193. *Unstable Intermediates. Part V.*[1] *Ozonides and Superoxides.*

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The preparation and properties of salts containing the ozonide ion, O_3^-, are described. In particular spectrophotometric and magnetic studies have been made which give structural information, and enable a distinction to be made between ozonides and superoxide ions. The transient formation of ozonide ions during the thermal decomposition of potassium hydroperoxide in concentrated aqueous potassium hydroxide and the photochemical decomposition of hydroperoxide ions in an alkali glass have been established.

When ozone is passed over powdered sodium or potassium hydroxide an orange solid ozonide is formed[2] which is remarkably stable. Recent studies[3,4] have indicated that this compound contains the ion O_3^-, which is paramagnetic, containing nineteen valence electrons.

Whilst the radicals OH, O^-, HO_2 and O_2^- are frequently postulated as transient intermediates in a variety of reactions (see, *e.g.*, refs. 5 and 6), the rôle of O_3^- as an intermediate has not been explored, and little attempt has been made to obtain direct physical evidence for the presence of any of these intermediates.

In Parts I, II, and IV we suggested that ultraviolet and electron spin resonance spectroscopy in combination are a powerful and sensitive method for detecting traces of unstable

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[1] Parts I—IV, Symons and Townsend, *J.*, 1959, 263; Gibson, Symons, and Townsend, *J.*, 1959, 269; Symons, *J.*, 1959, 277; Carrington, Dravnieks, and Symons, preceding paper.

[2] Wurtz, " Dictionnaire de Chimie pure et appliquée," Vol. II, p. 721, 1868.

[3] Kazarnovskii, Nikolskii, and Abletsova, *Doklady Akad. Nauk, S.S.S.R.*, 1949, **64**, 69.

[4] Whaley and Kleinberg, *J. Amer. Chem. Soc.*, 1951, **73**, 79.

[5] Uri, *Chem. Rev.*, 1952, **50**, 375.

[6] Symons, *J.*, 1953, 3956.

intermediates, so we have tried to use them in this study. The ultraviolet spectra of solutions of the superoxides in ammonia have been recorded [7] and the electron spin resonance spectrum has been described and interpreted.[8]

The conjugate acids of these ions are less stable and their identification depends far more on inference.[9,10] We therefore decided that in attempts to find reactions in which unstable intermediates of this sort might be formed, attention would be given to basic media.

Hydrogen peroxide decomposes readily in alkaline solution, though the mechanism is uncertain. The decomposition has been studied [11,12] at pH 9—13 but not in more concentrated alkali. Because of its simplicity we chose this reaction. When certain mixtures of aqueous sodium and potassium hydroxide are cooled clear glasses are formed, suitable for spectrophotometry; accordingly, dilute solutions of hydrogen peroxide in such low-temperature glasses were exposed to ultraviolet light, again in the hope that a sufficient build-up in radical concentration would occur to make identification possible.

EXPERIMENTAL AND RESULTS

Preparation of Ozonides.—Slow passage of dry ozonised oxygen over finely powdered sodium or potassium hydroxide at room temperature rapidly gave the corresponding ozonides as deep yellow powders. Dissolution of potassium ozonide in liquid ammonia gave a stable orange solution: the sodium salt was insoluble. The solids were stable for many hours in stoppered tubes and could be kept indefinitely at −78°. Attempts to prepare ozonides from lithium hydroxide and alkaline-earth metal hydroxides were unsuccessful.

Preparation of Superoxides.—Sodium superoxide is present as an impurity (*ca.* 10%) in "AnalaR" sodium peroxide.[8] Potassium superoxide, also contaminated with large quantities of the peroxide, was prepared by direct oxidation of potassium. The metal was distilled *in vacuo* (10^{-4} mm.) up a tube (40 cm. long) by means of a small electric furnace in several stages, and was deposited as a thin mirror on the walls of the reaction vessel. The side arm was removed at a constriction, and a small quantity of dried oxygen admitted. On slight warming of one section of the film, vigorous reaction occurred to give a deep yellow powder. This process was repeated until all the metal had been oxidised.

Spectrophotometry.—Spectra were measured with a Unicam S.P. 500 spectrophotometer. Diffuse reflectance measurements were made directly on the powdered solid by use of a Unicam attachment with lithium fluoride as a reference surface. The ozonides are not hygroscopic and the readings were reproducible under ordinary operating conditions.

Spectra of solutions of potassium ozonide in liquid ammonia were measured in 1 cm. stoppered quartz cells in a thermostatted cell holder. Coolant was circulated from a Townson and Mercer low-temperature thermostat by a small pump *via* lagged tubing. The temperature of the cells was estimated to be about −50°. Cold dry nitrogen was circulated through the cell housing to prevent misting of the cell surfaces. The cells were filled with solvent and solution with a pre-cooled dropping pipette, and were cooled in acetone at −78° before being placed in the housing. Thus atmospheric moisture was kept out.

Concentrations of ozonide solutions were estimated by comparing the areas under their electron spin resonance spectra, measured at 90° K, with the areas under similar spectra obtained from calibrated carbon specimens measured under identical conditions. Hence extinction coefficients for solutions in liquid ammonia were estimated. The results are given in Table 1 together with relevant details of the spectra of superoxides.[8] A typical spectrum is shown in Fig. 1.

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[7] Thompson and Kleinberg, *J. Amer. Chem. Soc.*, 1951, **73**, 1243.

[8] Bennett, Ingram, Symons, George, and Griffith, *Phil. Mag.*, 1955, **46**, 443; for the method of detection see Ingram, "Spectroscopy at Radio and Microwave Frequencies," Butterworths, London, 1955.

[9] Livingstone, Ghormley, and Zeldes, *J. Chem. Phys.*, 1956, **24**, 483.

[10] Gibson, Symons, and Townsend, *J.*, 1959, 269.

[11] Nicoll and Smith, *Ind. Eng. Chem.*, 1955, **47**, 2548.

[12] Erdey, *Acta. Chim. Acad. Sci. Hung.*, 1953, **3**, 95.

Spectra of irradiated glasses were measured at about 100° K in a Unicam S.P. 500 instrument fitted with a special cell holder.[15] Cells were filled and manipulated as in earlier experiments.[16] The results are given in Table 1 and a typical spectrum is shown in Fig. 2.

TABLE 1. *Details of spectra of superoxide and ozonide ions.*

$\varepsilon_{max.}$ is the molar extinction coefficient at the peak ($\lambda_{max.}$).

Compound	$\lambda_{max.}$ (mμ)	$\varepsilon_{max.}$	Remarks
$NaO_2 + Na_2O_2$	370	—	Diffuse reflectance (shoulder)
O_2^- in NH_3	380	—	Ref. 7
$NaO_3 + NaOH$	440	—	Diffuse reflectance
O_3^- in NH_3	435	2000	Solution
Irradiated HO_2^-	430	—	Irradiated in glass

Magnetic Measurements.—Initial measurements were made at wavelengths of 3 cm., 1·25 cm., and 8 mm., by use of standard " crystal-video " detection.[8,13] Later measurements were made at 3 cm. with phase-sensitive detection,[14] The results reported for the superoxides [8] have been confirmed, but the initial results mentioned by Bennett *et al.*[13] for solid ozonides have not. The present results show that under all conditions of measurement a single symmetrical line centred on a *g*-value of 2·012 ± 0·001 and having a total width at half-height of 25 ± 2 gauss is obtained. The curve reported earlier [13] is asymmetric having a shoulder on the high-field side with a *g*-value of about 2·003. This shoulder, close to the free-spin value, was probably caused by a small amount of impurity since no sign of any broadening in this region has been observed in the present study. Whilst it is true that such asymmetry would not be so well resolved at 3 cm. as at 1·25 cm., this is offset by the fact that a relatively narrow line is obtained, and the method of detection whereby the first derivative of the absorption line is recorded, is very sensitive to changes in line shape. The fact that small traces of diphenylpicrylhydrazyl added to the specimen can be clearly detected supports this contention. The results are given in Table 2 and Fig. 3.

FIG. 1. *Spectrum of solid sodium ozonide measured by diffuse reflectance methods.*

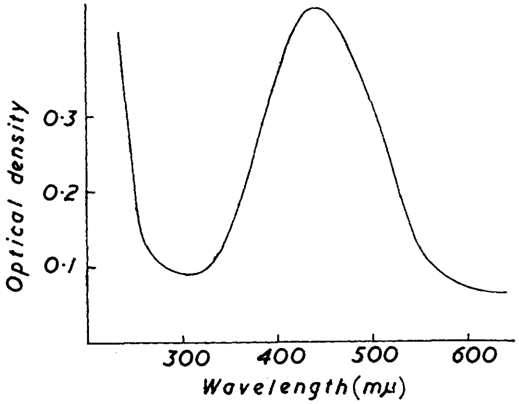
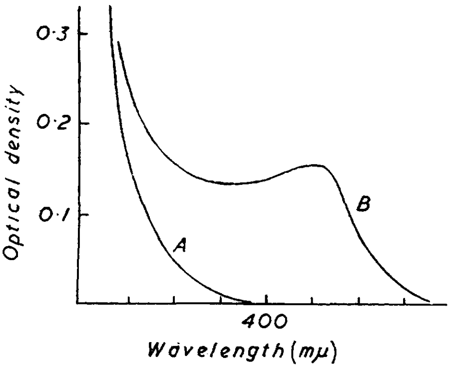


FIG. 2. *Spectrum of a glass composed of sodium and potassium hydroxides, water, and hydrogen peroxide, recorded at* 100° K, (*A*) *before irradiation,* (*B*) *after irradiation with* 3650 Å *light.*



Hydrogen Peroxide–Alkali System.—All reagents were carefully purified because it seemed probable that radical formation was induced by traces of impurities (see Discussion). Judactan " Batch tested " potassium hydroxide was dissolved in specially purified water [17] in Polythene vessels. Stock solutions were further purified at times by shaking with alumina and centrifuging. Hydrogen peroxide was 90% triply distilled material kindly supplied by Laporte Chemicals Ltd. Reaction mixtures were prepared in Polythene vessels and rapidly transferred to small

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[13] Bennett, Ingram, and Schonland, *Proc. Phys. Soc.*, 1956, **69**, *A*, 556.
[14] Gibson, Ingram, Symons, and Townsend, *Trans. Faraday Soc.*, 1957, **53**, 914.
[15] Symons and Townsend, *Spectrovision*, 1957, **4**, 5.
[16] Symons and Townsend, *J.*, 1959, 263.
[17] Smith and Symons, *Trans. Faraday Soc.*, 1958, **54**, 338.

silica tubes immediately before being frozen in liquid oxygen to quench the reaction. Subsequent measurements of electron spin resonance spectra were made at 90° K. Detectable signals were obtained only when the concentration of potassium hydroxide approached 8M and decayed rapidly at room temperature, a typical half-life being 2 min. Under these conditions a rapid evolution of oxygen occurred but there was no detectable coloration. The concentration of radicals was probably in excess of 10^{-4}M under good conditions: it did not appear to depend crucially upon the degree of purification.

TABLE 2. *Details of electron spin resonance spectra of superoxide and ozonide ions at 3 cm.*

	g-value	$\Delta_{\frac{1}{2}ht}$ (gauss) *	Δ_{MS} (gauss) †
NaO_2 (+Na_2O_2)	2·000 ± 0·005 ($g_\perp$) 2·175 ± 0·005 ($g_\parallel$)	250	—
NaO_3 (+NaOH)	2·012 ± 0·002	25	20
O_3^- in NH_3	2·012 ± 0·002	24	18
H_2O_2 in KOH (40%)	2·012 ± 0·003	25	19
Irradiated glass (2 min.)	2·012 ± 0·003	25	19
Irradiated glass (6 hr.)	2·008 ± 0·005	35	—

* $\Delta_{\frac{1}{2}ht}$ = full width at half-height. † Δ_{MS} = width between points of maximum slope.

Irradiation.—Specimens for spectrophotometric and electron spin resonance analysis were prepared and irradiated as described earlier.[14,16] A medium pressure 250 w mercury arc lamp was used, the light being filtered through several thicknesses of soda-glass so that only the 3650 Å band and possibly some of the 3130 Å band were effective. Good glasses were obtained from equimolar mixtures of potassium and sodium hydroxide solutions (*ca.* 8M) to which a few drops of hydrogen peroxide had been added immediately before cooling in liquid oxygen.

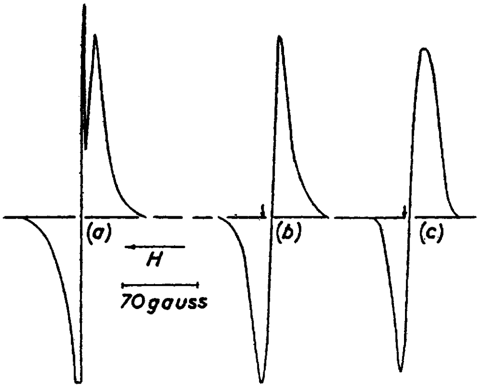

FIG. 3. *Electron resonance spectra:* (*a*) *sodium ozonide with diphenylpicrylhydrazyl,* (*b*) *sodium ozonide alone,* (*c*) *glass composed of sodium and potassium hydroxides, water, and hydrogen peroxide after irradiation. The curves are first derivatives of the signal and the arrow indicates the value g* = 2·003.

On irradiation a yellow colour rapidly developed, and an intense electron spin resonance signal was obtained after a few minutes' exposure. The rate of photolysis, however, rapidly decreased, possibly because of the internal filter effect of the coloured species. The ultraviolet spectrum of a glass irradiated for 6 hr. showed considerable absorption in the 370 mμ region (Fig. 2) as well as a peak at 435 mμ, and the electron spin resonance spectrum was broader and less symmetrical than that obtained initially.

On warming to −50° the colour and signal decayed relatively slowly in marked contrast with the behaviour of reactive radicals described previously.[14] This evidence of stability means that radicals such as OH of O^- should not be considered as possible causes of the colour or paramagnetism.

DISCUSSION

Structure of the Ozonide Ion.—Our spectrophotometric and electron spin resonance results confirm earlier evidence that the alkali-metal ozonides are salts containing the ion O_3^-. This ion has the same number of valency electrons as chlorine dioxide, and the electronic structure is probably similar to that suggested for chlorine dioxide by Walsh,[18] though the

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[18] Walsh, *J.*, 1953, 2266.

more detailed description given by Bennett, Ingram, and Schonland[13] is not appropriate since low-lying *d*-orbitals are not available for bonding in O_3^-. The first electronic transitions are remarkably similar, since chlorine dioxide has a series of bands in the 370 mμ region with a maximum extinction coefficient of about 2000.[19] This transition is described by Walsh[18] as

$$(a_2'')^2\,(b_2')^2\,(b_1')^2\,(b_1'') \longrightarrow (a_2'')\,(b_2')^2\,b_1')^2\,(b_1'')^2$$

and this formulation is presumably applicable to the spectrum of O_3^-. Using arguments similar to those given,[19] one would expect a smaller energy for this transition in O_3^- since the electron affinity of oxygen is greater than that of chlorine.

Despite the relatively high energy of this transition the fact that the *g*-value is appreciably different from the free spin value means that spin–orbit coupling is not negligible. The apparent absence of *g*-value variation must mean that $g_x \doteqdot g_y \doteqdot g_z = 2{\cdot}012$. This result can be compared with that for chlorine dioxide, for which the values $g_x \doteqdot g_z = 2{\cdot}02$ and $g_z = 2{\cdot}01$ are reported.[13]

The electron spin resonance spectrum for ozonide is very different from that for superoxide, which has a pronounced shoulder on the low-field side. A large variation in *g* is often observed for molecules having axial symmetry: the peak is due to molecules whose axes are nearly perpendicular to the applied field ($g_\perp$) whilst the shoulder is due to molecules nearly parallel ($g_\parallel$). The difference in intensity arises because there is a far greater probability of finding molecules with axial symmetry nearly perpendicular than nearly parallel to the fields.

Absence of detectable asymmetry from the electron spin resonance spectrum obtained from ozonide means that there is no axial symmetry. This means that the ion must be bent, as expected for molecules with 19 valency electrons,[18] and also that the unpaired electron is in an orbital which is spread over the whole ion.

Reaction Mechanisms.—The radical intermediate formed during the decomposition of hydrogen peroxide in alkali can be reasonably identified as ozonide rather than superoxide. Unfortunately, insufficient radicals were accumulated for spectrophotometric study, but the electron spin resonance results seem conclusive. The mechanism involved is obscure. We consider that catalysis by traces of impurities is important. Many transition-metal ions are oxidised to high valency states by hydrogen peroxide in alkaline solution, and the resulting oxyions then act as catalysts for the decomposition of hydrogen peroxide to oxygen and water, being themselves reversibly reduced during the process.[20] This reaction is thought to proceed by single electron-transfer stages and hence to involve free radicals. Since oxygen is a product, and in view of the stability of the ozonide ion, we suggest that steps such as (1), (2), and (3) are important, and that relatively large stationary concentrations of ozonide may accumulate:

$$O_2 + OH \rightleftharpoons HO_3 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$HO_3 + OH^- \rightleftharpoons O_3^- + H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$O_2 + O^- \longrightarrow O_3^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

The decomposition of ozone in aqueous alkaline solution has been studied by Forchheimer and Taube,[21] and by Weiss.[22] Weiss postulated that the yellow colour which develops at −40° in 40% potassium hydroxide solutions in contact with ozonised oxygen is due to superoxide. We have detected small concentrations of ozonide under these conditions but no superoxide. The reaction may well resemble that which occurs between ozone and solid hydroxides.

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[19] Buser and Honisch, *Helv. Chim. Acta*, 1952, **35**, 2547.

[20] Carrington and Symons, *J.*, 1956, 3373.

[21] Forchheimer and Taube, *J. Amer. Chem. Soc.*, 1954, **76**, 2099.

[22] Weiss, *Trans. Faraday Soc.*, 1935, **31**, 668.

Forchheimer and Taube,[21] using more dilute alkali, found that exchange of ^{18}O between water and oxygen was catalysed by ozone. One interpretation put forward was that the exchange

$$^{*}OH^- + OH \longrightarrow {}^{*}OH + OH^- \qquad (4)$$

was followed by steps (1), (2), and (3). The hydroxyl radicals in (4) are derived from ozone.[21] In view of the remarkable stability of solid ozonides we prefer this sequence for the exchange to the one involving the reverse of reaction (3), which was postulated originally.[21]

These reactions are probably significant also in the reaction between ozone and solid hydroxides, which could be initiated by the charge-transfer (5), followed either by (1) and (2), or (6) and (3).

$$O_3 + OH^- \rightleftharpoons O_3^- + OH \qquad (5)$$

$$OH + OH^- \rightleftharpoons O^- + H_2O \qquad (6)$$

Step (5) is energetically unfavourable, but nevertheless hydroxide in the absence of an excess of water is a relatively powerful reducing agent, since it reacts with manganate to give hypomanganate [20] and chromate to give hypochromate.[23]

Again the same separate stages are probably involved in the reaction between solid potassium ozonide and water.[24] The apparent independence of pH is possibly a result of the experimental method,[24] since most of the rapid reaction will have occurred close to the dissolving solid, and therefore in an environment largely independent of the bulk solvent.

Photolyses.—Since hydrogen peroxide and the hydroperoxide ion have very similar ultraviolet spectra and on photolysis decompose remarkably similarly,[25] the primary act of light absorption probably leads directly to (7) rather than being a photoionisation:

$$HO_2^- + h\nu \longrightarrow O^- + OH \qquad (7)$$

If this is so, then the very rapid build up in the concentration of ozonide must mean that this is an efficient step even in a rigid glass, and also that radical migration can occur so that steps (6) and (3) can be realised. Once the available oxygen in the glass has been consumed, however, it is probable that a build-up in the concentration of superoxide would occur, as a consequence of reactions such as (8).

$$O^- + HO_2^- \longrightarrow OH^- + O_2^- \qquad (8)$$

The results [Figs. 2 and 3(*c*)] reveal that there is some evidence, from the ultraviolet and electron spin resonance spectra of glasses irradiated for extended periods, for this contention.

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[23] Bailey and Symons, *J.*, 1957, 203.
[24] Kasarnowsky, Lipichin, and Tichomirov, *Nature*, 1956, **178**, 100.
[25] Baxendale and Wilson, *Trans. Faraday Soc.*, 1957, **53**, 344.