0.1225 g. and the average heat capacity of the reacting sodium hydroxide solution was 993.3 ± 0.9 gram calories per degree. The heat of reaction is expressed in kilogram calories per mole of organic reactant.

TABLE II

HEATS OF REACTION OF SOLID *d*-GLUCONIC ACID AND ITS MODIFICATIONS WITH 0.0102 *N* SODIUM HYDROXIDE

Acid reactant	Measurements	Mean heat of reaction	Av. dev.
d-Gluconic acid	2	− 6.91	0.03
d-Gluconic-δ-lactone	2	− 9.73	.03
d-Gluconic-γ-lactone	2	−10.22	.00

Discussion

From the data above the heats of reaction of the three forms of *d*-gluconic acid (aq.) with sodium hydroxide (aq.) have been calculated and are as follows:

d-Gluconic acid (aq.), $\Delta H = -12.37$ Cal.
d-Gluconic-δ-lactone (aq.), $\Delta H = -14.45$ Cal.
d-Gluconic-γ-lactone (aq.), $\Delta H = -15.81$ Cal.

In a similar manner, by proper treatment of the data, it can be shown that the thermal relations (ΔH in kg. cal.) of the three modifications in water solutions and in solid state are:

	Reaction	Aqueous	Solid
1	*d*-Gluconic = *d*-gluconic-δ-lactone	2.08	2.82
2	*d*-Gluconic = *d*-gluconic-γ-lactone	3.54	3.41
3	*d*-Gluconic-δ-lactone = *d*-gluconic-γ-lactone	1.46	0.59

The lower heat of conversion, 2.08, of *d*-gluconic acid into *d*-gluconic-δ-lactone than that, 3.54, for converting it into *d*-gluconic-γ-lactone gives experimental support to the inferences of Hedenburg and of Levene and Simms that the free acid dissolved in water attains an equilibrium between itself and *d*-gluconic-δ-lactone before the equilibrium with *d*-gluconic-γ-lactone.

Summary

1. The heats of solution in water to a dilution of 0.0003 ± mole of solute per mole of water at 25° for *d*-gluconic acid, *d*-gluconic-δ-lactone, *d*-gluconic-γ-lactone and sodium *d*-gluconate have been determined, as well as the heats of neutralization of the first three substances with 0.0102 *N* sodium hydroxide.
2. The thermal relations of the three modifications of *d*-gluconic acid in water solutions and in solid states have been calculated and it has been found that the transformation of *d*-gluconic-δ-lactone into *d*-gluconic-γ-lactone is an endothermic change.
3. The inferences of Hedenburg and of Levene and Simms concerning the equilibrium of the *d*-gluconic acid and its lactones find experimental support in the present work.

LINCOLN, NEBRASKA RECEIVED JULY 9, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Photochemistry of Mixtures of Chlorine and Ozone

BY A. C. BYRNS AND G. K. ROLLEFSON

In a recent article[1] we showed that, even at temperatures as high as 20°, pressure measurements were not an accurate measure of the amount of ozone decomposed when mixtures of chlorine and ozone were illuminated with blue light, due to the condensation of chlorine trioxide on the walls of the reaction vessel. This was shown by a comparison of the amount of oxygen calculated from the pressure increase with that found by freezing out all other gases with liquid air. There was also the qualitative observation that drops of liquid chlorine trioxide could be seen on the walls of the vessel. At the same time it was shown that chlorine trioxide acted as a catalyst for the thermal decomposition of ozone. A further study has now been made of the behavior of chlorine–ozone mixtures at 30°, where there should be no condensation of chlorine trioxide. The apparatus and technique used were essentially the same as in the earlier article, except for the use of a modified ozonizer which has been described by one of us. The temperature was hand regulated and a large Pyrex test-tube was used as a thermostat. For the work on stoichiometry, readings were taken at 0° so as to minimize the error due to thermal reaction before the gases could be frozen out with liquid air. The pressures of chlorine used varied from 10–50 cm. of sulfuric acid, and of ozone 30–82 cm.

At no time could any chlorine trioxide be observed on the walls of the reaction vessel at 30°, nor even when cooled to room temperature. However, there was in a few runs some evidence of

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(1) Rollefson and Byrns, THIS JOURNAL, **56**, 364 (1934).

color when the vessel was cooled to 0°. This places the maximum pressure of chlorine trioxide as slightly above the vapor pressure at 0° (2.6 mm.). However, it was observed that the oxygen found at liquid air temperatures was still much higher than calculated from the pressure increase, and that the discrepancy between the two continued to increase throughout the entire course of the runs. The magnitude of the variation is shown by Column 2 of Table I and it is obviously greater than can be accounted for by the chlorine trioxide formed.

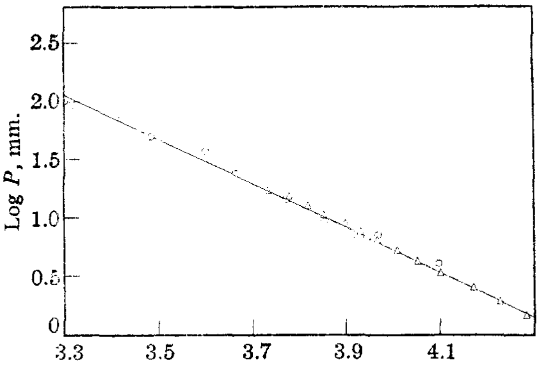

Fig. 1.

This indicates the presence of another reaction in addition to the formation of chlorine trioxide which leads to a pressure decrease. That it also occurs at lower temperatures as well as at 30° was shown by a run at 20°, where illumination was continued until no further increase in pressure occurred. Even at this temperature no chlorine trioxide could remain after the pressure became constant, due both to the thermal decomposition and the chlorine-sensitized photochemical decomposition of this compound to be discussed in a later section of this paper. The difference between the two oxygen values was found to be of the same magnitude as at 30°.

Conclusive evidence for the identity of the intermediate involved was furnished by a vapor pressure curve of a small amount of it which was isolated. Several runs were carried to completion at 30°, using the same chlorine for all of the runs. At the end of the first run the resulting mixture was cooled with liquid air and more ozone added without allowing the vessel to warm up. In this way any intermediate present at the end of the run was retained in the reaction vessel with the chlorine. That the intermediate was stable enough under these conditions to continue to increase in amount was indicated by further deviation in the oxygen values. All chlorine and oxygen was finally pumped from the reaction vessel at carbon dioxide–acetone temperature and a vapor pressure–temperature curve determined on the drop of liquid remaining in the vessel. In order to prevent solution of the intermediate in the sulfuric acid in the manometer, it was found necessary to have a buffer of inert gas between the manometer and the vessel. This was obtained by heating a section of the capillary connection next to the manometer, which decomposed the intermediate into chlorine and oxygen. In this manner the buffer was furnished by the decomposition products themselves, and at the pressures used there was little danger of error due to diffusion back into the vessel through the meter of capillary tubing. The results obtained have been compared in Fig. 1 with the vapor pressures determined by Goodeve and Powney[2] for chlorine heptoxide. It was not possible to cover the higher temperature range used by them due to the small amount of liquid available. Points obtained in this work are represented by triangles, while the data of Goodeve and Powney are represented by circles. The excellent agreement between the two sets of points can leave no doubt that this intermediate is chlorine heptoxide.

Further proof that this compound was chlorine heptoxide was obtained in the following manner. The gases remaining at the end of the runs, after pumping off oxygen at liquid air temperature, were frozen into a side tube attached to the line. This was repeated for several runs, after which all gases were pumped off as before at carbon dioxide–acetone temperature. A drop of colorless liquid was found remaining in the side tube at this temperature. The liquid dissolved slowly in water to give a strongly acid solution and the amount of acid present was determined by titration with sodium hydroxide. Half of the neutralized solution was boiled with acidified bisulfite, after which chloride was determined with silver nitrate and sodium chromate indicator on both portions. The amount of chloride was the same in both portions, and the total for the two portions was less than 5% of the acid found. This is further evidence for chlorine heptoxide, rather than some lower valence of chlorine.

The large error in stoichiometry which may be

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(2) Goodeve and Powney, *J. Chem. Soc.*, 2078 (1932).

introduced by the formation of this oxide is apparent from the equation for its formation

$$Cl_2 + 7O_3 = Cl_2O_7 + 7O_2$$

A systematic investigation was made of the effect of the variation of the initial pressures of chlorine and of ozone, and the incident light intensity, upon the amount of chlorine heptoxide formed. The results of these experiments appear in Table I. The differences between the calculated and observed values of oxygen at the end of the runs have been given the symbol Δ. The ratio Δ/O_3 shown in the third column of the table is a measure of the amount of chlorine heptoxide formed, besides indicating the error introduced if it is assumed that the net reaction is merely the decomposition of ozone.

It is seen that this ratio is proportional to the amount of ozone initially present, for constant chlorine pressure and incident light intensity. There is an increase, though a small one, with increasing chlorine pressure and incident light intensity *in the range covered by this investigation.*

TABLE I

Initial chlorine = 10.0 cm.

Initial O_3	Δ	Δ/O_3	Intensity
32.4	9.4	0.290	1.000
72.4	20.6	.285	1.000
Initial chlorine = 25.0 cm.			
35.6	13.6	0.382	1.000
39.9	14.4	.361	1.000
44.2	16.4	.372	1.000
47.7	18.0	.377	1.000
65.1	24.0	.369	1.000
74.2	25.0	.337	1.000
74.4	27.7	.372	1.000
81.6	29.4	.360	1.000
69.0	21.0	.304	1.000 (20°)
Initial chlorine = 50.0 cm.			
29.6	11.7	0.396	1.000
30.3	14.3	.472	1.000
56.7	25.0	.440	1.000
65.0	28.1	.433	1.000
66.2	28.6	.435	1.000
Initial chlorine = 25.0 cm.			
65.3	17.9	0.274	0.314
65.9	21.5	.326	.148
54.9	15.3	.279	.059

As it has been shown previously that one of the reactions occurring in mixtures of chlorine and ozone is the decomposition of ozone in the presence of chlorine trioxide, an attempt was made to isolate chlorine heptoxide as an intermediate in this reaction. The original work on this reaction involved thoroughly pumping off all gases from the liquid chlorine trioxide before admitting ozone for another run. To determine the presence of chlorine heptoxide in these mixtures a slightly different procedure was used. A small amount of chlorine trioxide was first made and purified in the reaction vessel. Ozone was then admitted and the two substances allowed to stand for several hours at room temperature, until most of the ozone had decomposed. Oxygen was then pumped off at liquid air temperature, after which more ozone was introduced without allowing the vessel to warm up. In this way any chlorine heptoxide formed would be retained. This was repeated four times and about 300 cm. of ozone was decomposed. Finally, all gases were thoroughly pumped off at carbon dioxide–acetone temperature, and the vessel warmed to 0°. The pressure was found to be 17 cm. The vessel was then recooled with carbon dioxide and repumped, after which four vapor pressure points were taken. When plotted on the vapor pressure curve for chlorine heptoxide these four points lie quite close to the curve drawn through the points shown in Fig. 1, so that we can say that chlorine heptoxide seems definitely to be produced in the chlorine trioxide catalyzed thermal decomposition. A slight modification of the tentative mechanism originally proposed for this reaction must be made to account for the formation of this oxide as a secondary product.

The original mechanism was as follows

$$ClO_3 + O_3 = ClO_2 + 2O_2 \tag{1}$$

$$ClO_2 + O_3 = ClO_3^* + O_2 \tag{2}$$

$$ClO_3^* + O_3 = ClO_2 + 2O_2 \tag{3}$$

$$ClO_3^* + O_3 = ClO_3 + O_3 + \text{k. e.} \tag{4}$$

$$ClO_3^* + M = ClO_3 + M + \text{k. e.} \tag{5}$$

where ClO_3^* represents an activated or perhaps peroxide structure for chlorine trioxide. In the absence of inert gases ozone acts as a chain terminator, in the above mechanism either through deactivation of ClO_3^* or by stabilizing rearrangement to the normal form. This is the step which must be modified to account for the formation of chlorine heptoxide as shown by the equations

$$ClO_3^* + O_3 = ClO_4 + O_2 \tag{4'}$$

$$ClO_3 + ClO_4 = Cl_2O_7 \tag{4''}$$

Provided the chain is not too short this would not affect either the form or stoichiometry of the net reaction under the conditions used for the investigation of the chlorine trioxide–ozone reaction. Qualitative evidence that the chain has an appreciable length is obtained from the work of Allmand and Spinks[3] in which a maximum quantum yield of 59 for the chlorine-sensitized decomposition of ozone was obtained. It is quite probable, in the light of the present evidence for the formation of chlorine heptoxide in this system, that the true quantum yield is actually higher than this by perhaps 25%. Furthermore, in the chlorine-sensitized decomposition of ozone, the formation of chlorine heptoxide plays a double part in terminating chains in that two molecules of chlorine trioxide are required for each molecule of chlorine heptoxide produced.

There are two other reactions which use up chlorine trioxide, the thermal and the chlorine-sensitized photochemical decomposition of the oxide. One may expect that under some conditions the thermal decomposition might play an important part in terminating chains, as has been postulated by Bodenstein, Padelt and Schumacher, and by Hamann and Schumacher[4] for the chlorine catalyzed thermal decomposition of ozone. The equation postulated by these authors was $ClO_3 + ClO_3 = Cl_2 + 3O_2$. We have made a number of experiments on the decomposition of liquid chlorine trioxide, by following the increase of pressure in the reaction vessel at several temperatures between 0 and 30°. Approximately 0.5 cc. of liquid chlorine trioxide was used so that the amount of liquid present could be considered constant. Heats of activation calculated from the temperature coefficients for two runs on the same batch of liquid oxide are shown in Table II.

TABLE II

Temp. intervals, °C.	Run I, *E*, k. cal.	Run II, *E*, k. cal.
0–5	26.4	20.3
5–10	26.8	22.8
10–15	26.5	16.7
15–20	25.1	22.9
20–25	..	21.3
	Av. 26.2	20.8 (omitting 16.7)

Another series was made using smaller amounts of liquid to determine the products of the reaction. This was done by freezing out all gases but oxygen with liquid air, as described previously, which enables one to determine the ratio of $O_2/\Delta p$. The values of this ratio obtained at three temperatures are shown in Table III.

TABLE III

Temp., °C.	Δp	pO_2	$O_2/\Delta p$
0	10.4	4.3	0.34
0	8.6	2.5	.35
10	7.1	2.8	.38
20	18.7	7.3	.39
20	62.6	25.8	.40
20	27.7	11.6	.42
20	22.7	9.3	.41
20	44.7	16.5	.37
30	3.9	9.0	.43
30	11.9	23.8	.50
30	10.0	19.4	.52
30	14.1	26.1	.54

Since under these conditions we are concerned with the decomposition of the liquid oxide the ratio expected from the equation postulated by Bodenstein and his co-workers would be 0.75. At the lower temperature used in the present work the values of the ratios found correspond more closely with the formation of chlorine dioxide and oxygen. The value obtained at 30° would correspond to about half of the chlorine trioxide being converted to chlorine dioxide and oxygen, and about half to chlorine and oxygen. If only chlorine dioxide and oxygen were produced the ratio would be 0.333, according to the equation $ClO_3(l) = ClO_2 + {}^1/_2O_2$. That chlorine dioxide is actually formed was further shown in the following qualitative experiment. A batch of chlorine trioxide was allowed to decompose at room temperature in the reaction vessel until there was no color of chlorine trioxide observed when the vessel was cooled in an ice-water bath. After pumping off oxygen at liquid air temperature, ozone was condensed into the vessel. Upon warming to 0° the walls of the vessel were found to be covered with a film of liquid chlorine trioxide. This experiment was repeated twice, with the same result each time. Another qualitative observation which confirms this view is one first noted by Bodenstein and his co-workers, that when a drop of liquid chlorine trioxide is decomposed in a small sealed tube by immersion in a hot-water bath the color first changes to the intense yellowish-green of chlorine dioxide, followed by a rapid decrease in color. Bodenstein and his co-workers identified the gas spectroscopically as the dioxide, although they did not bring such a mechanism for the thermal decomposition into their postulated mechanism for the chlorine-catalyzed thermal decomposition of ozone. Whether at all temperatures the first step is the formation of chlorine dioxide is still uncertain, although the higher ratios

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[3] Allmand and Spinks, *J. Chem. Soc.*, 599 (1932).

[4] Bodenstein, Padelt and Schumacher, *Z. physik. Chem.*, **B5**, 209 (1929); Hamann and Schumacher, *ibid.*, **B17**, 293 (1932).

obtained in the present work at 30° indicate that at least the final products at higher temperatures involve the formation of chlorine as well.

Although illumination of chlorine trioxide vapor in equilibrium with the liquid did not affect the rate of decomposition appreciably, it was found that when chlorine was present blue light caused a marked change in the rate of pressure increase. At high light intensity the products are apparently chlorine and oxygen as determined by the ratio $O_2/\Delta p$ having a value of 0.75, which corresponds to such an over-all equation as $ClO_3(l) = {}^1/_2Cl_2 + {}^3/_2O_2$. With low light intensity the value of the ratio $O_2/\Delta p$ was appreciably larger, as shown by some results tabulated in Table IV.

TABLE IV

Initial press. of Cl_2, cm.	Δp, cm.	pO_2, cm.	$O_2/\Delta p$
101.7	9.80	8.30	0.85
89.5	6.90	8.20	1.19
87.2	5.00	6.00	1.20
50.9	2.77	8.07	0.92
45.3	16.48	13.90	.84
30.0	10.00	8.50	.85
21.9	8.73	7.87	.90
10.7	4.95	3.98	.80

The variations apparently depend somewhat on the chlorine pressure. Some typical Δp *vs.* time curves are shown in Fig. 2. These show a variation which could be explained if we assume that some intermediate is formed which condenses out or at least causes a pressure decrease. After the dip has been passed the curves are regular and the dependence of the rate on the chlorine pressure and light intensity is shown by the data in Table V.

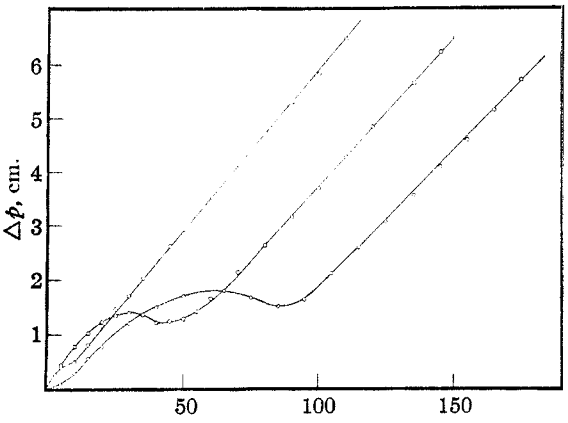

Fig. 2.

TABLE V

Initial Cl_2 in H_2SO_4	5.5	10.5	25.2	50.0
Rate cm./min......	0.112	0.113	0.116	0.112
Intensity.........	1.000	0.30	0.15	.06
Rate cm./min......	0.107	0.076	0.052	.025

These results also favor the assumption of an intermediate which is light sensitive.[5]

We may now turn to a discussion of the behavior of chlorine and ozone mixtures when illuminated. Some typical Δp *vs.* time curves obtained at 30° are shown in Fig. 3. These curves are definitely composite in nature and each curve may be divided into two parts. The last parts of all the curves are essentially similar and the rate appears to be dependent on the ozone pressure but independent of light intensity and chlorine pressure. Under the conditions prevailing in these experiments the rate of pressure increase is proportional to the rate of decomposition of the ozone, as it was found that the discrepancy due to the formation of chlorine heptoxide was proportional to Δp. Therefore we must conclude that in the first portions of the curves the rate of disappearance of ozone is actually as small as indicated. This is probably due to a slowness in building up the concentrations of the active intermediates so that the maximum rate is not attained until some time after the illumination is started. The absolute

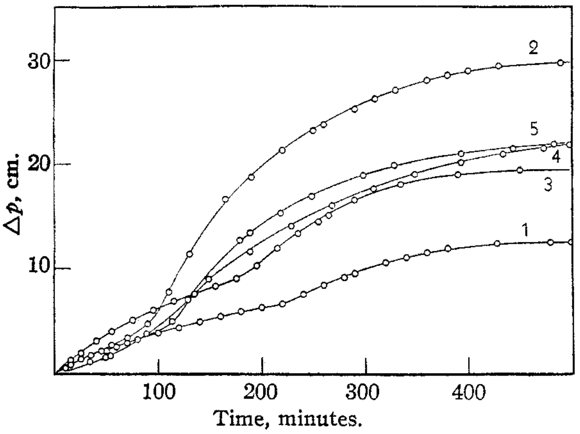

Fig. 3.—Δp-time curves for chlorine-ozone mixtures.

Initial Cl_2, cm.	Initial O_3, cm.	Light intensity	Run
25.0	35.6	1.000	1
25.0	81.6	1.000	2
50.0	56.7	1.000	3
25.0	65.0	0.314	4
25.0	66.0	0.148	5

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[5] An extended discussion of these results is contained in the Ph.D. thesis of A. C. Byrns, University of California, 1934.

value of this maximum rate is somewhat greater than can be accounted for by comparison with the rate of reaction of chlorine trioxide and ozone. However, we have found it necessary to consider two forms of the chlorine trioxide molecule, one of which is much more reactive than the other. If we assume that all or at least a large portion of these molecules are formed in this reactive state it would be possible to account for a much higher rate. It seems, therefore, that the quantitative elucidation of the behavior of chlorine–ozone mixtures is dependent on the chlorine trioxide molecule. The data available are not sufficient for such treatment at present but it must be emphasized that in all these studies it is necessary to do more than measure the pressure change as a function of time.

Summary

It has been shown that when mixtures of chlorine and ozone are illuminated with blue light two oxides of chlorine having the formulas ClO_3 and Cl_2O_7 are formed in appreciable quantities. The Cl_2O_7 is relatively inert chemically and tends to remain in the system unchanged once it is formed. The factors influencing the amount of this oxide formed have been studied. The ClO_3 undergoes a thermal decomposition, a chlorine-sensitized photodecomposition, and a reaction with ozone. One product of the latter reaction is Cl_2O_7. Evidence has been presented that one of the primary products in the thermal decomposition is ClO_2. The bearing of all these reactions on the previous observations of the chlorine-sensitized decomposition of ozone has been discussed.

Berkeley, California Received July 10, 1934

[Contribution No. 143 from the Experimental Station, E. I. du Pont de Nemours & Company]

The Influence of Lead Tetraethyl upon the Combination of Hydrogen and Oxygen

By H. G. Tanner

M. V. Poljakow and P. Stadnik[1] recently have reported that yields of hydrogen peroxide as high as 8 to 10% were obtained by the simple expedient of exploding electrolytic gas at reduced pressure in a vessel surrounded by liquid air. They attributed their success in part to the catalytic action of the platinum filament which was used to ignite the gas mixture. Their results and conclusions are novel and deemed of sufficient importance to warrant confirmatory experiments.

Using a 2:1 mixture of hydrogen and oxygen at total pressures between 40 and 120 mm., and apparatus built according to their specifications, the formation of hydrogen peroxide was confirmed qualitatively by the $TiCl_4$ test. Quantitative determinations, however, made by permanganate titration, showed that the yields obtained were only 0.2 to 0.3% of the weight of water simultaneously produced. In most of these experiments the reaction of the elements was practically complete. The theory advanced by Poljakow and Stadnik would attribute these lower yields to a lesser activity of the platinum filament. That any catalytic property of platinum was involved, either in their experiments or those mentioned above, does not appear probable, particularly in view of the fact that Poljakow and Stadnik reported that the temperature to which the filament was heated had very little effect upon the reaction. Heterogeneous catalytic reactions are usually quite sensitive to the temperature of the catalyst, and, therefore, the extent to which the filament functioned catalytically appears to be very small. This conclusion was checked experimentally by employing a spark to explode the mixture. Sparks were produced between tungsten terminals, and also between platinum terminals, but the yields of hydrogen peroxide were the same as before. These experiments prove that the platinum filament had no catalytic action and indicate that the formation of hydrogen peroxide under these conditions took place in the gas phase.

The latter conclusion led to the thought that the yield of hydrogen peroxide might be enhanced by the addition of catalysts which would function in the gas phase. From current theories of knock-inducing substances for engine fuels, one would expect to raise the peroxide yield by addition of knock-inducing reagents. Four experiments were performed in which nitrogen peroxide (obtained from the decomposition of lead nitrate) was introduced with the hydrogen–oxygen mixture into the reaction vessel. Explosions with this oxide present reduced the yield of hydrogen peroxide to zero. These results were not altogether surprising, since experimental conditions were not all that could be desired. The liquid air around the reaction vessel could have removed all but a trace of the nitrogen peroxide vapor prior to explosion. Furthermore, the nitrous acid which could have formed with the water condensed on the reaction vessel wall might have been just sufficient to destroy all the hydrogen peroxide simultaneously condensed. Therefore, conclusions about any effect which nitrogen peroxide may have had on this reaction cannot be drawn from these negative results.

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(1) Poljakow and Stadnik, *Phys. Z. Sowjetunion*, **3**, 227, 617 (1933).