

Liquid-liquid reaction of hydrogen peroxide and sodium hypochlorite for the production of singlet oxygen in a centrifugal flow singlet oxygen generator

Rong-rong Cui, Lie-zheng Deng*, Wen-bo Shi, He-ping Yang, Guo-he Sha, Cun-hao Zhang

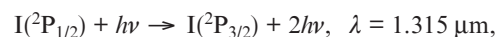
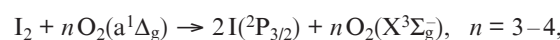
Abstract. An attempt is made to produce gas-phase singlet oxygen $O_2(a^1\Delta_g)$ in a liquid-liquid reaction between acidic hydrogen peroxide (AHP) and sodium hypochlorite (NaOCl). The attempt arises from the fact that basic hydrogen peroxide (BHP) has long been the prime source for producing singlet delta oxygen through its reaction with chlorine. However, BHP suffers from the defect of being unstable during storage. Exploratory experiments were performed in a centrifugal flow singlet oxygen generator (CF-SOG) with two streams of solutions, AHP and NaOCl, mixed in a slit nozzle and then injected into the arc-shaped concavity in the CF-SOG to form a rotating liquid flow with a remarkable centrifugal force. With the help of this centrifugal force, the product of the $O_2(^1\Delta)$ reaction was quickly separated from the liquid phase. The gas-phase $O_2(^1\Delta)$ was detected via the spectrum of $O_2(^1\Delta)$ cooperative dimolecular emission with a CCD spectrograph. Experimental results show that it is feasible to produce gas-phase $O_2(^1\Delta)$ from the AHP + NaOCl reaction, and the stronger the acidity, the more efficient the $O_2(^1\Delta)$ production. However, since in the AHP + NaOCl reaction, Cl_2 unavoidably appears as a byproduct, its catalytic action on the decomposition of H_2O_2 into ground-state O_2 remains a major obstacle to utilising the AHP + NaOCl reaction in producing gas-phase $O_2(^1\Delta)$. Qualitative interpretation shows that the AHP + NaOCl reaction is virtually the reaction of interaction of molecular H_2O_2 with molecular HOCl, its mechanism being analogous to that of reaction of BHP with Cl_2 , where HOCl is the key intermediate. It is difficult to form the intermediate HOCl via the H_2O_2 + NaOCl reaction in a basic medium, thus gas-phase $O_2(^1\Delta)$ cannot be obtained in appreciable quantities.

Keywords: chemical laser, singlet oxygen generator, chemical oxygen–iodine laser, hydrogen peroxide, sodium hypochlorite.

1. Introduction

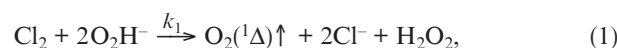
As a short-wavelength chemical laser capable of a very high continuous power output, the chemical oxygen–iodine laser (COIL), first successfully demonstrated by McDermott et al. [1] in 1978, has now nearly reached the engineering-wise maturity [2]. It operates on the nearly resonant energy transfer

from the singlet delta oxygen $O_2(a^1\Delta_g)$ to an atomic iodine atom which is produced from molecular iodine dissociated by $O_2(^1\Delta)$ [2]:



where, as the direct energy source, the method for $O_2(a^1\Delta)$ production is of vital importance for COILs.

At present, the most common method for the $O_2(a^1\Delta)$ production is the gas-liquid reaction of gaseous chlorine (Cl_2) with basic hydrogen peroxide (BHP) [2]. BHP is the solution formed by mixing excess hydrogen peroxide (H_2O_2) with such alkali as LiOH, NaOH and KOH. As the alkalinity of OH^- is much stronger than that of O_2H^- , almost all the OH^- ions change into O_2H^- ions as mixing proceeds, and the components in the BHP solution are H_2O_2 , H_2O , O_2H^- and alkali metal cations [3]. Hence, the Cl_2 + BHP reaction is virtually the reaction of Cl_2 with the O_2H^- ion [3, 4]:



$$k_1 \sim 10^8 \text{ M}^{-1} \text{ s}^{-1}.$$

Measured by Richardson et al. [4], the second order rate constant of reaction (1) is as high as $\sim 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

The shortcoming of the Cl_2 + BHP reaction system lies in the intrinsic instability of BHP, as in the alkaline solution, H_2O_2 is very easily decomposed. The catalysis in this case can be alkali, traces of transition metal ions of variable valence, and even the inner walls of the chamber [5–9]. Even after careful purification, BHP can be stored for no longer than 40 days [5], while BHP of common purity can preserve its potency for 1–10 days only even at a temperature as low as -20°C [10]. Our long-term experience in handling BHP shows that its potency will be completely lost after two weeks of storage at temperature of -10°C . Moreover, it is very likely that explosive decomposition will occur after a prolonged storage at room temperature.

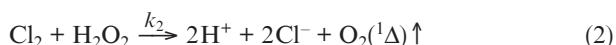
If BHP is substituted by non-basic (neutral or acidic) hydrogen peroxide (nBHP), the instability problem of BHP will be totally solved. nBHP may be stored for many years if proper stabiliser of H_2O_2 is added [11]. For example, the 50% wt. commercial H_2O_2 we purchased showed almost no change after being kept for three years in an ordinary polyethylene plastic barrel.

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The difficulty in substituting nBHP for BHP lies in that the $\text{Cl}_2 + \text{nBHP}$ reaction

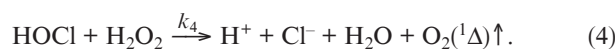


is considerably slower. The second order rate constant in reaction (2) was $35 \text{ M}^{-1} \text{ s}^{-1}$, as estimated by Davies et al. [12], far less than the rate constant of reaction (1).

For example, if we use 50% wt. H_2O_2 with the concentration $[\text{H}_2\text{O}_2] = 17.6 \text{ M}$, the characteristic time for $\text{O}_2(^1\Delta)$ production in the $\text{Cl}_2 + \text{nBHP}$ reaction is $(k_2[\text{H}_2\text{O}_2])^{-1} = 1.6 \text{ ms}$, which is much longer than the $\text{O}_2(^1\Delta)$ lifetime of $2 \mu\text{s}$ in water [13]. Therefore, it is impossible to obtain gas-phase $\text{O}_2(^1\Delta)$ in this reaction. Thus, the key is to find a Cl_2 substitute which can readily react with nBHP to produce $\text{O}_2(^1\Delta)$.

Fortunately, the Cl_2 substitute, hypochlorous acid (HOCl), has in fact long been discovered. Back in the 1960s, Seliger [14,15] already observed the red irradiation of the $\text{O}_2(^1\Delta)$ dimols when mixing acidic hydrogen peroxide (AHP) with sodium hypochlorite (NaOCl). We believe that in an acidic

medium, OCl^- would quickly combine with H^+ to form HOCl molecules, which would then react with H_2O_2 to form $\text{O}_2(^1\Delta)$:



Determined by Makower et al. [16], the second order rate constant in reaction (4) was as high as $1.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, so that the characteristic time for $\text{O}_2(^1\Delta)$ production in the $\text{Cl}_2 + \text{nBHP}$ reaction will be shortened to $0.6 \mu\text{s}$, even shorter than the $\text{O}_2(^1\Delta)$ lifetime of $2 \mu\text{s}$ in water [13]. Thus, theoretically it is feasible for the AHP + NaOCl reaction to produce gas-phase $\text{O}_2(^1\Delta)$.

The AHP + NaOCl reaction is a liquid-liquid reaction. Fast and even mixing of the two liquids, as well as good gas-liquid separation are the prerequisites for the favourable production of gas-phase $\text{O}_2(^1\Delta)$. In the past two years, originally with a view to improve the efficiency of the $\text{Cl}_2 + \text{BHP}$ reaction [17], we have designed and constructed a new type of a singlet oxygen generator (SOG), namely the centrifugal flow

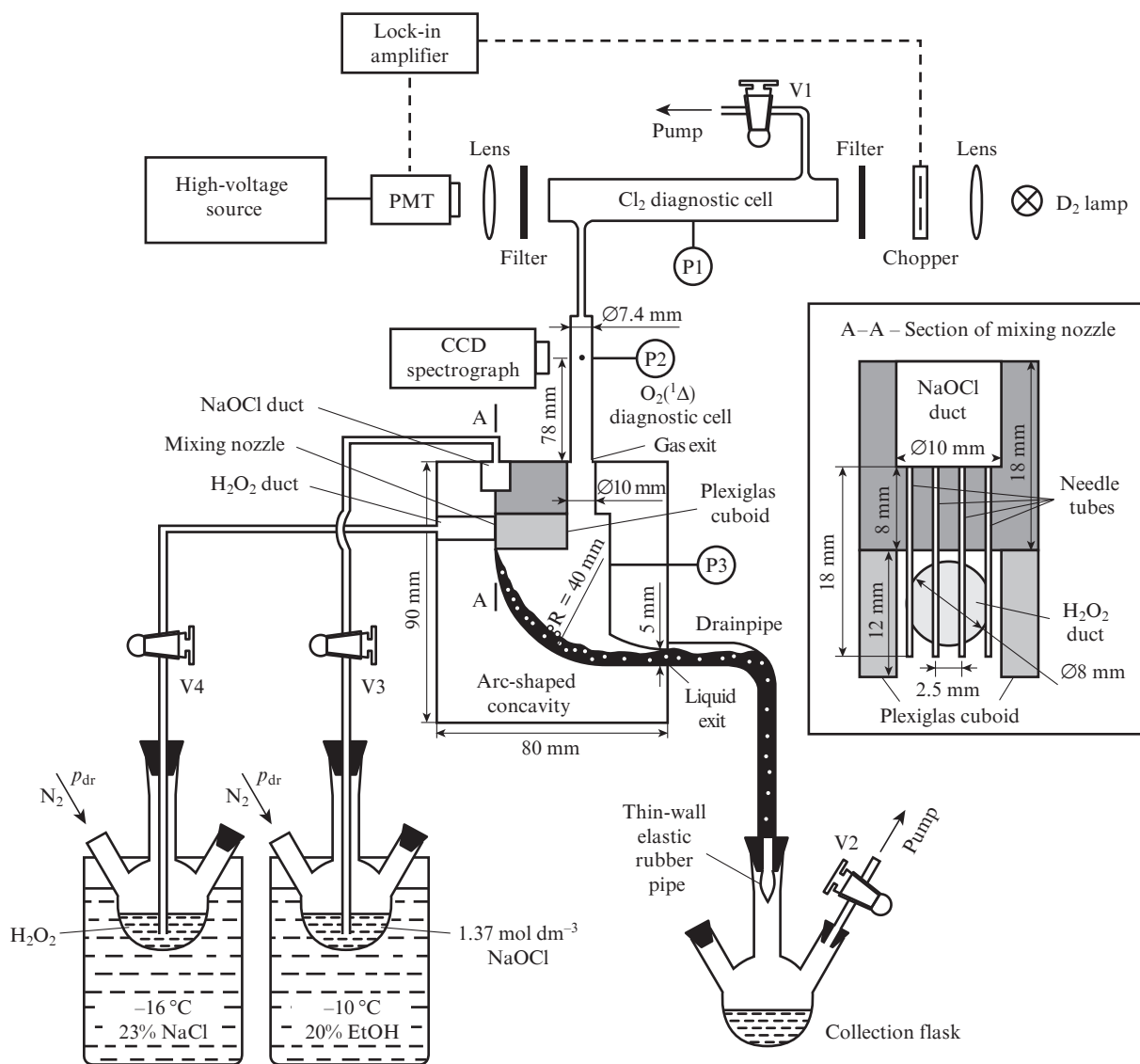


Figure 1. Schematic of the experimental setup (P1–P3 are manometers; V1–V4 are vacuum valves).

SOG (CF-SOG) in which the tremendous centrifugal force formed by a high-speed BHP liquid flowing over an arc-shape concavity was used to separate gas from liquid, so that the reaction efficiency was improved. We later adapted the CF-SOG to the liquid-liquid reaction of AHP + NaOCl.

2. Experimental setup

The experimental setup, which is similar to the CF-SOG used in [17], is schematically shown in Fig. 1. The reaction chamber in the CF-SOG is made of Plexiglas. On the left-top of the reaction chamber is a 10×0.74 -mm rectangle-cross-section mixing nozzle, which is virtually a 12-mm-long channel formed by attaching a cuboid Plexiglas block with a slot $0.74 \times 10 \times 12$ mm in size (depth \times width \times length) to the inner wall of the reaction chamber. The H_2O_2 duct is perpendicular to the NaOCl duct. Four needle tubes with an inner diameter of 0.390 mm drilled through the bottom of the NaOCl duct were inserted into the mixing nozzle. Through the four needle tubes the NaOCl solution was dropped into the H_2O_2 primary liquid flow, and then through the mixing nozzle was ejected onto the arc-shaped concavity to form a rotating liquid flow. The arc-shaped concavity has a width of 17 mm and a curvature radius of 40 mm. The 17×5 -mm rectangle-cross-section exit for liquid flow is located at the end of the concavity; through this exit the liquid flow runs into the drainpipe and is then drained into the collection flask. At the drainpipe outlet a thin-walled elastic rubber pipe is connected, which serves as a 'check valve' to isolate the reaction chamber from the collection flask. The $\text{O}_2(^1\Delta)$ diagnostic cell is a quartz tube with an inner diameter of 7.4 mm, connected with the gas exit. The light entrance to the CCD spectrograph is placed opposite at a distance of 78 mm from the gas exit, where the emission spectrum from the $\text{O}_2(^1\Delta)$ gas flow is detected. The manometers P1, P2 and P3 measure the pressures in Cl_2 , $\text{O}_2(^1\Delta)$ diagnostic cells and the reaction chamber, respectively. The Cl_2 diagnostic system, identical to that in [18], consists of a deuterium lamp, a chopper, two convex lenses, two filters, a Cl_2 diagnostic cell, a photomultiplier tube (PMT) and a lock-in amplifier. The Cl_2 partial pressure (p_{Cl_2}) was determined by measuring the 325-nm light absorption signal (S_{Cl_2}) in the Cl_2 diagnostic cell.

The AHP solution, in which the H_2O_2 concentration was constant and equal to 8.0 M and the HNO_3 concentration was variable at the four different concentrations 8, 4, 2, 0 M, was prepared by mixing H_2O_2 (50% wt.) with HNO_3 (65% wt.). The NaOCl solution came directly from commercial antiformalin, in which [NaOCl] was measured to be 1.4 M. The AHP and NaOCl solutions (500 mL each) were previously poured into one-litre flasks, and were kept cooled with saturated NaCl solution of -16°C and 20% (v/v) ethyl alcohol of -10°C , respectively. The driving pressure p_{dr} in the H_2O_2 and NaOCl flasks was maintained by N_2 at 15.0 kPa. Driven by the pressure, the volumetric flow rate for the H_2O_2 solution was about 25 mL s^{-1} , and for the NaOCl solution – about 1.7 mL s^{-1} , which corresponded to a 2.38-mmol s^{-1} molar flow rate for both NaOCl and Cl_2 ; the linear velocity of the mixed liquid flow was about 3.5 m s^{-1} , corresponding to a centrifugal acceleration of about $31g$ ($1g = 9.8 \text{ m s}^{-2}$).

3. Experimental results and discussions

Figure 2 shows typical dependences for the CF-SOG working cycle. Phase I represents the state before introducing the liquids into the reaction chamber, where the valves V1 and V2

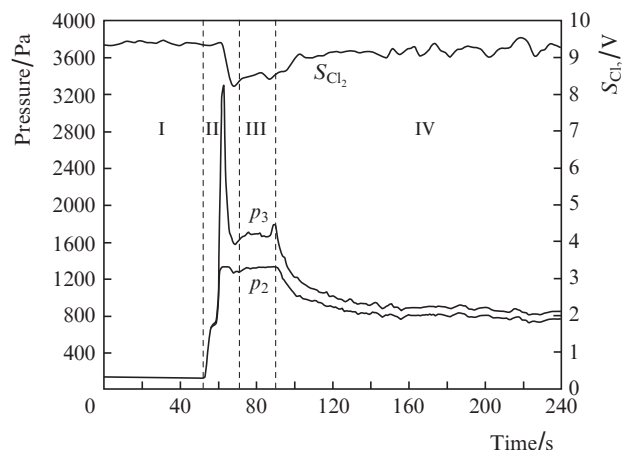


Figure 2. Typical dependences for four phases of the CF-SOG working cycle (from experiment 15 in Table 1). (I) before introducing the liquids; (II) starting to introduce liquids; (III) plateau phase of the AHP + NaOCl reaction; (IV) liquid flow cut off; p_2 and p_3 are the pressures measured with manometers P2 and P3, and S_{Cl_2} is the light absorption signal (S_{Cl_2}) in the Cl_2 diagnostic cell (see Fig. 1).

are opened. In phase II, the valves V3 and V4 are opened in sequence, so as to enable the NaOCl and AHP solution to enter successively into the reaction chamber, resulting in a violent pressure variation in the SOG. In phase III, the reaction of AHP + NaOCl proceeds smoothly. Finally, in phase IV, the valves V3 and V4 are shut and the liquid flow is cut off. The CCD spectrograph takes a frame of the spectrum at 4 second intervals. Figure 3 shows the spectra taken in phase III for different concentrations of HNO_3 , and Table 1 lists the average pressure values of phase III.

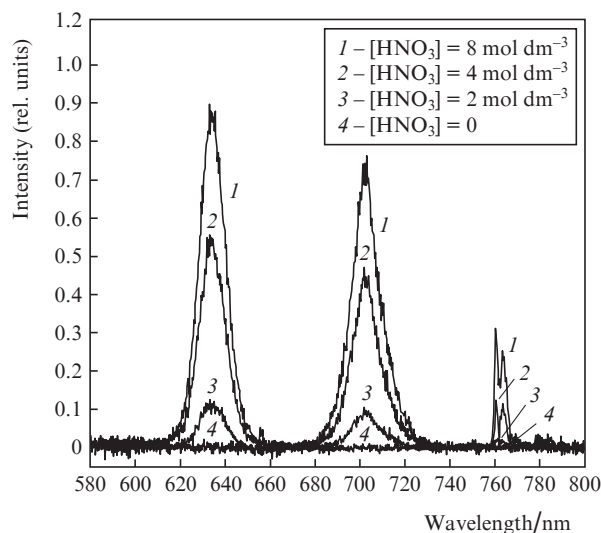


Figure 3. Emission spectra of the gas flow at the exit of the reaction chamber for different concentrations of HNO_3 .

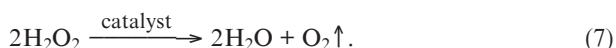
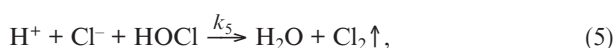
One can see from Fig. 2 that p_2 and p_3 decline slowly in phase IV when the liquid flow is cut off, and are unable to return to the original values in phase I after a very long time. It may thus be construed that the phenomenon resulted from two reasons. The minor reason could be the vaporisation of the liquid residue on the inner chamber wall, while the major

Table 1. Average values* of the pressures in the CF-SOG for different HNO₃ concentrations.

Experiment	[HNO ₃]/ mol dm ⁻³	<i>p</i> ₁ /Pa	<i>p</i> ₂ /Pa	<i>p</i> ₃ /Pa	<i>p</i> _{Cl₂} /Pa	<i>p</i> _{Cl₂} / <i>p</i> ₁
15	8.00	612.2	1320.6	1681.1	45.1	0.074
16	4.00	698.0	1259.1	1554.2	23.3	0.033
17	2.00	603.6	1256.6	1634.7	10.7	0.018
18	0	600.5	1257.7	1492.3	0	0
19	6.37**	605.2	1326.9	1945.1	0	0

*The average values of phase III during the CF-SOG working cycle (see Fig. 2.); **BHP with [KOH₂] = 6.37 M was used to replace AHP; the proportioning for the BHP is the same as that in Ref. [17].

reason may be attributed to a series of the gas-producing side reactions [for example, reactions (5)–(7)], which take place in the collection flask.



The unceasing bubbles from the mixed solution are the right proof for the existence of the side reactions.

In an acidic medium, reactions (5) and (6) would happen immediately after hydrochloric acid (HCl) is generated by reaction (4). Reaction (5) is the reverse reaction of Cl₂ hydrolysis. Based on the rate constant [19] and equilibrium constant [20] for Cl₂ hydrolysis, we can approximately estimate the third order rate constant *k*₅ to be on the order of 10³ M⁻² s⁻¹. Because the third order rate constant *k*₆ for reaction (6) is only on the order of 10⁻⁶ M⁻² s⁻¹ [21], it is very likely that reaction (5) is the predominant reaction for producing Cl₂. If NaOCl and AHP are not used up in the reaction chamber, the remaining NaOCl will convert into HOCl in the collection flask, and reaction (5) will proceed to produce Cl₂ until NaOCl is fully consumed. This point is further confirmed by the course that *S*_{Cl₂} slowly recovers to its original value of phase I after liquid flow has been cut off (see phase IV in Fig. 2).

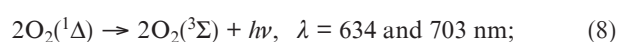
In reaction (7), H₂O₂ is catalytically decomposed into ground state oxygen by the catalysts in the solution. It proceeds as soon as the two solutions of NaOCl and H₂O₂ get in contact with each other. The catalysts are the byproduct Cl₂ and the impurities in the NaOCl solution. In an acidic medium, Cl₂ should serve as the main catalyst. Livingston et al. [21] believed that reactions (2) and (6) constitute a catalysis cycle of reaction (7). This can be proved by a simple experiment: in mixing the concentrated hydrochloric acid with H₂O₂, the mixed solution changes slowly even for a long time; when the concentration of Cl₂ produced by reaction (6) accumulates to a certain extent, the explosive decomposition will occur in the mixed solution.

In the alkaline medium, since no Cl₂ is generated, the catalyst can only be the impurities in the NaOCl solution (for example, commercial antiformin may contain a small amount of free alkali to improve the NaOCl stability). As the basic H₂O₂ solution is less stable [5–9], reaction (7) becomes faster in an alkaline medium. Table 1 shows that experiments 18, 19 are ‘alkaline’ experiments in which reactions (2)–(6) are unlikely to occur, but the pressures *p*₁, *p*₂, and *p*₃ are not markedly lower than those in the ‘acidic’ experiments 15–17. Especially

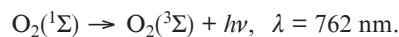
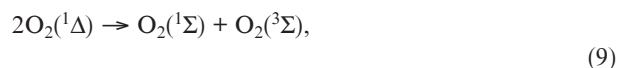
in experiment 19 where BHP was used, reaction (7) led to higher pressures for *p*₂ and *p*₃.

Note that, although the catalysis due to the impurities can be eliminated by further purification of NaOCl solution, it makes no sense to do so. Because only in the acidic medium gas-phase O₂(¹Δ) can be generated, side reactions (5) and (6), as well as the Cl₂ catalysis for H₂O₂ decomposition are in any case inevitable. Side reaction (5) decreases the utilisation of NaOCl, and side reaction (6) generates ground-state O₂, diminishing the yield of O₂(¹Δ). The most harmful is the Cl₂ catalysis, because of which the remaining unreacted H₂O₂ in the collection flask becomes unstable and, therefore, not reusable, forming a large amount of waste.

It was well known [22] that the two peaks at 634 nm and 703 nm in Fig. 3 arise from the O₂(¹Δ) dimolecular cooperative emission:



and the peak at 762 nm originates from the spontaneous radiation process of O₂(¹Σ) formed by the energy pooling of two O₂(¹Δ) molecules,



The presence of the three peaks in the spectrum proves that the AHP + NaOCl reaction has definitely produced gas-phase O₂(¹Δ). Moreover, one can see from Fig. 3 that the concentration of O₂(¹Δ) produced by the AHP + NaOCl reaction depends on the AHP acidity. The stronger the acidity, the more effective the O₂(¹Δ) production. This agrees with the observations by Seliger [14] in 1960. It may be asserted that this dependence is determined by the content of molecular HOCl. Since hypochlorous acid is weak, it exists principally in the form of OCl⁻ ions when pH > 9 and essentially in the form of molecular HOCl when pH < 6. Because the commercial antiformin contains a small amount of free alkali (NaOH) as a stabiliser for NaOCl, the NaOCl solution used in the above experiments exhibited some alkalinity, and hypochlorous acid existed mostly in the ion form. When the NaOCl solution is mixed with AHP, OCl⁻ will first combine with the excess H⁺ existing in AHP to form molecular HOCl [as in reaction (3)], then HOCl reacts with molecular H₂O₂ to produce O₂(¹Δ) [see reaction (4)]. Thus, the stronger the acidity, the higher the concentration of produced molecular HOCl when NaOCl is mixed with AHP, and the higher the O₂(¹Δ) yield.

The mechanism of O₂(¹Δ) production in the Cl₂ + BHP reaction, consisting of multiple reaction paths, was elucidated by Storch et al. [3] in 1983. The chief reaction path is shown in Fig. 4a. The nonpolar molecular Cl₂ will exhibit a dipole moment when it is induced by the negatively charged O atom from the HOO⁻ ion. Then, the positively charged Cl atom electrophilically attacks the negatively charged O atom to form a transition complex, in which the O–Cl bond gradually forms as the Cl–Cl bond gradually breaks up. After undergoing the electron transfer, the transition complex splits into HOOC (peroxyhypochlorous acid) and Cl⁻. Then, HOOC ionises to OOC⁻ and H⁺ ion, the OOC⁻ ion dissociates into O₂(¹Δ), and the H⁺ ion recombines with the excess HOO⁻ to form H₂O₂. In this reaction path, HOOC is the key intermediate to pro-

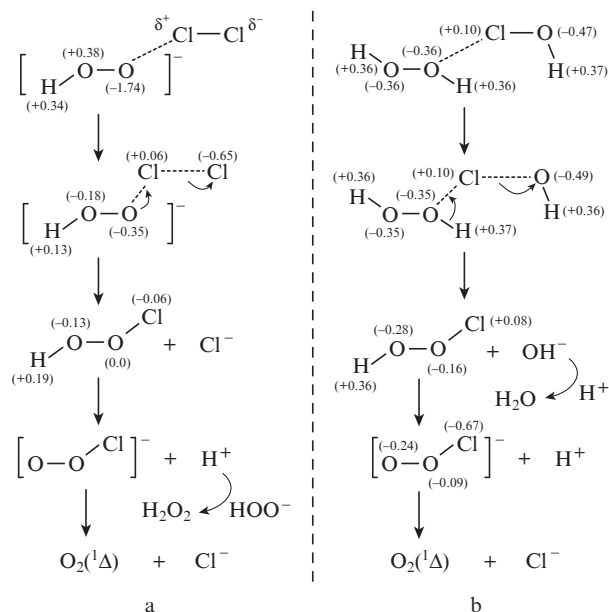


Figure 4. Reaction mechanisms of hydrogen peroxide with Cl_2 and HOCl : (a) the reaction mechanism of BHP with Cl_2 proposed by Storch [3] and (b) the postulated reaction mechanism of AHP with HOCl , in which the charge distribution was obtained from *ab initio* Gaussian calculations using the b3lyp/6-31+g(d,p) basis sets. Figures in bracket are the charges distributed in an atom, and δ^+ and δ^- are the induced charges in the induced dipole moment.

duce $\text{O}_2(^1\Delta)$, and only when HOCl has been generated $\text{O}_2(^1\Delta)$ is produced.

It should be pointed out that as early as 1994, Khan and Kasha [23] found experimentally that even in the absence of H_2O_2 the acidification of hypochlorite ClO^- alone may produce $\text{O}_2(^1\Delta)$. This reaction is completely different from the reaction of $\text{Cl}_2 + \text{BHP}$ or $\text{NaOCl} + \text{AHP}$. Nevertheless, recent theoretical computation by Jacobsen et al. [24] has shown that HOCl is the intermediate responsible for the production of $\text{O}_2(^1\Delta)$ via the acidification of ClO^- .

Comparing with the mechanism of the $\text{Cl}_2 + \text{BHP}$ reaction, we propose that to produce $\text{O}_2(^1\Delta)$, the intermediate, HOCl , must also be generated during the course of the $\text{HOCl} + \text{H}_2\text{O}_2$ reaction. Figure 4b shows the mechanism of the $\text{HOCl} + \text{H}_2\text{O}_2$ reaction that we proposed, and is similar to that of the $\text{Cl}_2 + \text{BHP}$ reaction. The differences are as follows.

(i) The Cl atom in HOCl is intrinsically positively charged and needs not be induced for its generation.

(ii) Two ions, H^+ and OH^- , need to be detached (simultaneously or in sequence) by the transition complex to form HOCl , while only one ion, Cl^- , needs to be detached in the $\text{Cl}_2 + \text{BHP}$ reaction.

(iii) As it is an acid reaction, no excess basic anions such as O_2H^- in the $\text{Cl}_2 + \text{BHP}$ reaction help to absorb H^+ ions formed during dissociation of by HOCl .

There are four possible types of $\text{NaOCl} + \text{H}_2\text{O}_2$ reactions: the strong basic reaction of $\text{OCl}^- + \text{HOO}^-$, the weak basic reaction of $\text{OCl}^- + \text{HOOH}$, the acid reaction of $\text{HOCl} + \text{HOOH}$ and the reaction of $\text{HOCl} + \text{HOO}^-$. Because HOCl is a weak acid and HOO^- is a strong base, and the weak acid cannot coexist with a strong base, the $\text{HOCl} + \text{HOO}^-$ reaction in fact does not exist. As mentioned above, to form HOCl , the Cl and O atoms must approach each other to form the Cl-O bond. *Ab initio* calculations using the Gaussian soft-

ware package with the b3lyp/6-31+g(d,p) basis sets showed that in $\text{OCl}^- + \text{HOO}^-$ and $\text{OCl}^- + \text{HOOH}$ reactions where the Cl and O atoms are both negatively charged, a relative high Coulomb barrier must be overcome when the Cl and O atoms approach each other, which makes it difficult for the reactions to take place. In contrast, for the $\text{HOCl} + \text{HOOH}$ reaction, the Cl atom is positively charged, and the Coulomb attractive force between the Cl and O atoms will greatly reduce the reaction barrier, thereby accelerating the reaction. Thus, we believe the above-said well explains why only in an acid medium the $\text{NaOCl} + \text{H}_2\text{O}_2$ reaction can produce gas-phase $\text{O}_2(^1\Delta)$.

4. Conclusions

Preliminary experiments have shown that by applying the centrifugal force in the CF-SOG, it is feasible to produce gas-phase $\text{O}_2(^1\Delta)$ from the liquid-liquid reaction of AHP + NaOCl . The disadvantage consists in that it is unavoidable for the AHP + NaOCl reaction to produce the byproduct, Cl_2 , which may catalytically decompose H_2O_2 to ground-state O_2 . As a result, the most unreacted H_2O_2 becomes unstable and, therefore, not be reusable, causing a great waste of the material. Meanwhile, the produced ground-state O_2 will also decrease the $\text{O}_2(^1\Delta)$ yield. Thus, side reaction (5) in which the byproduct, Cl_2 , is produced, and catalytic decomposition reactions (2) and (6), in which H_2O_2 is catalytically decomposed by Cl_2 into ground-state O_2 , make it impossible to use the AHP + NaOCl reaction to produce gas-phase $\text{O}_2(^1\Delta)$. The AHP + NaOCl reaction is only suitable for the situation where the material is not repeatedly used.

A qualitative analysis of the reaction mechanism shows that the AHP + NaOCl reaction is virtually the reaction of molecular H_2O_2 with molecular HOCl . Its reaction mechanism is analogous to that of $\text{Cl}_2 + \text{BHP}$, and HOCl is the key intermediate in both reactions. In a basic medium, it is difficult for the $\text{H}_2\text{O}_2 + \text{NaOCl}$ reaction to form the intermediate, HOCl . Thus, gas-phase $\text{O}_2(^1\Delta)$ cannot be obtained in appreciable quantities.

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