A PHOTOCHEMICAL REACTION INVOLVING ZINC OXIDE AND OXYGEN

BY JOHN McMORRIS AND ROSCOE G. DICKINSON

Zinc oxide has been found to act as a sensitizer in a number of photochemical reactions. In the course of the observation of some of these, Winther[1] found that when certain samples of zinc oxide were strongly illuminated, in the presence of air, by light filtered through ordinary glass, a substance appeared in the gas phase which was capable of oxidizing iodide to iodine. In view of its mode of preparation, its effect on iodide, and because it appeared to attack rubber membranes, the oxidizing substance was assumed to be ozone. However, Kistiakowsky[2] has remarked that the experiments showed only the presence of a volatile peroxide, and has suggested hydrogen peroxide as an alternative to ozone.

More elaborate experiments have been made by Jung and Kunau[3] with the purpose of ascertaining why only certain samples of zinc oxide produced the oxidizing substance. They prepared zinc oxide from pure zinc and oxygen, zinc carbonate, zinc sulfate and zinc nitrate and also prepared samples purposely contaminated with the oxides of several other metals. Again using the liberation of iodine from iodide as a detector, they found that only those samples which had been prepared by roasting the nitrate were active, and that even this activity disappeared on prolonged heating. It was accordingly suggested that a zinc oxynitrate was the photosensitizing agent rather than the oxide. Since considerable pains were taken to remove water, the oxidizing product was considered not to be hydrogen peroxide, and since the oxidizing product did not appear when nitrogen was employed in place of oxygen, the product was considered not to be nitrogen dioxide.

In these experiments a number of hours of passing oxygen over illuminated zinc oxide were required for the coloration of a small quantity of potassium iodide–starch solution, and since the quantity of oxidizing agent formed was evidently very small, the possibility of hydrogen peroxide formation from remaining traces of water does not appear to us to be convincingly excluded. Moreover, nitrogen dioxide likewise remains as a possibility; its absence when nitrogen is used instead of oxygen might well arise from the necessity of oxygen as a reactant rather than as a mere

[1] O. Winther, Z. wiss. Phot., 21, 168 (1921).

[2] G. B. Kistiakowsky, "Photochemical Processes," The Chemical Catalog Co., New York, 1928, p. 156.

[3] G. Jung and E. Kunau, Z. physik. Chem., 15B, 45 (1931).

vehicle to convey to the test solution nitrogen dioxide photochemically liberated from the solid.

Interest attaches to the question as to whether ozone can really be formed from oxygen through the agency of radiation in the near ultraviolet since the energy of light quanta in this spectral region is distinctly smaller than that involved in either the direct photochemical or the mercury-sensitized formation of ozone. We have accordingly undertaken experiments with the particular object of identifying the oxidizing substance by chemical tests.

Test Solutions.—The problem was, then, to distinguish between ozone, hydrogen peroxide and nitrogen dioxide contained in minute amount in a stream of oxygen. We have examined a number of the tests for this purpose which are to be found described in the literature, and have found some of them too insensitive and others fallacious. The tests which we have finally used are given in Table I.

TABLE I

TESTS FOR DISTINGUISHING OZONE, HYDROGEN PEROXIDE AND NITROGEN DIOXIDE

	Reagent solution	Coloration produced	Substance giving coloration
1	KI–starch	Blue	O_3, H_2O_2, NO_2
2	Neutral KI with cresol red	Red	O_3, H_2O_2
3	Fluorescein	Decoloration	O_3
4	$FeCl_3$ with $K_3Fe(CN)_6$	Blue or green	H_2O_2, NO_2
5	Sulfanilic acid with α-naphthylamine	Red	NO_2

Neutral potassium iodide with starch is sensitive but, of course, does not distinguish between ozone, hydrogen peroxide and nitrogen dioxide. However, the action of ozone or of hydrogen peroxide on potassium iodide renders the solution alkaline, while the action of nitrogen dioxide in low concentration leaves it neutral ($4NO_2 + 2KI = 2KNO_3 + I_2 + 2NO$). Consequently the presence of ozone or hydrogen peroxide may be detected by adding a suitable indicator to a potassium iodide solution through which the gas has been bubbled. We have used cresol red for this purpose.

The bleaching of an alkaline solution very dilute in fluorescein has been proposed[4] as a specific test for ozone. We have found this reagent, when prepared so dilute as to have a barely distinct color, to be decolorized by about the same quantity of ozone which would give a detectable color to an equal volume of potassium iodide–starch solution. The fluorescein reagent was found not to be attacked by oxygen nor by dilute solutions of hydrogen peroxide or nitrogen dioxide.

It has been stated[5] that an aqueous solution of ferric chloride and potassium ferricyanide is reduced by hydrogen peroxide to give Prussian blue but

[4] L. Benoist, *Compt. rend.*, **168**, 612 (1919); N. Allen, *Ind. Eng. Chem., Anal. Ed.*, **2**, 54 (1930).

[5] E. Keiser and L. McMaster, *Am. Chem. J.*, **39**, 96 (1908).

is unaffected by ozone or nitrogen dioxide. We have, however, found the blue coloration to be produced by nitrogen dioxide as well as hydrogen peroxide but not by ozone. This was shown in the case of nitrogen dioxide by adding to the iron reagent either a dilute solution of nitric and nitrous acids obtained by passing into water a small amount of nitrogen dioxide prepared by heating lead nitrate, or by adding a very dilute solution of sodium nitrite.

A specific reagent for nitrite (and hence for nitrogen dioxide) is afforded by an acetic acid solution of sulfanilic acid and α-naphthylamine (Griess–Ilosva reaction).[6] The reagent is colorless and is not colored by hydrogen peroxide; a large concentration of ozone gives a yellowish coloration. With nitrite the reagent forms a red dye and furnishes an extremely delicate test for NO_2.

Identification of the Oxidizing Product.—In the conduct of a series of experiments, zinc nitrate was first dehydrated and baked in a casserole at about 350° until brown fumes of nitrogen dioxide were no longer evident. The oxide was then pulverized and placed in a Pyrex tube 30 cm. in length and of 1 cm. bore fitted with ground-in end joints. The tube was surrounded by an electric furnace and the oxide roasted for at least two hours more at 350° in a stream of oxygen. Without removing the oxide from the tube, the furnace was removed and replaced by a Pyrex water-jacket through which tap water flowed in an annular space of 5 mm. A horizontal type Pyrex mercury arc lamp with an arc length of 25 cm. was placed alongside about 2 cm. from the oxide. An oxygen stream was maintained whose rate of flow was about 100 cc./min.; after passing through the zinc oxide tube, the oxygen bubbled through pure water or a reagent solution contained in a small test-tube. A plug of glass wool served to prevent any particles of oxide from being swept into the reagent.

The results of experiments made with three different samples of oxide are given in Table II; in this table, the experiments are listed in the order made. Samples 1 and 3 were made from commercial c. p. zinc nitrate, sample 2 was made from zinc nitrate prepared from c. p. zinc and nitric acid. In the experiments with sample 1, the oxygen was first bubbled through 6 N sulfuric acid (p_{H_2O} about 14 mm.); in the other experiments it was bubbled through concentrated sulfuric acid. It is evident from these results that we have been able to verify the appearance of an oxidizing substance in the issuing gas when zinc oxide from the nitrate is illuminated through glass in a stream of oxygen. However, in view of the positive tests given by the sulfanilic acid–α-naphthylamine solution and the absence of such a test when illumination was omitted, and in view of the failure to bleach fluorescein solution, we believe we have shown that the oxidizing substance is not ozone but is in fact nitrogen dioxide. It is

[6] F. Usher and B. Rao, *J. Chem. Soc.*, **111**, 789 (1917).

possible that a small amount of hydrogen peroxide might have been formed in addition to nitrogen dioxide but experiments 15 and 16 render this improbable.

TABLE II

RESULTS OF ILLUMINATING ZINC OXIDE AND OXYGEN

Expt.	Sample of oxide	Duration of test, hrs.	Illumi-nation	Reagent	Result	Substance identified
1	1	2	Ill.	(1)	Slight blue	Oxidizing agent
2	1	12	Dark	(1)	No color	. . . . . .
3	1	6	Ill.	(4)	Blue color	H_2O_2 or NO_2
4	1	6	Ill.	(5)	Pink color	NO_2
5	1	12	Dark	(5)	No color	. . . . . .
6	2	12	Ill.	(5)	Pink Color	NO_2
7	2	12	Dark	(5)	No color	. . . . . .
8	2	12	Ill.	(5)	Pink color	NO_2
9	2	12	Ill.	(3)	No change	No O_3
10	2	4	Ill.	(5)	Pink color	NO_2
11	3	3	Dark	(5)	No color	. . . . . .
12	3	3	Ill.	(5)	Pink color	NO_2
13[a]	3	6	Ill.	(5)	No color	. . . . . .
14[b]	3	3	Ill.	(5)	No color	. . . . . .
15	3	3	Ill.	(5)	Pink color	NO_2
16	3	8	Dark	(2)	Trace of pink	. . . . . .
17	3	8	Ill.	(2)	Trace of pink	No O_3 or H_2O_2

Key to reagents: (1) KI–starch solution; (2) neutral KI solution with subsequently Congo red; (3) fluorescein solution; (4) $FeCl_3$–$K_3Fe(CN)_6$ solution added to water through which the gas had bubbled; (5) sulfanilic acid–α-naphthylamine solution.

[a] $K_4Fe(CN)_6$ solution used in water jacket.

[b] Pure dried nitrogen was used in this experiment instead of oxygen.

It is interesting that, in agreement with the experiments of Jung and Kunau, no nitrogen dioxide was obtained when (Expt. 14) nitrogen was used in place of oxygen.

In Expt. 13 a 0.065 formal solution of potassium ferrocyanide was flowed through the condenser jacket instead of tap water. This solution in the thickness used (5 mm.) transmitted the visible freely but fairly completely removed the ultraviolet. The negative result obtained with this filter showed that the effective wave lengths lie in the ultraviolet region.

In conclusion, then, it may be said that those experiments which have been carried out in such a way as to distinguish between hydrogen peroxide, ozone and nitrogen dioxide have always indicated nitrogen dioxide. It is still possible that ozone may have been the product in experiments made by other investigators, but there appears to be no reason for assuming that such was the case.

Summary

Experiments have been made in which zinc oxide (prepared from zinc nitrate) was strongly illuminated, in the presence of oxygen, by mercury

arc radiation filtered through water and Pyrex glass; in these experiments nitrogen dioxide (not ozone as previously supposed) appeared in the gas. Radiation in the near ultraviolet but not in the visible was found to be effective.

PASADENA, CALIFORNIA

THERMODYNAMIC PROPERTIES OF FUSED SALT SOLUTIONS. VI. RUBIDIUM BROMIDE IN SILVER BROMIDE

BY EDWARD J. SALSTROM

The investigation described in this paper represents a continuation of a series of studies dealing with the thermodynamic properties of fused salt solutions. The present system, rubidium bromide in silver bromide, concludes that particular phase of the investigation dealing with the change in activity of silver bromide upon dilution with an alkali metal bromide.[1]

Experimental Part

The rubidium bromide was prepared by the neutralization of its hydroxide with pure hydrobromic acid. The neutralization was carried out in a platinum cylinder. After obtaining the rubidium bromide by crystallization from its saturated solution the salt was finally dried by fusing it in a quartz dish. The remaining materials, apparatus and procedure were similar to those previously described in the lithium bromide–silver bromide investigation.[1a]

Briefly the method consisted of applying a reversible bromine gas electrode to the study of fused salt solution cells of the type, Ag(s), AgBr(l), RbBr(l), $Br_2(g)$. Hydrolysis and oxidation products occasioned by the filling and sealing of the cell container were removed by bubbling dry hydrogen bromide gas through the melt for at least two hours. Bromine gas generated by electrolysis of fused lead bromide was then bubbled over a treated[2] graphite rod dipping into the melt. After equilibrium was reached, readings were taken at regular temperature intervals in both ascending and descending series. Both series were in complete agreement. The exact composition of each solution was finally determined by electrolytic analysis of the cell contents.

Table I gives the observed results plus a correction to take care of the thermoelectric effect[3] involved in each cell. Figure 1 presents the results

---

[1] (a) Salstrom and Hildebrand, THIS JOURNAL, **52**, 4650 (1930); (b) Salstrom, *ibid.*, **53**, 1794 (1931); *ibid.*, **53**, 3385 (1931).

[2] Salstrom and Hildebrand, *ibid.*, **52**, 4641 (1930).

[3] Ref. 2, p. 4644.