

PHOTOCHEMICAL FORMATION OF HYDROGEN PEROXIDE FROM WATER. PART II. IN PRESENCE OF BASIC ZINC CARBONATE AND OXIDES OF CADMIUM, TIN AND THORIUM

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The photochemical formation of hydrogen peroxide from water has been found to take place in presence of basic zinc carbonate. A study of this reaction in presence of zinc carbonate and zinc oxide in the ultra-violet light from a mercury-vapour lamp has shown that zinc carbonate is more photoactive than zinc oxide in this reaction: Besides cadmium oxide which is already known to sensitise this reaction (*vide* 'Chemical Action of Light' by N. R. Dhar, p. 263), stannic oxide and thorium have also been found to act as photosensitisers. A comparative study of the photoactivity of these three oxides has been carried out.

In a previous communication (*vide* Part I of the present series, *J. Indian Chem. Soc.*, 1944, 21, 97) it has been described that as a result of the photosensitising activity of zinc oxide, prepared by different methods, it was found that oxide prepared from carbonate by ignition has the greatest activity. This led to the idea that zinc carbonate itself might prove to be a sensitizer for the photochemical formation of H₂O₂ from water.

A number of tests for the detection of minute amounts of hydrogen peroxide are described in the literature. On examination, however, it was found that some of them were not as sensitive and specific as they were claimed to be. The following tests were finally employed for the detection of hydrogen peroxide in this investigation.

(i) The brown solution of ferric chloride (0.4%) and potassium ferricyanide (0.8%) is decomposed by reducing agents with the formation of Prussian blue. Hydrogen peroxide reduces ferricyanide to ferrocyanide which reacts with ferric chloride present to form Prussian blue. The limit of identification is known to be about 0.08×10^{-6} g. of hydrogen peroxide. This test could not be employed in the case of those test solutions which contained stabilisers because many organic substances were capable of reducing ferricyanide.

(ii) A neutral solution of potassium iodide containing starch is coloured blue due to the liberation of iodine in the presence of small quantities of hydrogen peroxide. The limit of identification has been found to be about 0.03×10^{-6} g. of hydrogen peroxide. Although this test is fairly sensitive, it is given by ozone as well as NO₂. The action of O₃ or H₂O₂ on potassium iodide, however, renders the solution alkaline, while the action of NO₂ in small concentration leaves it neutral. Consequently the presence of hydrogen peroxide or ozone is detected by adding a suitable indicator, such as cresol red, to a potassium iodide solution (*vide* McMorris and Dickinson, *J. Amer. Chem. Soc.*, 1932, 54, 4248).

(iii) Hydrogen peroxide causes a yellow colour to develop in acidic solutions of titanium sulphate (0.2%). This test is a specific test for hydrogen peroxide though not very sensitive. The sensitivity is about 1.24×10^{-6} g. of hydrogen peroxide.

EXPERIMENTAL

In a few preliminary experiments, aqueous suspensions of zinc carbonate (basic carbonate C. P., Merck) each containing about 0.2 g. of the powder in 30 c. c. of conductivity water in presence and absence of a small amount of stabiliser such as phenol or glycerol, were exposed in open pyrex flasks to sunlight for a period of about five hours. After exposure the contents of the flasks were filtered and the filtrates were divided into four portions and tested for H₂O₂ employing the tests mentioned above.

Hydrogen peroxide was detected. Similar experiments carried out with stannic oxide, thorium and cadmium oxide revealed the presence of hydrogen peroxide, after exposure to

sunlight. The observations led the authors to undertake a detailed study of the sensitising action of the above mentioned powders, employing artificial ultraviolet light, in addition to sunlight. Cadmium oxide has been observed by previous workers to act as a sensitiser in this reaction as already mentioned in our previous communication, but as far as the present authors are aware, no detailed study of this sensitiser has been carried out in this connection.

Preparation of Sensitisers

Zinc carbonate was prepared by precipitating an aqueous solution of zinc sulphate with a solution of sodium carbonate. The resulting precipitate after washing was dried at 100°. In addition to this sample, Merck's C. P. basic zinc carbonate was also employed. Two samples of cadmium oxide were obtained from the sulphate and the nitrate respectively by precipitation with alkali and igniting the resulting powders at 500°. The colour of the two samples was chocolate-red. Stannic oxide was prepared by precipitating a cold aqueous solution of stannic chloride with ammonia, and thorium dioxide from the corresponding nitrate by precipitation with alkali. The resulting samples were ignited at 1000°. All the above powders were passed through 150 mesh.

The chemicals employed in the preparation of the above samples were Merck's "Guaranteed Reagents" or "Extra Pure" chemicals. The experimental details and the method of estimation of hydrogen peroxide, adopted in this investigation, were the same as those described in our previous communication (*loc. cit.*). The stabiliser used was either phenol or glycerol, the quantity employed being such that the solution was always 0.1 M with respect to the stabiliser.

The Sensitising Action of Zinc Carbonate and Zinc Oxide

(i) These experiments were performed with the object of comparing the sensitising activity of zinc carbonate and zinc oxide. For this purpose an aqueous suspension (conductivity water) of the powder containing phenol as a stabiliser was exposed to the total ultraviolet light from a mercury vapour lamp in a quartz flask, which was placed at a distance of 15 cm. from the lamp. The flask was shaken at intervals during illumination. The results are summarised in Table I in which c represents the amount of hydrogen peroxide formed in moles, M, Merck's sample, C.I., the sample of zinc oxide prepared from carbonate by ignition and S.P., the sample prepared from sulphate by precipitation.

TABLE I

Powder	Powder (0.1 g.), water (25 c.c.), phenol (0.1 M), exposed to total ultraviolet for 2 hours.			
	Zinc carbonate (M)	Zinc carbonate (S.P.)	ZnO (C.I.)	ZnO (S.P.)
$c \times 10^6$	1.63	1.15	1.10	0.83

TABLE II

Powder	Powder (0.2 g.), water (30 c.c.), phenol (0.1 M), exposed to sunlight for 9 hours.		
	Zinc carbonate (M)	Zinc carbonate (S.P.)	ZnO (S.P.)
$c \times 10^6$	26.4	19.6	18.7

(ii) In these experiments aqueous suspensions of the powder were exposed in open Pyrex flasks to sunlight. After a period of 9 hours the flasks were removed and the hydrogen peroxide content of each was estimated. The results are shown in the following table.

The results as given in Tables I and II indicate that zinc carbonate supplied by Merck is more active than zinc oxide in sensitising this reaction. The sample of zinc carbonate that was prepared in the laboratory was comparatively less active than Merck's zinc carbonate.

*Photochemical Formation of Hydrogen Peroxide from Water in presence of
Oxides of Cadmium, Tin and Thorium*

In the following experiments, the reaction was studied in the presence of powders mentioned above employing ultraviolet light from a mercury vapour lamp as well as sunlight. The results are given in Tables III to VI. In these tables the letters S.P. have the same significance as mentioned above, while N.P. indicate the sample prepared from nitrate by precipitation. The quantities of H_2O_2 , obtained when zinc oxide (S.P.) was used as sensitiser, are also given for the sake of comparison.

TABLE III

Powder (0.1 g.), water (15 c.c.), exposed to light from a quartz mercury vapour lamp focussed by a glass condenser for 2 hours.

Powder	ZnO (S.P.)	CdO (S.P.)	CdO (N.P.)
$c \times 10^6$	0.5	0.4	0.3

TABLE IV

Powder (0.2 g.), water (30 c.c.), phenol (0.1 M), exposed in open Pyrex flasks to sunlight for 5 hours.

Powder	ZnO (S.P.)	CdO (S.P.)	CdO (N.P.)
$c \times 10^6$	12.55	1.65	1.35

TABLE V

Powder (0.1 g.), water (25 c.c.), phenol (0.1 M), exposed to total ultraviolet light from a quartz mercury vapour lamp for 6 hours.

Powder	ZnO (S.P.)	Stannic oxide	Thoria
$c \times 10^6$	1.86	0.71	0.38

TABLE VI

Powder (0.2 g.), water (30 c.c.), phenol (0.1 M), exposed to sunlight for 9 hours.

Powder	ZnO (S.P.)	Stannic oxide	Thoria
$c \times 10^6$	18.7	5.1	0.7

The results shown in Tables III and IV indicate that cadmium oxide prepared from sulphate is more active than that prepared from nitrate, as in the case of zinc oxide. The brown coloured oxide gradually turned white during exposure. It can also be seen from the above tables that the photoactivity of the oxides of cadmium, tin and thorium is much less than that of zinc oxide.

DISCUSSION

Iodide test is one of the most sensitive tests for H_2O_2 , but as this test is also given by NO_2 and O_3 , particular care has to be taken to eliminate the possibility of the existence of traces of the latter substances, while employing this test for the detection of small quantities of H_2O_2 . NO_2 is best detected by Griess Ilosva reaction which consists in the formation of red colouration on the addition of an acetic acid solution of sulphanilic acid and α -naphthylamine to the test solution. O_3 is best detected by its bleaching action on a dilute alkaline solution of fluorescein. The importance of carrying out these elimination tests in an investigation like the present one is emphasised by the following observation made during the course of this investigation. While carrying out preliminary tests with different sensitisers it was observed that the filtrate from an exposed sample containing aqueous suspension of Merck's Cr_2O_3 gave an instantaneous colouration with a neutral starch-iodide solution. The sample

kept in the dark also behaved in a similar manner. On carrying out elimination tests, both the filtrates were found to contain traces of NO_2 , but no H_2O_2 or O_3 , indicating that the sample of Cr_2O_3 , was contaminated with some nitrite. A pure sample of Cr_2O_3 , prepared by us, never gave a positive test with starch-iodide solution.

Incidentally, the above observation gave rise to the idea that the reaction between nitrite and iodide is probably catalysed by traces of chromium chloride and chromium sulphate, which were found to be present in the above filtrates.

Zinc carbonate supplied by Merck was found to be much more active than the sample of zinc carbonate prepared in the laboratory. This is apparently due to the fact that the average size of the particles in the case of Merck's sample was smaller than that of the particles in the sample prepared by the authors, but it may also be due to a difference in the chemical composition of the two samples of zinc carbonate, as the latter is known to possess a variable composition depending upon the conditions of its preparation. The extent to which each of the two factors is responsible for the observed difference in sensitising power cannot, however, be decided unless special care is taken to use powders having particles of the same average size.

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