Thermodynamic and Kinetic Aspects of the Stability of Sir P. C. Ray's Mercurous Nitrite Compound*

Asim K Das

Different thermodynamic and kinetic aspects of the stability of mercurous nitrite discovered accidentally in 1896 by P. C. Ray's group have been critically analysed in this review article. It has been concluded that mercurous nitrite is thermodynamically unstable but it gains the kinetic stability which may originate from the overpotential factor in the gas evolution in its redox decomposition. It may also arise from strengthening the Hg^I–Hg^I bond which undergoes cleavage at the rate determining step (rds) in the disproportionation of Hg_2^{2+} or its oxidation by the one-electron oxidant like NO_2^-. The Hg^I–Hg^I bond is strengthened through the formation of the relatively weaker Hg^I–O bond (i.e. nitrito linkage) compared to the Hg^I–N bond (i.e. nitro linkage) in mercurous nitrite.

Introduction

Mercurous nitrate $Hg_2(NO_3)_2$ is well known for a long time but before 1896, mercurous nitrite $Hg_2(NO_2)_2$ was unknown. P. C. Ray's accidental discovery of mercurous nitrite in 1896 is a scientific serendipity [1,2]. This discovery of mercurous nitrite created a storm among the chemists throughout the globe and it was immediately noticed and cited by *Nature* magazine (May 28 issue of 1896) [3]. Different aspects of the chemistry of the unusual compound, mercurous nitrite were explored and published by P. C. Ray in a series of papers [3,4].

The constituent ions of mercurous nitrite are themselves unstable [5] and in fact, they are only stable under some restricted condi-

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tions. Redox decomposition of mercurous nitrite is another possibility for its instability. In fact, mercurous nitrite is only stable under some restricted conditions. In fact, P.C. Ray's claim of mercurous nitrite formation in the reaction of dilute nitric acid with excess mercury was refuted by Potts and Allred in 1966 [6]. X-ray crystal structure studies on mercurous nitrite carried out by different workers were also inconclusive [7,8]. Thus it created a confusion regarding the existence of the mercurous nitrite. In 2001, Goswami and Bhattacharya, proposed a structure of mercurous nitrite in the journal, *Resonance* [9]. But their proposed structure could not be theoretically supported to explain the stability of the compound. However, all these confusions were removed and P.C. Ray's claim of mercurous nitrite was reestablished in 2011 by Chakravorty et al [10] through the X-ray crystal structure determination of mercurous nitrite prepared in the same procedure as done by P.C. Ray's group.

In fact, many unstable inorganic (e.g. ammonium nitrite) and organic nitrites like alkyl ammonium nitrites (e.g. RNH_3NO_2, $R_2NH_2NO_2$, R_3NHNO_2), mercurialkyl nitrites and mircurialkylaryl-ammonium nitrites were synthesized by P. C. Ray [3,4]. This is why, he was rightly addressed as the '**master of nitrite**'/'**doctor of nitrite**'. In general, the nitrites are unstable and explosive in some cases. Such nitrites are kinetically stable in pure from mainly due to the overpotential arising from the gas evolution [5,11] in their redox decomposition. For mercurous nitrite, the stability may also arise from strengthening the Hg^I–Hg^I bond which undergoes cleavage at the rate determining step (rds) in the disproportionation of Hg_2^{2+} or its oxidation by the one-electron oxidant like NO_2^- through the formation of the relatively weaker Hg^I–O bond (i.e. nitrito linkage) compared to the Hg^I–N bond (i.e. nitro linkage) in mercurous nitrite. Impurities may catalyse their decomposition.

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1. Discovery of Mercurous Nitrite

P. C. Ray's group was involved to prepare calomel (mercurous chloride, Hg_2Cl_2) for electrodes. To prepare calomel, mercurous nitrate ($Hg_2(NO_3)_2$) solution is treated with dilute HCl.

$$Hg_2(NO_3)_2 + HCl \rightarrow Hg_2Cl_2(\downarrow) + 2HNO_3$$
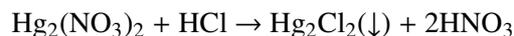
For the preparation of calomel in the above standard route, Ray's group was engaged to prepare $Hg_2(NO_3)_2$ in the reaction of dilute HNO_3 (1:4) with excess mercury. During the preparation of $Hg_2(NO_3)_2$, yellow crystalline needles were found to deposit on the Hg-surface. On standing, the yellow crystalline solid (in contact with the mother liquor) converted into the transparent crystalline solids which were identified as Marignac's salt (i.e. basic mercurous nitrate).

The yellow crystals were immediately separated from the mother liquor and analysed. They were decomposed in boiling water and it produced Hg^0, Hg^{2+} and NO_2^- (estimated in the reaction with urea). The observed molar ratio (Hg^0: Hg^{2+} : NO_2^- = 1 : 1 : 2) established the yellow crystals as $Hg_2(NO_2)_2$ [1,2]. It was the discovery of mercurous nitrite (*Scheme* 1).
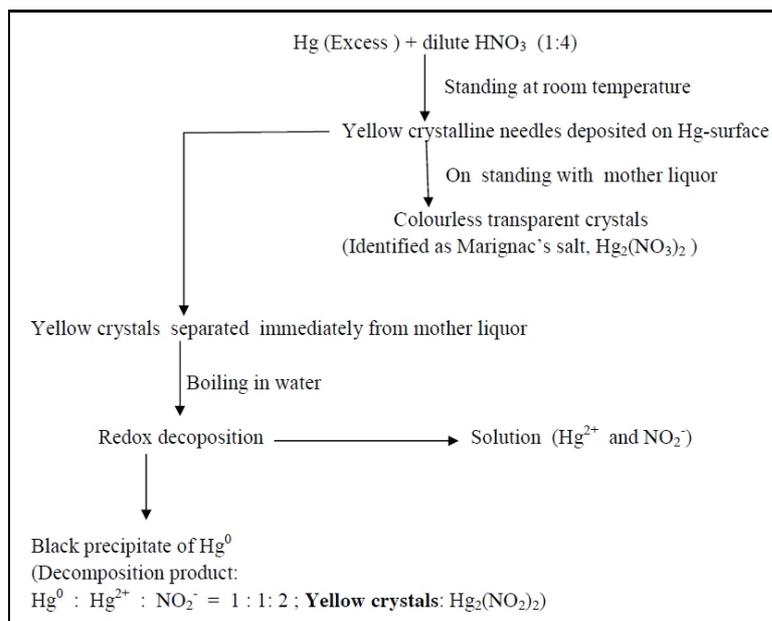
Let us consider the standard reduction potential values of the following redox couples of mercury:
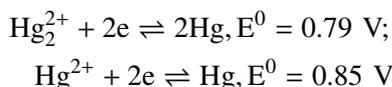
$$Hg_2^{2+} + 2e \rightleftharpoons 2Hg, E^0 = 0.79 \text{ V};$$
$$Hg^{2+} + 2e \rightleftharpoons Hg, E^0 = 0.85 \text{ V}$$

In terms of the standard reduction potential values, elemental mercury can be oxidized only upto Hg(I), i.e. Hg_2^{2+}, (but not upto Hg^{2+}) by the oxidizing agents whose potential values lie in the narrow range > 0.79 V but < 0.85 V. The common oxidizing agents including nitric acid (cf. $E^0(NO_3^-/NO_2^-) = 0.94$ V, E^0 $(NO_3^-/NO) = 0.95$ V) generally do not satisfy this condition and when mercury is treated with an excess of the oxidizing agent,

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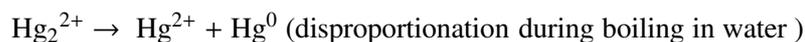
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Hg (Excess ) + dilute HNO₃  (1:4)

              │ Standing at room temperature
              ▼
Yellow crystalline needles deposited on Hg-surface

              │ On  standing with  mother liquor
              ▼
Colourless transparent crystals
(Identified as Marignac's salt, Hg₂(NO₃)₂ )

Yellow crystals  separated  immediately from mother liquor

              │ Boiling in water
              ▼
Redox decoposition  ───────────▶  Solution  (Hg²⁺ and NO₂⁻)

              │
              ▼
Black precipitate of Hg⁰
(Decomposition product:
Hg⁰ :  Hg²⁺ :  NO₂⁻  =  1 : 1: 2 ; Yellow crystals: Hg₂(NO₂)₂)
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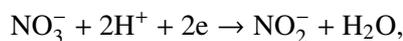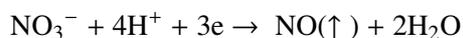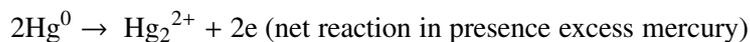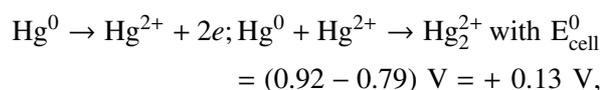
Scheme 1: P. C. Ray's synthesis of mercurous nitrite.

it is totally converted into Hg^{2+}. But when mercury is taken in excess (at least 50%), Hg(I), i.e. Hg_2^{2+}, can be produced because Hg can readily reduce Hg^{2+} to Hg_2^{2+} (i.e. $Hg^0 + Hg^{2+} \rightarrow Hg_2^{2+}$) [12]. Formation of mercurous nitrite occurs in a slightly acidic condition in the reaction of elemental mercury (in excess) with dilute HNO_3. The overall involved reactions are:

$$Hg^0 \rightarrow Hg^{2+} + 2e; Hg^0 + Hg^{2+} \rightarrow Hg_2^{2+} \text{ with } E^0_{cell}$$
$$= (0.92 - 0.79) \text{ V} = + 0.13 \text{ V},$$

$$2Hg^0 \rightarrow Hg_2^{2+} + 2e \text{ (net reaction in presence excess mercury)}$$

$$NO_3^- + 4H^+ + 3e \rightarrow NO(\uparrow) + 2H_2O$$

$$NO_3^- + 2H^+ + 2e \rightarrow NO_2^- + H_2O,$$
$$Hg_2^{2+} + 2NO_2^- \rightarrow Hg_2(NO_2)_2 (\downarrow) \text{ (yellow crystals)}$$

$$Hg_2(NO_2)_2 \rightarrow Hg_2^{2+} + 2NO_2^- \text{ (on boiling in water)},$$

$$Hg_2^{2+} \rightarrow Hg^{2+} + Hg^0 \text{ (disproportionation during boiling in water)}$$

Formation of mercurous nitrite occurs in a slightly acidic condition in the reaction of elemental mercury (in excess) with dilute HNO_3.

$$2NO_2^- + 2H^+ + OC(NH_2)_2 \text{ (urea)} \rightarrow CO_2 + 2N_2 + 3H_2O$$

Reaction of elemental mercury with dilute HNO_3 indicates that both the ions Hg_2^{2+} and NO_2^- produced are stable in a dilute acidic condition and they combine to crystallize as the yellow needle crystals. However, there is a question of stability of $Hg_2(NO_2)_2$ as noted by Ray himself.

2. Thermodynamic Stability of the Hg_2^{2+} Species with respect to Disproportionation

Possibility of its disproportionation can be analysed by considering the following Latimer EMF diagram [5].

$$Hg_2^{2+} + 2e \rightleftharpoons 2Hg, E^0 = 0.79 \text{ V}; 2Hg^{2+} + 2e \rightleftharpoons Hg_2^{2+}; E^0 = 0.92 \text{ V}$$

$$2Hg^{2+}/Hg_2^{2+}: E = E^0 + \frac{0.06}{2} \log [Hg^{2+}]^2/[Hg_2^{2+}], E^0 = 0.92 \text{ V}$$

Disproportionation: $Hg_2^{2+} \rightleftharpoons Hg^{2+} + Hg^0; E^0_{cell} = (0.79 - 0.92) \text{ V} = -0.13 \text{ V}$

E^0_{cell} for the said disproportionation reaction is negative and under the standard condition, the said disproportionation reaction is not thermodynamically possible. But, if under the experimental condition, formal potential of the $2Hg^{2+}/Hg_2^{2+}$ couple can be lowered down sufficiently to make E^0_{cell} positive, then the disproportionation reaction becomes thermodynamically possible. In fact, formation of the insoluble products like $Hg(OH)_2$, HgS, etc or stable complexes like $Hg(CN)_4^{2-}$ of Hg^{2+} lowers down the potential of the $2Hg^{2+}/Hg_2^{2+}$ couple sufficiently to allow the said

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disproportionation reaction thermodynamically [5]. In the acidic condition preventing the formation of insoluble $Hg(OH)_2$, Hg_2^{2+} survives from its disproportionation. However, it has been noted that at pH $\geq$ 5.6, due to the precipitation of $Hg(OH)_2$, disproportionation of Hg_2^{2+} becomes thermodynamically possible [3].

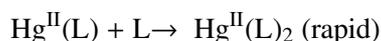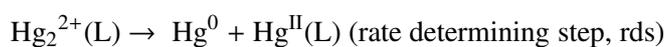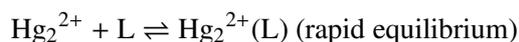Factors stabilizing Hg_2^{2+} and preventing its disproportionation can be rationalized also by considering the following comproportionation reaction (in general) [6].

$$Hg^0 + Hg^{II}L_x \rightleftharpoons Hg^I_2L_y + (x–y)L$$
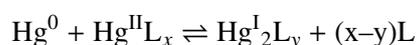
It indicates the following conclusions.

(i) Higher stability of $Hg^I_2L_y$ compared to that of $Hg^{II}L_x$ prevents the disproportionation of $Hg^I_2L_y$.

(ii) Hg^I–L bond should not be very strong because it will weaken the Hg–Hg bond of the Hg_2^{2+} species to favour the heterolytic cleavage of the bond leading to the said disproportionation reaction.

(iii) The reagent which can stabilize Hg^{II} either through the formation of stable complexes or insoluble precipitates will favour the disproportionation reaction. The possible rate process is [12]:

$$Hg_2^{2+} + L \rightleftharpoons Hg_2^{2+}(L) \text{ (rapid equilibrium)}$$

$$Hg_2^{2+}(L) \rightarrow Hg^0 + Hg^{II}(L) \text{ (rate determining step, rds)}$$

$$Hg^{II}(L) + L \rightarrow Hg^{II}(L)_2 \text{ (rapid)}$$

(iv) Here it is worth mentioning that for the oxidation of Hg_2^{2+} by the one-electron oxidant like nitrite, the rate determining step (rds) is also the cleavage of the Hg^I–Hg^I bond [12]. Thus to stabilize the Hg^I_2–cluster kinetically as in $Hg_2(NO_2)_2$ with respect to its redox decomposition, the Hg^I–Hg^I bond is also to be strengthened.

(v) L should not be oxidizing (both kinetically and thermodynamically) to oxidize Hg^I to Hg^{II}. Similarly, L should not be reducing to reduce Hg^I to Hg^0.

3. Thermodynamic and Kinetic Stability of NO_2^-

To consider the possibility of disproportionation of nitrite, we are to consider the following EMF diagram [5].

$$NO_3^- \xrightarrow{0.94} NO_2^- \xrightarrow{1.0} NO \text{ (Acidic condition)}$$
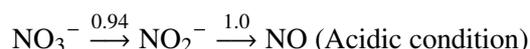
Disproportionation of NO_2^-: $3\,NO_2^- + 2H^+ \rightleftharpoons 2NO + NO_3^- + H_2O$

$E^0_{cell} = E^0\,(NO_2^-/NO) - E^0\,(NO_3^-/NO_2^-) = (1.0 - 0.94)\,V = 0.06\,V$

It indicates that in the acidic condition, NO_2^- which may be considered also to remain as nitrous acid HNO_2 having the pK_a value 3.2 [3,13] is thermodynamically unstable with respect to its disproportionation. It may be noted that the E^0_{cell} (= 0.06 V) for the said disproportionation reaction is only slightly positive and the reaction involves the gas evolution of NO and it experiences the overpotential (a kinetic barrier) which disfavours the process kinetically. Thus NO_2^- as HNO_2 (nitrous acid) the gains the kinetic stability to some extent with respect to its redox decomposition through the disproportionation reaction in the mild acidic condition. However, in the strongly acidic condition, nitrite disproportionates more readily.

It is interesting to point out that the favour in disproportionation of NO_2^- which mainly remains as HNO_2 (nitrous acid) in the acidic media can be rationalized [5,14] in terms of the bondings in the products and reactants (*Scheme* 2). In this disproportionation process, the number of O–H bonds remains unchanged but there is a net increase in the number of N–O π-bonds. The odd unpaired electron (denoted by a dot in Scheme 2) in NO remains in the antibonding π-molecular orbital (π^*-MO) [5] and thus the π-bond order in NO becomes 1.5. It is evident that 4 π-bonds (= 2 × 1.5 + 1) are produced at the cost of 3 π-bonds. Besides this, the lone pair-lone pair repulsion between N and O of nitrous acid is effectively reduced in the disproportionation products (cf. the N-lone pair is involved in making a coordinate covalent bond with oxygen in nitric acid).
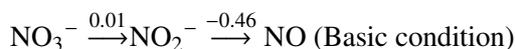
Scheme 2: Disproprotionation of nitrous acid (HNO_2).

It may be noted that NO_2^- which is resonance stabilised is thermodynamically stable in a basic condition.

$$NO_3^- \xrightarrow{0.01} NO_2^- \xrightarrow{-0.46} NO \text{ (Basic condition)}$$

$$E^0_{cell}(\text{disproportionation}) = E^0 (NO_2^-/NO)$$

$$- E^0 (NO_3^-/NO_2^-) = (-0.46 - 0.01) \text{ V} = -0.47 \text{ V}$$

Thus besides the kinetic barrier (overpotential due to evolution of NO gas), E^0_{cell} for disproportionation in a basic condition is highly negative (i.e. thermodynamic barrier). Thus NO_2^- is both thermodynamically and kinetically stable in a basic condition with respect to its disproportionation but Hg_2^{2+} ion is unstable in the basic condition due its favoured disproportionation.

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4. Possibility of Redox Decomposition of $Hg_2(NO_2)_2$

In the acidic condition, NO_2^- as a reducing agent (whose reducing power is measured by $E^0 (NO_3^-/NO_2^-) = 0.94$ V) cannot reduce Hg_2^{2+} (cf. E^0 for the couple $Hg_2^{2+}/2Hg = 0.79$ V) because for this reaction, E^0_{cell} is negative.

$$Hg_2^{2+} + NO_2^- + H_2O \longrightarrow 2Hg + NO_3^- + 2H^+$$

$$E^0_{cell} = E^0 (Hg_2^{2+}/2Hg) - E^0 (NO_3^-/NO_2^-)$$

$$= (0.79 - 0.94) \text{ V} = -0.15 \text{ V}.$$

But, in the acidic condition, NO_2^- as an oxidising agent (whose oxidising power is measured by $E^0 (NO_2^-/NO) = 1.0$ V) can oxidise Hg_2^{2+} (cf. E^0 for the couple $Hg^{2+}/ Hg_2^{2+}= 0.92$ V) because for this reaction, E^0_{cell} is positive.

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$$2 NO_2^- + 4H^+ + Hg_2^{2+} \longrightarrow 2NO + 2Hg^{2+} + 2H_2O$$

$$E^0_{cell} = E^0 (NO_2^-/NO) - E^0 (Hg^{2+}/Hg_2^{2+}) = (1.0 - 0.92) \text{ V} = 0.08 \text{ V}$$

The above reaction for which E^0_{cell} is slightly positive is kinetically disfavoured to some extent due to the overpotential factor for the release of NO gas. There is another source of kinetic barrier for the oxidation of Hg_2^{2+} by the one electron oxidant like NO_2^- (cf. $NO_2^- + 2H^+ + e \rightarrow NO + H_2O$). For the one-electron oxidant, the rate determining step (rds) is the cleavage of the Hg^I–Hg^I bond [12].

$$Hg^I\text{–}Hg^I - e \longrightarrow Hg^I + Hg^{II} \text{ (rds)}; Hg^I - e \longrightarrow Hg^{II} \text{ (fast)}$$
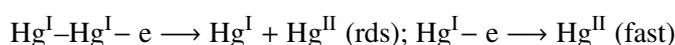
It will be discussed later that the Hg^I–Hg^I bond is strengthened by the formation of weaker Hg^I–O bond rather than the stronger Hg^I–N bond. Thus mercurous nitrite in an acidic condition does not have the thermodynamic stability but it possesses the kinetic stability to some extent with respect to its redox decomposition.

5. Comparison of the Stability of $Hg_2(NO_2)_2$ and $Hg_2(NO_3)_2$

NO_3^- is slightly less powerful as an oxidizing agent ($E^0 (NO_3^-/NO)$ = 0.95 V) than NO_2^- ($E^0 (NO_2^-/NO)$ = 1.0 V) in the acidic condition. In addition to this thermodynamic factor, kinetically, NO_3^- is a poorer oxidant than NO_2^- because of the stronger N–O bond in nitrate and in their oxidizing action, the N–O bond is to be ruptured [5]. There is no question of reducing action and disproportionation of nitrate. Thus there is no possibility of redox decomposition of $Hg_2(NO_3)_2$. It makes $Hg_2(NO_3)_2$ more stable than $Hg_2(NO_2)_2$.

6. Structure of $Hg_2(NO_2)_2$

It is shown in *Figure* 1. From the crystal structure [10], it is seen that mercury binds through the oxygen of nitrite. The molecular view of $Hg_2(NO_2)_2$ shows that the molecule is planar and centrosymmetric. Each Hg^I centre is unsymmetrically bonded to two oxygen atoms of the nitrite ion to produce a four membered chelate ring in which the nitrite ion approximately acts as a

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Figure 1. Molecular view
of discrete $Hg_2(NO_2)_2$ (Ref.
10).
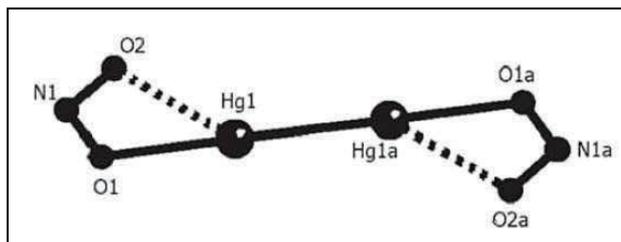
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bidentate chelating ligand (i.e. $\eta^2- NO_2^-$). Here one Hg^I–O interaction (denoted by . . .) is weaker and it may be described as a noncovalent interaction. The other Hg^I–O covalent interaction is stronger. The shorter (i.e stronger) and longer (i.e. weaker) Hg^I–O distances are 220 pm and 261 pm respectively. The Hg^I–Hg^I distance is 254 pm. In the crystal structure, it has been noted that there exists the weaker intermolecular Hg^I–O interactions and each O2 centre noncovalently interacts with two Hg^I-centres and each Hg^I-centre participates in such three weak interactions.

7. Hg^I–N Bond vs. Hg^I–O Bond and Kinetic Stability of $Hg_2(NO_2)_2$

In terms of the HSAB (hard and soft acids and basis) theory [5], the Hg^I–N bond (i.e. nitro linkage) is preferred to the Hg^I–O bond (i.e. nitrito linkage) and in fact, the Hg^I–N bond is shorter and stronger than the Hg^I–O bond. The stronger Hg^I–N bond will weaken the Hg^I–Hg^I bond to favour the heterolytic cleavage of the Hg^I–Hg^I bond. From the kinetics and mechanistic studies, it has been suggested that the heterolytic cleavage of the Hg^I–Hg^I bond is the rate determining step (rds) of the disproportionation reaction of Hg_2^{2+}. It has also been argued that this is also the rate determining step for the oxidation of Hg_2^{2+} by the one electron oxidant like NO_2^- (cf. $NO_2^- + 2H^+ + e \longrightarrow NO + H_2O$).

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Thus to stabilize the Hg_2^{2+} cluster with respect to its disproportionation and oxidation by nitrite, the weaker Hg^I–O nitrito linkage is preferred [6]. In fact, Goswami et al theoretically proposed in 2001 in Resonance [9] the structure of $Hg_2(NO_2)_2$ by considering the Hg^I–N nitro linkage. But from their studies on X-ray crystal structure of mercurous nitrite in 2011 [10], it was estab-

lished that there exists the Hg^I–O bond (i.e. nitrito linkage) not the Hg^I–N bond (i.e. nitro linkage). Thus the crystal structure determination contradicted their earlier proposed structure.

## 8. Conclusion Regarding the Stability of $Hg_2(NO_2)_2$

From the above discussion, now we are at the right position to draw the conclusions regarding the stability of mercurous nitrite. The major points to explain the stability of mercurous nitrite are mentioned here.

(i) In the acidic condition preventing the formation of insoluble $Hg_2(OH)_2$, mercurous ion (Hg_2^{2+}) is thermodynamically stable with respect to its disproportionation.

(ii) In the mild acidic condition NO_2^- is thermodynamically slightly unstable with respect to its disproportionation but it is kinetically stable to some extent due to the overpotential in the NO gas formation.

(iii) Though reduction of Hg_2^{2+} by NO_2^- is not thermodynamically possible, oxidation of Hg_2^{2+} by NO_2^- is thermodynamically slightly favoured in the acidic condition but the process is kinetically disfavoured due to the overpotential factor. There is another source of kinetic barrier for the oxidation of Hg_2^{2+} by the one electron oxidant like NO_2^- (cf. $NO_2^- + 2H^+ + e \rightarrow NO + H_2O$). For the one-electron oxidant, the rate determining step (rds) is the cleavage of the Hg^I–Hg^I bond.

$$Hg^I\text{–}Hg^I - e \longrightarrow Hg^I + Hg^{II} \text{ (rds)}$$
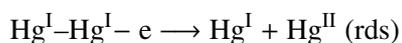
In mercurous nitrite, the relatively weaker Hg^I–O bond (i.e. nitrito linkage) compared to the Hg^I–N bond (i.e. nitro linkage) strengthens the Hg^I–Hg^I bond to disfavor kinetically the oxidation of Hg_2^{2+} by nitrite.

Here it is worth mentioning that all the above conclusions are made by considering the standard redox potentials (E^0) but in reality, it needs the consideration of the related formal potentials.

In fact, Goswami et al theoretically proposed in 2001 in Resonance [9] the structure of $Hg_2(NO_2)_2$ by considering the Hg^I–N nitro linkage. But from their studies on X-ray crystal structure of mercurous nitrite in 2011 [10], it was established that there exists the Hg^I–O bond (i.e. nitrito linkage) not the Hg^I–N bond (i.e. nitro linkage).

In mercurous nitrite, the relatively weaker Hg^I–O bond (i.e. nitrito linkage) compared to the Hg^I–N bond (i.e. nitro linkage) strengthens the Hg^I–Hg^I bond to disfavor kinetically the oxidation of Hg_2^{2+} by nitrite.

(iv) From the standpoint of kinetics and mechanism of the disproportionation reaction of Hg_2^{2+}, it has been suggested that the heterolytic cleavage of the Hg^I–Hg^I bond is the rate determining step (rds). In mercurous nitrite, the relatively weaker Hg^I–O bond (i.e. nitrito linkage) compared to the Hg^I–N bond (i.e. nitro linkage) strengthens the Hg^I–Hg^I bond to disfavor kinetically the disproportionation of Hg_2^{2+}.

All these indicate that in an aqueous mild acidic condition, both Hg_2^{2+} and NO_2^- ions can coexist (in presence of excess mercury) kinetically but not thermodynamically and they can form the yellow crystals of $Hg_2(NO_2)_2$. Thus kinetic stability is playing a crucial role in the overall stability of $Hg_2(NO_2)_2$.

Acknowledgements

Suggested Reading

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