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IRON COMPOUNDS IN HIGH OXIDATION STATES. II *. REACTION BETWEEN Na_2O_2 AND $FeSO_4$

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ABSTRACT

In continuing our study dealing with the design of new synthetic procedures to obtain highly oxidized iron compounds, we have investigated the behaviour of the Na_2O_2–$FeSO_4$ system. The results obtained differ significantly from those previously reported for the analogous BaO_2–$FeSO_4$ system. Ferrates(V) and (VI) can now be obtained and the nature of the final products depends on the ratio between the initial amounts of the reagents. A simple way of preparing soluble ferrates(VI) is also described.

INTRODUCTION

In trying to establish new preparative procedures for highly oxidized iron derivatives, that do not imply conditions as extreme as those reported in the literature, in a recent publication [1], we studied the oxidizing ability of BaO_2 towards $FeSO_4$. In this system, the iron derivatives obtained are always ferrates(IV) which become stabilized through perovskite or related structures.

From a thermodynamic view, Ba^{2+} plays a significant role in stabilizing this concrete oxidation state in solid phases. This suggests that the nature of the iron derivatives, which could be obtained by the action of an oxidizing agent such as the peroxide, might be influenced by the nature of the cation present.

To progress with this hypothesis, we have researched the processes occurring on heating samples containing Na_2O_2–$FeSO_4$ mixtures. As far as we know, there is no information in the literature dealing with these reactions.

In the absence of bibliographic antecedents, we have speculated a priori about the possible reaction schemes. Two generic reaction types seem to be

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* For Part I, see ref. 1.

the most reasonable to "describe" the complete processes

$$nFeSO_4 + mNa_2O_2 \rightarrow pNa_zFeO_x + qSO_3 + rO_2$$

$$n'FeSO_4 + m'Na_2O_2 \rightarrow p'\,Na_{z'}FeO_y + sNa_2SO_4$$

Competitive and/or side reactions (probably involving the decomposition of some reagent) might proceed together with the main process. The fact that each one of the schemes implies different amounts of evolved gases leads us to think that thermal analysis is actually a suitable technique to obtain significant information concerning to the Na_2O_2–$FeSO_4$ system.

The results reported in this paper refer, as well as those previously described in Part I of this work, to the phenomenological behaviour of the system. The formal kinetic study of both systems has been performed by isothermal and non-isothermal procedures. The results obtained will be reported and discussed in a forthcoming paper.

EXPERIMENTAL

The experimental conditions and techniques used are largely the same as those reported in Part I of this work [1]. Therefore, only specific aspects will be described here.

Powdered sodium peroxide raw material is a highly hygroscopic and CO_2-absorbing material [2]. Although the solid was handled with the necessary precautions, the above characteristics must also be taken into account in order to explain the results observed.

To make the samples, precise amounts of both reagents were mixed and ground in an agate mortar. This process was carried out in a glove-box in the presence of P_4O_{10} and NaOH. The samples were stored in sealed flasks in a desiccator over P_4O_{10} and NaOH.

Preliminary experiments show that the greatest resolution between consecutive processes, as well as the maximum accuracy in the weight variation determinations, is achieved when the thermal analyses are performed under the following conditions: heating rate, 6°C $\min^{-1}$; sample mass, 100 mg; cylindrical alumina crucibles; dynamic, dry N_2 atmosphere. As DTA reference, calcined Al_2O_3 was used.

RESULTS AND DISCUSSION

Thermal analysis

To obtain information about the system, a series of nine samples, whose $Na_2O_2/FeSO_4$ molar ratios (R) ranged from 0.5/2 to 7/2, was prepared.

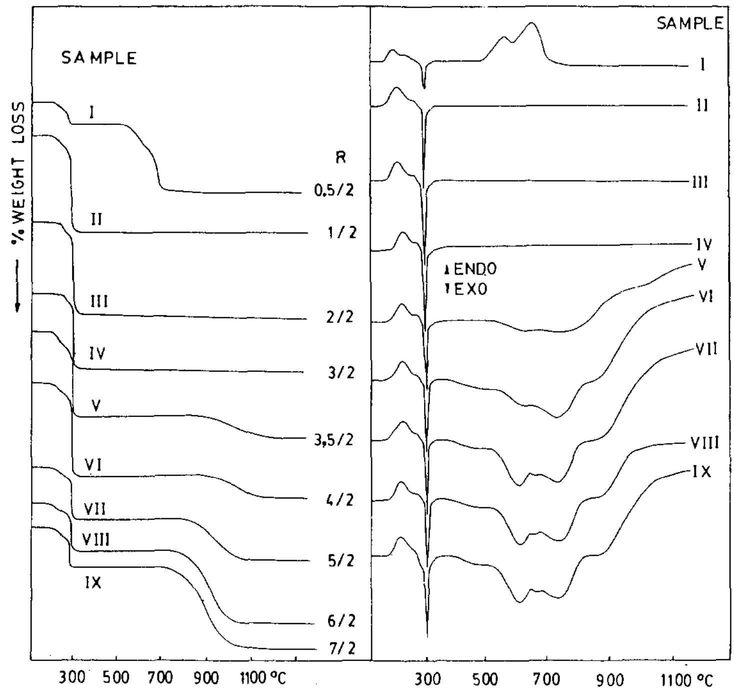

Fig. 1. TG (left-hand side) and DTA (right-hand side) plots of the samples. (Dynamic nitrogen atmosphere, 6°C min^{-1}.)

Figure 1 shows the respective TG and DTA curves for these samples.

As it can be noted in all cases, the first weight loss occurs in two consecutive stages between ~ 130 and ~ 350°C. The first stage is accompanied by a small endothermic peak in the DTA curve at ~ 250°C; the second stage, which is much more quantitatively significant than the first, occurs very rapidly, and is associated, with a sharp and intense exothermic peak at 300°C. The relative magnitude of the weight loss in this last stage decreases as the $Na_2O_2/FeSO_4$ ratio increases.

The above process is the only one observed for samples II–IV ($R = 1/2$, 2/2 and 3/2, respectively). Besides this, in the case of sample I ($R = 0.5/2$) there is an additional two-stage endothermic weight loss between 525 and 675°C. Samples V to IX ($R = 3.5/2$, 4/2, 5/2, 6/2 and 7/2, respectively) undergo a second process between 700 and 1100°C. This process also involves a weight loss. TG curves show only a single step but the DTA curves indicate that the process involved is very complex. Thus, they display an exothermic effect beginning at ~ 600°C that shows maxima at 650 and 730°C. This effect overlaps with an endothermic peak centred at ~ 1000°C. The intensity of the exothermic peak increases with the $Na_2O_2/FeSO_4$ ratio.

At this point, the following considerations can be made based on the thermal behaviour described: (1) the attack on $FeSO_4$ by Na_2O_2 always occurs at 300°C. According to the exothermic nature of the process, it implies that oxidation from Fe(II) to higher valences is very likely; (2) the small weight loss shown by all the samples at a lower temperature must be due to the moisture adsorbed by the very hygroscopic reagents during their handling *; (3) the process occurring between 525 and 675°C in the case of sample I ($R = 0.5/2$) can be associated with the decomposition of unreacted $FeSO_4$ [1]. In all the remaining cases ($R \geqslant 1/2$) $FeSO_4$ is fully consumed in the 300°C reaction; (4) the complex process occurring above 600°C for samples V–IX ($R \geqslant 4/2$) begins with an exothermic step without mass variation. This step probably involves the oxidation of the iron derivatives formed at 300°C. The subsequent endothermic step might be due to the decomposition of the products resulting from the previous reactions.

Identification of the reaction products

Gases

According to that suggested above, the only gaseous products that might be evolved during the reaction processes are SO_3 and SO_2 coming from $FeSO_4$, and O_2 from Na_2O_2.

The gas evolved when a sample to be determined is heated in a tubular furnace (under a dry N_2 stream) was absorbed through a concentrated NaOH solution. The solution was then tested for SO_2 by means of acid fuchsin [3a], and SO_3 by rhodizonate and Ba^{2+} [3b]. The results obtained are summarized in Table 1.

Solids

Given that our interest is focused mainly on the possibility of obtaining highly oxidized iron derivatives, we have qualitatively tested the solid reaction products for the presence of Fe(VI) among their hydrolysis products. The appearance of the characteristic purple-violet colour of the FeO_4^{2-} ion [4] is indicative of the presence of iron with an oxidation number higher than III in the solids. The results are included in Table 1.

The remaining solid products have been identified by means of physical methods.

IR spectroscopy

Ferrate groups can also be identified by means of IR spectroscopy (KBr pellets) and by using the values reported in the literature for the FeO_4^{n-} ($n = 2, 3, 4$) group vibrations [5–9].

The IR spectra of the different samples heated at 400, 750 and 1000°C were recorded and some of these are shown in Fig. 2.

The analysis of these spectra leads to the following observations.

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* A blank sample of Na_2O_2 behaves similarly. See also refs. 1 and 2.

TABLE 1

Chemical identification of the reaction products

Sample	*R*	Gases				Solids		
		T (°C) = 400		400–1000		400	700	1000
		SO_2	SO_3	SO_2	SO_3	Fe(VI)	Fe(VI)	Fe(VI)
I	0.5/2	–	+	–	–	–	–	–
II	1/2	–	+	–	–	–	–	–
III	2/2	–	+	–	–	–	–	–
IV	3/2	–	+	–	–	–	–	–
V	3.5/2	–	+	–	–	–	–	–
VI	4/2	–	+	–	+	–	+	–
VII	5/2	–	–	–	+	–	+	–
VIII	6/2	–	–	–	+	–	+	–
IX	7/2	–	–	–	+	–	+	–

Samples VII–IX, that give negative results to both tests, must evolve only O_2 when heated at 400°C.

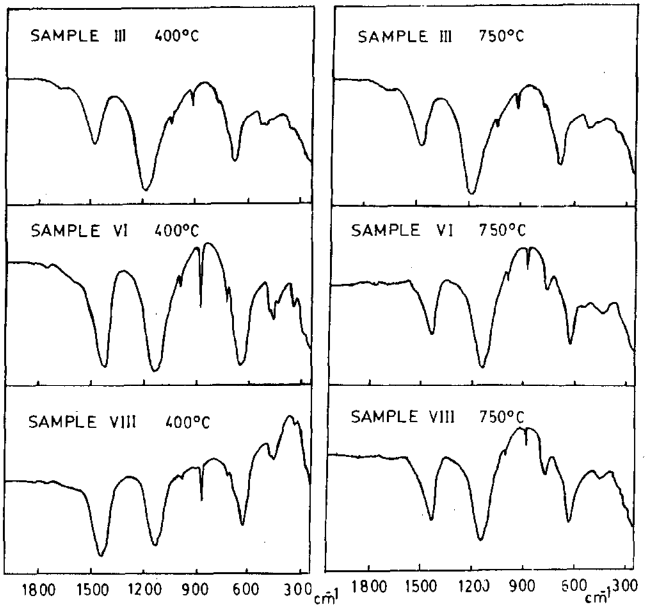

Fig. 2. IR spectra of samples III ($R = 2/2$), VI ($R = 4/2$) and VIII ($R = 6/2$) heated at 400°C (left-hand side) and 750°C (right-hand side).

(1) The bands at 780 and 330 cm^{-1}, that can be assigned to the vibrations of tetrahedral FeO_4^{n-} groups [5–9], only appear in the spectra of samples VI–IX heated at 750°C.

(2) In all cases, the spectra of the samples heated at 400°C show a band centred at 460 cm^{-1}, which is characteristic of the Fe–O bond in oxides.

(3) All the spectra show bands at 1180 and 660–680 cm^{-1} assignable to sulphate vibrations [10a].

(4) Likewise, the presence of Na_2CO_3 as impurity is revealed by the appearance (in all the spectra) of bands at 1420 and 875 cm^{-1} [10b].

X-ray diffraction

In Fig. 3 we have included some X-ray powder diffraction patterns obtained when the samples were heated at 400, 750 and 1000°C.

The following solid crystalline phases can be identified.

(1) Peaks assignable to Na_2SO_4 appear in the patterns of all samples calcined at any one temperature. The anhydrous compound has two main crystalline forms [11]. In the present case, the prevailing phase has the structure of naturally occurring thenardite.

(2) When samples are heated at 400°C, the patterns of those of $R \geqslant 1$ show peaks characteristic of two polymorphic forms of sodium ferrite, $NaFeO_2$ [12]. Samples I and II ($R < 1$) yield Fe_2O_3 [13] as reaction product. In this last case, the presence of small amounts of Fe_3O_4 can also be detected [14].

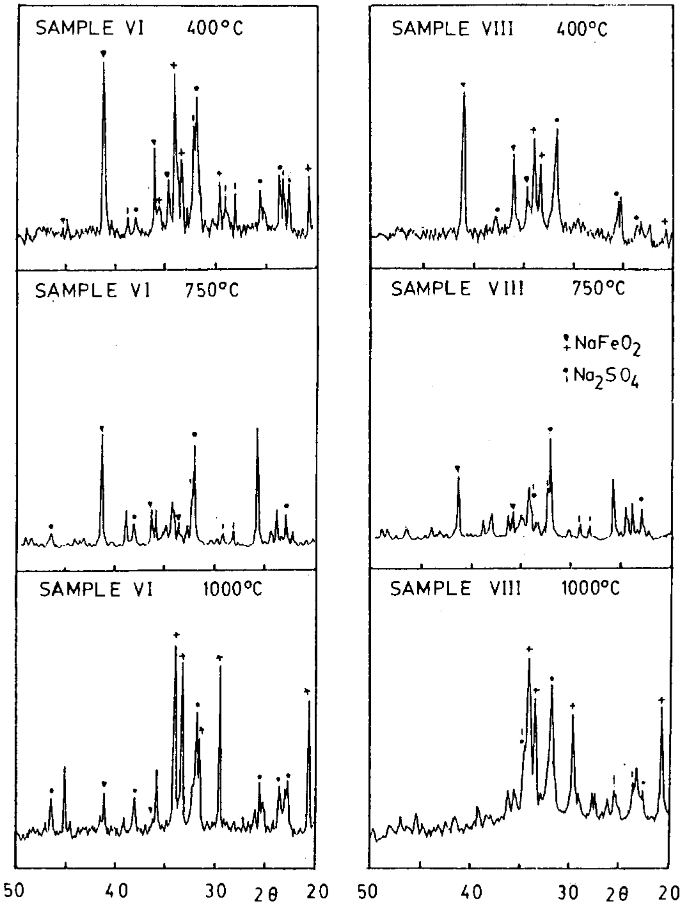

Fig. 3. X-ray powder diffraction patterns of the samples VI ($R = 4/2$) and VIII ($R = 6/2$) heated at 400, 750 and 1000°C.

(3) The Na_2SO_4 peaks remain in the patterns of samples VI ($R = 4/2$) and VIII ($R = 6/2$) heated at 750°C, but the disappearance of the peaks of one of the $NaFeO_2$ phases can be noted. The intensity of the peaks of the remaining $NaFeO_2$ form decreases as the Na_2O_2 content in the sample increases. New peaks appear that cannot be assigned to any known phase.

(4) The patterns of these two samples (VI and VIII) heated at 1000°C lack peaks of the iron derivative(s) formed at 750°C but they again show those of sodium ferrite.

Na_2CO_3 peaks are absent [15] in the patterns of all the samples. Accordingly, this compound, shown by IR spectroscopy, must contaminate the samples in very small amounts.

Stoichiometry of the reactions between $FeSO_4$ and Na_2O_2

As stated above, the first oxidative attack on $FeSO_4$ always occurs at 300°C. Taking into account the TG data and based on the reaction products identified, it is possible to propose the equation

$$FeSO_4 + 3/2\ Na_2O_2 \rightarrow Na_2SO_4 + NaFeO_2 + 1/2\ O_2 \qquad \text{(a)}$$

as representative of the idealized stoichiometric net reaction occurring at that temperature. Both $NaFeO_2$ and Na_2SO_4 show no single crystalline form.

Notwithstanding, to go to completion, this reaction would require at least a stoichiometric R value of 3/2. Given that reaction is observed in all cases at 300°C it can be assumed that eqn. (a) is a combination of others describing simpler processes. Indeed, with the results reported, the reactions occurring for samples for which $R \leqslant 3/2$ could be written as

$$FeSO_4 + 1/2\ Na_2O_2 \rightarrow 1/2\ Fe_2O_3 + 1/2\ Na_2SO_4 + 1/2\ SO_3 \qquad \text{(b)}$$

and

$$FeSO_4 + Na_2O_2 \rightarrow NaFeO_2 + 1/2\ Na_2SO_4 + 1/2\ SO_3 + 1/4\ O_2 \qquad \text{(c)}$$

In fact, these last two equations support the fact that formation of $NaFeO_2$ phases must not proceed, initially at least, through the direct reaction (equation a) but by means of a mechanism involving the appearance of Fe_2O_3 as intermediate

$$FeSO_4 + 1/2\ Na_2O_2 \rightarrow 1/2\ Fe_2O_3 + 1/2\ Na_2SO_4 + 1/2\ SO_3 \qquad \text{(b)}$$

followed by

$$1/2\ Fe_2O_3 + 1/2\ Na_2O_2 \rightarrow NaFeO_2 + 1/4\ O_2 \qquad \text{(d)}$$

This step-by-step scheme also explains why SO_3 is detected among the gases evolved on heating samples of $R > 3/2$ (up to $R < 5/2$). Although the stoichiometric ratio required for its complete consumption is 3/2, the evolved SO_3 (gas) could only react completely in the presence of a significant excess of Na_2O_2 (solid).

Thus, the reaction scheme for the process at 300°C in the case of samples with $R > 3/2$ might formally be described as

$$FeSO_4 + n\ Na_2O_2 \rightarrow NaFeO_2 + NaSO_4 + 1/2\ O_2 + (n - 3/2)\ Na_2O_2 \qquad \text{(e)}$$

with an excess of Na_2O_2 remaining in the system.

The above results indicate that, for samples V–IX ($R > 3/2$), a new oxidative attack occurs on increasing the temperature. The remaining Na_2O_2 oxidizes the $NaFeO_2$ produced at 300°C leading to the formation of a compound in which the oxidation state of iron will be higher than III. In accordance with the DTA data, the larger the excess of Na_2O_2 in the system, the higher the oxidation state attainable.

The IR spectra of samples VI and VIII heated at 750°C show bands at 330 and 780 cm^{-1} assignable, as stated, to FeO_4^{n-} ($n = 2, 3, 4$) groups. The X-ray diffraction patterns of these samples show some peaks that cannot be assigned to any known phase (not even by comparison with the patterns of similar phases, such as Na_2CrO_4 or Na_3CrO_4).

The process occurring can probably be represented by means of some of the following equations

$$3\ Na_2O_2 + 2\ NaFeO_2 \rightarrow 2\ Na_4FeO_4 + O_2$$

$$Na_2O_2 + NaFeO_2 \rightarrow Na_3FeO_4$$

$$3\ Na_2O_2 + 2\ NaFeO_2 \rightarrow 2\ Na_2FeO_4 + 2\ Na_2O$$

although these reactions are not necessarily exhaustive.

However, the first one (yielding ferrate(IV)) can be rejected given that, as shown by the TG curves, the oxidative process occurs without a weight loss.

The products from the former stages decompose above 800°C. The decomposition processes again lead essentially to the formation of $NaFeO_2$. The "sodium ferrite" is actually the product of the thermal decomposition of the sodium ferrates, regardless of the oxidation state of iron in them [5]. Na_2SO_4, at temperatures of the order of 900°C, melts and, in the presence of heavy metals, can also decompose with the evolution of SO_3 [16].

Thermochemical calculations

Although the calculations implied involve an appreciable degree of uncertainty, we have considered it interesting to make an estimation of the thermodynamic feasibility of the reactions proposed.

The variation of enthalpy associated with reaction (a) is $\Delta H_R(a) = -25$ kcal (mol $FeSO_4$)$^{-1}$, measured by means of DSC. From this value, and using literature data concerning the formation of reagents and products [17], we have made a rough estimation * of $\Delta H_f^0(NaFeO_2)$. The calculated value, 102 kcal mol^{-1}, refers to "mean $NaFeO_2$" regardless of the crystalline structure **. Using this value, the lattice energy of "$NaFeO_2$" has been determined through a Born–Haber cycle and is found to be $U = 2128$ kcal mol^{-1}. This same magnitude estimated from Kapustinskii's equation [1] yields $U_k = 2023$ kcal mol^{-1}, this giving an indication of the reliability of the calculations.

Now, the thermodynamic data, given in Table 2, can be determined.

As it can be noted, all the proposed reactions would be exoenergetic at 573 K ***.

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* The idealized nature of the stoichiometric equation contributes to the approximate character of the calculation.

** The word "mean" must be considered in the sense that, as we have stated above, the sodium ferrite obtained does not show a single crystalline form. However, the empirical calculations performed obviate the actual structure of the solids.

*** Given the nature of the approximations used, the wide coherence of the obtained results seems satisfactory. Thus, the only inconsistency observed among the calculated data with respect to the experimental results refers to $\Delta H_R^{298}(c)$. This departure should not be surprising and can be attributed to the approximations involved in the calculations.

TABLE 2

ΔH_R and ΔG_R (kcal) for the proposed reactions

Reaction	ΔH_R^{298}	ΔG_R^{573}
(b) $FeSO_4 + 1/2\ Na_2O_2 \rightarrow 1/2\ Fe_2O_3 + 1/2\ Na_2SO_4 + 1/2\ SO_3$	−26.5	−61.5
(d) $1/2\ Fe_2O_3 + 1/2\ Na_2O_2 \rightarrow NaFeO_2 + 1/4\ O_2$	+58.0	+51.0
(c) = (b)+(d) $FeSO_4 + Na_2O_2 \rightarrow NaFeO_2 + 1/2\ Na_2SO_4 + 1/2\ SO_3 + 1/4\ O_2$	+31.5	−10.5
(a) = (c)+(f) $FeSO_4 + 3/2\ Na_2O_2 \rightarrow NaFeO_2 + Na_2SO_4 + 1/2\ O_2$	−25	−56.5
(f) $1/2\ SO_3 + 1/2\ Na_2O_2 \rightarrow 1/2\ Na_2SO_4 + 1/4\ O_2$	−56.5	−46.0

The energy required by step 2 (reaction d) of the two-stage mechanism of $NaFeO_2$ formation can be provided by the previous formation of Fe_2O_3. However, although this mechanism seems to be the more probable, the direct process (reaction a) should not be left aside on a thermodynamic basis. In this way, $NaFeO_2$ formation might occur through two different but simultaneous mechanisms.

Crystallization of potassium ferrate(VI)

As an interesting indirect result, we can present an advantageous alternative to Schreyer's procedure [18] in order to obtain crystallized K_2FeO_4.

Procedure

(1) Thoroughly mix, in an agate mortar, sufficient Na_2O_2 and anhydrous $FeSO_4$ to obtain a molar $Na_2O_2/FeSO_4$ ratio equal to 3.0. Carry out the process in a dry-box in the presence of P_4O_{10} and NaOH. Heat the sample (in a tubular furnace under a dry N_2 stream) at 700°C for 1 h.

(2) Dissolve a 25-g portion of the product obtained in 100 ml of 5 M NaOH solution ensuring that the temperature of the solution does not rise above 5°C. Centrifuge the resulting dark solution for 10 min (to remove the solid hydrolysis products, mainly hydrated Fe(III) oxides), filter it through a sintered glass plate (No. 4) of large surface area to minimize the time of filtration. Collect the filtrate over 25 g of solid KOH.

(3) The solution obtained is then saturated, with continuous stirring, with solid KOH. This process must be performed at 20°C to avoid the crystallization of KOH hydrates. Maintain the stirring for 10 min and then filter through a sintered glass plate (No. 3).

(4) Wash the purple solid on the plate with 10 ml of hexane, to wash down the excess of water, and then with four or five small portions of absolute ethanol. Transfer the solid to a beaker with 100 ml of absolute ethanol and stir for 10 min. Repeat this operation three times. Filter the solid again and dry it with 50 ml of dry ether. During this operation, protect

the filter with a P_4O_{10} tube. Store the product in a vacuum desiccator over P_4O_{10}.

CONCLUDING REMARKS

In the presence of sufficient Na_2O_2 ($R \geqslant 1$), the reaction between Na_2O_2 and $FeSO_4$ leads unequivocally and systematically to the formation of sodium ferrite as the product of the first oxidative process at 300°C. Lower Na_2O_2 contents yield Fe_2O_3. However, an excess of Na_2O_2 does not affect the nature of the iron derivative obtained.

Like the analogous BaO_2 reaction [1], the main driving force of the process is the highly exoenergetic (sodium) sulphate formation. However, when R is lower then $5/2$, the presence of SO_3 gas is still detected among the reaction products. On the other hand, unlike the behaviour observed for the BaO_2–$FeSO_4$ system, Fe_2O_3 is identified as reaction product only in the case of samples of $R < 1/2$. This result suggests that, when $R > 1$, the iron(III) oxide (from which the $FeSO_4$ precursor comes) will be formed initially but it will react immediately (with the required amount of Na_2O_2) to give sodium ferrite. Thus, it can be reasonably assumed that the Fe_2O_3 formed in situ is always an intermediate to $NaFeO_2$ formation.

Hence, the reaction between Na_2O_2 and $FeSO_4$ is different from that observed in the case of BaO_2. The formation of Fe_2O_3 and SO_3 in the first stage of the process suggests that its mechanism may be similar to that of $FeSO_4$ oxidation by means of O_2. This last process involves an initial attack of $FeSO_4$ with the formation of iron(III) oxosulphate and sodium oxide. The immediate decomposition of $Fe_2O(SO_4)_2$ would yield Fe_2O_3 and SO_3 [19]. Then, the reaction would proceed as stated above.

Along with the difference indicated, the main difference between both systems lies in the processes occurring at higher temperatures. In the present case, the appearance of phases containing iron in high oxidation states occurs at ~ 600°C only when Na_2O_2 is no longer consumed by SO_3 neutralization, that is to say, for samples of $R > 3/2$. Moreover, the fact that, under these conditions, $NaFeO_2$ oxidation occurs without weight variation eliminates the possibility of sodium ferrate(IV) formation. Likewise, the IR and analytical results indicate the presence of iron(V) and/or (VI) in the oxidation products: both types of ferrate might be among the products. If the Na_3FeO_4 phase resulted in being amorphous as is the potassium salt [5], it could obviously be assumed that the crystalline phase observed, when there is an appreciable excess of Na_2O_2 ($R \geqslant 6/2$) *, is Na_2FeO_4.

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* From which potassium ferrate(VI) can be crystallized. For lower R values ($3/2 < R < 6/2$) the X-ray diffraction patterns show, besides definite peaks, a component due to an amorphous material.

In any case, regardless of the uncertainty about the precise nature of the oxidized products obtained, two outstanding features must be emphasized:

(1) in contrast to the behaviour of the BaO_2–$FeSO_4$ system whose ultimate products are always ferrates(IV), the iron oxidation state (IV) does not result in being stabilized in any case. In addition, the average oxidation state reached here depends on the initial relationship between the amounts of reagents. Hence, a comparison between both systems shows the key role of the cation (through the available lattices) in the stabilization of the oxidation states determined in spite of the fact that we are using the same formal oxidizing agent (the peroxide ion) and similar working conditions *.

(2) the products obtained by oxidation of the sodium ferrite also have a great interest as precursors (by hydrolysis) of the FeO_4^{2-}(aq). Thus far, the utilization of the soluble ferrates(VI) in the bacteriological and chemical treatment of waste water [20] has been hindered by the lack of a suitable industrial preparative method. The simple procedure described here stands to remove this obstacle.

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