JOURNAL OF CATALYSIS 4, 691–696 (1965)

An Infrared Study of the Photocatalytic Reaction between Titanium Dioxide and Silver Nitrate

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Received March 9, 1965

An infrared study has been made of the photoinduced discoloration of mixtures of titanium dioxide and silver nitrate. Attenuated total reflectance and conventional transmission measurements have been made on samples before and after exposure to ultraviolet radiation. Some evidence has been obtained for the hypothesis that the black end product of the photoreaction is metallic silver. A model is proposed for localized electron-trapping centers at the titanium dioxide surface, at energies ranging from 0.136 to 0.62 eV below the conduction band.

INTRODUCTION

The ultraviolet-induced darkening of mixtures of titanium dioxide and silver compounds has been reported by several authors (*1–4*).

In the specific case of titanium dioxide–silver nitrate mixtures reports agree that the mixture darkens in the presence of ultraviolet radiation from a near white to a heavy black coloration and that this process is considerably accelerated in the presence of moisture. For example, a paste of titanium dioxide pigment in an aqueous solution of silver nitrate will be heavily blackened during a few seconds of exposure. There is disagreement regarding the nature of the black end product of this photoreaction. Some authors claim an oxidation of the silver ions to black silver oxide (*1, 3*), while others advance the view that the reaction is one of reduction to metallic silver (*2, 4*). The role of the titanium dioxide is assumed to be that of a photocatalyst in each case.

Much of the published evidence is based on reflectance measurements in the visible region upon the black discoloration. The featureless nature of these reflection spectra poses a real difficulty in a definite interpretation. In the work described here, some measurements have been made in the infrared region in order to obtain additional information on this problem. The original object was to identify if possible any characteristic absorptions of the silver oxide (Ag_2O) claimed as the black end product by the supporters of the photooxidation theory.

SAMPLE PREPARATION

The titanium dioxide was a commercially available pure grade; the major impurity levels were quoted as, arsenic less than 1 ppm, antimony less than 100 ppm, and lead less than 50 ppm. X-ray examination showed it to be anatase. Electron micrographs revealed a particle size of the order of 0.3 microns. The samples used were obtained from a mixture of 10 g of TiO_2 to 10 ml $0.1\,N$ $AgNO_3$ solution (Analar quality). This was made into a paste, dried at 80°C for 2 days, and ground. These operations were carried out in darkness. The resulting powder was stored in a dark dessicator until required. Experiments were conducted on dry powder and on a paste of the powder and water.

TECHNIQUES

All infrared spectra were measured with a Unicam SP-100 double-beam spectrophotometer. Depending on the spectra investigated two techniques proved to yield useful information: (a) *Attenuated Total Reflectance,* yielding total reflectance spectra closely related to normal absorption spectra; (b) *thin self-supporting discs,* yielding conventional transmission spectra. In the range 375–700 cm^{-1} a KBr prism and polythene filter were used and the slit-width of the instrument was set at 11, giving maximum energy. In the range 650–2150 cm^{-1}, a rock salt prism and grating monochromator were used with the slit-width being set at 11. In the range 2000–8000 cm^{-1} a rock salt prism only was used. The slit was set at 8 giving approximately the same energy as in the range 650–2150 cm^{-1} with slit 11, enabling spectra to be conveniently displayed.

ATTENUATED TOTAL REFLECTANCE (ATR)

The attenuated total reflectance technique first developed by Fahrenfort (*5*) is based on the phenomenon of total reflection of light at the interface between media of differing refractive indices. It is claimed that the resultant spectrum is closely related to the conventional transmission spectrum.

The spectra shown in Figs. 1–5 were taken using a KRS-5 thallium bromide iodide prism. The sampling procedures followed closely the techniques recommended by the manufacturers of the ATR unit.* Dry powders were spread uniformly over the prism face and firmly compacted

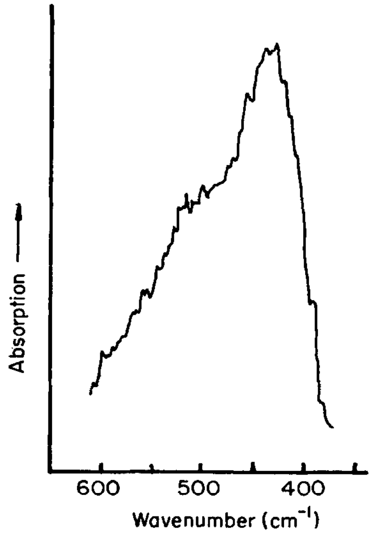

FIG. 1. Attenuated total reflectance spectrum of TiO_2.

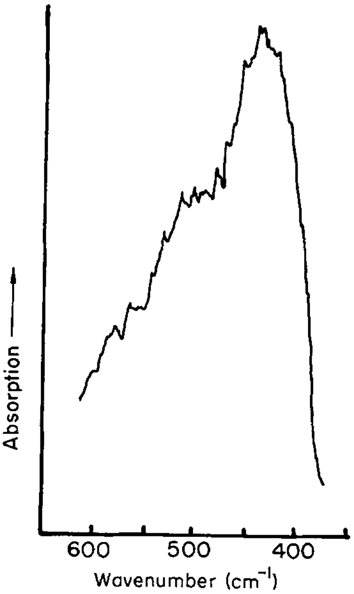

FIG. 2. Attenuated total reflectance spectrum of a $TiO_2/AgNO_3$ solution paste (unexposed).

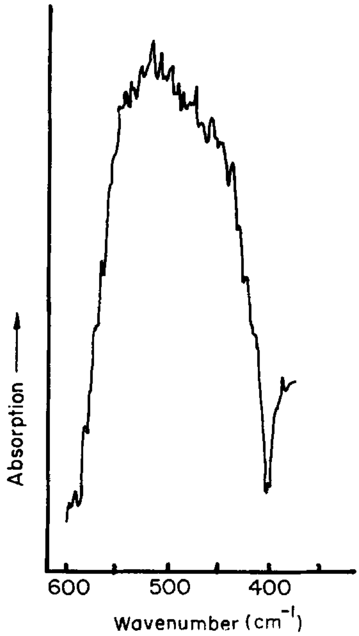

FIG. 3. Attenuated total reflectance spectrum of Ag_2O.

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* Research and Industrial Instruments Company, London, England.

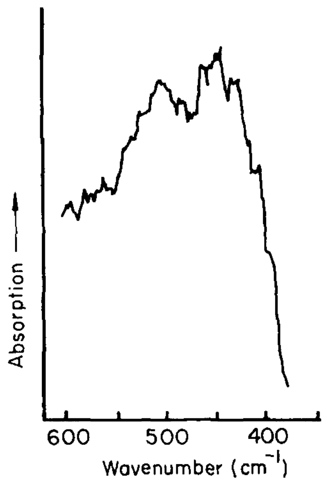

FIG. 4. Attenuated total reflectance spectrum of a 1:1 mixture of TiO_2/Ag_2O.

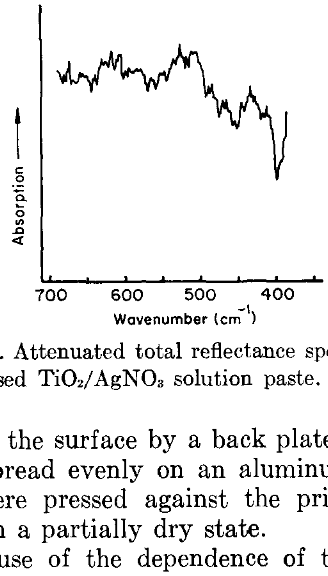

FIG. 5. Attenuated total reflectance spectrum of an exposed $TiO_2/AgNO_3$ solution paste.

against the surface by a back plate. Pastes were spread evenly on an aluminum plate and were pressed against the prism face when in a partially dry state.

Because of the dependence of the total reflection on the angle of incidence of the light upon the prism, this could be adjusted so as to display the characteristic features of the spectrum. The reference beam was appropriately attenuated to obtain a convenient recording. Figures 1–5 were obtained using an angle of 40°.

RESULTS AND INTERPRETATIONS

The broad peaks at about 420 cm^{-1} (Fig. 1) and about 500 cm^{-1} (Fig. 3) correspond, respectively, to the lattice vibrations for TiO_2 and Ag_2O; these observations are in good agreement with known data (*6*). Because of the characteristic broad absorptions of the two substances it was expected that they would not be resolved completely. In order to estimate the type of spectrum anticipated for a mixture an investigation was carried out with a 1:1 by weight mixture. The general broadening of the absorption in the range 375–700 cm^{-1} is shown in Fig. 4. The shoulder at about 500 cm^{-1} shows the behavior that should be anticipated for the mixture.

The titanium dioxide–silver nitrate paste prepared in the dark shows the characteristic absorption of TiO_2 in the range 375–700 cm^{-1} (see Fig. 2). After removing the prism the semidry paste was exposed to ultraviolet irradiation until a thin but dense black surface had been produced, the sample was then replaced against the prism, and the characteristic spectrum of Fig. 5 was obtained. This spectrum shows little resemblance to that of either TiO_2 or Ag_2O. The masking of the features of the TiO_2 spectrum after irradiation can only be explained by assuming that the thin black layer formed at the surface of the sample does not allow the infrared radiation to penetrate to a depth that would bring it in contact with the titanium dioxide. The explanation becomes quite probable when consideration is given to the optics of the ATR system and allowance is made for the interchange of infrared energy being largely restricted to the prism–sample interface. If, however, it is accepted that the thin layer of black material does not allow any appreciable interaction of the radiation with the TiO_2, it follows that it must itself interact with the incident radiation. Examining the spectrum and noting that a Ag_2O absorption should show up at 500 cm^{-1}, it is deduced that either such an absorption does not exist or is not strong enough to reveal itself. The latter possibility has been invalidated by the above argument.

TRANSMISSION SPECTRA

Because of the high scattering power of TiO_2 it proved very difficult to transmit enough energy to the detector with most of the more conventional sampling techniques. However, transmission spectra were eventually obtained through thin self-supporting discs of the sample.

In order to be able to transmit energy through the discs it was necessary to make them extremely thin. About 50 mg of the powder was weighed and made into a thin 16-mm diameter disc using a paper ring for support, giving an areal density of about 20 mg/cm^2. The operation was carried out in a KBr disc die. A pressure of about 2000 lb/sq inch was applied to make the discs; they were very fragile, and extreme care had to be exercised during the operation.

With this technique it was possible to transmit enough energy through the disc to actuate the Golay detector of the instrument. The spectra shown in Figs. 6 and 7

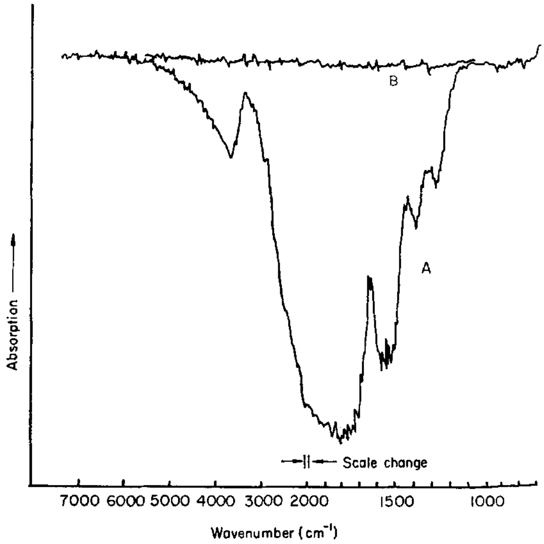

FIG. 6. A. Transmission spectrum of gauze-compensated *unexposed* dry $TiO_2/AgNO_3$ disc. B. Transmission spectrum of gauze-compensated *exposed* $TiO_2/AgNO_3$ disc.

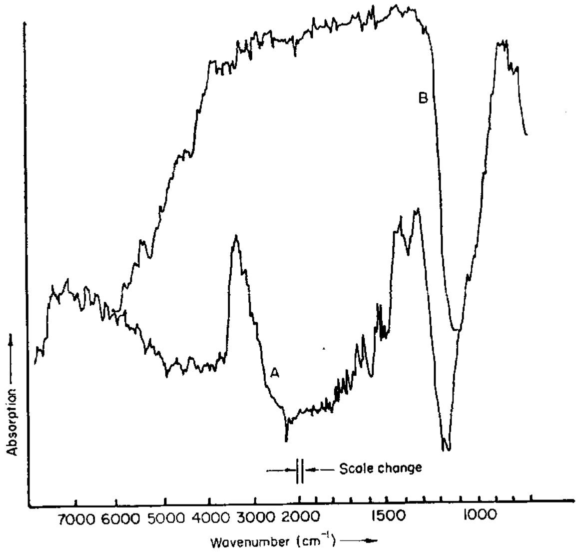

FIG. 7. A. Transmission spectrum of TiO_2 blank disc-compensated *unexposed* dry $TiO_2/AgNO_3$ disc. B. Transmission spectrum of TiO_2 blank disc-compensated *exposed* $TiO_2/AgNO_3$ disc.

were measured with a heavily damped pen and a slow scanning speed of about 5 sec/wave number.

It proved impossible to transmit enough energy in the lower range 375 to 650 cm^{-1} in view of the comparatively smaller energy output of the instrument in that region. In the 650 to 8000 cm^{-1} region, compensation of the reference beam was achieved either by placing metal gauzes or blank pigment discs. Blank pigment discs carefully compensated have the obvious advantage of eliminating the effective absorptions of the titanium dioxide. A study can, therefore, be made of the changes due to ultraviolet irradiation. Good compensation is, however, difficult, especially when dealing with thin and fragile discs.

RESULTS AND INTERPRETATION

Figure 6A shows the spectrum of a titanium dioxide–silver nitrate powder disc compensated by metal gauze before exposure to ultraviolet irradiation. There is a characteristic valley between 1100 and 5000 cm^{-1}. The peaks at about 1300 cm^{-1} and about 1400 cm^{-1} can be identified as NO_3 absorptions. The absorptions at about 1650 and 3300 cm^{-1} are due to the presence of moisture (*8*). Figure 7A shows the same region of the spectrum, the reference beam being compensated with a blank TiO_2 disc. After exposing the samples to prolonged ultraviolet irradiation, in moist conditions to accelerate the darkening process, the valley disappears in the gauze-compensated case and is replaced by a continuous absorption between 650 and 8000 cm^{-1} (Fig. 6B), while in the TiO_2 blank-compensated sample a strong absorption between 1100 and 5000 cm^{-1} is produced (Fig. 7B). Comparing the spectra before and after irradiation it becomes apparent that a new wide infrared absorption has emerged between 1100 cm^{-1} (0.136 eV) and about 5000 cm^{-1} (0.62 eV). It has been established that it does not appear even after considerable irradiation of titanium dioxide without the silver nitrate, in normal laboratory environments. It seems therefore that we must associate the absorption band either with only the black compound formed on irradiation or with some interaction brought about by the formation of the black compound at the surface of the titanium dioxide.

For the purpose of discussing the probable nature of this absorption, it will be assumed that the blackening observed is due to the formation of colloidal silver; this has been identified by X-ray analysis (*13*). There is no reason to suggest that the observed absorption band can be associated with colloidal silver particles alone. In fact silver is known to be a good infrared reflector. The possibility that such an absorption can be linked to the scattering properties of the small silver particles is excluded because this would be a gradual effect that would neither justify the sharp absorption edge at 0.136 eV nor the width of the band. This width suggests an electronic absorption which can easily be thought to be associated with a continuous distribution of energy states from 0.136 eV to about 0.62 eV.

In connection with this absorption it may be helpful to recall that a similar type of band has been observed by Filimonov (*9*). This author has established the emergence of an infrared absorption at about 3000 cm^{-1} when finely dispersed titanium dioxide samples were irradiated with light in the region of intrinsic absorption in a vacuum. The absorption persisted after the irradiation, provided the vacuum was maintained. Admission of air or oxygen to the sample quickly restored the transmittance of the samples to their original magnitude. Filimonov interpreted the observed bands in terms of donor impurity levels at the surface. The absorption is thought of as due either to electronic transitions from the donor levels to the conduction band or by transitions within the conduction band. Adsorption of oxygen results in the trapping of these electrons by the oxygen, with the consequent elimination of the absorption band.

A model based on the same general principles can be proposed by postulating trapping levels localizing charge carriers at the surface. This will be possible considering the structurally imperfect nature of defects associated with the surface. On illuminating the crystals the number of electrons available to be localized increases. Oxygen can be thought to be associated with electrons trapped at such imperfect centers, the oxygen thereby becoming adsorbed. Because of the high electron affinity of oxygen, it is reasonable to suggest (*10*) that the electron trap is modified, probably to a deep-lying level. Desorption of oxygen and creation of charge carriers by irradiation is likely to increase the concentration of the electrons trapped at such imperfect centers. Thus the observed absorption band is created by localized electronic energy states below the conduction band.

Concentrating on the postulated system of a surface trap and localized electron it is seen that this will constitute an excess negative charge which may be able to attract a silver ion from its environment. A silver ion associated with the trapped electron will look very much like a silver atom and in turn is likely to promote the formation of further atoms. This type of mechanism proposed for formation of groups of silver atoms is very similar to those considered in connection with the photolysis of silver in silver halides (*11*).

A further discussion of possible mechanisms producing the photochemical reaction has been given elsewhere (*13*). The system with which we are concerned here consists of a surface trap–electron–silver system as compared to Filimonov's (*9*) surface trap–electron–oxygen system. Following the arguments of Volkenstein on the electronic theory of catalysis (*12*) silver or oxygen are associated with the surface via the trapped electron. The silver atom has a considerably smaller electron affinity than oxygen and is therefore not very likely to modify the electronic state to a large extent. The infrared band can, therefore, be attributed to excitation of electrons from this system to the conduction bands. It may be argued that excitation of the trapped electron destroys the silver atom. This, however, is of secondary importance because the atom at the center may always have combined with other silver ions to form the groups mentioned above. Also a process of recombination for the excited electron with the trapping system is possible. This way of interpreting the infrared absorption leads us to visualize "surface centers" that are responsible for the observed photochemical change.

Accepting such a picture, electronic energy levels can be assigned to the system of an imperfection–localized electron–silver ranging from 0.136 eV down to about 0.62 eV below the conduction band. The shape of the absorption indicates that there is a sharp rise in the concentration of these levels at 0.136 eV, remaining constant at 0.62 eV where it gradually decreases, giving rise to the observed tail down to 0.98 eV, the limit of the instrument.

ACKNOWLEDGMENT

The authors wish to thank Dr. R. S. Theobald for his help in developing the infrared techniques described here.

REFERENCES

1. SBROLLI, W., AND BERTOTTI, E., *Ann. Chim. (Rome)* **49,** 1143 (1959).

2. GEOTZ, A., AND INN, E. C. Y., *Rev. Mod. Phys.* **20,** 131 (1948).

3. FÖRLAND, K. S., *Intern. Symp. Reactivity of Solids, Gothenburg, 1952.*

4. CLARK, W. C., AND VONDJIDIS, A. G., *Nature* **203,** 635 (1964).

5. FAHRENFORT, J., *Spectrochim. Acta* **17,** 694 (1961).

6. LAWSON, K. E., "Infra-red Absorption of Inorganic Substances," Chapman and Hall, London, 1961.

7. SMITH, I. T., Paint Research Station, Teddington, England. Private communication.

8. PIMENTAL, G. C., AND MCCLELLAN, A. L., "The Hydrogen Bond." Freeman, San Francisco, 1960.

9. FILIMONOV, V. N., *Opt. Spektry.* **5,** 709 (1958).

10. VOLKENSTEIN, F. F., *Advan. Catalysis* **12,** 187 (1960).

11. MITCHELL, J. W., "Chemistry of the Solid State." Butterworths, London, 1955.

12. VOLKENSTEIN, F. F., "The Electronic Theory of Catalysis on Semiconductors." Pergamon, New York, 1963.

13. VONDJIDIS, A. G., M.Sc. thesis, London, 1964; Bristol College of Science and Technology Research Report, 1964.