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# Titanium Dioxide Catalyzed Photooxidation of Mercury

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Yellow coloration of $TiO_2$ (anatase) was observed on uv irradiation in the presence of Hg vapor and $O_2$. The effect was most pronounced with light of 390–420 nm, corresponding to the absorption edge of $TiO_2$. At room temperature, the yellow color darkened with continued irradiation, and finally a dark brown surface layer was formed in which HgO was identified. At 170°C, only yellow coloration of the $TiO_2$ was observed, and there was a saturation in Hg content corresponding to the quantity of acidic as well as of basic OH groups on the surface. A grey instead of a yellow tone appeared with $TiO_2$ the basic $OH^-$ groups of which had been exchanged for $H_2PO_4^-$ ions. Hg of oxidation state +1, exclusively, was found on phosphate-covered $TiO_2$. Mercury(I) was found also in the beginning of the photooxidation reaction on untreated or alkali-treated $TiO_2$; later on, there was only $Hg^{2+}$ present. One $O_2$ molecule is consumed for each chemisorbed Hg atom at 60°C and at low uptakes. Water is formed in this reaction. The photooxidation is apparently caused by OH radicals, arising from the basic $OH^-$ groups, together with a chemisorbed oxygen species, very likely $O_2^-$. The reaction is reversible: the yellow color fades slowly in darkness if water vapor is present, and metallic Hg distills off. The same reactions were observed qualitatively with rutile as well as with anatase, and with zinc oxide, tin dioxide, or cerium dioxide.

## INTRODUCTION

It is well known that organic substances are oxidized when they are irradiated with ultraviolet light in the presence of certain oxides. This phenomenon was originally observed with titanium dioxide (*1–5*). It is of profound importance in view of the use of $TiO_2$ as a pigment. Under anaerobic conditions, titanium dioxide is reduced and turns mauve, blue, or grey. If oxygen is present, however, the titanium dioxide is continually reoxidized while the organic material, e.g. the binder of a paint, is destroyed ("chalking" of the paint). Occasionally a yellow discoloration of $TiO_2$ has been observed (*6–9*). It has been attributed to formation of a peroxide species on the $TiO_2$ surface or to slight reduction of the $TiO_2$. We found, however, that a yellow color appears always when $TiO_2$ is irradiated with ultraviolet light in the presence of mercury vapor and oxygen. Mercury is chemisorbed on the surface in this reaction, and mercuric oxide, HgO, is finally formed in considerable quantities if the reaction is allowed to proceed at room temperature.

It was found in earlier investigations (*10–12*) that the surface of $TiO_2$ contains hydroxyl groups which react amphoterically. A total of 440 μeq/g of OH groups was found for the anatase powder used in this study. Half of this quantity reacts fairly strongly acidic; these OH groups are neutralized by NaOH at equilibrium concentrations of ca. 0.01 *N*. The other OH groups react very weakly acidic, corresponding to a p*K* of 12–13. It is assumed

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that the weakly acidic OH groups are identical with the 220 $\mu$eq/g of $OH^-$ ions which undergo exchange for $H_2PO_4^-$ ions on treatment with phosphoric acid. Exchange reactions have also been observed with several other acids. It is thought that these basic $OH^-$ groups are coordinated to one Ti atom, while the acidic OH groups are coordinated to two Ti atoms (*11, 12*). Of course, the bonding is neither purely ionic nor purely covalent. The OH groups are stable up to 150°C, and they are almost completely driven off as water at 350°C. There are indications that the OH groups take part in the photooxidation reactions of $TiO_2$.

## METHODS

### *Materials*

Most experiments were performed using a fine-particle size anatase, "P 25", produced by flame hydrolysis of $TiCl_4$ by Degussa at Rheinfelden, Germany. This material, which contains ~5% of rutile, has been described in detail (*10, 11*); its main impurity is chloride (60 $\mu$eq/g). The specific surface area is 56 $m^2/g$ (BET method, 16.2 $Å^2/N_2$ molecule). This material, if not surface-treated, will henceforth be designated $TiO_2$–u.

Other $TiO_2$ preparations, rutile as well as anatase, were prepared by hydrolysis of $TiCl_4$ or $Ti(OC_2H_5)_4$, respectively. Rutile prepared from $TiCl_4$ was also obtained from British Titan Products Ltd. (code no. Cl/D391); very similar material has been described in detail (*13*). Commercial pigments which had not undergone surface treatment for prevention of photoactivity were used as well; they were obtained from Farbenfabriken Bayer, Krefeld-Uerdingen.

Phosphate-covered $TiO_2$ ($TiO_2$–$PO_4$) was prepared by suspending 1 g of $TiO_2$ "P 25" in 6 ml 0.05 *M* $H_3PO_4$ solution and evaporating to dryness. Similarly, $TiO_2$–Na was prepared using 6 ml 0.1 *M* NaOH. The quantities were chosen so that there was an excess of $H_3PO_4$ or NaOH in comparison to the quantities of basic or acidic OH groups (220 and 440 $\mu$eq/g, respectively).

### *Irradiation*

As a source of ultraviolet light, a mercury high-pressure lamp was used (model Q 81 of Original Hanau Quarzlampen GmbH.) which had its maximum output at long wavelengths near 366 nm. Occasionally, sunlight was used. Wavelength dependency of the effects was tested using a Zeiss MPQ II spectrophotometer with a hydrogen lamp for wavelengths below 325 nm. $TiO_2$ was applied as a thin film on a glass slide which was placed, together with a drop of mercury, in the usual cuvettes made of quartz glass. The cuvettes were closed by a lid in order to keep the atmosphere saturated with Hg vapor. The monochromator was set at definite wavelengths, and the color of the sample was observed where it was hit by the beam after specified times. In addition, the presence of chemisorbed mercury was checked by testing with diphenyl carbazone.

### *Analysis*

The oxidation state of chemisorbed mercury was determined by treating the samples with a saturated solution of diphenyl carbazone in toluene. Water was added to the suspension which then was agitated vigorously. After separation of the phases, there was a red color in the aqueous layer if only Hg(I) was present, while the organic layer turned slightly pink. If only Hg(II) was present, the toluene layer was blue, and the aqueous phase remained colorless. Both color effects could be observed in the presence of both oxidation states. For quantitative analysis, all mercury was oxidized by treatment with nitric acid (35%), and the solution was titrated against 0.01 *M* EDTA solution using the back-titration technique (*14*).

### *X-Ray Diffraction*

A Siemens Kristalloflex IV X-ray diffractometer was used with Cu *Kα* radiation for the diffractograms. The sample holder was made by etching a pit of approximately 1 mm depth into a glass plate.

### *Kinetics of Oxygen Uptake*

Oxygen consumption was measured in the set-up shown in Fig. 1. The bottom of

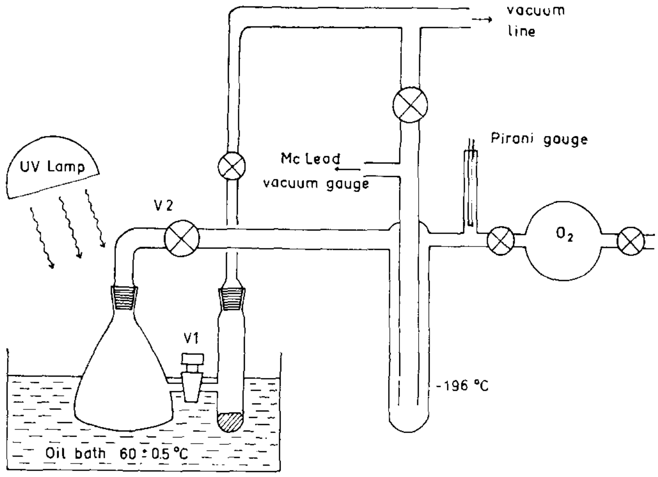

FIG. 1. Experimental arrangement for measuring oxygen consumption during chemisorption of mercury.

the flask was covered with a $TiO_2$ layer of 2–4 mm thickness; 0.5 g of $TiO_2$-u covered an area of 10.75 $cm^2$. Samples of 1 g were used with $TiO_2$-Na and $TiO_2$–$PO_4$. The trap was cooled with liquid nitrogen the level of which was kept in the same position during all pressure readings. Pressure was measured by use of a McLeod gauge of 500-ml compression volume. The flask and the reservoir were kept at 60°C by a constant temperature oil bath. The $TiO_2$ was outgassed for 20 hr at 60°C in darkness; valves 1 and 2 were closed, and dry oxygen was admitted to the pressure measuring part. Rough adjustment of the desired pressure was facilitated by means of a Pirani gauge. After reading the pressure and estimating the gas quantity from the known volume, valve 2 was opened, and the drop in pressure was followed until it was constant. Then, after opening valve 1, uv illumination was started, and the pressure measured periodically. The volumes of the various parts of the apparatus had been previously measured by introducing known gas quantities and measuring the pressures, the trap and flask being kept at —196°C and 60°C, respectively. The total volume was 1205 ml; a pressure change of $10^{-3}$ Torr corresponded to 0.0708 $\mu$mole gas. At the termination of the experiment, the $TiO_2$ was recovered from the flask and its mercury content was determined.

## RESULTS

### *Qualitative Observations*

A yellow color always appeared when $TiO_2$ was irradiated with near ultraviolet light in the presence of mercury vapor and oxygen. Small $O_2$ partial pressures, e.g., $10^{-2}$ Torr, were sufficient. The phenomenon can be easily produced by placing $TiO_2$ and a drop of mercury in a petri dish. Covering with the lid ensures an atmosphere saturated in Hg. On illumination, the $TiO_2$ powder turns yellow on the surface exposed to light within a day. The reaction is considerably accelerated by putting the petri dish on a hot plate, e.g., at 170°C, thus increasing the Hg partial pressure. Yellow color is noticeable within 30 min under such conditions.

At 170°C, the reaction comes to an end when all illuminated $TiO_2$ is yellow. At room temperature, however, there is a gradual increase in tone, and finally the whole surface is covered by a dark brown layer. No discoloration is observed above 300°C, and samples already turned yellow become white again.

These color effects are only observed when $TiO_2$ is exposed to oxygen, mercury vapor, and ultraviolet light at the same time. Sunlight is effective, too, but the reaction is faster under an uv lamp, obviously due to the greater illumination density.

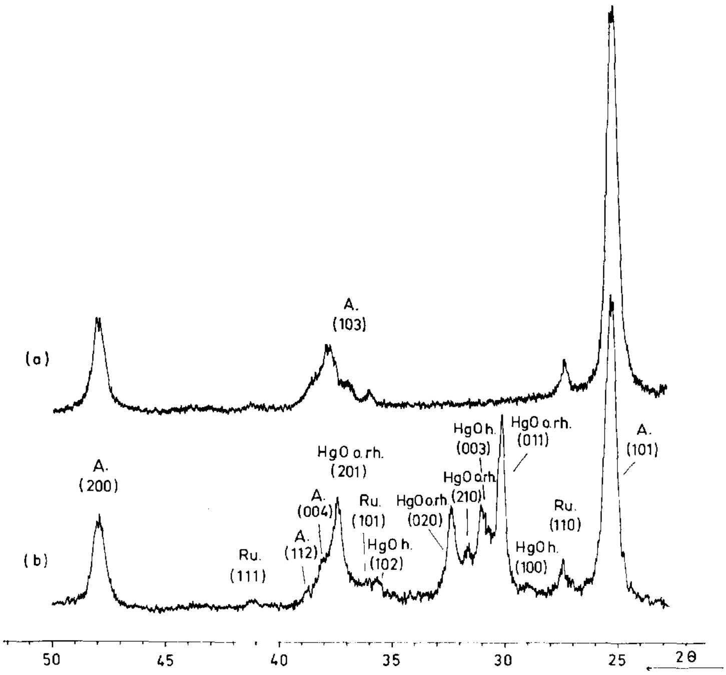

FIG. 2. X-Ray diffractograms of $TiO_2$ "P 25" (a) before and (b) after uv irradiation at 25°C in the presence of mercury.

Samples were compressed in the glass holders used in the X-ray diffractometer, and were irradiated, first at 170°C and then at room temperature until a dark brown surface layer had formed. The resulting diffractogram (Fig. 2) showed new diffraction lines which could be identified as the main reflections of orthorhombic and of hexagonal (*15*) HgO (Table 1). As judged from the intensity of the reflections, there was more orthorhombic than hexagonal HgO present. Weak HgO reflections were already noticeable with yellow samples with an overall Hg content of 420 μmole/g.

Chemical analysis confirmed the presence of mercury in the yellow samples. Predominantly, mercury in the +1 oxidation state was detected in the early stages of the reaction. After long standing of such samples, all mercury was in the +2 oxidation state. The existence of mercury in the +1 oxidation state was confirmed by treatment with aqueous alkali: The samples turned dark grey by disproportionation to Hg and $Hg^{2+}$. This behavior was not shown by samples kept for 12 hr or more. After irradiation for several hours, mercury(II) was found, too, and predominantly mercury(II) was observed after prolonged reaction.

On treatment with potassium iodide solution, freshly prepared samples assumed a greenish-yellow hue while preparations which had been stored for some time turned orange-red. This behavior is in accordance with the presence of mercury(I) or mercury(II) ions, respectively. The fresh preparations, in contrast to older samples, reduced $KI_3$ solution, indicating again, the presence of a reducing species.

Similar behavior as with untreated $TiO_2$ was observed with $TiO_2$–Na, the sample in which acidic protons were replaced by sodium ions. There was a qualitative impression that discoloration at 170°C and formation of HgO at room temperature proceeded faster with this sample. However, $TiO_2$ in which basic surface $OH^-$ ions were replaced by phosphate ions showed different behavior: There was only grey to yellowish-grey discoloration, and only mercury(I)

TABLE 1

IDENTIFICATION OF X-RAY REFLECTIONS OBSERVED AFTER UV IRRADIATION AT 25°C OF $TiO_2$ IN THE PRESENCE OF Hg AND $O_2$

(The surface of the sample was covered with a dark brown layer; the Hg content of the total sample was 855 μmole/g.)

| $d_{obsd}$ (Å) | Identification substance | (*hkl*) | $d_{ASTM}$[a] (Å) | $I/I_{0\,ASTM}$[a] |
|---|---|---|---|---|
| 3.515 | Anatase | (101) | 3.51 | 100 |
| 3.248 | Rutile | (110) | 3.245 | 100 |
| 3.085 | HgO (hexagonal) | (100) | 3.101 | 50 |
| 2.967 | HgO (orthorhombic) | (011) | 2.967 | 100 |
| 2.905 | HgO (hexagonal) | (101) | 2.920 | 100 |
| 2.885 | HgO (hexagonal) | (003) | 2.896 | 60 |
| 2.833 | HgO (orthorhombic) | (210) | 2.834 | 80 |
| 2.764 | HgO (orthorhombic) | (020) | 2.759 | 60 |
| 2.519 | HgO (hexagonal) | (102) | 2.523 | 80 |
| 2.492 | Rutile | (101) | 2.489 | 41 |
| — | Anatase | (103) | 2.435 | 9 |
| 2.406 | HgO (orthorhombic) | (201) | 2.408 | 65 |
| 2.378 | Anatase | (004) | 2.379 | 22 |
| 2.328 | Anatase | (112) | 2.336 | 9 |
| 2.191 | Rutile | (111) | 2.188 | 22 |
| — | HgO (hexagonal) | (103) | 2.117 | 10 |
| 1.895 | Anatase | (200) | 1.891 | 33 |

[a] *d* values and intensities for hexagonal HgO from (*15*).

could be detected in all stages. No HgO was formed. This observation implies that surface OH groups might take part in the photooxidation reaction. Therefore, $TiO_2$ which had been dehydroxylated by outgassing at 400°C was used in another test together with dry oxygen. There was pronounced reduction in the rate and the intensity of the yellow coloration. It cannot be excluded that traces of moisture originating from the glass vessels had found access to the $TiO_2$.

Photoactivity in the oxidation of mercury was observed with all tested $TiO_2$ preparations, anatase as well as rutile. Commercial pigments which had not been surface treated with the aim of prevention of photoactivity developed the same yellow color as the other samples. Yellow colors and dark brown surface layers formed also on ZnO, $SnO_2$, and $CeO_2$. MgO, $\gamma$-$Al_2O_3$ and $SiO_2$ were inactive.

The effective wavelengths of light were determined using the monochromator of a spectrophotometer. Only where the sample was hit by the beam, could color effects be observed and mercury detected. The results of these experiments are described in Table 2. The test for mercury was positive in the spectral range 470–300 nm although exposures of 24 hr or more were necessary. Slight yellow coloration after 24 to 48 hr was observable in the range 450–310 nm. A distinct yellow color was noticed after 1.5 to 2 hr only in the range 420–370 nm, with maximum intensity at 410–390 nm. Light of wavelengths shorter than 310 nm produced no yellow color; in particular, the Hg resonance line at 253.7 nm was ineffective.

### *Quantitative Observations*

Thin layers of $TiO_2$ were prepared on a glass slide, and the mercury content was determined after irradiation under standard conditions of illumination intensity and temperature (170°C) using a closed system (petri dish). The mercury content was determined as function of irradiation time using an optically "thin" layer (5.09 mg/$cm^2$) and as function of layer thickness, expressed as mass thickness, at constant

TABLE 2

Dependence on Wavelength of Color Effects and Hg Chemisorption (Reaction Temperature, 60°C)

| Wave-length (nm) | Time of irradiation (hr) | Color | Test for Hg |
|---|---|---|---|
| 500 | 48.0 | — | – |
| 470 | 24.0 | — | + |
| 460 | 24.0 | — | + |
| 450 | 48.0 | Slightly yellow | + |
| 440 | 8.0 | Yellow | + |
| 430 | 18.0 | Yellow | + |
| 420 | 20.0 | Yellow | + |
| 410 | 1.5 | Distinctly yellow | + |
|  | 18.0 | Brown | + |
| 400 | 2.7 | Yellow | + |
|  | 39.0 | Dark brown | + |
| 390 | 2.6 | Yellow | + |
|  | 24.0 | Dark brown | + |
| 380 | 2.7 | Distinctly yellow | + |
|  | 23.0 | Yellow-brown | + |
| 370 | 1.5 | Slightly yellow | + |
|  | 24.0 | Yellow | + |
| 360 | 1.5 | — | + |
|  | 9.3 | Yellow | + |
| 350 | 1.5 | — | + |
|  | 41.0 | Yellow | + |
| 340 | 48.0 | Slightly yellow | + |
| 330 | 48.0 | Slightly yellow | + |
| 320 | 48.0 | Slightly yellow | + |
| 310 | 32.0 | Very slightly yellow | + |
| 300 | 25.0 | — | + |
| 290 | 24.0 | — | – |

illumination for 24 hr. The results are presented in Figs. 3 and 4, respectively.

As can be seen from Fig. 3, saturation was achieved at 170°C within a few hours. The saturation uptake was approximately 220 $\mu$mole Hg/g. When the heating was stopped, there was additional uptake of mercury with no apparent saturation within 72 hr. It proved convenient for the speedy preparation of samples rich in Hg content to preadsorb mercury at 170°C and then to have the reaction proceed at or near room temperature.

Figure 4 shows that the mercury uptake was proportional to mass thickness up to a mass thickness of approximately 6–8 mg/cm$^2$. Up to this point, the $TiO_2$ layers can be considered as optically thin. At higher mass thicknesses, the loss in uv light by absorption and scattering is limiting the Hg uptake within a fixed period of 24 hr. This period is quite sufficient to obtain saturation with thin layers (Fig. 3). The saturation uptake of Hg can be estimated from the slope of the linear portions of the curves in Fig. 4. The results are shown in Table 3. While virtually identical curves were observed for $TiO_2$–u and $TiO_2$–Na, considerably less Hg was bound on the surface of $TiO_2$–$PO_4$. The saturation value for $TiO_2$–u and $TiO_2$–Na coincided well with the concentration of either strongly acidic or basic OH groups on the

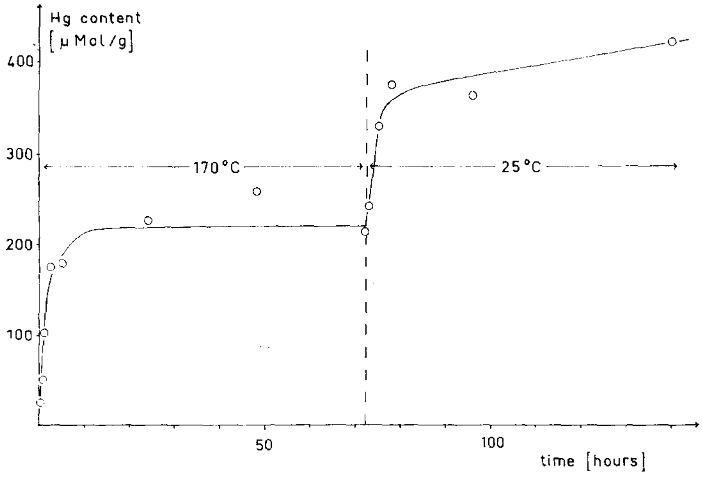

Fig. 3. Hg uptake of $TiO_2$-u as function of time, using an optically thin layer, at 170 and at 25°C.

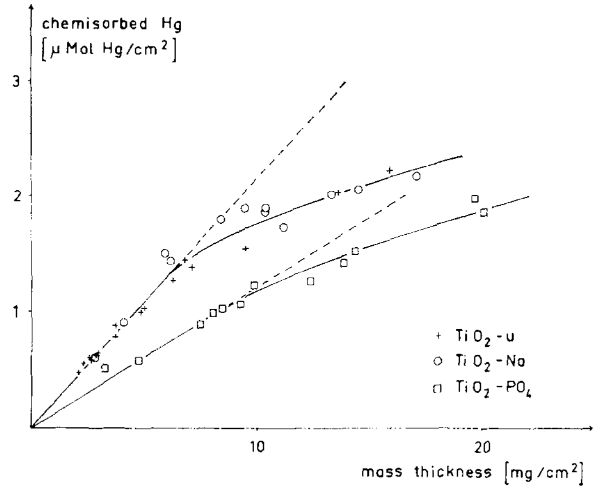

FIG. 4. Hg uptake at 170°C as function of mass thickness after 24 hr of uv irradiation.

surface. The fact that surface treatment with phosphoric acid influences color effects and the quantity and oxidation state of chemisorbed mercury implies that the basic OH groups take part in the reaction.

In another series of experiments, the quantity of oxygen consumed in the reaction was estimated. The reaction was run at 60°C because the vapor pressure of mercury ($25 \cdot 10^{-3}$ Torr) is higher at this temperature than at room temperature; the use of greased joints prohibited higher reaction temperatures. $TiO_2$ was spread on the bottom of the flask (Fig. 1) in a layer of ca. 2–4 mm thickness, i.e., an optically thick layer. The quantity of oxygen consumed was estimated from the decrease in its pressure. There was some rapid uptake of oxygen while the mercury supply was still shut off (see the section on kinetics). The oxygen consumption after admission of Hg and starting the uv irradiation is compared with the final Hg content in Table 4. This table shows clearly that the ratio of $O_2$ consumption and Hg uptake is 1, at least in the beginning stages of the photooxidation reaction and at low $O_2$ pressures. Because an optically thick layer was used, the mercury distribution was uneven within the sample. The reaction is much slower at 60°C than at 170°C. It was not possible, for experimental reasons, to have the reaction run to saturation.

It was noticed that water is formed in the course of the reaction and condensed in the cooling trap. A smaller drop in pressure was observed, and water condensed in the McLeod gauge, when the cooling of the trap with liquid nitrogen was omitted. The pressure dropped considerably, and water condensed in the trap, when it was cooled at the termination of oxygen uptake. An exact estimate of the quantity of water

TABLE 3

INFLUENCE OF SURFACE TREATMENT ON SATURATION Hg UPTAKE OF $TiO_2$ "P 25" (DETERMINED FROM SLOPES IN FIG. 3)

| Sample | Hg uptake (μmole/g) |
|---|---|
| $TiO_2$-u | 216 |
| $TiO_2$-Na | 216 |
| $TiO_2$-$PO_4$ | 122 |

TABLE 4

OXYGEN CONSUMPTION AND MERCURY UPTAKE OF $TiO_2$ "P 25" DURING UV IRRADIATION AT 60°C

| Sample | $O_2$ consumption (μmole/g) | Hg uptake (μmole/g) | Ratio $O_2$:Hg |
|---|---|---|---|
| $TiO_2$-u | 16.6 | 15.6 | 1.06 |
| | 42.8 | 42.1 | 1.02 |
| | 67.4 | 72.3 | 0.93 |
| $TiO_2$-Na | 20.3 | 19.9 | 1.02 |
| $TiO_2$-$PO_4$ | 14.7 | 12.1 | 1.21 |

formed was not possible, since substantial parts of the apparatus were at different temperatures compared with the standard conditions. Approximately 3 μmole of $H_2O$ were liberated as compared with a Hg chemisorption of 3.6 μmole. Furthermore, some fading of the yellow color of the $TiO_2$ was observed on cooling of the trap. The quantitative results warrant confirmation under better experimental conditions.

In order to obtain information on the composition of the mercuric surface complex of substances with relatively high mercury contents, a sample containing 420 μmole Hg/g was thermally decomposed. The evolved oxygen was collected by means of a Toepler pump and was measured gas volumetrically. Since it is well-known that organic contaminants reduce $TiO_2$ at higher temperatures with formation of CO, care was taken to use only greaseless vacuum connections between the sample and the nearest cold trap. Temperature was raised in steps of 50°C. First signs of decomposition were noticeable at 250°C; at 300°C a red color, similar to that of mixtures of $TiO_2$ and HgO, was observed. Rapid decomposition occurred at 400°C, and after 5 hr at 450°C, a final volume of 362 μmole $O_2$/g was collected. The identity of the gas was checked by gas chromatography. The results indicate that there are at least two oxygen atoms bound for each chemisorbed Hg atom if one assumes that 220 μmole/g of Hg were chemisorbed and 200 μmole/g of HgO had formed. There is some indication that peroxides, in addition to chemisorbed mercury may exist on the $TiO_2$ surface.

### *Kinetics of Oxygen Chemisorption*

The arrangement shown in Fig. 1 was used also for kinetic measurements of the oxygen uptake in the coadsorption of mercury and oxygen at 60°C. On admitting oxygen to the sample outgassed at 60°C in darkness, there was some adsorption of oxygen which came to an end after 30 min (Fig. 5). Similar observations have been described in the literature (*16*). The quantity adsorbed at a pressure of $\sim 40 \cdot 10^{-3}$ Torr corresponded to 0.3–0.4 μmole $O_2$/g. On start of the uv irradiation, there was an initial rapid decrease of the $O_2$ pressure which gradually reached a constant value after the major fraction of the available oxygen was consumed. Typical curves for the samples $TiO_2$–u, $TiO_2$–Na and $TiO_2$–$PO_4$ are shown in Fig. 5. It is seen immediately that $TiO_2$–u and $TiO_2$–Na behave very similarly, while oxygen uptake is much slower for $TiO_2$–$PO_4$. On admitting further oxygen, there was again some adsorption in the dark, and greatly increased adsorption under uv irradiation. In a total of 11 adsorption runs, 67.2 μmole $O_2$/g were adsorbed on $TiO_2$–u. The quantity of oxygen consumed in each run was approximately proportional to the starting pressure.

The initial rate of $O_2$ uptake varied to some extent from 20 to 35 nmole/min without any apparent relationship to pressure or preadsorbed quantity. The adsorption curves could be surprisingly well-represented by Elovich kinetics. Linear plots were obtained when $\Delta p$ was plotted against $\log(t + t_0)$ with $t_0 = 100$ min for $TiO_2$–u, 60 min for $TiO_2$–Na, and 30 min for $TiO_2$–$PO_4$. Consecutive adsorption curves on the same samples fitted the Elovich equation equally well (see Fig. 6).

### *Reverse Reaction in Darkness*

The yellow coloration of $TiO_2$ in the presence of Hg and $O_2$ is a reversible process. It was noticed that yellow samples became gradually white again if they were kept in darkness in open air. On closer inspection of this phenomenon, it was found that the presence of water is necessary for this fading. As has been mentioned, water which can be frozen out on a cold finger is liberated in the course of photooxidation of mercury. Fading did not occur if the samples were stored in a desiccator over phosphorus pentoxide. It occurred more quickly, within ca. 16 hr, if the samples were kept in air saturated with water vapor. Sometimes, a slight grey color was noticeable under these conditions. No mercury could be detected in the samples after fading of the yellow color. If the reaction was allowed to proceed at low $H_2O$ and $O_2$ pressures in a vacuum system, condensation of

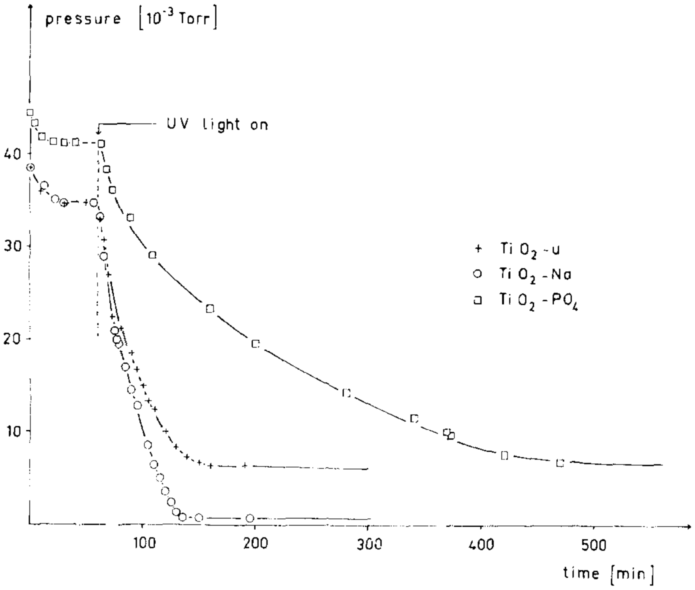

FIG. 5. Kinetics of oxygen chemisorption on uv irradiation in the presence of constant Hg pressure ($25 \cdot 10^{-3}$ Torr). $T = 60°C$.

mercury could be observed upon cooling of a "cold finger" to −196°C. The fading phenomena were observed only with yellow material; HgO that had formed catalytically at room temperature was stable.

The conclusion is that a reducing species is formed on adsorption of water and oxygen on the yellow $TiO_2$ surface. Possible species are $H_2O_2$ or $HO_2^-$, $HO_2\cdot$ or $O_2^-$. Mercuric oxide, HgO, is slowly reduced by aqueous $H_2O_2$. On treatment of yellow $TiO_2$ with aqueous $H_2O_2$, there was gas evolution and change in color after a short induction period. In the end, a light yellow color of more greenish than reddish quality became apparent; frequently, a grey shade due to metallic mercury could be noticed. A similar, light yellow color is observed when untreated $TiO_2$ is dispersed in $H_2O_2$ solutions. The grey product obtained on irradiation of $TiO_2$–$PO_4$ in the presence of Hg and $O_2$ turned yellow immediately when $H_2O_2$ was added, no gas evolution was noticed.

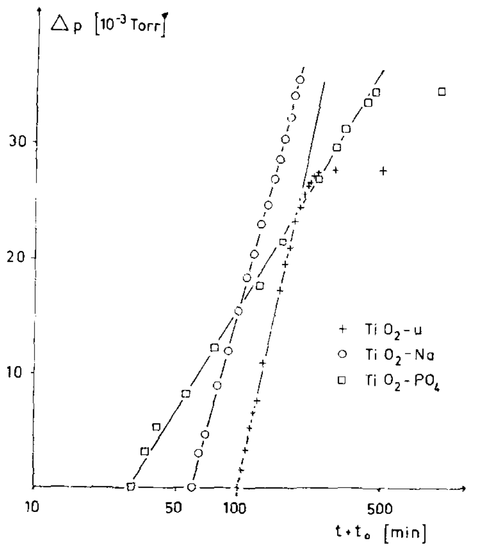

FIG. 6. Elovich plots of the kinetics of oxygen chemisorption (see Fig. 5).

## DISCUSSION

Titanium dioxide always develops a yellow color when it is exposed to mercury vapor, oxygen, and ultraviolet light simultaneously. All three factors are necessary, although partial pressures of $10^{-3}$ Torr (vapor pressure of mercury at room temperature) to $10^{-2}$ Torr are sufficient. After such treatment, the $TiO_2$ always contains mercury of oxidation stages +1 or +2. No chemisorbed mercury and no color is found if one of the factors $TiO_2$, Hg, $O_2$, and uv quanta is lacking. Earlier observations of a yellow coloration of $TiO_2$ must very probably be attributed to photooxidation of mercury. From the descriptions of experiments in the literature, one can conclude that mercury had been used in manometers and diffusion pumps.

The nature of the color-bearing species is not yet known. The possibility that the color is caused by a peroxide species cannot be altogether excluded although the yellow color that develops on adsorption of hydrogen peroxide on $TiO_2$ (*5*) is of a somewhat different hue, paler and less reddish. All attempts to detect the presence of hydrogen peroxide on irradiated, yellow $TiO_2$ by chemical means were unsuccessful. A similar yellow tone develops and mercury is chemisorbed when zinc oxide is irradiated in the presence of Hg and $O_2$. No yellow surface species forms on immersion of pure zinc oxide in hydrogen peroxide. This leads us to the assumption that the yellow color of irradiated $TiO_2$ or ZnO is caused by the chemisorption of mercury.

The yellow color deepens with time and finally turns dark brown, almost black under uv irradiation at room temperature. The presence of HgO was established in such samples. No HgO formed at elevated temperatures, e.g., at 170°C. Instead, the reaction stopped when approximately 220 $\mu$mole/g of mercury were chemisorbed. In contrast, finely divided HgO obtained in the photocatalyzed reaction at room temperature decomposed slowly at 170°C. The temperature of 170°C seemed well-suited for these experiments because most molecular water is driven off the $TiO_2$ surface while surface OH groups are just stable (*10*).

The most active wavelengths of light are observed in the region of the absorption edge of anatase. Although absorption rises most steeply near 390 nm, there is measurable absorption (and a decrease in reflectance) at wavelengths up to 420 nm and higher. No yellow color was discernable within reasonable times of illumination at wavelengths longer than 450 nm. However, traces of mercury could be detected chemically if light up to 470 nm was used. Strangely, photoactivity decreased with increasing energy of the uv light. Perhaps, this can be explained by the diminishing output of the tungsten lamp with decreasing wavelength; however, the output of the hydrogen lamp is constant from 330 to 240 nm.

The saturation mercury uptake at 170°C of approximately 220 $\mu$mole/g coincides with the quantities of basic and of fairly strongly acidic OH groups on the surface of $TiO_2$ "P 25." This led to the assumption that surface OH groups might be involved in the photooxidation mechanism. This was confirmed by the observation of water evolution and by the markedly reduced activity of $TiO_2$ outgassed at 350°C. Studies with $TiO_2$ samples treated with alkali or with phosphoric acid point to the basic OH groups as the active ingredient. $TiO_2$ in which the basic OH groups had been replaced by $H_2PO_4^-$ groups showed quite different behavior: a grey shade developed instead of the yellow color, only mercury of oxidation state +1 could be detected, and oxygen uptake was considerably slower. No HgO was formed by this material.

It is well-established that exclusion of water inhibits photooxidation of binders by $TiO_2$ pigments; the relevant literature is cited in a recent paper by Völz *et al.* (*17*). The observation that photoactivity is inhibited by addition of fluorides, too, (*4*) confirms our assumption that the basic OH groups are involved in the reactions since these groups are easily exchanged for $F^-$ ions (*18*). We assume that $OH^-$ ions on the surface form OH radicals on uv irradiation. The OH radicals will oxidize organic substances as well as mercury. Phenol was identified as a reaction product of uv irradiation of benzene in the presence of $TiO_2$ when oxygen was excluded; 4-nitropyrocatechol was formed from *p*-nitrophenol (*19*).

The formation of OH radicals upon irradiation of $TiO_2$ pigments suspended in water was recently confirmed by ESR spectroscopy (*17*). Absorption of uv quanta produces pairs of electrons and holes. Trapping of photochemically produced holes by

$OH^-$ ions on the surface has already been postulated for magnesium oxide (*20*). There are several ways for the electrons to be trapped: They can form $Ti^{3+}$ ions from $Ti^{4+}$ ions; they can be localized in anion vacancies, giving rise to F or S centers (*21*), or they may form $O_2^-$ ions with adsorbed oxygen (*9, 22*). $Ti^{3+}$ ions and F or S centers give rise to grey or blue colors.

There is one fundamental difference, however, between oxidation of organic substances and of mercury in the presence of $TiO_2$: Oxygen is necessary for the oxidation of mercury, whereas organic substances are oxidized as well in the absence of oxygen. $TiO_2$ is reduced then, and turns blue. The oxidation capacity under anaerobic conditions is limited, and the reaction comes to an end when the surface layer is fully reduced. Our results indicate that both OH radicals and chemisorbed oxygen, presumably $O_2^-$ ions, are needed for the photocatalyzed oxidation of mercury. One must remember in this context that one molecule of oxygen is chemisorbed for each Hg atom at low coverages. Therefore, an $O_2$ species, either $O_2^-$ or $O_2^{2-}$, is likely to exist in the surface complex.

The existence of another species, besides OH radicals, on irradiated $TiO_2$ surfaces was confirmed by the reaction with tetranitromethane. This species displays reducing properties. Tetranitromethane in aqueous solution at pH 3 reacts characteristically with $HO_2$ radicals which are formed by $O_2^-$ ions in acidic media (*23, 24*):

$$C(NO_2)_4 + HO_2 \rightarrow H^+ + C(NO_2)_3^- + NO_2 + O_2.$$

Formation of nitroform, $HC(NO_2)_3$, was observed only when the $TiO_2$ suspension was irradiated with uv light (*19*). The presence of $O_2$ was not essential, however, since nitroform was also found when oxygen was carefully excluded. Since reduction of tetranitromethane by OH radicals is very unlikely, it is concluded (*19*) that tetranitromethane is able to accept photoproduced electrons directly. Oxidation of OH radicals would yield O atoms which ought to oxidize nitroform destructively. These reactions will be described in detail in a later publication.

The acidic OH groups on the surface of $TiO_2$ also seem to be involved in the photooxidation of mercury. Despite the lack of basic OH groups, photooxidation is observed with $TiO_2$–$PO_4$, albeit in a qualitatively and quantitatively different manner.

Mercury(I) surface compounds are formed exclusively. Only mercury(I) salts but no stable mercury(I) oxides, hydroxides, or peroxides are known. We conclude, therefore, that mercury(I) ions are bound in a salt-like fashion by acidic surface sites. So far as is known, only binuclear $Hg_2^{2+}$ species are stable. No ESR signals of paramagnetic $Hg^+$ ions could be detected, although such ions must occur intermediately: Mercury vapor is monatomic, and the concentration of physisorbed Hg atoms on the $TiO_2$ surface is certainly small. There was no change in weight when $TiO_2$ "P 25" was exposed to nearly saturated Hg vapor *in vacuo;* a quartz spring balance was used, the sensitivity was 5 $\mu$mole Hg/g. Another indication of the salt-like nature of the binding of the chemisorbed mercury ions is the observation of water evolution in the course of the photooxidation reaction. Thus, the observed reactions can be described schematically as shown in Fig. 7.

Mercury(I) ions seem not to be stable on the surface on untreated $TiO_2$. Only $Hg^{2+}$ ions can be detected by chemical means after standing for a few hours.

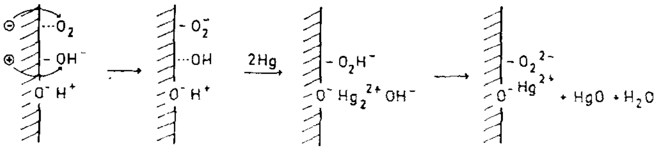

FIG. 7. Schematic representation of the observed reactions in the photooxidation of mercury on $TiO_2$ surfaces after production of an electron-hole pair by absorption of a quantum of uv light.

Darkening caused by the formation of metallic mercury was frequently observed; finely divided mercury vaporizes easily, of course. The gradual disappearance of mercury(I) can be explained by a disproportionation reaction which is caused by the basic surface OH groups, analogous to that observed on treatment of mercury(I) salts with alkali. In agreement with this explanation, formation of dark metallic mercury was observed when $TiO_2$ was added to $Hg_2(NO_3)_2$ solutions.

There must be a species present in yellow $TiO_2$ which forms a reducing species with adsorbed water. The bleaching of yellow $TiO_2$ in darkness is very slow, however, even in saturated water vapor. One explanation might be that formation of this reducing species with adsorbed water requires a relatively high activation energy. Clearly, the oxidation reactions under uv irradiation are much faster than the fading reaction.

It is perhaps worth mentioning here that reversible color changes are observed also with $TiO_2$ doped with various transition metal ions, e.g., iron ions. Such material turns yellow under uv illumination and returns to a white state in darkness. However, this phenomenon is not limited to the surface but occurs in the bulk of the particles. It ought not to be influenced by exterior conditions such as water vapor pressure.

Further investigations of these phenomena are needed to elucidate the mechanism of photooxidation as well as of the fading reaction. It is of interest to note here that zinc oxide pigments, which behave similar to $TiO_2$ in the photooxidation of mercury, are generally reported not to give rise to chalking phenomena of paints (*17*). However, there exists a recent paper dealing with chalking of zinc oxide paints (*25*).

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