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Alkali and Alkaline Earth Metal Ozonides

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Data published in the Soviet and foreign literature on alkali and alkaline earth metal ozonides are described systematically and critically discussed. The methods of their preparation, physicochemical properties and reactivities have been examined. Certain concepts concerning the mechanism of the formation of ozonides have been presented.
The bibliography includes 87 references.

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I. GENERAL INFORMATION ABOUT ALKALI METAL OZONIDES

As early as the middle of the nineteenth century certain investigators[1,2] noted that alkali metal hydroxides react with ozone to form coloured products, the nature of which was not established. However, the studies in this field up to 1949 were largely qualitative.

Baeyer and Villiger[3] suggested that the coloured products of the reaction of ozone with KOH and RbOH are salts of the hypothetical ozonic acid H_2O_4. Bach[4] believed that the reaction of ozone with potassium hydroxide takes place according to the equation

$$KOH + O_3 \rightarrow KO_4H .$$

The first attempt to investigate the nature of ozonides was made in 1912. Traube[5] showed that the products of the reaction of ozone with potassium hydroxide contain, apart from the two higher potassium oxides K_2O_2 and K_2O_4 and the unreacted potassium hydroxide, a small amount of an orange substance. At room temperature the substance immediately decomposed to K_2O_4. Traube suggested that K_2O_4 is a product of the decomposition of a higher potassium oxide, which he called "ozonate".

In a later study Traube[6] attempted to determine the amount of oxygen evolved on decomposition of potassium "ozonate". He regarded potassium "ozonate" as a compound in which an oxygen molecule is joined by subsidiary valences to one or two KOH molecules, i.e. $KOH.O_2$ or $(KOH)_2.O_2$. According to Traube, these formulae emphasise the capacity of ozonides to evolve molecular oxygen on interaction with water. He represented the conversion of potassium ozonide into the tetroxide as a two-stage process: in the first stage "potassium ozonate" undergoes intramolecular oxidation according to the equation

$$2(KOH)_2 \cdot O_2 = 2K_2O_2 + 2H_2O + O_2 , \quad (1)$$

and in the second stage the potassium peroxide formed reacts with another "ozonate" molecule to produce potassium tetroxide and hydroxide:

$$K_2O_2 + (KOH)_2 \cdot O_2 = K_2O_2 \cdot O_2 + 2KOH . \quad (2)$$

To test the hypothesis that metal ozonides do not contain hydrogen, Strecker and Thienemann[7] investigated the reaction of ozone with pure metals dissolved in liquid ammonia. When ozone was introduced into the blue solution of potassium in liquid ammonia, a white mass was formed initially and then the blue colour disappeared and a dark-brown precipitate and a dark-orange solution were produced. According to the author's hypothesis, the precipitate contained an admixture of a compound of the metal with ozone. Precipitates with admixtures of sodium, rubidium, and caesium ozonides were obtained in this way. The stability of the precipitates decreased from caesium to sodium, as noted previously by Manschot and Kampschulte[8]. Strecker and Thienemann did not succeed in obtaining pure preparations of the "ozone compounds" and in determining accurately their composition because of the marked contamination of the reaction products by ammonium nitrate and nitrite. Therefore it was necessary to investigate the reaction of ozone with ammonia. Strecker and Thienemann[7] showed that nitrates and nitrites are formed in the reaction of ozone with liquid ammonia according to the following equations:

$$2NH_3 + 4O_3 \rightarrow (NH_4)NO_3 + 4O_2 + H_2O , \quad (3)$$

$$2NH_3 + 3O_2 \rightarrow (NH_4)NO_2 + 3O_2 + H_2O . \quad (4)$$

They observed[7] that, when ozone is passed through liquid ammonia, an intense orange colour appears in solution, and rapidly disappears when ammonia is evaporated. The same phenomenon was noted by Manschot and Kampschulte[8]. Strecker and Thienemann suggested that, as with alkalis, an unstable ammonia compound is formed in this system and is readily converted into ammonium nitrate and nitrite.

In 1927 Fichter and Bladergroen[9] published the results of studies in which "potassium ozonide" was obtained on passing fluorine through a concentrated potassium hydroxide solution at −20°C. The resulting preparations were coloured brown. Fichter and Bladergroen suggested that they obtained the same products as Baeyer and Villiger in the reaction of ozone with potassium hydroxide.

Thus in the studies published up to 1949, there was no unanimity concerning the composition of the ozonation products. The reason was that investigators were unable to isolate in a pure form and to elucidate the nature of the coloured substances obtained in the reaction of ozone with alkali metal hydroxides. These substances were called "ozonates" and compositions identical with

those of derivatives of the hypothetical ozonic acid in the form of normal-(K_2O_4) and acid (KHO_4) salts were attributed to them. Later these compounds were regarded as molecular compounds of oxygen with one or two molecules of alkali: $KOH...O_2$ or $(KOH)_2...O_2$.

The present interest in the chemistry of inorganic ozonides was aroused by the work of Kazarnovskii and coworkers[10-14], where the possibility of isolating alkali metal ozonides in a crystalline state was demonstrated for the first time. Crystalline KO_3 (purity about 91%) and very small amounts of NaO_3 (purity up to 90%) and RbO_3 and CsO_3 (purity up to 66%) were obtained.

II. MODERN CONCEPTS CONCERNING ALKALI METAL OZONIDES

A recent study of the physicochemical properties of alkali metal ozonides[10,15] showed that they are higher oxides $M^+O_3^-$ with the molecular ion O_3^-. The presence of the molecular ion O_3^- in ozonides was first established by magnetic[10] and X-ray diffraction[12,16] measurements and was confirmed by spectrophotometry[17,18] and electron spin resonance[17-21].

Two resonating structures with a single free valence were attributed to the O_3^- ion on the basis of magnetic data[10,22]. Measurements of magnetic susceptibility confirm this[10]. $\chi_g = +12.5 \times 10^{-6}$ was found at 20°C, whence $\chi(\text{corr}) = +13.6 \times 10^{-6}$; this gives $\mu = 1.76$ Bohr magnetons, which is close to the theoretical value 1.73 Bohr magnetons for a single unpaired electron.

According to Pauling's data[22], the O–O bond length is 1.35 Å and the <OOO angle between the oxygen atoms is 108°. Starting with the angular form of the O_3 molecule, with an angle of 116° ± 0.5° between the O–O–O bonds and an O–O distance $r = 1.278 \pm 0.002$ Å, Smith[23] found by extrapolation that, like ozone, the O_3^- ion is non linear and has an angle of 110° ± 5° and a distance r = 1.34 ± 0.05 Å, which agrees well with Pauling's data. X-Ray diffraction study[16] showed that the O_3^- ion has an angular configuration with <OOO = 100° and $r = 1.19$ Å, which agrees well with the data of Herman and Giguere[18], who determined the O–O bond length in the O_3^- ion as 1.22 Å on the basis of the infrared spectrum of ammonium ozonide. They also showed[18] that the O_3^- ion does not show a tendency towards dimerisation, in contrast with the isoelectronic NO_2^{2-} ion[24,25], and with the NO_2 molecule.

In an E.S.R. study of potassium ozonide specimens at room temperature and the temperature of liquid nitrogen, Piskunov et al.[19] confirmed the data of Bennet et al.[20] and Marshall and van Osterburg[21]. The closeness of the g-factor to two and also the occurrence of appreciable exchange interaction confirm the above hypothesis that the magnetism of the molecular ion O_3^-, which is responsible for the observed paramagnetic resonance in KO_3, is of the free radical type[19]. The O_3^- ion, which has an odd number of electrons, is the carrier of the enormous chemical reactivity of ozonides, which may be regarded as unusually longlived free radicals. Measurements of the g-factor for perpendicular and parallel orientations of KO_3 gave $g_\perp = 2.012 \pm 0.002$ and $g_\parallel = 2.005 \pm 0.003$.

Nikol'skii et al. estimated the heat of formation of alkali metal ozonides[11] from the known heats of formation of KO_3 (−62.1 kcal mole^{-1})[14] and an estimate of the lattice energy. Table 1 lists the heats of formation of alkali metal ozonides which they calculated.

The values of r_0 in Table 1 were calculated by the same investigators on the hypothesis that the unit cells of ozonides are constructed in the same way as the corresponding unit cells of azides, which was not confirmed in subsequent studies[16,26]. The author of the review also estimated the heats of formation of alkali metal ozonides from the elements by a comparative calculation[27]. Initially a check was made to find if the variation of the properties of compounds of Group I elements is linear. The following compounds were chosen for the comparison: oxides, peroxides, superoxides, hydroxides, chlorides, perchlorates, nitrates, carbonates, and sulphates. The resulting values are also listed in Table 1.

Table 1. Heats of formation of alkali metal ozonides[11].

Compound	r_0, Å	n	U, kcal	S_M*, kcal	I_M*, kcal	$-\Delta H$, kcal		
						from Ref.11	from calculated data (Ref.15)	from Ref.28
$(LiO)_3$	3.09	7	(161) (215)***	36.4	123.8	36	70±10	63±
NaO_3	3.29	8	154	26.0	118.0	45	60±10	—
KO_3	3.52	9	148	21.5	99.6	62.1**	—	—
RbO_3	3.68	10	143	20.5	95.9	62	57±10	—
CsO_3	3.84	10	137	18.8	89.4	64	57±10	—

* Data taken by Nikol'skii et al.[11] from a handbook[29].
** Value obtained from experimental data[14].
*** Estimated by Wood and D'Orazio[28].

Wood and D'Orazio[28] estimated by an extrapolation procedure the lattice energy of lithium ozonide as 215 ± 10 kcal mole^{-1} and from this value calculated the heat of formation of the ozonide as −63 ± 15 kcal mole^{-1}. They also estimated the absolute entropy and the free energy of formation of LiO_3, which are 60 e.u.[14] and 45 kcal mole^{-1} respectively.

Using the crystallographic data of Zhdanov and Zvonkova[12], Kazarnovskii and coworkers[14] calculated the lattice energy of KO_3 as 149 kcal mole^{-1}. Knowing the lattice energy and the heat of formation of KO_3, they estimated the electron affinity of the ozone molecule as 66.5 kcal mole^{-1}. This is three times greater than for the oxygen molecule (E_{O_2} = 22 kcal mole^{-1} [30]).

Wood and D'Orazio[28] estimated the electron affinity of the ozone molecule as 44 ± 10 kcal mole^{-1} and that of the oxygen molecule as 14.9 kcal mole^{-1}. These data are much lower than those quoted in other studies[14,30]. In addition, Wood and D'Orazio[28] estimated the heat of formation of the gaseous ozonide ion: $\Delta H[O_3^-\ (\text{gas})] = -11 \pm 10$ kcal mole^{-1}.

Solomon and Kacmarek[31] showed that in the visible region the spectra of solutions of alkali metal ozonides in liquid ammonia are independent of the cation and have a characteristic maximum at 450 nm.

The reactivity of ozonides has been little investigated. The principal studies dealt with the reactivity of potassium ozonide. Alkali metal ozonides react with water according to Eqn. (5), forming oxygen and the hydroxide:

$$2MO_3(\text{solid}) + H_2O(\text{liq}) \rightarrow 2MOH(\text{solid}) + \tfrac{3}{2}O_2 . \qquad (5)$$

Hence it follows that solid ozonides may serve as sources of oxygen.

III. ALKALI METAL OZONIDES

1. Lithium Ozonide

Lithium ozonide has not been obtained in a pure form but its tetrammine $Li(NH_3)_4.O_3$ is known. The tetrammine was synthesised[32] by the reaction of an ozone–oxygen mixture containing 3% of ozone with lithium hydroxide moistened with liquid ammonia ($LiOH : NH_3 = 5 : 0.2$) at −112°. The ozone-treated hydroxide was extracted with liquid ammonia. The tetrammine of lithium ozonide was salted-out from liquid ammonia solution with trifluoromethane. After the evaporation of trifluoromethane and ammonia at −126° and −78°C respectively, the solid red residue consisted of $Li(NH_3)_4.O_3$ with a considerable admixture of LiOH. The standard enthalpy of formation of the tetrammine of lithium ozonide from the elements is -135 ± 5 kcal mole^{-1}.

Several months before the publication of this study[32], the author of the review carried out experiments on the synthesis of lithium ozonide from lithium hydroxide and lithium peroxide[33]. The system was treated with ozone at −110°C, almost at the liquefaction limit of ozone, in a reactor with a screw stirrer for 3 h. The system was extracted with liquid ammonia, after the evaporation of which a thick oily dark-orange liquid remained at the bottom of the vessel. Analysis showed that the lithium : oxygen ratio was 1 : 2.56. The results of the experiments suggest that one can reliably assume that lithium hydroxide and peroxide react with ozone to form compounds of the ozonide type, as shown by the characteristic colour and the analytical lithium : oxygen ratio.

Probably the reason why lithium ozonide is not formed by a method similar to that employed for sodium and potassium ozonides and only a tetrammine is obtained, is the small radius of the lithium ion Li^+ (0.60 Å). The complex ion $Li(NH_3)_4^+$, which is larger than Li^+, can combine with the unstable O_3^- ion.

Wood and D'Orazio[28] estimated the LiO_3 lattice energy as 215 ± 10 kcal mole^{-1}. The heat of formation of LiO_3 calculated from this value is -63 ± 15 kcal mole^{-1}. Wood and D'Orazio[28] estimated the absolute entropy of LiO_3 as 20 e.u. and the entropy and free energy of formation of LiO_3 as 60 e.u. and 45 kcal mole^{-1} respectively and from these results calculated the enthalpies and free energies of the following reactions:

$$2LiO_3 \rightarrow Li_2O + {}^5/_3 O_2 \quad \begin{matrix}\Delta H = -16 \text{ kcal mole}^{-1} \\ \Delta F = -44 \text{ kcal mole}^{-1}\end{matrix}; \qquad (6)$$

$$2LiO_3 \rightarrow Li_2O_2 + 2O_2 \quad \begin{matrix}\Delta H = -26 \text{ kcal mole}^{-1} \\ \Delta F = -46 \text{ kcal mole}^{-1}\end{matrix}; \qquad (7)$$

$$LiO_3 \rightarrow LiO_2 + O_2 \quad \begin{matrix}\Delta H = +2 \text{ kcal mole}^{-1} \\ \Delta F = -19 \text{ kcal mole}^{-1}\end{matrix}. \qquad (8)$$

2. Sodium Ozonide

Sodium ozonide was first isolated by Nikol'skii et al.[11] in 1951, In a study of the reaction of dehydrated powdered sodium hydroxide (98.2%) with an ozone–oxygen mixture (8–9% O_3) at a temperature between −50° and −60°C, they observed that[11] the alkali acquired an intense yellow colour. Extraction with liquid ammonia at the same temperatures yielded a dark-red solution from which, after evaporation of liquid ammonia, a quasicrystalline dark-red product containing up to 90% of sodium ozonide, 2–3% of sodium hydroxide, and 4.6% of water was precipitated; the water was bound to the hydroxide as a hydrate.

The authors noted that sodium ozonide is extremely unstable and decomposes at room temperature with liberation of oxygen and the formation of sodium superoxide according to the equation

$$NaO_3 \rightarrow NaO_2 + {}^1/_2 O_2 . \qquad (9)$$

According to Nikol'skii et al.[11], the process reaches completion after 53 h.

Simultaneously with the work of Nikol'skii et al.[11], Whaley and Kleinberg[15] investigated the nature of the products of the reaction of ozone with alkali metal hydroxides. They confirmed[15] the data of Nikol'skii et al.[11], according to which treatment of sodium hydroxide with ozone at −60°C results in the formation of a yellow substance soluble in liquid ammonia. In addition, Whaley and Kleinberg[15] allowed ozone to react with sodium hydroxide at room temperature and showed that the resulting yellow product is insoluble in liquid ammonia and stable at room temperature. The authors believe they obtained sodium ozonide, although it was not isolated in a pure form. Its presence in the ozone-treatment product was demonstrated by an indirect method—magnetic measurements. McLachlan et al.[17] also noted that treatment of sodium hydroxide with ozone at room temperature results in the formation of a yellow substance. They suggested that the colour is due to the presence of sodium ozonide; the ozonide did not dissolve in liquid ammonia, and the ozone-treated alkali was stable for several hours on storage in closed tubes.

Griffith et al.[34], who investigated the ultraviolet spectra (200–600 n.m.) of sodium hydroxide treated with ozone at room temperature, showed that the spectra are identical with those obtained for a solution of potassium ozonide in liquid ammonia. On the basis of these data, they suggested that sodium ozonide is formed also above 0°C. In addition it was established[15,35] that, when sodium hydroxide is treated with ozone both at room temperature and below 0°C, the superoxide NaO_2 is formed together with the ozonide.

Evidently the data on the synthesis and properties of sodium ozonide are contradictory. Nikol'skii et al.[11] isolated sodium ozonide synthesised at −60°C; it is soluble in liquid ammonia and unstable at room temperature. Whaley and Kleinberg[15] and other investigators[17,34] confirmed these data and showed in addition that the reaction of ozone with sodium hydroxide takes place also at room temperature. Sodium hydroxide treated with ozone at room temperature is stable but sodium ozonide could not be extracted from it with liquid ammonia. Whaley and Kleinberg[15] put forward two explanations. The first is that sodium ozonide may exist in two crystalline forms. This hypothesis was not confirmed by experiment. The second explanation is that, in the reaction between ozone and sodium hydroxide at room temperature, the yield of sodium ozonide is extremely low and its particles are surrounded and protected by sodium hydroxide, which prevents their thermal decomposition and hinders the solubility of the ozonide in liquid ammonia, but this is unlikely.

Subsequently the possibility of the formation of sodium ozonide both above and below 0°C was demonstrated[36]. Moreover it was shown that, in the reaction with ozone, sodium superoxide is formed together with the ozonide. The study of the extraction of sodium ozonide from ozone-treated sodium hydroxide with liquid ammonia showed that the isolation of sodium ozonide synthesised above 0°C involves greater experimental difficulties than the isolation of sodium ozonide synthesised at negative tempera-

tures. The difficulties consist in the fact that sodium ozonide synthesised above 0°C instantly decomposes when the stream of ozone is stopped. The yellow colour of the product remaining after the decomposition of sodium ozonide is due to the presence of sodium superoxide formed in the reaction with ozone. Probably this is in fact the source of the above contradictions concerning the different properties of sodium ozonide synthesised at different temperatures.

The studies [36] on the preparation of sodium ozonide via sodium superoxide showed that, as with potassium and caesium [37], the reaction $MO_2 + O_2 \rightarrow MO_3 + O_2$ is possible also for NaO_2. However, the reaction of ozone with sodium superoxide is only of theoretical value for the explanation of the mechanism of the reaction with ozone owing to the low yield of the ozonide and the difficulty of carrying out the process [36].

Differential thermal analysis of sodium ozonide [38] showed that its decomposition is accompanied by an exothermic effect at $-10° \pm 2°$, due to the vigorous evolution of oxygen; this is consistent with the nature of the thermal decomposition of other alkali metal ozonides. Comparison of the heating curves for alkali metal ozonides reveals a regular increase of thermal stability with increasing atomic number of the element.

Thermogravimetric study of sodium ozonide [38] on a McBain balance made it possible to determine the degree of conversion of sodium ozonide and the rate of its decomposition at $-10°$, $-20°$, 0°, and +10°C. It is striking that the highest rate of decomposition of the ozonide is observed at the beginning of the decomposition process. Thermal decomposition of NaO_3 at $-20°$ and $-10°$C proceeds up to the formation of NaO_2. Above 0°C the thermal decomposition of sodium ozonide is accompanied by the reaction of the NaO_2 formed with the water of crystallisation present in sodium ozonide and proceeds up to the formation of NaOH. At $-20°$ and $-10°$C water does not enter into the reaction. The density [30] of NaO_3 is in the range 1.56–1.60 g cm^{-3}. The bright brown-red crystals of sodium ozonide exhibit pleochroism in polarised light: the crystals are coloured pale-yellow in the N_p direction and red-brown in the N_g direction. The sodium ozonide crystals are monoaxial and positive. The refractive indices are $N_p = 1.405$ and $N_g = 1.49$.

It should be noted that analysis of sodium ozonide involves considerable experimental difficulties. Direct sampling is impossible because of the extreme instability of sodium ozonide at room temperature. Therefore a special technique was developed for the analysis of sodium ozonide [40], which was subsequently employed for the analysis of other unstable ozonides.

In a preliminary X-ray diffraction study [41] a tetragonal cell with the parameters $a = 10.43$ Å, $c = 6.88$ Å, and $c/a = 0.660$ was provisionally ascribed to sodium ozonide. In a later investigation [52] these values were revised. Indexing of the X-ray diffraction patterns by means of Hall's curves yielded satisfactory agreement between the measured interplanar spacings and the values calculated for a body-centred tetragonal lattice with the ratio $c/a = 0.660$ and the parameters $a = 11.65$ Å and $c = 7.66$ Å. The space group $I4/mmm$ was chosen provisionally.

3. Potassium Ozonide

Potassium ozonide was first isolated in a crystalline state in 1949 by Kazarnovskii et al. [10] in the reaction of an ozone–oxygen mixture with potassium hydroxide below 0°C followed by extraction with liquid ammonia. The preparations obtained contained up to 83–88% KO_3 with KOH as the main impurity. In recent years a number of studies were carried out in order to find new methods for the synthesis of potassium ozonide. It was shown that potassium ozonide can be formed above 0°C at +5°C [43] and +40°C [44]. The highest yield of potassium ozonide was achieved when ozone was allowed to react with powdered potassium hydroxide in a fluidised bed [43,44]. It was shown [44] that the fluidised bed method makes it possible to extend greatly the temperature range in which potassium hydroxide can react with ozone not only in the anhydrous state, but also in the hydrated form.

The synthesis of potassium ozonide at positive temperatures is important for practical purposes. Potassium ozonide is also formed when ozone is allowed to react with potassium alkoxides [45,46]. In the reaction of ozone with potassium t-butoxide and t-perbutoxide, KO_3 is formed in yields of about 10 and 40% respectively. However, the ozonide cannot be isolated with liquid ammonia from the ozone-treated alkoxides, since the alkoxides are also soluble in ammonia [45,46]. In addition, potassium ozonide can be obtained by treating potassium superoxide with ozone [37,45,47,48]. The studies carried out in the Laboratory of Peroxy-Compounds at the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences [37] and based on the estimation of the heat of the reaction

$$KO_2 + O_3 \rightarrow KO_3 + O_2 + 28 \text{ kcal} \qquad (10)$$

showed that, when KO_2 is treated with ozone at 40°C, potassium ozonide is formed in the same yield as in the reaction of ozone with potassium hydroxide and can also be successfully extracted with liquid ammonia.

Other methods for the synthesis of potassium ozonide are known [9,17,49]. Among the available methods, treatment with ozone of a suspension of potassium hydroxide [50] and particularly a suspension of KO_2 in Freons [51] is of considerable interest. The yield of potassium ozonide in the reaction of ozone with potassium hydroxide by the method of Kazarnovskii and coworkers [10] and in the reaction of ozone with potassium superoxide in a fluidised bed set up by a stream of ozonised oxygen [37] does not exceed 5–9%. The yield of the ozonide is largely promoted by two factors—an increase in the area of contact with ozone and an increase in the concentration of ozone.

A method involving the reaction of ozone with potassium superoxide in the liquid phase was developed to intensify the process. Freon-12 [52], which exhibits selective solubility in relation to an ozone-oxygen mixture, dissolving ozone alone, was employed as a solvent for ozone; in addition, it is inert with respect to KO_2 and KO_3. It has been shown [51] that, in the reaction of ozone with potassium superperoxide suspended in Freon-12, an ozonide product containing up to 80% KO_3 is obtained without extraction with liquid ammonia. Potassium ozonide was analysed by the method of Petrocelli and Capotosto [53]. The new method for the synthesis of alkali metal ozonides in Freons leads to the possibility of obtaining concentrated oxonides in a single stage without extraction with liquid ammonia and evaporation in a vacuum.

Potassium ozonide is a red crystalline substance stable only on storage in a hermetically sealed container below 0°C. The study of the kinetics of the spontaneous decomposition of potassium ozonide by chemical methods [13] showed that the reaction proceeds according to the equation $2KO_3 \rightarrow 2KO_2 + O_2$ and has the following thermodynamic parameters: $\Delta H^\circ_{298} = -11.6$ kcal, $\Delta S^\circ_{298} = 33$ e.u., and $\Delta F^\circ_{298} = -21.6$ kcal.

The dissociation of potassium ozonide is an irreversible reaction. The decomposition of KO_3 is autocatalytic with an induction period of 1.67, 20.54, and 205 days at +18.0°, −9°, and −18°C. In the subsequent active period, the rate of decomposition of potassium ozonide increases sharply; the activation energy is 22−23 kcal mole^{-1}. It has been shown by electron spin resonance (ESR) [19] that the decomposition of KO_3 at 22°C over a period between 2 and 7 days takes place approximately according to an exponential law with a time constant of 0.02 h^{-1}. It was established by differential thermal analysis [54] that the limit of the thermal stability of potassium ozonide is at 60° ± 2°C. At this temperature KO_3 is entirely converted into KO_2. To elucidate the mechanism of the decomposition of potassium ozonide, magnetic measurements were made [55] at room temperature and at 0°C. The observed deviations from additivity, which are far outside the limits of the error of the measurements, suggest the intermediate formation of a highly paramagnetic product. It is reasonable to postulate that this product is atomic oxygen, the magnetic susceptibility of which is several times greater than those of KO_3 and KO_2.

At the beginning of the decomposition the oxygen content in the solid phase increases, passes through a maximum when the degree of decomposition of potassium ozonide is about 60%, and then falls to zero for 100% decomposition. The two main elementary steps in the decomposition of potassium ozonide to potassium superoxide and oxygen may be described by the following equations:

$$\begin{gathered} KO_3 \rightarrow KO_2 + O, \\ KO_2 + O \rightarrow KO_2 + O_2, \\ \hline 2KO_3 \rightarrow 2KO_2 + O_2. \end{gathered}$$

The density of potassium ozonide is 1.990 g cm^{-3} [39]. Externally potassium ozonide crystals do not exhibit cleavage planes, the grains are formless, and show pleochroism, noted in an earlier study by Azarov and Korvin [16]. They are coloured pale-yellow in the N_p direction and red-brown in the N_g direction. The crystals are monoaxial, negative, and exhibit appreciable double refraction. The refractive indices are $N_p = 1.391$ and $N_g = 1.670$. The heat of formation of KO_3 was determined by measuring its heat of solution in dilute sulphuric acid [14] and amounts to 62.1 ± 0.9 kcal mole^{-1}.

The solubility of potassium ozonide in liquid ammonia was measured in two ways. In a study of the phase diagram for the NH_3-KO_3 system by an isothermal method, and by visual observations over a range of temperatures [56] (the "visual polythermal" method), it was established that the maximum solubility of 14.82 g/100 g NH_3 is attained at −35°C. Determinations of the vapour pressures of saturated solutions of potassium ozonide in liquid ammonia established [32] that the solubility of KO_3 at −63.5°C is approximately 12 g/100g NH_3.

Potassium ozonide is a powerful oxidant and contains 46 wt.% of active oxygen. It reacts instantly with water both at room temperature and at 0°C, with liberation of oxygen via the intermediate formation of OH radicals. In a study of isotope exchange between free hydroxy-radicals and water in 1957, Kazamovskii et al. [57] proposed the following mechanism for reaction (5):

$$\begin{gathered} KO_3 + H_2O^x = KO^xH + O_2, \\ \cdot OH + H_2O^x = \cdot{}^xOH + H_2O, \\ \cdot O^x H + \cdot O^x H = H_2O^x + {}^3/_2\, O_2^x, \\ \cdot O^x H + \cdot OH = H_2O_2^x. \end{gathered} \qquad (11)$$

Not more than 15% of the hydroxy-radicals are converted into H_2O_2 by reaction (11).

The reaction of hydroxy-radicals generated by potassium ozonide with hydrogen peroxide solution was investigated at 0°C [58]. When KO_3 is introduced into water, instantaneous reaction with liberation of oxygen and the formation of KOH and H_2O_2 is observed. The degree of consumption of OH in the formation of H_2O_2 is 18−24%. In hydrogen peroxide solutions, the formation of H_2O_2 is less pronounced and at $[H_2O_2] = 0.3$ M becomes zero.

A mixture of potassium ozonide powder and ice was investigated by the ESR method with slow increase of temperature from −196° to 0°C [59]. As the mixture is gradually heated to a temperature slightly above 0°C, a sharp decrease of signal intensity and the appearance against its background of a narrow signal with a g- factor of 2.011 are observed. The authors [59] believe that the observed signal is probably due to free hydroxy-radicals formed in the reaction of potassium ozonide with water:

$$KO_3 + H_2O \rightarrow KOH + OH + O_2. \qquad (12)$$

The reactions of formic and acetic acids with hydroxy-radicals and molecular oxygen, generated by potassium ozonide, have been investigated. The experiments at room temperature with aqueous formic acid solutions yielded carbon dioxide, oxygen, and hydrogen peroxide as the products. The reaction with anhydrous formic acid results in the formation of carbon dioxide, oxygen, carbon monoxide, and hydrogen [60]. The reaction with acetic acid vapour is instantaneous, goes virtually to completion, and is accompanied by a blue luminescence. The principal products are carbon dioxide, carbon monoxide, molecular hydrogen, water, and a small amount of methane [61]. Potassium ozonide is inert with respect to F_2O_3 dissolved in Freon-13 in the temperature range between −183° and 103° [62]. The reaction of potassium ozonide with water vapour and carbon dioxide was studied in greater detail. In the temperature range 0−20°C, potassium ozonide reacts vigorously with water vapour, active oxygen being completely liberated with formation of potassium hydroxide dihydrate [63]. At +24°C and 50% humidity potassium ozonide grains fully decompose in 30 h under the action of water vapour. During the first two hours, 87% of oxygen is removed. The average rate of liberation of oxygen during the active period is 10.9 ml g^{-1} h^{-1} but at the same temperature and 100% humidity the average rates of evolution of oxygen is 29.6 ml g^{-1} h^{-1}. [64]

The reaction of potassium ozonide with carbon dioxide takes place only in the presence of water vapour via a stage involving the complete hydrolysis of the ozonide with subsequent formation of potassium carbonate and its hydrates. The rate of evolution of oxygen is determined by the rate of diffusion of water vapour [63,94]:

$$\begin{gathered} 2KO_3 + H_2O \rightarrow 2KOH + {}^5/_2\, O_2, \\ 2KOH + CO_2 \rightarrow K_2CO_3 + H_2O. \end{gathered} \qquad (12a)$$

In the absence of moisture the reaction between KO_3 and CO_2 does not occur. The potassium bicarbonate present in the reaction products is determined by potentiometric titration with acid. The ready formation of potassium carbonate increases the possible usefulness of potassium ozonide as a life-supporting agent [64].

Zhdanov and Zvonkova [12] found from the X-ray diffraction pattern of the powder that potassium ozonide has a lattice close to the tetragonal lattice of potassium azide (KN_3) with the parameters $a = 6.094$ Å and $c = 7.056$ Å. However, the absence from the diffraction pattern of the important reflection with an index of 121, according to their data, does not confirm the hypothesis of a linear configuration of the O_3^- ion. Therefore they believe [12]

that the symmetry of KO_3 is probably lower than that of KN_3. In the light of new data on the structure of the ozone molecule [23], it has been suggested that the KO_3 lattice may be of a different type. As stated above, Smith [23] found that the O_3^- ion is not linear but angular with an angle of 110° ± 5° and $r = 1.34 \pm 0.05$ Å. Since these values are close to the corresponding data for the NO_2^- ion, for which the angle $<O-N-O = 115° \pm 4°$ and $r = 1.34 \pm 0.03$ Å, Smith postulated that the structures of KO_3 and KNO_2 are similar. On the basis of the correspondence of the X-ray diffraction data (l and d) for KO_3 and KNO_2, he believes it to be likely that KO_3 has a monoclinic unit cell of the KNO_2 type and with the same coordination.

Azarov and Korvin [16] showed that potassium ozonide has a body-centred tetragonal unit cell with the parameters $a = 8.597 \pm 0.002$ Å and $c = 7.08 \pm 0.002$ Å; the space group is $I4/mcm$. In view of the similarity of the reflection intensities of KO_3 and KN_3, they believe that these structures are derived from the CsCl structure, where each N_3^- or O_3^- ion occupies a Cl^- site and K^+ occupies a Cs^+ site. They calculated from the coordinates of the atoms that the O_3^- ion is not linear but angular with an angle of 100° and $r = 1.19$ Å.

4. Rubidium Ozonide

Rubidium ozonide was first isolated in 1951 by Nikol'skii et al. [11] The reaction between rubidium hydroxide and ozone was carried out at −30°C with subsequent extraction by liquid ammonia. After the evaporation of liquid ammonia, orange quasi-crystalline rubidium ozonide preparations were isolated with an RbO_3 content between 55 and 66% (the residue was RbOH).

The high percentage of the impurity is due to the considerable solubility of RbOH in liquid ammonia (at −40°C 100 ml of liquid ammonia dissolves 0.9 g of RbOH).

In 1966 96.6% pure rubidium ozonide was obtained [65]. This high rubidium ozonide content was achieved by employing as the starting material rubidium superoxide (93.3%), which in turn was prepared by atomising metallic rubidium in an oxygen and argon atmosphere with the aid of a special sprayer and apparatus described in detail by Vol'nov and Matveev [66]. The reaction of ozone with rubidium superoxide was carried out at 0°C for 50 min in a fluidised bed set up with a stream of ozonised oxygen. Before extraction the ozone-treated rubidium superperoxide contained 70.5% RbO_3.

At room temperature rubidium ozonide decomposes slowly according to the equation

$$RbO_3 \rightarrow RbO_2 + {}^1/_2 O_2 . \qquad (13)$$

The density of rubidium ozonide is 2.75 g cm^{-3} [67]. Polycrystalline RbO_3 specimens exhibit pleochroism; they are coloured pale-yellow in the direction of the smallest refractive index and dark-brown in the direction of the largest refractive index; $N_p = 1.456$, $N_m = 1.576$, and $N_g = 1.750$. The rubidium ozonide crystals are optically biaxial.

The solubility of rubidium ozonide in liquid ammonia in the temperature range between −48° and −84° has been investigated. The RbO_3-NH_3 system is of the type with a simple eutectic at a temperature between −82° and −83°C. The eutectic mixture contains 4.0% RbO_3 (4.3 g of RbO_3 in 100 g of NH_3). [68]

5. Caesium Ozonide

The literature data on the synthesis of caesium ozonide up to 1963 may be regarded as merely exploratory, since pure caesium ozonide had not been obtained up to that time.

In a study of the reaction of ozonised oxygen with CsOH, Manchot and Kampschulte [8] noted that CsOH becomes coloured red, the colour disappearing on subsequent heating to 140−160°C. Traube [6] carried out the reaction of ozone with carefully dehydrated CsOH at temperatures between 20° and 0°C. The coloured product was decomposed by water with evolution of 2% of oxygen and the formation of a very small amount of hydrogen peroxide. When [ozone-treated] caesium hydroxide was stored in the cold, the colour persisted for 14 days. An unstable coloured product with the empirical composition CsOH.O was obtained by Strecker and Thienemann [69] in the reaction of ozone with a solution of metallic caesium in liquid ammonia. Because of the considerable solubility of CsOH in liquid ammonia (1.0 g/100 ml NH_3), the purest preparation obtained by Nikol'skii et al. [11] contained 67.3% $CsOH_3$ and 31.2% CsOH.

In order to prepare pure caesium ozonide, the reaction of caesium superoxide with an ozone−oxygen mixture in a fluidised bed was employed above 0°C [37,48] using the method of Vol'nov and Matveev [66]. Caesium superoxide reacted with ozone in a fluidised bed produced by a stream of an ozone−oxygen mixture containing up to 8% of ozone. After extraction with liquid ammonia, a product containing up to 92.5% of caesium ozonide was obtained [66]. Caesium ozonide is extremely unstable with respect to moisture and carbon dioxide. The caesium ozonide content in the ozone-treated superoxide and in the ozonide itself after extraction with liquid ammonia was found by determining the active oxygen and Cs_2O [48].

In order to determine the limit of the thermal stability of caesium ozonide and to discover the processes occurring during its decomposition, a differential heating curve was recorded on a Kurnakov differential thermal analyser [70]. At the same time measurements were made of the amount of oxygen evolved on heating. The heating curve showed two effects. An exothermic effect, which begins at 70°C and has a maximum at 100°C, corresponds to the decomposition of CsO_3 to CsO_2 and is accompanied by the evolution of oxygen. An endothermic effect at 408°C corresponds to the fusion of CsO_2 with subsequent decomposition to the oxide and liberation of oxygen. The density and the refractive index of caesium ozonide were measured [71]. In transmitted polarised light CsO_3 crystals are coloured dark cherry red and exhibit pleochroism. In the direction of the minimum refractive index, their colour is pale yellow, and in the direction of the maximum refractive index dark cherry red. In thick layers the crystals absorb light almost completely and become opaque. The crystals belong to the middle category and are optically monoaxial and positive. The refractive indices are $N_m = 1.523$ and $N_g = 1.69$. The density measured by hydrostatic weighing is 3.19 g cm^{-3} and the X-ray density is 3.22 g cm^{-3}. Like sodium and potassium ozonides, caesium ozonide has the lowest density compared with the peroxide and the superoxide:

	Cs_2O_2	CsO_2	CsO_3
d_4^{20}	4.47	3.80	3.19

But in the series of ozonides its density is a maximum:

	NaO_3	KO_3	RbO_3	CsO_3
d_4^{20}	1.6	1.99	2.75	3.19

Caesium ozonide crystallises with a body-centred tetragonal lattice, having the parameters $a = 9.75$ Å, $c = 8.75$ Å, and $c/a = 0.9$.[26] The space group is $I4/mcm$.

IV. ALKALINE EARTH METAL OZONIDES

The problem of the formation of alkaline earth metal ozonides remained open until recently. Manchot and Kampschulte[8] noted that, in the reaction of an ozone-oxygen mixture containing 8 wt.% of ozone with magnesium, strontium, and barium oxides at room temperature, ozone was decomposed and at −80°C barium oxide acquired an intense yellow colour, calcium oxide was less strongly coloured, and the colour of magnesium oxide was insignificant. They suggested that these coloured compounds are ozonides. However, this hypothesis was not confirmed either by chemical analysis or other methods. Blumental[72] repeated the experiments of Maschot and Kampschulte and reported the formation of "some kind" of substance which does not decolourise potassium permanganate solution but liberates iodine from acid potassium iodide solutions. Strecker and Thienemann[73] oxidised solutions of metallic barium and calcium in liquid ammonia with an ozone−oxygen mixture. With calcium, they obtained a brown precipitate, which fully decomposed on evaporation of ammonia and was not analysed. These data exhaust the early information about the products of the reaction of alkaline earth metals with ozone.

The first calcium, strontium, and barium ozonides were synthesised in 1966.[74] On the hypothesis that the reaction of ozone with alkaline earth metal hydroxides is described by the equation

$$M(OH)_2 + 2O_3 \rightarrow M(O_3)_2 + H_2O + {}^1/_2 O_2 \ , \qquad (14)$$

the thermodynamic functions for this reaction with calcium, strontium, and barium hydroxides were estimated[74]. The results are presented in Table 2.

Table 2. Estimation of the enthalpies of formation of alkaline earth metal ozonides from the elements and the enthalpy and free energy of reaction (14) (±10 kcal).

Compound	ΔH^0_{298} for formation from elements	By reaction (14)	
		ΔH^0_{298}	ΔF^0_{298}
$Ca(O_3)_2$	−169	−69	−83
$Sr(O_3)_2$	−161	−68	−81
$Ba(O_3)_2$	−157	−67	−80

The values of ΔH°_{298} for the formation of the ozonides from the elements were estimated by comparative calculation[27]. It was shown[74] that, in the reaction of ozone with calcium, strontium, and barium hydroxides at −100°C, the latter become coloured yellow, the colour intensity increasing from calcium to barium.

An ESR study of the resulting coloured precipitates at the temperature of liquid nitrogen showed the presence of a typical spectrum of the ozonide ion with $g = 2.01$. The thermal stability of the ozonides increases from calcium to barium. Calcium ozonide decomposes appreciably at −35°C, strontium ozonide a little below 0°C, and barium ozonide at 0°C.

The results of the ESR study suggest that the coloured products are formed in the reaction of the ozone−oxygen mixture with solid alkaline earth metal hydroxides and are ozonides containing the paramagnetic ion O_3^-.

V. AMMONIUM AND TETRAMETHYLAMMONIUM OZONIDES

The capacity for the formation of an ozonide is not characteristic solely of alkali and alkaline earth metals but also of the ammonium ion and its derivatives.

In 1907 Manchot and Kampschulte[8] were the first to predict the possibility of the existence of ammonium ozonide. They found that, when dilute ozone is passed through liquid ammonia, a dark-orange colour is produced, which persists until the liquid is heated. They discovered that the colour is most intense at −70°C and disappears at −60°C. Strecker and Thienemann[7] also observed a short-lived colour when dilute ozone was passed through liquid ammonia, although the product isolated contained mainly ammonium nitrate. Experiments carried out in the Laboratory for Peroxy-Compounds at the Institute of General and Inorganic Chemistry on the reaction of ozone with solutions of metallic calcium in liquid ammonia showed that the solutions assume a bright-orange colour which gradually disappears as ammonia is evaporated[75].

Ammonium ozonide was first isolated in 1962 by Solomon et al.[76] by the reaction of ozone with liquid ammonia at a temperature below −100°C. The absorption spectrum of ammonium ozonide in a mixture with trifluoromethane is analogous to the spectra of other ozonides. The use of a solvent was necessary to keep the system in the liquid state at the low temperature required for the stabilisation of ammonium ozonide. A peak at 450 nm, characteristic of the ozonide ion, was observed in the spectrum of ammonium ozonide. Moreover, the ESR spectra of potassium, tetramethylammonium, and ammonium ozonides were recorded to identify ammonium ozonide. The presence of the ozonide ion was demonstrated in all these compounds. The results are presented in Table 3.

Table 3.

Compound	g-factor
KO_3	2.0124
$(CH_3)_4NO_3$	2.0144
NH_4O_3	2.0119

Ammonium ozonide is stable only below −126°C. It decomposes according to the equation

$$2NH_4O_3 \rightarrow NH_4NO_3 + {}^1/_2 O_2 + 2H_2O \ . \qquad (15)$$

Herman and Giguere[18] also showed that ammonium ozonide begins to decompose at temperatures below −126°C and at −90°C the decomposition is complete.

In 1929 Traube and Kyhbier[77] treated tetramethylammonium hydroxide with ozone and obtained a red substance to which they attributed the formula $(CH_3NOH)_2.O_2$. Tetramethylammonium ozonide was first isolated and identified by Solomon et al.[78] It was obtained by the reaction of ozone with tetramethylammonium hydroxide at

25°C. The absorption spectrum of the solution of tetramethylammonium ozonide in liquid ammonia has an absorption maximum at 450 nm, characteristic of all ozonides.

Tetramethylammonium ozonide dissolves in liquid ammonia at −63°C to the extent of 1.3 ± 1 g/100 g NH_3. It is stable up to 25°C and at 25°C decomposes completely over a period of 48 h. The heat of formation of $[N(CH_3)_4]O_3$ from the elements is 49.5 ± 4 kcal mole^{-1}.

VI. SOME HYPOTHESES CONCERNING THE MECHANISM OF THE FORMATION OF OZONIDES

The formation of alkali metal ozonides by the mechanism proposed by Kazarnovskii[11,79] proceeds via an unstable complex of the type $M^+O^-H^+O_3^-$ and a subsequent further reaction with ozone:

$$2\,MOH + 2\,O_3 \rightarrow 2\,MOH \cdot O_3\,, \quad (16)$$
$$2\,MOH \cdot O_3 + 2\,O_3 \rightarrow 2\,MO_3 + 2\,HO_2 + 2\,O_2\,, \quad (17)$$
$$2\,HO_2 \rightarrow H_2O + 1.5\,O_2\,, \quad (18)$$
$$MOH + H_2O \rightarrow MOH \cdot H_2O\,, \quad (19)$$
$$3\,MOH + 4\,O_3 \rightarrow 2\,MO_3 + MOH \cdot H_2O + 3.5\,O_2\,. \quad (20)$$

The overall result is the formation of a mixture of the alkali metal ozonide and the monohydrate of the hydroxide with a simultaneous conversion of a large amount of ozone into oxygen. The activation energy for the reaction of potassium hydroxide with ozone has been estimated as 3.1 kcal.[80]

The following considerations can be put forward concerning the above mechanism for the formation of alkali metal ozonides. The mechanism is based on two hypotheses: the hypothesis of the formation of the unstable complex $MOH.O_3$ of sodium, potassium, rubidium, or caesium (but not lithium) hydroxides with an ozone molecule [reaction (16)] and the hypothesis of the participation of the radical HO_2 [by reaction (17)] in the formation of the ozonides of these elements.

According to Eqn. (20), the ratio of the metal hydroxide monohydrate to the ozonide is 1:2, which means that in the reactions of ozone with sodium and potassium hydroxides the ozonide contents should be 71% and 66.4% respectively. However, it has been shown that not more than 4−5% NaO_3 is detected in the ozone-treated sodium hydroxide[36,81]. This contradiction was eliminated in a mechanism for the formation of ozonides put forward subsequently[82]. Probably the reaction of ozone with alkali metal hydroxides takes place mainly on the surfaces of the solid hydroxides. Isotopic analysis of oxygen in potassium ozonide[75] synthesised from $K^{18}OH$ with the natural composition showed that the oxygen of the hydroxide is involved in the formation of the ozonide.

On the basis of the fact that potassium ozonide is formed also by the reaction $KO_2 + O_3 \rightarrow KO_3 + O_2$ from the superoxide and ozone[11,37,83] and data[80] for the catalytic decomposition of ozone on the KOH surface, it is more probable that atomic oxygen is responsible for the formation of ozonides.

The mechanism proposed for the formation of ozonides[82] presupposes the successive occurrence of the following reactions:

$$3\,O_3 + 2\,MOH \rightarrow 3\,O_2 + 2\,MOH \cdot O + O\,, \quad (21)$$
$$2\,MOH \cdot O + O \rightarrow 2\,MO_2 + H_2O\,, \quad (22)$$
$$2\,O_3 + 2\,MO_2 \rightarrow 2\,MO_2 \cdot O + 2\,O_2\,, \quad (23)$$
$$2\,MO_2 \cdot O \rightarrow 2\,MO_3\,, \quad (24)$$
$$5\,O_3 + 2\,MOH \rightarrow 5\,O_2 + 2\,MO_3 + H_2O\,. \quad (25)$$

Reaction (21) has been confirmed by the data of Schwab and Hartman[80] and the results obtained in a study of the reaction of ozone with sodium hydroxide[36]. The occurrence of reaction (22) has been demonstrated in a study of the reaction of potassium hydroxide with atomic oxygen generated in a glow discharge[84]. Reactions (23) and (24) are components of reaction (10). The overall equation (25) is based on the three experimentally demonstrated intermediate reactions and is consistent with the decomposition of ozone in which n moles of oxygen and n atoms of oxygen should be formed from n moles of ozone.

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The data presented in the review show that recently there has been a considerable growth of interest in compounds included in the class of inorganic ozonides. The chemistry of ozonides has been attracting the attention of investigators both in the Soviet Union and abroad.

Evidently the main studies are devoted to problems of the synthesis, structure, and physicochemical properties of ozonides. Very few investigations deal with the reactions of these substances with various classes of compounds: solid, liquid, gaseous, inorganic, and organic. There has been no work at all on the stabilisation of ozonides.

The study of these processes will characterise more fully this new class of compounds and will bring nearer their practical application. The accumulation of experimental data on the synthesis and properties of ozonides and the mechanisms of their formation will help in the elucidation of the mechanism of the formation of important inorganic radicals.

Inorganic ozonides, which are powerful oxidants and sources of oxygen, are very promising substances and further intensification of the study of their synthesis and properties and also ways for their stabilisation will lead to their wider practical application.

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