At lower pressures the detonation velocity in the flask remains at 1800 m sec^{-1} (Fig. 3*b*) but the formation of the detonation wave in the lower flask takes place after a considerable delay, as indicated by the increase in the horizontal distance between the starting points of the upper and lower bands. The detonation wave is apparently broken up on leaving the capillary to enter the lower flask, although the combustion continues to spread at a low velocity. Only at the lower closed end of the flask does the pressure increase sufficiently for the formation of a detonation wave. At low pressures, even in the upper flask, the detonation wave is formed not close to the ignition point but at the lower almost closed end of the tube (Fig. 3*c*).

When the spectrum of the flame in the flasks was recorded, only sodium lines were observed. The sodium *D* doublet was clearly seen on the photograph of the spectrum from a single spark. When 30–40 successive sparks were recorded on one film, the brightness of the doublet showed a corresponding increase, but no lines other than those of sodium were observed. Thus the glow observed in our experiments during the sparking of ozone is a secondary effect due to the excitation of lines from sodium, introduced with trace impurities. This excitation takes place under the influence of high temperature, when the decomposition of the ozone is for the most part complete. In the shock wave the temperature is higher, so that formation of the wave produces the glow repeatedly even when no undecomposed ozone is present in the gas.

SUMMARY

The conditions for the passage of a gaseous-ozone detonation through 20 cm capillary tubes in a closed apparatus at low gas pressures, up to 300 mm Hg, have been studied. The detonation is transferred through the capillary only at gas pressures above a certain boundary value (p_b). For given apparatus dimensions, the plot of p_b against the reciprocal of the capillary diameter is approximately linear. The transfer of the detonation through the capillary involves detonation waves along the capillary at ~1800 m sec^{-1}. At 264 mm Hg the detonation wave passes unhindered through a 0.799 mm diameter capillary. At lower pressures the detonation wave breaks down on leaving the capillary and is reformed after a slight delay.

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INVESTIGATION OF THE MECHANISM OF OXYGEN EVOLUTION AT A SILVER ELECTRODE USING THE OXYGEN ISOTOPE ^{18}O

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During anodic polarisation both bulk and surface oxygen compounds are formed on a silver electrode[1,2], of the type Ag_2O at a potential of 1.2 V, and Ag_2O_2 (AgO) at 1.4 V. Thus the electrochemical evolution of oxygen (above 1.6 V) takes place on an already oxidised silver surface.

It was suggested in earlier work on the electrochemical[3] and photoelectrochemical[4] characteristics of a silver anode that oxygen evolution takes place *via* the formation and decomposition of higher oxygen compounds of silver. According to more recent results and theoretical ideas[5], the rate-determining stage in this process is the reaction of chemisorbed oxygen (oxide) with hydroxide ions undergoing discharge under the influence of the electric field.

The aim of the present work was to confirm experimentally this reaction mechanism by using ^{18}O as a tracer, as was done previously for the same reaction at a platinum electrode[6]. The principle of this method is that the oxygen in the bulk silver compounds is "labelled" with ^{18}O, after which it is detected by analysing the initial portions of gaseous oxygen evolved at such an electrode when solutions not enriched with ^{18}O are electrolysed. This method has been used[7] to investigate the effect of the nature of the metal oxides on the fractionation of the oxygen isotopes during electrolysis. When the oxides Ag_2O_2, PbO_2, and MnO_2 enriched with ^{18}O were used as anodes[7], it was found that the isotopic composition of the oxygen evolved from alkaline solutions was not derived from that of the oxides. The American workers explain this result by the occurrence of exchange of oxygen atoms between the metal oxides and the solvent, and do not deny that silver oxides may take part in oxygen evolution.

EXPERIMENTAL

Two identical apparatuses (Fig. 1) were used, one filled with 1 *N* KOH solution enriched with ^{18}O and the other with ordinary 1 *N* KOH. The apparatus consisted of three sections, in which were placed the silver test electrode *1*, the platinum auxiliary electrode *2*, and the reference electrode *3*, which consisted of a strip of palladium saturated with hydrogen in the same solution. The volume of solution in the anode compartment did not exceed 3–4 ml. The

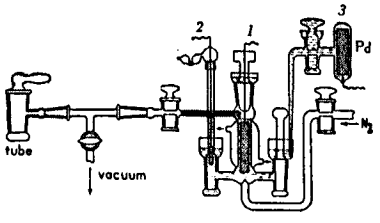

Fig. 1. Measuring apparatus.

test electrode was a rolled up strip of silver 0.1 mm thick and of apparent surface area 31 cm². Before an experiment the surface of the silver was treated with 4 *N* NH_4OH to remove any oxides, and then mechanically cleaned and polished with powdered glass. After this the electrode was degreased in boiling 4 *N* KOH, washed in hot twice distilled water, dried at 70°, and placed in the cell filled with ^{18}O-enriched 1 *N* KOH, in which it was first subjected to repeated anodic and cathodic polarisation over the potential range 0–1.2 V for 30 min. The electrode prepared in this manner was polarised anodically at a constant potential for 6–7 h. The polarisation potentials were respectively 1.22–1.24 V (formation of the oxide Ag_2O) and 1.55 V (formation of Ag_2O_2). The amount of Ag_2O formed was determined from the quantity of electricity which had passed, and that of Ag_2O_2 from the magnitude of the arrest on the cathodic charging curve obtained. A solution of 1 *N* KOH was simultaneously saturated with nitrogen in a similar cell, and the tubes for the removal of samples of gaseous oxygen were evacuated. All experiments were carried out at 20° [the central part of the cell (Fig. 1) was fitted with a jacket connected to a precision thermostat].

After the termination of the anodic polarisation, the test electrode was removed from the cell, quickly (within 30 sec) and carefully rinsed in a stream of twice distilled water and in ordinary 1 *N* KOH, and placed in an atmosphere of nitrogen in the second cell. The anodic potentials of the electrode in the absence of polarisation were 1.16–1.17 V and 1.4–1.46 V respectively. After a given time, gaseous oxygen was evolved at the electrode at a potential of 1.9–2.0 V, the first five portions of which, each 1 cm³ in volume, were collected at atmospheric pressure over the solution, and then transferred to the previously evacuated tubes. In a control experiment the gas was withdrawn under these same conditions. The tubes containing the samples were analysed in a mass spectrograph of type MI 1301, with an accuracy of 1–2%.

We also investigated the rate of exchange of oxygen atoms between silver oxides and water both during electrolysis and in its absence. The silver electrode, covered with the appropriate oxide into which the ^{18}O isotope had been introduced, was left for a definite time in ordinary alkali solution (0.5–0.9 ml) in a test-tube. The appearance of ^{18}O in the alkali was determined by mass-spectrographic analysis of a sample of the gaseous oxygen evolved at a platinum anode on electrolysis of this solution in a microcell. Simultaneously in the second cell, as described above, the first five samples of oxygen were evolved at the silver electrode, and also analysed in the mass spectrograph. In this way the rate of exchange could be calculated from the measured time dependence of the number of ^{18}O atoms which had passed from the surface of the silver into the water and into the gaseous oxygen, since the total number of ^{18}O atoms introduced into the surface was known.

TABLE 1.

Ag_2O, 10^6 g-equiv.	Time	^{18}O in samples of O_2, %				^{18}O in control sample, %
		1	2	3	4	
5.2	1 min	0.220	0.205	0.196	—	0.196
8.4	»	0.215	0.208	0.200	0.192	0.192
6.6	»	0.234	0.213	0.202	—	0.202
8.4	18 h	0.239	0.222	0.205	0.202	0.199
8.4	30 »	0.223	0.218	0.214	0.210	0.203
5.9	42 »	0.224	0.220	0.216	0.202	0.202

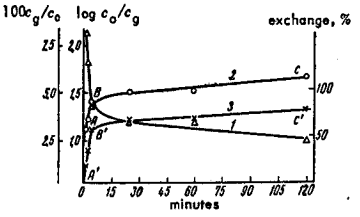

Fig. 2. The $Ag|Ag_2O|Ag_2O_2^*-1$ *N* KOH system. Variation with time of: 1) proportion of ^{18}O atoms ($100\ c_g/c_0$) which have passed from the oxide surface into the gaseous oxygen; 2) $\log c_0/c_g$; 3) percentage exchange of oxygen atoms between $Ag_2O_2^*$ and H_2O during electrolysis under conditions such that $c_g = 0.1c_0$ at $t = 0$.

TABLE 2.

Ag_2O_2, 10^6 g-equiv.	Time	^{18}O in samples of O_2, %					^{18}O in control sample, %
		1	2	3	4	5	
5.3	1 min	0.578	0.430	0.318	0.277	0.260	0.199
5.0	2.5 »	0.465	0.380	0.310	0.273	0.245	0.199
5.3	4.5 »	0.385	0.330	0.265	0.244	0.236	0.199
5.9	25 »	0.365	0.321	0.275	0.246	0.213	0.201
4.8	1 h	0.324	0.305	0.256	0.231	0.212	0.199
7.2	2 »	0.337	0.291	0.252	0.228	0.218	0.197
5.5	4 »	0.268	0.265	0.243	0.227	0.223	0.200
5.2	9 »	0.244	0.239	0.234	0.223	0.212	0.201
4.9	18 »	0.220	0.213	0.210	0.205	0.195	0.195

DISCUSSION

The experimental results are presented in Table 1 (for the Ag | Ag_2O–solution system, $\varphi_0 = 1.17$ V after polarisation was switched off), Table 2 (for the Ag | Ag_2O | Ag_2O_2–solution system, $\varphi_0 = 1.45–1.46$ V), and Fig. 2. All experiments were carried out with water containing 19% ^{18}O.

It is evident from Table 1 that the isotopic composition of the gaseous oxygen is practically independent of that of the lower oxide of silver Ag_2O. This can be explained by the very rapid oxidation of Ag_2O to Ag_2O_2 at the potentials of oxygen evolution, by the reaction

$$Ag_2O + 2OH^- \rightarrow Ag_2O_2 + H_2O + 2e,$$

during which, according to our results, only ~0.3% of all the ^{18}O atoms have sufficient time to pass from the Ag_2O into the Ag_2O_2, and hence can be detected in the O_2.

In the case of Ag_2O_2 (see Table 2) the ^{18}O isotope introduced into the oxide at 1.55 V is detected in the initial portions of oxygen evolved on electrolysis in ordinary 1 *N* KOH. The number of ^{18}O atoms found in the oxygen gas is ~8% of the number introduced into the oxide (if the sampling time of the gas is 1–2 min). Thus this result does not agree with the data in ref. 7.

Curve *1* in Fig. 2 shows the variation of the proportion of ^{18}O atoms (as a percentage corrected for the control), which have passed from the $Ag_2O_2^*$ surface into the gaseous oxygen, with the time between the termination of polarisation of the silver electrode in the solution containing ^{18}O and the withdrawal of oxygen samples during electrolysis of the ordinary solution.

Curve *2* in Fig. 2, which shows the variation with time of the logarithm of the ratio of the number c_0 of ^{18}O atoms introduced into the oxide to the number c_g collected in the gas, has two well defined linear portions AB and BC. Extrapolation of the section BA gives $\log c_0/c_g = 1$ at $t = 0$, when the percentage exchange is zero. Hence, it follows that, under the experimental conditions, only 10% of the total number of ^{18}O atoms introduced into the oxide can be detected in the gaseous oxygen. During the electrochemical oxygen evolution (1.9–2.0 V) in an ordinary solution the test electrode is covered with freshly deposited oxides which are no longer enriched with the ^{18}O isotope, and obviously only the ^{18}O atoms in the outer layers of the electrode surface can enter the oxygen gas. This apparently explains the maximum enrichment of ~8% observed in our experiments in the initial samples of oxygen. However, a complete understanding of the results is possible only if allowance is made for the exchange of oxygen atoms between the oxides and the water.

Curve *3* in Fig. 2 shows the variation in the percentage exchange of oxygen atoms between Ag_2O_2 and H_2O with time during electrolysis under conditions such that $c_g = 0.1\,c_0$ at $t = 0$. It is similar in shape to curve *2*. The exchange reaches approximately 60% during the first 5 min (section $A'B'$), whereas it changes by only ~10% during the next 2 h. This is probably due to a strengthening of the bond between the oxygen atoms and the silver surface with time, and to diffusion of oxygen atoms from deeper layers in the oxide.

Table 3 and Fig. 3 give the time dependence of the percentage exchange of oxygen atoms between the oxides and water and of $\log c_0/c$ (where c is the number of ^{18}O atoms in the surface at time t) for the systems Ag | Ag_2O | $Ag_2O_2^*$ – 1 *N* KOH (curves *1* and *1'*) and Ag | Ag_2O^* – 1 *N* KOH (curves *2* and *2'*), measured directly from the enrichment of the water with ^{18}O in the absence of electrolysis. The linear change in $\log c_0/c$ with time indicates that both reactions follow first-order kinetics, the rate of the former reaction ($Ag_2O_2^* - H_2O$) being three times as great as that of the latter ($Ag_2O^* - H_2O$). This points to the oxygen being more firmly bound to the silver in Ag_2O than in Ag_2O_2.

The experiments have shown that the rate of exchange in the case of Ag_2O_2 is considerably greater when oxygen is evolved at this oxide. Thus from the results illustrated in

TABLE 3.

Composition of oxide	Amount of oxide, 10^6 g-equiv.	Time, h	Vol. of water, cm³	^{18}O in H_2O, %	^{18}O in control sample, %	% exchange $100c_{H_2O}/c_0$	Rate constant, 10^6 sec^{-1}
Ag_2O_2	1.14	4	0.7	0.204	0.200	15	1.09
»	1.25	9	0.5	0.217	0.201	38	1.45
»	1.03	16	0.75	1.211	0.197	60	1.60
»	1.65	18	0.9	0.213	0.195	57	1.30
Ag_2O	0.84	18	0.55	0.206	0.199	27	0.49
»	0.84	30	0.55	0.213	0.203	42	0.51
»	0.6	42	0.55	0.212	0.202	57	0.55

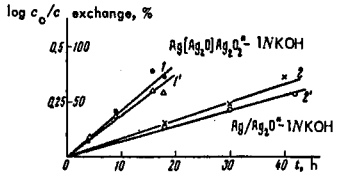

Fig. 3. Variation with time of the percentage exchange between oxygen atoms of oxides and of water, and of $\log c_0/c$, measured in absence of electrolysis for the following systems: 1) and 1') Ag|Ag_2O|$Ag_2O_2^*$ – 1 *N* KOH; 2) and 2') Ag|Ag_2O^* – 1 *N* KOH.

Fig. 3, the exchange current is $\sim 10^{-6}$ A cm^{-2} when electrolysis is not occurring, whereas during electrolysis (Fig. 2, curve *1*, section AB) it is increased a hundredfold and becomes $\sim 10^{-4}$ A cm^{-2}. The stability of the link between the oxygen and the silver in Ag_2O_2 obviously diminishes during electrolysis, the oxide being made more labile and easily passing into the still more unstable peroxide Ag_2O_3. As a result, oxygen atoms from deeper layers of the oxide can take part in the exchange reaction, and the rate of exchange is increased.

The present investigation has established the participation of the higher silver oxide Ag_2O_2 in the anodic evolution of oxygen, this oxide conferring a potential of 1.4 – 1.45 V on the electrode after the polarising current has been switched off. Thus experimental confirmation has been obtained for the mechanism suggested for this reaction in ref. 5.

On the basis of the above results, it may be supposed that oxygen evolution at a silver electrode proceeds according to the following scheme.

1. Formation of silver oxides on the surface of the silver electrode:

$$Ag\,|\,Ag_2O\,|_n + 2pO^*H^- - 2pe \rightarrow Ag\,|\,Ag_2O\,|_{n-p}\;\; Ag_2O_2^*\,|_p + pH_2O. \quad (1)$$

2. Further oxidation of the surface with the formation of chemisorbed oxygen or an unstable peroxide compound Ag_2O_3:

$$Ag\,|\,Ag_2O\,|_{n-p}\;\; Ag_2O_2^*\,|_p + 2pOH^- - 2pe \rightarrow Ag\,|\,Ag_2O\,|_{n-p}\;\; Ag_2O_2^*O\,|_p + pH_2O. \quad (2)$$

3. Reaction of the chemisorbed oxygen (oxide) with hydroxide ions undergoing discharge, which governs the overall rate of oxygen evolution on silver and corresponds to the so-called electrochemical mechanism of overpotential:

$$Ag\,|\,Ag_2O\,|_{n-p}\;\; Ag_2O_2^*O\,|_p + 2pOH^- - 2pe \rightarrow Ag\,|\,Ag_2O\,|_{n-p}\,|\,Ag_2O_2\,|_p + pO^*O + pH_2O. \quad (3)$$

This does not exclude the possibility of the reaction

$$Ag\,|\,Ag_2O\,|_{n-p}\;\; Ag_2O_2^*O\,|_p \rightarrow p/2\,O^*O + Ag\,|\,Ag_2O\,|_{n-p}\;\; Ag_2O_2\,|_p, \quad (4)$$

corresponding to a recombination mechanism of overpotential. Unfortunately, without water 100% enriched with ^{18}O, and in view of the high rate of exchange of oxygen atoms between Ag_2O_2 and H_2O during electrolysis, the

method used does not allow us to distinguish between reactions (3) and (4). However, the electrochemical mechanism appears to be the most probable if all the results obtained both for the oxygen overpotential on silver and for the surface condition of anodically polarised silver are taken into account.

SUMMARY

1. The role of Ag_2O and Ag_2O_2 in anodic oxygen evolution has been elucidated by a tracer method using ^{18}O.
2. It has been established that Ag_2O_2 ($\varphi_0 = 1.4-1.45$ V) plays a part in the reaction.
3. A mechanism is suggested for oxygen evolution at a silver | silver oxide electrode, which involves the participation of higher oxygen compounds of silver.
4. The rate of exchange of oxygen atoms between the silver oxides and water has been measured, and it has been shown that, in the case of the oxide Ag_2O_2, the rate is considerably increased when oxygen evolution is occurring on the oxide. The exchange current increases from $\sim 10^{-6}$ to $\sim 10^{-4}$ A cm^{-2}.

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THERMAL DECOMPOSITION OF NITRATE ESTERS. II. THERMAL DECOMPOSITION OF PENTAERYTHRITYL TETRANITRATE

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Pentaerythrityl tetranitrate (PETN) is practically the only nitrate ester used abroad as the explosive charge in certain types of ammunition, detonator capsules, and detonating cord. One of its most important properties is high chemical stability compared with that of other nitrate esters. The reasons for the enhanced stability have not been established, but some workers[1] have related it to higher molecular symmetry. Another characteristic property of PETN is the following. In order to reduce its sensitivity towards mechanical shock, it is sometimes desirable to employ PETN not in the pure state but as a melt with trotyl. Unexpectedly, experiments have shown that addition of trotyl as well as other nitro-compounds sharply reduces the stability of PETN.[2]

The present work was undertaken to investigate the decomposition of PETN under various conditions as well as the effect of certain additives, in order to explain the above peculiarities.

EXPERIMENTAL

The PETN was twice recrystallised from acetone (with cooling), m.p. 141.3°. The dimensions of the crystals were less than 1 mm. The decomposition was studied manometrically using a Bourdon glass manometer described in the first communication of this series[3].

Decomposition of PETN in a Melt

In order to compare the nature and rate of decomposition of PETN with those of other nitrate esters, the melting points of which are much lower, it is useful to study the decomposition above the melting point of the explosive, *i.e.* in the melt. Using the usual non-automatic technique, this can be done in the range 145°–171°. At higher temperatures the decomposition is too fast, the half-life becoming comparable with the duration of heating of the vessel. The experiments were carried out at moderate degrees of filling of the vessel δ†, in order to observe stages in the decomposition other than the initial.

Pressure–time and rate of gas evolution–time curves (Fig. 1) show that the general course of the decomposition is similar to that for other nitrate esters (nitroglycerin, ethylene glycol dinitrate, and nitrocellulose). Gas evolution begins immediately after the reaction vessel is placed in the thermostat, proceeds at an increasing rate, passes through a maximum, and then falls. The gas phase gradually becomes yellow, the intensity of the colour passes through a maximum, and finally, towards the end of the decomposition, the gas again becomes colourless.

As in the case of nitroglycerin and nitroglycol, increase of δ leads to a reduction of the initial rate of gas evolution, the effect being strongest for small δ. The maximum rate also falls with increase in δ, but this is only true for small δ, when the pressure of the breakdown products is low and the acceleration caused by them is not yet much in evidence.

To make a comparison with other nitrate esters, Fig. 2 shows curves for nitroglycerin, ethylene glycol dinitrate, and diethylene glycol dinitrate. It is seen that the rate of decomposition of PETN at 140° is intermediate between those of the first two nitrate esters; initially‡ it is approximately 50% of that for nitroglycerin and one and a half times greater than for ethylene glycol dinitrate. The course of the decomposition at various temperatures (Fig. 1) is in general similar. This is shown more clearly in Fig. 3 where the curves $V = f(t)$ have been adjusted to the same scale. Over a considerable extent of the decomposition the variation with

† The degree of filling δ is defined as the ratio of the volume of the substance to that of the vessel; since the densities of the explosive at high temperatures are unknown, room-temperature volumes were employed in the calculations.

‡ During the later stages of the decomposition the difference between the rates remains approximately the same so that their ratio decreases.