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THE REACTIONS OF SOME COMPOUNDS OF ZINC, CADMIUM AND MERCURY WITH THE MOLTEN LITHIUM CARBONATE–SODIUM CARBONATE–POTASSIUM CARBONATE EUTECTIC

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ABSTRACT

The reactions of $ZnCl_2$, $CdCl_2$, $CdCO_3$, $CdSO_4$, Hg_2Cl_2, Hg_2SO_4, $HgCl_2$ and $HgSO_4$ with the molten alkali metal carbonate eutectic were investigated by thermogravimetry. Reaction products were analysed by various techniques.

Zinc and cadmium compounds were found to react with the eutectic showing one weight-loss step in their thermograms for the evolution of carbon dioxide and produced corresponding metal oxides. Mercury compounds, on the other hand, reacted with the eutectic exhibiting two or three weight-loss steps due to the formation of stable intermediates consisting of various basic mercury carbonates which ultimately decomposed to give a mixture of metallic mercury, oxygen and carbon dioxide. The temperature ranges of the reactions and their stoichiometries have been established.

INTRODUCTION

The alkali metal carbonate melt is a versatile high-temperature liquid. The melt has been used as an electrolyte in fuel cells [1], as a scrubbing medium for the removal of sulfur dioxide from flue gases and sulfur from coal undergoing gasification [2], as a non-toxic bath containing silicon carbide for the carburization of mild steel [3], and as a highly basic solvent for the preparation of oxy compounds of some transition metals [4].

The carbonate melt can act as a reaction medium as well as a Lux–Flood base, i.e., a donor of oxide ions evolving CO_2 which can be quantitatively determined using a thermobalance. For this reason, thermogravimetry has been employed in recent years for the investigation of chemical reactions in the molten carbonate eutectic. Thus, the reactions of acidic oxides and oxyanions of the main group elements [5], metal oxides and oxyanions of Group VB and VIB elements [6], some transition metal cations [7], iron(II) oxalate and basic nickel(II) carbonates [8], and some compounds of manganese [9] with the molten carbonate eutectic have been published recently. This paper now reports the thermogravimetric investigations of the reactions of some compounds of zinc, cadmium and mercury with the eutectic.

EXPERIMENTAL

Materials

Analar (Alfa) anhydrous Li_2CO_3, Na_2CO_3 and K_2CO_3 were dried at 130°C for 3 h, mixed in the eutectic ratio (32.1 : 33.4 : 34.5 wt.%, respectively) and melted in a cylindrical gold crucible placed in a silica tube at 450°C. Carbon dioxide gas was passed through the melt for 5 h by means of silica tubing connected to a gold tube dipping into the melt. The melt was solidified and finely ground in a dry box. The aqueous solution of the carbonate eutectic showed a negative test for hydroxide ions; this indicated that the melt was free from oxide impurity. The eutectic was melted at 397 ± 2°C under both carbon dioxide and argon atmospheres and compared with the reported value of 397°C [10].

Laboratory reagent grade (BDH) $ZnCl_2$ was purified according to the method of Kerridge [11] (found: Zn, 47.9; Cl, 51.9%; calcd. for $ZnCl_2$: Zn, 48.0; Cl, 52.0%). AnalaR (BDH) Hg_2Cl_2, $HgCl_2$ (99.6%), Analar (Alfa) $CdSO_4$ (ultrapure), $CdCl_2$ (99%), and laboratory reagent grade (BDH) $CdCO_3$, Hg_2SO_4 and $HgSO_4$ (99%) were all dried at 120°C for 3–5 h.

Procedure and analysis

The eutectic and each reactant were weighed in a 5-cm^3 gold crucible which was then heated on a thermobalance at 2° min^{-1} under both carbon dioxide and argon atmospheres at a flow rate of 20 cm^3 min^{-1} to determine their reaction temperature ranges and the amount of gaseous products, which were identified by infrared spectroscopy and mass spectrometry. The melt-insoluble products were separated by filtration, cooled to room temperature, washed quickly with aqueous KOH solution to remove the solidified carbonate melt, and then with methanol and acetone. The dried product was identified by the X-ray diffraction method. The product was dissolved in HCl to convert it into chlorides and the solution was examined by a hand-spectroscope to detect the presence of alkali metals. Zinc, cadmium and mercury were determined by atomic absorption spectroscopy.

Instrumentation

Thermogravimetric analysis was carried out on a Stanton TR-01 thermobalance. Infrared and mass spectra were obtained on a Perkin-Elmer 457 grating spectrometer and a JEOL D100 mass spectrometer, respectively. The X-ray diffraction measurements were carried out on a Siemens counter-tube goniometer by using nickel-filtered Cu K_α radiation. For atomic absorption measurements a Varian Techtron AA6 spectrophotometer was employed.

RESULTS AND DISCUSSION

Zinc(II) chloride

Zinc(II) chloride reacted with the carbonate eutectic showing a one-step weight loss due to evolution of carbon dioxide between 188 and 467°C. The solidified reaction mixture on stirring with water deposited a white residue which, analysed by X-ray and chemical methods, was found to be zinc(II) oxide. The experimental value of weight loss compared with that of a calculated value as shown in Table 1 and the analysis of the reaction products confirmed the following stoichiometry of this reaction.

$$ZnCl_2 + CO_3^{2-} \rightarrow ZnO + 2Cl^- + CO_2 \qquad (1)$$

As the weight loss took place in one step, quantitatively converting $ZnCl_2$ to ZnO, it was obvious that no stable intermediate existed in this reaction. This result may be supported by the observation of Kerridge and Sturton [12] who could not find any thermally stable species on heating Na_2CO_3 with molten $ZnCl_2$, nor could Dollimore and Griffiths [13] or Mu and Perlmutter [14] detect any stable carbonate or basic carbonate species during thermal study of $ZnC_2O_4 \cdot 2H_2O$ and $ZnCO_3$. However, Duval [15] mentioned the existence of a species, $ZnCO_3 \cdot 4ZnO$, stable to 880°C during the thermal study of basic zinc carbonate.

In a separate experiment, a mixture of $ZnCl_2$ and the eutectic was heated to 800°C, solidified, disssolved in water and an insoluble residue filtered. The residue was found to be ZnO and the filtrate contained no zinc(II) species. Thus, there was no indication even of the existence of any oxyanion of zinc in the reaction as normally found in alkaline solutions.

Cadmium(II) carbonate

When heated with the eutectic, $CdCO_3$ was found to decompose to CdO and CO_2 in a single weight-loss step. The thermogram gave no indication of the existence of any stable basic carbonate and showed the quantitative loss of CO_2 in accordance with the following decomposition reaction.

$$CdCO_3 \rightarrow CdO + CO_2 \qquad (2)$$

The temperature range for the decomposition of $CdCO_3$ alone to the above products under air or nitrogen has been reported [14] to be 280–375°C. This is close to that found under argon in this work.

TABLE 1

The reactions of some compounds of zinc, cadmium and mercury with the carbonate eutectic under argon (a) and carbon dioxide (b)

Reactant	No. of wt. loss steps	Temp. range (°C)	Temp. of max. rate (°C)	Wt. loss (%)	
				Found	Calc.
$ZnCl_2$	1 (a, b)	188–467	332	31.12 ± 1.10	32.28
$CdCO_3$	1 (a)	270–480	360	26.37 ± 0.48	25.52
	(b)	370–485	400		
$CdCl_2$	1 (a, b)	325–626	480	23.65 ± 0.68	24.00
$CdSO_4$	1 (a, b)	380–526	423	20.94 ± 0.51	21.10
Hg_2Cl_2	3 i(a, b)	180–320	270	49.60 ± 1.50	50.88
	ii(a)	378–485	400	58.15 ± 0.78	60.06
	(b)	440–550	532		
	iii(a, b)	580–730	668	97.05 ± 0.68	97.67
Hg_2SO_4	2 i(a, b)	380–500	443	48.05 ± 0.87	48.31
	ii(a, b)	520–760	600	89.96 ± 2.13	92.75
$HgCl_2$	3 i(a, b)	120–320	230	14.96 ± 0.38	14.59
	ii(a)	380–480	397	22.15 ± 0.87	22.57
	(b)	450–540	518		
	iii(a, b)	550–760	650	97.42 ± 2.55	95.99
$HgSO_4$	2 i(a, b)	370–500	467	50.29 ± 0.42	49.86
	ii(a)	500–730	623	87.17 ± 2.53	87.85
	(b)	610–730	684		

(1) When a reaction shows more than one weight-loss step, the value is shown as the combined loss at the end of that step.

(2) (a, b) indicates that the temperature range is the same under both argon and CO_2.

(3) The concentration of each reactant varied from 0.5 to 1.7 *m*.

As shown in Table 1, the initial decomposition temperature was found to depend on the nature of the gas under which $CdCO_3$ was heated. Thus, it was found to be 100°C higher under CO_2 than under argon. The reported final temperature (375°C), on the other hand, was close to that found under argon (480°C) and CO_2 (485°C).

On heating $CdCO_3$ with the eutectic to about 900°C, a grey sublimate of cadmium metal was deposited on the cooler parts of the apparatus. The mixture was solidified and a product, insoluble in water, was analysed to be mainly CdO with some cadmium metal. The filtrate contained no soluble cadmium species.

It was therefore concluded that $CdCO_3$ simply decomposed to CO_2 and CdO which was partly reduced to metal on heating to 900°C. There was no indication of the existence of a basic carbonate nor of any cadmium oxyanion in this system.

Cadmium(II) chloride

The thermogravimetric analysis indicated that $CdCl_2$ reacted with the eutectic in a single weight-loss step evolving a quantitative amount of CO_2 in support of reaction (3).

$$CdCl_2 + CO_3^{2-} \rightarrow CdO + 2Cl^- + CO_2 \qquad (3)$$

A residue of CdO was obtained from the aqueous solution of the solidified melt. The filtrate showed the absence of cadmium oxyanion species.

Cadmium(II) sulfate

This was found to react with the eutectic in a manner similar to the above reaction producing CdO and CO_2. The one-step quantitative weight loss supported the following stoichiometry of the reaction.

$$CdSO_4 + CO_3^{2-} \rightarrow CdO + SO_4^{2-} + CO_2 \qquad (4)$$

Both $CdCl_2$ and $CdSO_4$ reacted with the eutectic at high temperature in a manner similar to $CdCO_3$ without the formation of any oxyanion species.

Mercury(I) chloride

The thermogram of the reaction of Hg_2Cl_2 and the eutectic showed three weight-loss steps. The first step showed a weight loss of 49.60 ± 1.50% between 180 and 320°C. The temperature range for the second step depended on the atmosphere as shown in Table 1. The third step was between 580 and 730°C with a total weight loss of 97.05 ± 0.68%. The gaseous products collected at 270, 532 and 668°C were found to contain CO_2 in the first step and a mixture of CO_2 and O_2 in the last two steps. Metallic mercury was found to be evolved in all the steps.

To identify the intermediates, four reaction mixtures were collected by heating the chloride and the eutectic at 250, 350, 570 and 750°C. Their infrared spectra were found to be similar to that of the eutectic with two additional bands at 450 and 515 cm^{-1} in the first three mixtures. The X-ray diffraction patterns of the mixtures were found to be complicated. However, they showed all the *d*-spacings for the carbonate eutectic with low-intensity additional lines which could be assigned to LiCl, NaCl, KCl and HgO.

On dissolving each mixture in water and separating the insoluble products, it was observed that there was no insoluble product in the last mixture. The analysis showed the presence of chloride and the absence of mercury ions in the filtrates. All the insoluble products, though varied in colour from brown, yellow-brown to yellow-grey, showed two bands at 485 ± 5 and 587 ± 7 cm^{-1} in their infrared spectra and their X-ray diffraction patterns were found to be similar to that of HgO. The products dissolved in dilute HNO_3 and the solutions showed the presence of mercury(II) ions and the absence of alkali metals. It was concluded that the insoluble product in each case was HgO.

At the end of first weight loss of 49.60 ± 1.50% as compared with 51.81%, the stoichiometry of the reaction may be represented by the equation

$$Hg_2Cl_2 + CO_3^{2-} \rightarrow HgO + 2Cl^- + Hg + CO_2 \qquad (5)$$

At the end of the second reaction, the weight loss of 58.15 ± 0.78% could be compared with 59.28% calculated for the following reaction

$$2Hg_2Cl_2 + 2CO_3^{2-} \rightarrow Hg_2O + 4Cl^- + 2Hg + 2CO_2 + \tfrac{1}{2}O_2 \qquad (6)$$

The above stoichiometry was supported by weight losses and by analyses of the reaction products with the exception of the insoluble product which was found to be HgO rather than Hg_2O. The latter oxide might have existed momentarily before decomposing to its elements and thus producing an overall weight loss of 97.05 ± 0.68% as compared with a calculated value of 97.67% for the following final reaction

$$Hg_2Cl_2 + CO_3^{2-} \rightarrow 2Cl^- + 2Hg + CO_2 + \tfrac{1}{2}O_2 \qquad (7)$$

Alternatively, three weight-loss steps and the analytical results for the products may be explained by the initial formation and the decomposition of Hg_2CO_3 to a basic carbonate as expressed in the following reaction sequence.

$$\begin{array}{l} 10Hg_2Cl_2 + 10CO_3^{2-} \rightarrow 10Hg_2CO_3 + 20Cl^- \\ 10Hg_2CO_3 \rightarrow HgCO_3 \cdot 9HgO + 10Hg + 9CO_2 \\ \hline 10Hg_2Cl_2 + 10CO_3^{2-} \rightarrow HgCO_3 \cdot 9HgO + 20Cl^- + 10Hg + 9CO_2 \end{array} \qquad (8)$$

The calculated weight loss for the above reaction of 50.88% is comparable with the experimental value of 49.60 ± 1.50%.

The second step may be represented by eqn. (9) with a calculated weight loss of 60.06% compared with the experimental value of 58.15 ± 0.78%.

$$10Hg_2Cl_2 + 10CO_3^{2-} \rightarrow HgCO_3 \cdot 8HgO + 20Cl^- + 11Hg + 9CO_2 + \tfrac{1}{2}O_2 \qquad (9)$$

The basic carbonate formed in the second step would have decomposed to Hg, O_2 and CO_2 to account for the final weight loss. The sum of eqns. (8) and (9), and the decomposition of the above basic carbonate give the same overall reaction stoichiometry as expressed in eqn. (7).

The X-ray diffraction pattern of the solid reaction products containing mercury carbonate or basic carbonate along with carbonates and chlorides of alkali metals were complex and not conclusive. However, the infrared spectra of the products did contain two bands at 452 and 515 cm^{-1} which could be attributed to the basic carbonate as the corresponding bands in pure HgO or in the hydrolysed insoluble products appeared at 485 ± 5 and 587 ± 7 cm^{-1}, respectively.

Thus, the thermogravimetric weight losses of the reaction of Hg_2Cl_2 with the eutectic may well be explained by the initial formation of Hg_2CO_3 and its decomposition to be above-mentioned basic carbonates which finally decomposed to CO_2, O_2 and Hg.

In a separate experiment, solutions of Na_2CO_3 and Hg_2Cl_2 were mixed and a yellow-brown precipitate was obtained. On washing, the colour of the precipitate changed to brown. After drying, the infrared spectrum and the X-ray diffraction pattern indicated it to be HgO. It was concluded that mercury carbonate or basic carbonate produced above, or in the reaction of Hg_2Cl_2 with the eutectic would have hydrolysed during washing to form HgO. In the old literature, $HgCO_3$ has been described to be formed by the action of CO_2 on an alkaline solution of $HgCl_2$ [17]. However, according to a recent report [18] all experiments designed for the preparation of $HgCO_3$ gave only HgO or ill-defined basic carbonate. It is, therefore, not surprising that during the present study the existence of $HgCO_3$ or basic carbonate could not be confirmed after washing the mixture with water.

Mercury(I) sulfate

The thermogram of the reaction of Hg_2SO_4 with the eutectic showed a weight loss in two stages. In the first stage $48.05 \pm 0.87\%$ weight loss was registered between 380 and 500°C. In the second stage the weight loss was found to occur between 520 and 760°C, showing a total of $89.96 \pm 2.13\%$ loss. The volatile products were found to contain mixtures of $CO_2 + Hg$ and $CO_2 + O_2 + Hg$ during the first and second stages of the reaction, respectively.

In order to identify non-volatile species formed at the end of each stage, reaction mixtures were collected at 510 and 770°C. After solidifying, the infrared spectra of the mixtures were found to be similar to that of the eutectic with an extra band at 916 cm^{-1} in both the mixtures and a band at 450 cm^{-1} and a shoulder at 515 cm^{-1} in the first mixture only.

On dissolving the mixtures in water, an insoluble residue was obtained only in the first mixture. The residue was identified to be HgO by the infrared and the X-ray diffraction methods. The filtrate in each case was found by chemical tests to contain sulfate and there was no indication of the presence of mercury cations. The presence of sulfate in the solid mixtures was confirmed by the infrared band at 916 cm^{-1} due to ν_4 vibration of the sulfate ion [19]. Its presence in the filtrates may be taken to indicate the exchange of sulfate from Hg_2SO_4 by carbonate from the eutectic; thus, supporting the formation of mercury carbonate species during the course of this reaction. As discussed in the Hg_2Cl_2 reaction, the presence of infrared bands in the solid mixtures at frequencies lower than those expected for HgO may be indicative of the formation of a basic mercury carbonate. The band at 450 cm^{-1} and a shoulder at 515 cm^{-1} could be due to such a species.

From the above results and discussion the first weight loss may account for the following reaction.

$$10Hg_2SO_4 + 10CO_3^{2-} \rightarrow HgCO_3 \cdot 9HgO + 10SO_4^{2-} + 9CO_2 + 10Hg \qquad (10)$$

The absence of any insoluble product in the second mixture indicates the decomposition of mercury basic carbonate to CO_2, O_2 and Hg without the formation of any other species containing mercury. The final reaction may be represented by eqn. (11) with a calculated weight loss of 92.75% as compared to the experimental value of 89.96 ± 2.13%.

$$Hg_2SO_4 + CO_3^{2-} \rightarrow SO_4^{2-} + CO_2 + 2Hg + \tfrac{1}{2}O_2 \qquad (11)$$

It is interesting to note that the basic carbonate of the same composition ($HgCO_3 \cdot 9HgO$), when formed in a low-temperature range (180–320°C), as in the Hg_2Cl_2 reaction, was converted to $HgCO_3 \cdot 8HgO$ but when formed in a high-temperature range (380–500°C), as in the sulfate reaction, was found to decompose without forming any stable intermediate.

Mercury(II) chloride

This chloride reacted with the eutectic to show a weight loss in three steps. The first weight loss of 14.96 ± 0.38% took place between 120 and 320°C. At the end of the second step the combined weight loss was 22.15 ± 0.87% and took place between 380 and 480°C under argon but between 450 and 540°C under CO_2. The third weight loss was observed in both argon and CO_2 between 500 and 760°C and the total loss was found to be 97.42 ± 2.55%.

The analysis of gaseous products from each step indicated that only CO_2 evolved in the first step and a mixture of CO_2, O_2 and Hg in the last two steps.

In order to identify stable intermediates at the end of each step, $HgCl_2$ and the eutectic were heated under argon and samples collected at 340, 500 and 800°C and analysed as described in the previous mercury compound reactions. It was found that mercury basic carbonates were formed at the end of first and second steps and there was no mercury compound left in the solid mixture at the end of the third step. As found in the previous reactions the basic carbonates of mercury were converted to HgO by hydrolysis when washed with water.

The first weight-loss step of the reaction of $HgCl_2$ may be represented by the following sequences

$$\begin{array}{l} 10HgCl_2 + 10CO_3^{2-} \rightarrow 10HgCO_3 + 20Cl^- \\ 10HgCO_3 \rightarrow HgCO_3 \cdot 9HgO + 9CO_2 \\ \hline 10HgCl_2 + 10CO_3^{2-} \rightarrow HgCO_3 \cdot 9HgO + 20Cl^- + 9CO_2 \end{array} \qquad (12)$$

The calculated weight loss for the above step is 14.59% compared with 14.96 ± 0.38 as found experimentally.

The reaction at the end of second step may be expressed by eqn. (13) with a calculated weight loss of 22.57% compared with the experimental value of 22.15 ± 0.87%.

$$10HgCl_2 + 10CO_3^{2-} \rightarrow HgCO_3 \cdot 8HgO + 20Cl^- + 9CO_2 + Hg + \tfrac{1}{2}O_2 \qquad (13)$$

The final step may be represented by eqn. (14) with a calculated weight loss of 95.99% as compared with the experimental value of 97.42 ± 2.55%.

$$HgCl_2 + CO_3^{2-} \rightarrow 2Cl^- + Hg + CO_2 + \tfrac{1}{2}O_2 \qquad (14)$$

Mercury(II) sulfate

The thermogravimetric results showed that $HgSO_4$ reacted with the eutectic in two stages. The first reaction took place between 370 and 500°C with a weight loss of 50.29 ± 0.42% while the second reaction occurred between 500 and 730°C under argon and between 610 and 730°C under CO_2 atmosphere showing a total weight loss of 87.17 ± 2.53%. In fact, the thermogram showed an inflection at 500°C under argon but a distinct plateau between 500 and 610°C under CO_2 gas.

Gaseous products in both weight-loss steps consisted of a mixture of Hg, CO_2 and O_2. The infrared spectra of the solid mixtures collected at 500 and 750°C were similar to that of the eutectic with an additional sulfate band at 619 cm^{-1} in both the mixtures and a broad band at 460 cm^{-1} due to a basic carbonate in the first mixture only. On dissolving in water, the basic carbonate was found to be converted to insoluble HgO and there was no residue in the second mixture. The filtrates contained sulfate and no soluble mercury species.

The stoichiometry of the reaction due to the first weight loss of 50.29 ± 0.42% compared with a calculated value of 49.86% may be represented by eqn. (15).

$$10HgSO_4 + 10CO_3^{2-} \rightarrow HgCO_3 \cdot 4HgO + 10SO_4^{2-} + 5Hg + 9CO_2 + \tfrac{5}{2}O_2 \qquad (15)$$

Equation (16) represents the overall reaction with a calculated weight loss of 87.85% compared with the experimental value of 87.17 ± 2.53%.

$$HgSO_4 + CO_3^{2-} \rightarrow SO_4^{2-} + Hg + CO_2 + \tfrac{1}{2}O_2 \qquad (16)$$

The final products of the reactions of mercury compounds were similar and consisted of alkali metal chlorides or sulfates, O_2, CO_2 and Hg. The initial reaction temperatures were lower in the chloride reactions as compared with the sulfate reactions. This may be due to the melting points of the chlorides being lower than those of the sulfates. Thus, for example, the melting points of Hg_2Cl_2 and $HgCl_2$ are 302 and 277°C and those of the corresponding sulfates are 335 (decomposes) and 850°C, respectively. The melting points of the chlorides may have been lowered further by the eutectic, thus forming a semi-liquid mixture and causing the Hg_2Cl_2 and $HgCl_2$ reactions to commence at 180 and 120°C, respectively, as against at 370–380°C for the sulfate reactions.

The lower reaction temperatures of the chlorides may also be responsible for the existence of two stable basic carbonates as compared with only one intermediate in the sulfate reactions.

The composition of two basic carbonates as determined by the weight loss, infrared and chemical methods was found to be similar in the reactions of mercury(I) and (II) chlorides as was the basic carbonate formed in the Hg_2SO_4 reaction, but $HgSO_4$ produced a basic carbonate with a different composition.

The thermograms of the reactions of zinc and cadmium compounds showed no stable intermediate, although the melting point and the initial reaction temperature of $ZnCl_2$ were comparable to those of Hg_2Cl_2 and those of cadmium compounds to mercury sulfates. This may be taken to indicate that there were either direct reactions between zinc as well as cadmium compounds with the eutectic resulting in the formation of the respective metal oxides, or carbonate species, if formed, were not stable under the experimental conditions.

As the reactions were studied under both argon and carbon dioxide, it was found that the stability range of the intermediates formed during certain reactions and that of $CdCO_3$ when heated with the eutectic was increased under carbon dioxide. The increased stability of an intermediate under carbon dioxide may well be taken as due to the existence of carbonate or basic carbonate species.

It was also found that when a carbonate species was formed at a higher temperature, its stability range was independent of the atmosphere. Thus, for example, $HgCO_3 \cdot 9HgO$ was indicated in the chloride and Hg_2SO_4 reactions. This species showed increased stability under carbon dioxide when formed in the chloride reactions at comparatively low temperatures. In the Hg_2SO_4 reaction it was formed at a high temperature and its stability range was found to be the same under both argon and carbon dioxide.

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