studied for a long time, since the beginning of the 20th century, mainly by Liebhafsky and coworkers.¹⁻³ More recently, this reaction has been used in demonstration experiments to undergraduate students.⁴



In the mechanism accepted, the following pathways have been suggested:



In neutral solutions, in which the H^+ activity (a_H) is approximately equal to 10^{-7} , one can predict, based on the

*e-mail: augusti@ufmg.br

standard potentials (E°) of the respective half-reactions and by applying the Nernst equation, that both reactions, as stated in equations 2 and 3, are thermodynamically favored processes. In acidic solutions, however, the iodide-catalyzed oxidation of H_2O_2 to O_2 no longer occurs.⁴

In equation 2, which is believed to be the rate-determining step,⁴ it is proposed that H_2O_2 is reduced to H_2O whereas iodide (I^-) is oxidized to hypoiodous acid (HOI). In equation 3, the oxidation of H_2O_2 to O_2 is accomplished by the reduction of hypoiodous acid to iodide. The oxidation of H_2O_2 to O_2 , as shown in equation 3, is however an intricate process⁵ for which a detailed mechanism has not been previously described.

Owing to an outstanding sensitivity, speed, and selectivity, electrospray ionization mass spectrometry (ESI-MS) has been extensively used to elucidate reaction mechanisms, especially in solutions of polar solvents, via the detection and identification of reactants, products, and intermediates, most particularly of transient species occurring at very low concentrations,⁶⁻²⁵ including complex and high-molecular weight species.²⁶ Under the most commonly used electrospray operating conditions, only rarely the electrochemical processes seem to affect the identity and the relative abundances of the ions in an ESI mass spectrum.²⁷ Furthermore, there is overwhelming evidence that electrospray ionization is successful in the characterization of solution-phase species via a study of the corresponding gas-phase ions.^{28, 29}

Although a number of studies^{1-3, 5} on the iodide-catalyzed hydrogen peroxide decomposition have been previously reported, the detection and characterization of key intermediate species have not been so far accomplished. Hence, electrospray ionization mass spectrometry (and tandem mass spectrometry) is employed to furnish such sort of elucidatory information on this old reaction. High level *ab initio* calculations are also performed to evaluate the relative stabilities of short-lived intermediates and to appraise their most favored dissociation channels upon collision-induced dissociation (CID).

Experimental

Chemicals were obtained from Sigma-Aldrich (Milwaukee, WI, USA) or Merck (Whitehouse Station, NJ, USA) and used with no further purification. All the aqueous solutions were prepared with Millipore MilliQ water.

Hydrogen peroxide decomposition

In a typical procedure, 100 mL of an aqueous solution containing H_2O_2 ($7.0 \times 10^{-2} \text{ mol L}^{-1}$) and KI ($2.4 \times 10^{-4} \text{ mol L}^{-1}$)

at pH 6 was continuously stirred and the solution temperature kept constant at 25 ± 2 °C. The evolution of O_2 was continuously supervised by using a home-built glass apparatus. It was observed that the maximum rate of O_2 formation was reached at pH close to 6.

Mass Spectrometry

The ESI-MS and ESI-MS/MS experiments were performed using a commercial LCQ Advantage ion trap mass spectrometer (Thermo Finnigan, San Jose, CA). The spectra were obtained as an average of 50 scans, each requiring 0.2 s. Typical ESI conditions were as follows: heated capillary temperature, 200 °C; sheath gas (N_2) flow rate, 20 units (*ca.* 0.30 L min^{-1}); spray voltage $\pm 4.5 \text{ kV}$; capillary voltage 25 V; tube lens off set voltage, 25 V. For tandem mass spectra, the precursor ion of interest was first isolated and then fragmented by collision-induced dissociation (CID) with helium. The collision energy was set to a value at which product ions were produced in measurable abundance. The isolation width used in the MS/MS experiments was 2 *m/z* units.

Computational details

Geometries have been fully optimized and frequency calculations have been carried out using Møller-Plesset Perturbation (MP2), CCSD, and DFT levels of theory. Real harmonic frequencies assure that all stationary points found in the potential energy surfaces are true minima. For DFT calculations, the PBE expressions for exchange and correlation functional have been used.³⁰ For all methods, the inner shell electrons (1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d) of iodine were treated by the effective core potential of Hay and Wadt (LANL2DZ)³¹ and the valence electrons (5s, 5p, 5d) were included explicitly in the calculations, using the associated double-z basis set with the original³¹ contraction exponent augmented with d polarization function (exponent 0.244). The O and H atoms were described by the 6-311++G(d,p) Pople's basis sets.^{32, 33} Single point calculations on CCSD fully optimized geometries were performed at MP4 and CCSD(T) levels of theory aiming to improve the electronic energies. All quantum chemical calculations were performed using Gaussian 2003 suite of programs.³⁴ To assess the quality of our approach, the I_2 dissociation free energy has been estimated to be $34.2 \text{ kcal mol}^{-1}$ at CCSD(T) level of theory, only $1.3 \text{ kcal mol}^{-1}$ smaller than the experimental dissociation energy. The harmonic frequency is estimated to be 210 cm^{-1} , which may be compared to the experimental value of 214.5 cm^{-1} .³⁵ The I-I bond distance was estimated to be 2.743 \AA , about 0.077 \AA larger than the experimental value of 2.666 \AA .³⁵

Results and Discussion

Monitoring of the iodide-catalyzed decomposition of H_2O_2 by ESI-MS

ESI-MS monitoring was performed aiming to identify possible transient species formed *in situ* in an aqueous solution containing H_2O_2 and iodide. The analyses were carried out in the negative ion mode and typical spectra are shown in Figure 1.

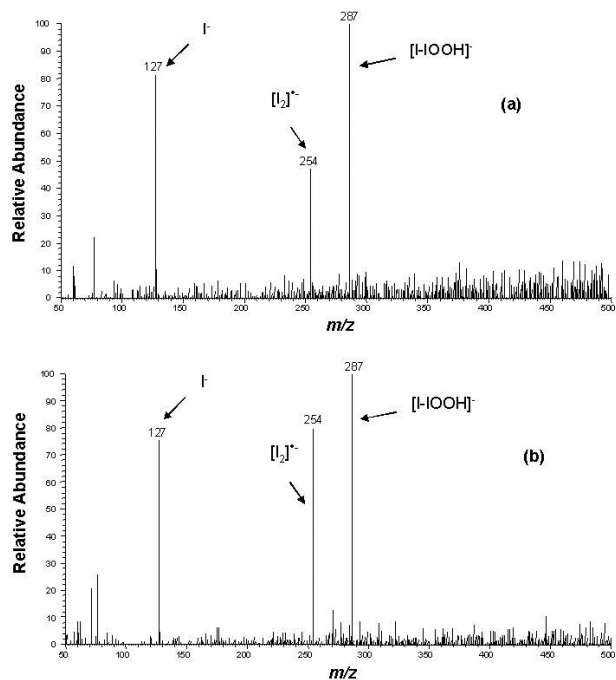


Figure 1. ESI(-)-MS of an aqueous solution of H_2O_2 and iodide after a reaction time of (a) 2 min; (b) 30 min ($[H_2O_2] = 7.0 \times 10^{-2} \text{ mol L}^{-1}$; $[KI] = 2.4 \times 10^{-4} \text{ mol L}^{-1}$; pH 6).

The ESI(-)-MS revealed the predominant presence of the following ions: m/z 127 (iodide), m/z 254 (I_2^*), and m/z 287. The mass-selection and fragmentation (Figure 2) of the later anion yielded exclusively the product ion of m/z 254 (I_2^*) via the loss of a neutral fragment with a nominal mass of 33 Da attributed to be the peroxide radical ($\cdot OOH$). In addition, the anion of m/z 254 detected in the ESI(-)-MS shown in Figure 1 is probably resulting from an in-source process that involves successive collisions of the anion of m/z 287 with the buffer gas.

Based on this fragmentation pattern, which clearly reveals the atom connectivity in the anion of m/z 287, the structure $[I-IOOH]^-$ was thus proposed. Other structures for the gaseous anion of m/z 287, supposedly the ion-dipole complex of hypiodous acid ($[IO\cdots H\cdots OI]^-$) and the complex of iodide with iodic acid ($[OIOHI]^-$), were not taken into consideration since they are obviously not

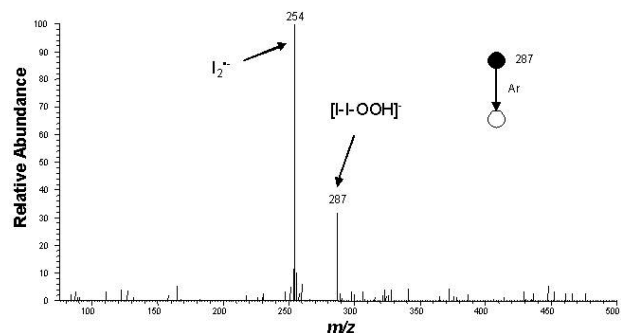


Figure 2. CID experiment of the anion of m/z 287 proposed to be the unstable specie $[I-IOOH]^-$.

consistent with the MS/MS data (Figure 2). Hence, the $[I-IOOH]^-$ anion is proposed to be present in solution as a result of an equilibrium of the type $I^- + IOOH \rightarrow [I-IOOH]^-$, and then promptly transferred to the gas phase by the ESI process (note that the I^- concentration is relatively high which likely favors the product formation). The neutral and short-lived IOOH species, which is assumed to be a key intermediate in the iodide-catalyzed decomposition of H_2O_2 to H_2O and O_2 (see discussion following this paper), is thus resulting from a net replacement of H by I in the H_2O_2 molecule.

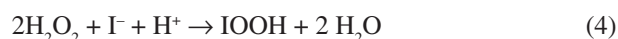
The I-I bond, present in the $[I-IOOH]^-$ anion, is probably very similar to that formed as a result of the interaction between iodide (I^-) and iodine (I_2) to generate the well-known triiodide (I_3^-) anion. Furthermore, the exclusive loss of peroxide radical ($\cdot OOH$), as a result of the CID of the $[I-IOOH]^-$, is consistent with the weakness of the I-O chemical bond, which is probably related to a very inefficient overlap between the 2p and 5p atomic orbitals of oxygen and iodine, respectively (results of high level *ab initio* calculations on the relative stability and favored dissociation channels for the $[I-IOOH]^-$ anion will be presented following this paper).

The relative intensities of these anions (*i.e.* of m/z 127, 254, and 287), estimated from the ESI(-)-MS at varied times (Figure 1), stayed approximately constant during the reaction monitoring which thus strongly indicates that the reaction reaches an steady state after a reaction time as short as 2 min. Note that possible anions derived from hypiodous acid (HOI) (proposed to play an important role in the disproportionation of H_2O_2 to H_2O and O_2 as stated in equations 2 and 3), such as IO^- of m/z 143 and even $[I-IOH]^-$ of m/z 271, were not detected at all in the ESI(-)-MS (Figure 1). This finding thus indicates that either the HOI concentration stays in a very low level as the reaction proceeds or, most probably, HOI does not play an important role in such mechanistic process. Furthermore, the participation of I_2 as a possible and important intermediate in such reaction process (as the presence of the anion I_2^* of

m/z 254 in the ESI(-)-MS of Figure 1 could suggest) was discharged since UV spectroscopy measurements of the reaction solution did not reveal its presence at all.

A mechanistic proposal for the iodide-catalyzed decomposition of H_2O_2 to H_2O and O_2

Based on the data obtained via ESI-MS monitoring, it can be postulated that the decomposition of H_2O_2 to H_2O and O_2 occurs via two distinct pathways, as outlined in equations 4 and 5:



In equation 4, the key intermediate IOOH is suggested to be formed via a straightforward interaction between H_2O_2 and I^- . In this equation, H_2O_2 is reduced to H_2O whereas iodide (I^-) is oxidized to IOOH. Subsequently, as shown in equation 5, the species IOOH is proposed to quickly decompose to O_2 and HI . Finally, note that HIO and I_2 are no longer included in these novel reaction pathways and, in addition, the combination of equations 4 and 5 yields equation 1, which represents the overall decomposition of H_2O_2 to H_2O and O_2 .

Therefore, the data presented herein support the formation of the key intermediate IOOH, which seems to play a major role in the decomposition of H_2O_2 to O_2 . In fact, the participation of the unstable specie HIO_2 (with the same molecular formula than IOOH) as an essential intermediate in the iodide-catalyzed decomposition of H_2O_2 was previously proposed by Liebhaftsky and coworkers several years ago.⁵ Note also that in the overall process for the decomposition of H_2O_2 to H_2O and O_2 (equation 1) there is no net consumption of iodide. This anion thus acts as a catalyst for such a process, being consumed in equation 4 and subsequently restored, as stated in equation 5. These simple reaction pathways (Equations 2, 4 and 5) appears therefore do describe properly the mechanism of disproportionation of H_2O_2 to H_2O and O_2 , but the reaction mechanism may be more complex with, for instance, the participation of radical species such as HO^\bullet , HOO^\bullet , and I^\bullet .

Theoretical calculations

To verify the gas-phase stability of the $[I_2OOH]^-$ anion and also to evaluate its main dissociation channels, high level *ab initio* calculations were performed and the results are displayed in Table 1.

Table 1. Free energies for the formation of I_2OOH^- (from IOOH and I^-) and its main dissociation channels calculated at different levels of theory¹

<i>Ab initio</i> Method	ΔE / (kcal mol ⁻¹)	$\Delta G^{\text{therm } 1}$ / (kcal mol ⁻¹)	ΔG / (kcal mol ⁻¹)
$[I_2OOH]^- \rightarrow IOOH + I^-$			
PBE/6-311++G**	39.61	-6.69	32.72
MP2/6-311++G**	32.22	-7.18	25.04
MP4SDQ/6-311++G**	30.70	-7.18	23.52
CCSD/6-311++G**	29.28	-7.08	22.20
CCSD(T)//CCSD/6-311++G**	32.92	-7.18	24.92
$[I_2OOH]^- \rightarrow I_2^\bullet + HOO^\bullet$			
PBE/6-311++G**	28.83	-11.08	17.74
MP2/6-311++G**	30.08	-11.07	19.00
MP4SDQ/6-311++G**	22.16	-11.07	11.09
CCSD/6-311++G**	19.26	-11.30	7.96
CCSD(T)//CCSD/6-311++G**	24.44	-11.07	13.36
$[I_2OOH]^- \rightarrow I_2O^\bullet + HO^\bullet$			
PBE/6-311++G** ²	49.19	-12.03	37.16
MP2/6-311++G**	52.36	-11.85	40.51
MP4SDQ/6-311++G**	40.05	-11.85	28.20
CCSD/6-311++G**	34.80	-12.47	22.33
CCSD(T)//CCSD/6-311++G**	39.70	-11.85	27.85
$[I_2OOH]^- \rightarrow I_2OO^\bullet + H^\bullet$			
PBE/6-311++G** ²	70.36	-7.39	62.97
MP2/6-311++G**	81.24	-13.11	68.13
MP4SDQ/6-311++G**	79.62	-13.11	66.51
CCSD/6-311++G**	76.43	-14.19	62.25
CCSD(T)//CCSD/6-311++G**	76.42	-13.11	63.31

¹ ΔG^{therm} was evaluated at 298K and includes the zero point energy; ² deMon package has been used.

All the theoretical calculations indicate that the formation of $[\text{I}_2\text{OOH}]^-$ from IOOH and I^- is a thermodynamically favored process. For instance, the CCSD(T) //CCSD /6-311++G** *ab initio* method (the most accurate level of theory employed herein, see Table 1) shows that the free energy for the $[\text{I}_2\text{OOH}]^-$ species is found to lie about 25 kcal mol⁻¹ below the reactants IOOH and I^- (Figure 3).

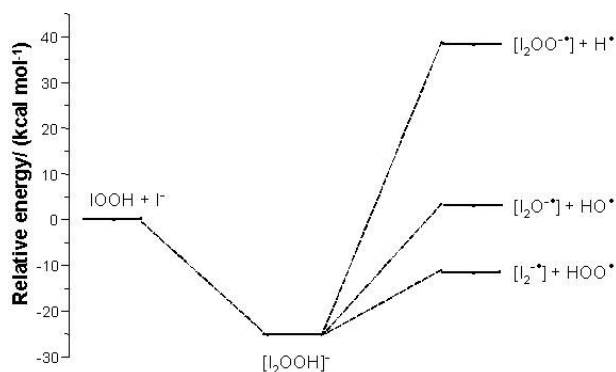


Figure 3. Diagram showing the relative energies for the formation of $[\text{I}_2\text{OOH}]^-$ (from IOOH and I^-) as well as the free energies involved in its main dissociation channels.

Furthermore, all the *ab initio* methods indicate that the decomposition of $[\text{I}_2\text{OOH}]^-$ leading to $[\text{I}_2]^-$ and $\cdot\text{OOH}$ is the preferential decomposition channel in comparison with the alternative routes investigated herein (see Table 1). For instance, calculations at the CCSD(T) //CCSD /6-311++G** level indicates that the free energy for this dissociation channel lies about 13 kcal mol⁻¹ above $[\text{I}_2\text{OOH}]^-$, clearly indicating that this is the most favored decomposition channel (Figure 3). Conversely, the decomposition channels of $[\text{I}_2\text{OOH}]^-$ to yield (a) IOOH and I^- ; (b) $[\text{I}_2\text{O}]^-$ and $\cdot\text{OH}$; (c) $[\text{I}_2\text{OO}]^-$ and H^\bullet were found to be less favored by about (a) 25 kcal mol⁻¹; (b) 28 kcal mol⁻¹; and (c) 63 kcal mol⁻¹, respectively (Figure 3). This is a remarkable result since the decomposition of $[\text{I}_2\text{OOH}]^-$ to produce the closed shell species IOOH and I^- , instead of the relatively unstable radical species $[\text{I}_2]^-$ and $\cdot\text{OOH}$, would be the natural assumption. The optimized structures for the $[\text{I}_2\text{OOH}]^-$ anion and also for all the species formed as the result of its fragmentation, calculated at the CCSD(T) //CCSD /6-311++G** level of theory, are shown in Figure 4. For the optimized structure of the $[\text{I}_2\text{OOH}]^-$ anion, for instance, the I-I, O-O, and I-O bond lengths were found to be 3.06, 1.44, and 2.18 Å, respectively. These values are comparable with the bond lengths calculated for $[\text{I}-\text{I}]^-$ and $\cdot\text{O}-\text{OH}$ (3.29 Å and 1.32 Å, respectively), and for IO-OH (2.06 Å).

These findings are thus consistent with the experimental results in which the $[\text{I}_2\text{OOH}]^-$ anion of m/z 287 was proposed to be formed in solution via an interaction between IOOH and I^- and then transferred to the gas phase

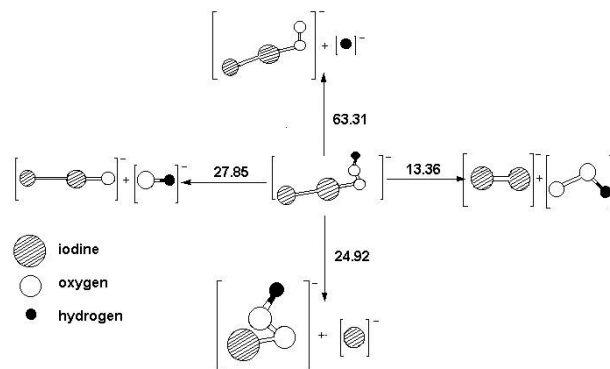


Figure 4. Optimized structures calculated at the CCSD(T)/6-311++G(d,p) level of theory for the several species formed upon the dissociation of the anion $[\text{I}_2\text{OOH}]^-$. The energies involved in each dissociation channel are given in kcal mol⁻¹.

under the ESI conditions, as previously stated. Note also that calculations are in fully agreement with the CID results on the $[\text{I}_2\text{OOH}]^-$ anion, which fragmented exclusively via the loss of a peroxide radical ($\cdot\text{OOH}$, 33 Da) to yield the $[\text{I}_2]^-$ anion of m/z 254 (Figure 2).

Conclusions

The combined Electrospray Ionization Mass Spectrometry monitoring and high level *ab initio* calculations revealed that IOOH, an unstable and reactive species proposed to be generated *in situ* as a result of the reaction of H_2O_2 and iodide in aqueous solution, is likely a key intermediate that take part in the overall mechanism that leads the decomposition of H_2O_2 to H_2O and O_2 . The refined set of information provided by ESI-MS certainly could not be achieved by other techniques thus revealing the exceptional ability of ESI-MS to directly monitor processes that take place in condensed phase.

Acknowledgments

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