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Electron Spin Resonance Studies of the Surface Chemistry of Rutile

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Abstract: The electron spin resonance spectra of precipitated rutile powders dried in air and subjected to various gas and vacuum treatments have been studied. Two signals (both triplets) obtained with the sample dried in air have been attributed to the presence of O_2^+ on the surface. Outgassing at higher temperatures leads to the disappearance of the two triplets and appearance of a new asymmetric signal, due to formation of Ti(III) ions. Experiments also indicate that these Ti(III) ions do not assume interstitial positions but are present at regular lattice positions. If outgassing of the sample is done at 500° for 3 hr the Ti(III) ions produced are close to the surface and are completely oxidized to Ti(IV) at room temperature on admission of oxygen. However, use of hydrogen gas for reducing TiO_2 leads to formation of Ti(III) ions even in the bulk of the material. Finally, outgassing of a sample exposed to oxygen at room temperature following an initial high-temperature outgassing yields a new signal (doublet) which is identified as the O_2^- species at the surface.

Properties of rutile single crystals have been studied by electron paramagnetic resonance techniques by Chester, Gerritsen, and others.[2-5] In these investigations oxygen-deficient single crystals prepared by outgassing and treatment with hydrogen and transition element doped single crystals of rutile were used. A study of the defect structure of single-crystal rutile is of fundamental importance; however, it is not helpful in understanding the catalytic and other surface properties of rutile powders where the influence of the surface defects generally predominates over that due to impurities and defects in the bulk of the material. The usefulness of epr techniques in studying the properties of various powdered material has been demonstrated by Burns[6] and by Walters and Estle.[7] Kazanskii, *et al.*,[8] have recently utilized this technique to elucidate the nature of the adsorbed species on a sample of anatase.

In the present investigation some important observations have been made which should prove useful in understanding the surface properties of rutile powders and which are not encountered in studies on single crystals.

Experimental Section

A. Materials. The rutile sample was furnished by the National Lead Co. Titanium Division, South Amboy, N. J. It was prepared by addition of titanium tetrachloride to aqueous ammonia. After heating the mixture for 30 min to 85° and cooling to 25°, the pH was adjusted to 6.5. The mixture was then filtered; the residue was warmed and then dried at 500° in air for 2 hr. The surface area was 40 m^2/g. It was determined by the BET method with nitrogen and using the value of 16.2 A^2 for the area of a nitrogen molecule. An X-ray analysis showed only the presence of crystalline rutile. The nature of the amorphous material which constituted the bulk of the samples was not treated by the X-ray method. The impurities as determined by emission spectroscopy were (in

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(1) (a) Frankford Arsenal; (b) Princeton University.

(2) (a) P. F. Chester, *Bull. Am. Phys. Soc.*, **5**, 72 (1960); (b) *J. Appl. Phys.*, **32**, 866 (1961); (c) *ibid.*, **32**, 2233 (1961).

(3) H. J., Gerritsen, S. E., Harrison, H. R. Lewis, and J. P. Wittke, *Phys. Rev. Letters*, **2**, 153 (1959).

(4) H. J. Gerritsen and H. R. Lewis, *Phys. Rev.*, **119**, 1010 (1960).

(5) E. Yamaka and A. G. Barnes, *ibid.*, **135**, A144 (1964).

(6) G. Burns, *J. Appl. Phys.*, **32**, 2048 (1961).

(7) G. K. Walters and T. L. Estle, *ibid.*, **32**, 1854 (1961).

(8) V. B. Kazanskii, D. V. Nikitina, G. B. Pariskhi, and V. F. Kieselev, *Dokl. Akad. Nauk SSSR*, **151**, 369 (1963).

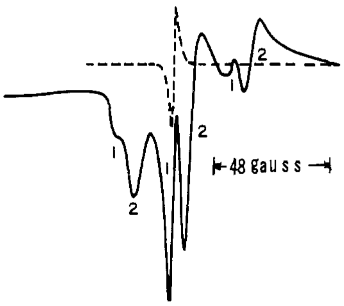

FIG. 1

Figure 1. Esr (x band) spectrum of rutile dried at 500° for 2 hr and outgassed at room temperature for 24 hr (dotted line, DPPH, $g = 2.0036$).

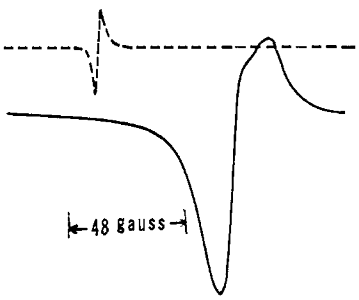

Figure 2. Esr (x band) spectrum of high-temperature vacuum outgassed rutile (dotted line, DPPH, $g = 2.0036$).

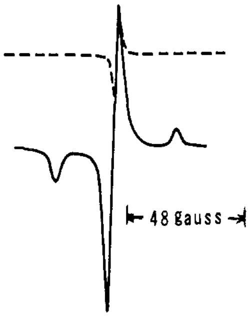

Figure 3. Esr (x band) spectrum of rutile treated in oxygen at 500° for 3 hr (dotted line, DPPH, $g = 2.0036$).

ppm) Si <350, Fe <14, Al <10, Mo <10, V <3, Cu <1, Mg <1, and Mn <0.5.[9]

Oxygen (General Dynamics Corp.) was dried over silica gel. Hydrogen and deuterium (CP grade, Matheson Co.) were passed through a deoxo unit prior to use. Nitric oxide and nitrogen dioxide (CP grade, Matheson Co.) were used directly from the tank.

B. Apparatus. The outgassing and gas treatment of the samples were carried out in a gas-handling apparatus consisting of a Cenco Hyvac pump, a multistage oil diffusion pump, and an ion gauge. During the degassing process the samples were protected from oil vapors from the diffusion pump by liquid nitrogen traps. A vacuum of 10^{-8} torr could be attained in this system.

The sample tubes were made of Vycor brand quartz (5 mm o.d. and 4 mm i.d.). The tubing was annealed in an oxypropane flame for 10 min to remove any esr signal. Approximately 25 mg (2-cm length) of rutile as taken in the tube for experiment, and the quartz tube was attached to the vacuum system by a quartz–Pyrex graded seal.

For the 9.5-kMc/sec measurements, a Varian spectrometer (Model V4500) with a TE_{104} mode dual cavity was used. The magnetic field was controlled by a Fieldial regulator V-FR-2100. For the 35.5-kMc/sec measurements a Varian spectrometer (Model V4561) was used.

Measurements at 4.2 and 1.6°K using 9.5-kMc/sec frequency were carried out with standard equipment modified for liquid helium work. The modulation was 400 cps and a standard Varian-type narrow-band amplifier was used in the detection system.

1,1-Diphenylpicrylhydrazyl (DPPH) was used as a standard for g measurements.[10] Unless otherwise stated all measurements were carried out at liquid nitrogen temperatures.

Results

The standard sample was the material received from the supplier, heated to 500° for 2 hr, cooled in air, and then outgassed at room temperature for 24 hr. The sample showed a complex esr spectrum (Figure 1) consisting of two sets of lines, no. 1 and 2. Each set has a triplet with a sharp symmetrical line and two satellites at an equal distance of 34 gauss from the central line, asymmetric in shape and differing in phase from each other. The central line had an intensity ten times greater than that of the satellites. The g value of the central line for the no. 1 set was 2.002 while that for the no. 2 set was 1.999. The width of the central line was about 5 gauss.

The no. 1 set saturated more readily with microwave power than the no. 2 set. Thus, using a modulation amplitude of 4.5 gauss at power levels less than 40 mw triplet no. 1 was sharp and well defined while the no. 2 set was weak. The intensity of both sets increased with power. At 220-mw power the signal due to triplet no. 1 showed saturation while that due to triplet no. 2 did not, so that triplet no. 2 dominated the spectrum.

Outgassing. Outgassing the standard sample in a vacuum system at room temperature or at 200° produced no significant changes in the nature of the esr spectrum.

Outgassing at 400° produced a new signal, no. 3, at $g_{av} = 1.95$ which was 29.8 gauss broad (Figure 2). This signal was anisotropic with $g = 1.959$ and 1.946. Triplets no. 1 and 2 were also observed. These esr characteristics were unchanged when the sample was investigated at 35.5 kMc/sec. This confirmed the assignment of g values. The sample was slightly discolored.

Outgassing the sample at 500° increased the signal at $g_{av} = 1.95$ while the two triplets no. 1 and 2 became very weak. The color of the sample was bluish gray. Addition of oxygen at room temperature to a sample that had been degassed at 500° produced a large increase in the intensity of triplet no. 1 (Figure 3). The broad band no. 3 at $g = 1.95$ disappeared. There was no evidence of triplet no. 2. If this sample was degassed at room temperature, a new line, no. 4 (Figure 4), was produced at the low-frequency side of triplet no. 1 distorting the low-field satellite of triplet no. 1.

Readmission of oxygen removed the no. 4 line and restored triplet no. 1 to its original symmetrical shape. The process of forming the no. 4 line and removing it by admission and pumping off of oxygen was reproducible at all temperatures from that of liquid nitrogen to 150°. Outgassing above 400° produced only the broad signal no. 3 at $g = 1.95$. All the above esr measurements were made at the temperature of liquid nitrogen. If the measurements were made at room temperature, signal no. 3 at $g = 1.95$ became very broad (80-gauss width) and consequently was difficult to study in detail because

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(9) Impurity analyses were furnished by the courtesy of Dr. K. Herrington of the National Lead Co.

(10) C. H. Townes and J. Turkevich, *Phys. Rev.*, **148**, 11 (1950).

of its low intensity. If the measurement was carried out at 4.2°K, signal no. 3 became sharp, strong, and more symmetrical. Its width was 28.1 gauss at 4.2°K and 21.9 gauss at 1.6°K. From the variation of the width with temperature and assuming a direct relaxation process, a spin–lattice relaxation was found approximately to be 3.5×10^{-8} sec at 4.2°K and a spin–spin relaxation of 2.0×10^{-8} sec.

If the standard sample was pretreated with oxygen at 500° for 3 hr before outgassing, the same set of phenomena was observed. However, the outgassing treatment had to be more drastic (higher temperature and longer time).

Oxygen Treatment. Addition of oxygen to the standard sample at room temperature produced an enhancement of triplet no. 1 and apparently suppressed triplet no. 2.

Treatment with oxygen at 500° for 3 hr and cooling in oxygen suppressed triplet no. 2, and only triplet no. 1 was observed (Figure 3). The width of the central line was again 5 gauss, and the two satellites were symmetrically located 33 gauss on either side of the central line and had opposite phase. The ratio of heights of the central line to that of either satellite was approximately 10. Power saturation studies showed that in samples so treated with oxygen, triplet no. 1 did not saturate. Triplet no. 2 could not be observed at the highest microwave power of 220 mw that was available. If the sample was evacuated at room temperature, both triplets no. 1 and 2 were observed and the power *vs.* signal intensity revealed the same behavior of the signals as those of the standard sample that had not been treated with oxygen at 500°.

Examination at 35.5 kMc/sec showed the triplet with the same g values. Treatment with oxygen at 600° and above eliminated both the no. 1 and 2 triplets.

Hydrogen Treatment. No substantial change in the esr spectrum of the standard sample was observed after treatment up to 300° for 3 hr in the flow of hydrogen gas.

Treatment at 500° for 3 hr reduced signal no. 1 by a factor of 3 while it sharpened the central peak to 4 gauss. Signal no. 2 was not affected.

Treatment at 600° for 1 hr decreased the no. 1 and 2 peaks and produced the no. 3 peak at $g = 1.95$. The sample was discolored. If this sample was treated with oxygen at room temperature, signal no. 1 reappeared, but only part of signal no. 3 at $g = 1.95$ disappeared. This was undoubtedly due to the fact that some of the defects responsible for the $g = 1.95$ signal were located in the bulk of the material where they were produced by hydrogen gas treatment and could not be removed by the oxygen gas.

The results with deuterium treatment were the same as those produced by the hydrogen. No new signals were observed and the spectra obtained had the same characteristics as those obtained with hydrogen treatment.

Treatment with Oxides of Nitrogen. When the standard samples after outgassing at 500° for 3 hr were exposed to nitrogen dioxide, the no. 3 peak at $g = 1.95$ disappeared and triplet no. 1 appeared. The discoloration was removed. The nitrogen dioxide treatment also caused the complete disappearance of signal no. 3 produced by previous hydrogen treatment. As previously pointed out this did not lose its intensity completely on subsequent oxygen treatment.

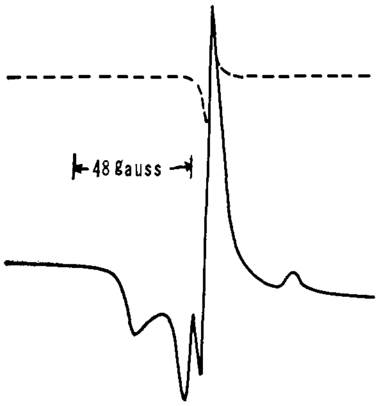

Figure 4. Esr (x band) spectrum of rutile initially outgassed at 500° and reoutgassed at room temperature following oxygen addition at room temperature.

Nitric oxide had the same effect on the esr spectrum of outgassed rutile as nitrogen dioxide.

Discussion

The esr spectra that have been observed are not due to a carbonaceous impurity because signals no. 1 and 2 are triplets and no. 4 is anisotropic. Signals due to carbon are usually symmetric. The g value of 1.959 for no. 3 eliminates this signal as a carbon signal since the latter occurs near $g = 2$. Furthermore any carbon present should be removed by treatment with oxygen at 500°. In the case of the samples studied signal no. 1 was enhanced by such a treatment.

The signals observed are not due to a hydrogen-containing species since their number does not change with treatment of the specimen with deuterium. The presence of a hyperfine structure should also have been revealed by comparison of results obtained with 9.5 *vs.* 35.5 kMc/sec.

The esr signals are not due to electrons or holes in traps greater than 600 cal since γ irradiation of the sample does not give an esr signal at room temperature. Therefore they are not true F centers.

Signal at $g = 1.959$. The esr signal no. 3 at $g = 1.959$ is assigned to the Ti(III) ion. Thus Chester[2b] and Gerritsen[11] have obtained in oxygen-deficient rutile a signal at $g_z = 1.940$, $g_x = 1.972$, and $g_y = 1.975$ which they attributed to the Ti(III) ion at liquid helium temperatures. Since the signal was not observed at room temperature, the spin-orbit coupling must relax the signal too rapidly for observation. The crystal field must be lower than cubic or axial. The presence of an asymmetric signal at liquid nitrogen temperature with $g_\perp = 1.959$ and $g_\parallel = 1.946$, confirmed by the proper frequency dependence of the signals, indicates that the crystal field surrounding the Ti(III) is tetragonal.

The g values for a tetragonal crystal field are given by

$$g_\parallel = 2.0023 - (2\lambda/\delta)$$

$$g_\perp = 2.0023 - (8\lambda/\Delta)$$

If we use $\lambda = 154\ \text{cm}^{-1}$ for titanium we obtained $\Delta =$

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(11) H. J. Gerritsen in "Paramagnetic Resonance," Vol. 1, W. Low, Ed., Academic Press Inc., New York, N. Y., 1963, pp 3–12.

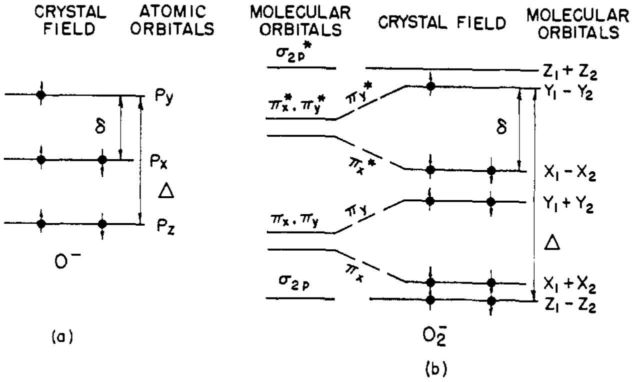

FIG. 5

Figure 5. (a) Electronic energy levels of O^-. (b) Electronic energy levels of O_2^-.

22,000 cm^{-1} and $\delta = 7200$ cm^{-1}. There is a wide variation in the values reported for the crystal-field parameters for Ti(III) compounds.[12] Thus for $KTi(C_2O_4)_2 \cdot 2H_2O$ the values of Δ and δ are 8800 and 7700 cm^{-1}, while for $OsTi(SO_4)_2 \cdot H_2O$ the values are 396 and 1430 cm^{-1}.

The crystal structure of rutile reveals the locale of the strong tetragonal crystal field. In a perfect lattice, there is only one type of Ti atom and it is situated in a environment of tetragonal symmetry with four oxygen atoms at distance of 1.944 A and two oxygen atoms at a distance of 1.988 A from the titanium atom.[13] The formation of Ti(III) can take place either by removal or displacement of one or both of the two axial oxygens at 1.988 A from the titanium atom, the removal or displacement of one or more of the four planar oxygen at 1.944 A, or by the titanium slipping into an interstitial position. The first possibility, the removal or displacement of one or two of the axial oxygen atoms, will give us the required tetragonal field. The other two possibilities would produce a crystal field of symmetry lower than tetragonal. The signal would then have three components g_x, g_y, and g_z. This we did not observe. However, a crystal field of symmetry lower than tetragonal has been observed by Chester[2b] in single crystals.

At liquid helium the line became more symmetric and narrower. The crystal-field parameter δ must become smaller approaching the value $\Delta/4$ due to changes in the lattice parameters with temperature. Most of the line width must come from spin–lattice relaxation as evident from the narrowing of the line from liquid nitrogen temperature to those of liquid helium. The Ti(III) ions must be separated from each other by a distance greater than 6 A. Otherwise the broadening would contribute to the line width to make the latter greater than the observed 30 gauss.

Triplet no. 1 represents a signal from the same species with $g_x = 2.024$, $g_y = 2.002$, and $g_y = 1.980$. This is confirmed by measurements at 35.5 kMc/sec which give the same g values and also by power saturation studies which showed that the three signals had the same saturation characteristics. The two satellites are symmetrically placed about the central peak, indicating that the paramagnetic species is located in an orthorhombic environment.

An environment of higher symmetry would produce two g values, $g_\perp$ and $g_\parallel$, or even one g value. The fact that two of the g values are greater than 2.0023, the value of the free electron, indicates that the spin-orbit constant is negative and that we are dealing with a paramagnetic species in which the p electrons or the d electrons are in shells which are more than half-filled. This eliminates titanium as the source of the triplet no. 1 and suggests that this triplet is due to oxygen.

If it is a negatively charged oxygen atom, O^-, then the p hole will be split by the crystal field into three levels (Figure 5a) with the following g values.

$$g_x = 2.0023 - \frac{2\lambda}{E_y - E_z} = 2.0023 - \frac{2\lambda}{\Delta}$$

$$g_y = 2.0023$$

$$g_z = 2.0023 - \frac{2\lambda}{E_y - E_x} = 2.0023 - \frac{2\lambda}{\delta}$$

Since it is a hole, its λ is negative. Therefore two of the g values are greater than 2.0023 and the third equal to 2.0023, whereas only one of the observed values is greater than 2.0023 and the other is less than 2.0023, while the third g value is 2.0023. This cannot be explained by the presence of a temperature-independent paramagnetism since the same set of g values is obtained by measurement at 9.5 kMc as at 35.5 kMc. This also indicates the absence of a local magnetic field which might produce a uniform shift in all g values. The signal is not observed at 4.2 and 1.6°K and is not broadened by gaseous oxygen. The latter fact would eliminate O_2^- which we find in other systems is broadened by gaseous O_2.

Furthermore, an analysis to the second order of the g values for O_2^- cannot account for the observed g values (Figure 5b).[14] This gives the following values for $\Delta \gg \delta \gg \lambda$

$$g_y = 2.0023 - \frac{\lambda^2}{\delta^2} + \frac{\lambda^2}{\Delta\delta}$$

$$g_x = 2.0023 + \frac{2\lambda}{\Delta} - \frac{\lambda^2}{\delta^2} - \frac{\lambda^2}{\Delta\delta}$$

$$g_z = 2.0023 + \frac{2\lambda}{\delta}$$

Kanzig and Cohen's[14] notations Δ and E correspond to our notation δ and Δ, respectively, and λ is the effective spin–orbit splitting of the molecule O_2^-. Having 108 cm^{-1} as the value of λ for oxygen, we see that an experimental situation may arise such that g_x can be less than 2 when g_y and g_z are greater than 2. However a quantitative analysis of our signals using these equations leads to an internal inconsistency. If we set for g_x the experimental value of 1.98, we obtain for δ a value of 700 cm^{-1}, but this requires that g_z be set to 2.02 which leads us to a δ value of 10,000 cm^{-1}. This discrepancy of a factor of 14 in the δ value obtained from the equations used to interpret the O_2^- signal leads us to the conclusion that the observed triplet no. 1 cannot be due to the O_2^- species.

We have assigned this signal to O_2^+ in rutile lattice for reasons to be given below. We have adopted for

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[12] G. E. Pake, "Paramagnetic Resonance," W. A. Benjamin Inc., New York, N. Y., 1962, p 62.

[13] A. Von Hippel, *et al.*, *J. Phys. Chem. Solids*, **23**, 779 (1962).

[14] W. Kanzig and M. H. Cohen, *Phys. Rev. Letters*, **3**, 509 (1959).

the theoretical discussion of our system the treatment by Schlichter[15] for the Cl_2^- color center. To the first order the g values are given by (Figure 6) (with λ negative)

$$g_x = 1.98 - 2.0023 + (\lambda/\Delta)$$

$$g_y = 2.0023$$

$$g_z = 2.02 = 2.0023 - (\lambda/\delta)$$

where λ is the spin-orbit coupling constant for oxygen which we take to be 108 cm^{-1}. δ and Δ are the difference in energy between the state of the unpaired spin and the excited and lower states which can couple with the former. For O_2^+ it is the energy separation between the state of unpaired spin characterized by the molecular orbital π_y^* and the lowest state σ_{2p}, on the one hand, and π_x^*, on the other hand (Figure 6). Using the above equations for g values we obtain $\delta = \Delta = 5000\ cm^{-1}$.

The unusual nature of the O_2^+ species requires some comment. The ionization constant for the oxygen atom is 13.55 ev, while for the oxygen molecule it is 12.8 ev. However, titanium dioxide has a very large dielectric constant which for crystalline rutile varies from 86 to 170 Debye units depending on the orientation of the crystal. In the interior of the crystal, the ionization energy will vary inversely as the square of the dielectric constant[16] and this circumstance would lower the ionization of O or O_2 to a small fraction of an electron volt. The effect on the surface will not be as great, but certainly might be sufficiently appreciable to make the ionization of O or O_2 energetically favorable.

Triplet no. 2 ($g_x = 1.977$, $g_y = 1.999$, $g_z = 2.022$) with the central line shifted to $g_y = 1.999$ (a shift of 4.5 gauss with respect to the central line of triplet no. 1) has the same structure as triplet no. 1. Its behavior is different in two respects. It does not saturate with microwave power as readily as triplet no. 1. Its intensity decreases on admission of oxygen at high temperature. It is not affected as readily as the triplet no. 1 by hydrogen gas, and it is not produced by treatment with NO.

This triplet no. 2 was assigned to the O_2^+ in the lattice of anatase, which is invariably present in small amounts in rutile. The high intensity of this triplet at higher power levels is due to its relatively short spin-lattice relaxation time. The fact that it was not observed in the standard sample in the presence of oxygen could result from line broadening or its disappearance in the wings of the enhanced signal of triplet no. 1. The enhancement of triplet no. 1 was accompanied by considerable broadening of the wings of the central signal without changing its peak-to-peak width. That the disappearance of triplet no. 2 may not have resulted from line broadening can be reasoned as follows: triplet no. 2 has a much shorter spin-lattice relaxation time than triplet no. 1; therefore, the presence of oxygen should have a less broadening effect on triplet no. 2. Since there was no broadening of triplet no. 1, it can be concluded that triplet no. 2 was unaffected. It possibly disappeared into the wings of triplet no. 1.

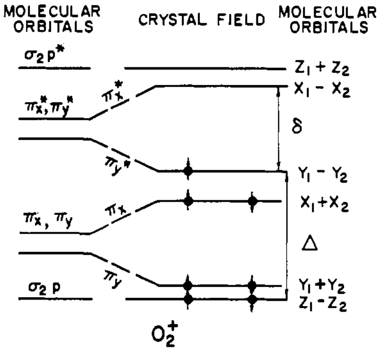

FIG. 6

Figure 6. Electronic energy levels of O_2^+.

It is possible to explain the difference between the two triplets. It is based on a difference in crystal structure; triplet no. 1 is due to O_2^+ adsorbed on a rutile lattice, and triplet no. 2 is due to the same species adsorbed on a small amount of anatase which is transformed into rutile on further heat treatment. This difference in lattice characteristics of these two forms of TiO_2 might account for the small but uniform shift in their g values. And this might also account for the difference of at least one order of magnitude in the relaxation times of the two signals and the difference in their behavior on treatment with oxygen, hydrogen, and nitric oxide. It is the lattice vibrations that modulate the spin-orbit interaction, which is the mechanism of the spin-lattice relaxation. The difference in crystal-lattice characteristics can have pronounced effect on the relaxation times.

Signal no. 4 (Figure 4) can be partially resolved from triplet no. 1 since it is suppressed by the addition of gaseous and reappears on evacuation. Its g values as obtained using 35.5 kMc/sec are 2.0106 and 2.0216. The species responsible for this signal must be O_2^-. Its behavior with gaseous oxygen suggests that the decrease in intensity of the signal is due to the exchange reaction

$$O_2^- + O_2 \longrightarrow O_2 + O_2^-$$

Kasai[17] reported for O_2^- in barium zeolite g values of 2.0046, 2.0090, and 2.057, and for sodium zeolite 2.0016, 2.0066, and 2.113. Fujita[18] finds for O_2^- on zinc oxide g = 2.0133, 2.010, and 2.04, and for O_2^- on porous silica produced by ultraviolet irradiation of H_2O_2, g = 2.0023, 2.0144, and 2.0302. It is quite possible that in our case the O_2^- species on the surface of TiO_2 has three values of g with the third value coinciding with 2.002, the main line of triplet signal no. 1.

The mechanism for the formation of the various species detected by the esr is as follows. On evacuation at high temperature the TiO_2 loses oxygen from the surface producing a Ti^{4+} which dissociates

$$Ti^{4+} \longrightarrow Ti^{3+} + \text{hole}$$

The Ti(III) gives the signal at g = 1.959. The hole is

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(15) C. P. Schlichter, "Principles of Magnetic Resonance," Harper & Row, Publishers, New York, N. Y., 1963, p 195.

(16) C. Kittel, "Introduction to Solid State Physics," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1956, p 356.

(17) P. H. Kasai, *J. Chem. Phys.*, **43**, 3322 (1965).

(18) Y. Fujita and J. Turkevich, unpublished work.

not seen in esr. On admission of oxygen

$$Ti^{3+} + O_2 \longrightarrow Ti^{4+} + O_2^-$$

while

$$O_2 + \text{hole} \longrightarrow O_2^+$$

Acknowledgment. The authors acknowledge with gratitude the assistance of Howard C. Guertler and Donald Isagan with the experimental work. The work at Princeton University was supported by the U. S. Atomic Energy Commission.

An Electron Spin Resonance Study of Tetra- and Pentacyanopyridine Anion Radicals[1a]

M. Thomas Jones[1b]

Contribution No. 1220 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware. *Received June 16, 1966*

Abstract: The anion radicals of tetra- and pentacyanopyridine have been studied by esr. The nitrogen hyperfine splittings have been interpreted in terms of the relationship between π-electron spin densities and ^{14}N coupling constants based upon the Karplus–Fraenkel treatment of ^{13}C. Moreover, the relevance of these results to the question of whether a permanent Jahn–Teller distortion has occurred in the radical prepared by reduction of tricyano-*s*-triazine is considered. These results plus calculations of the expected nitrogen hyperfine splittings from the anion radical of tricyano-*s*-triazine suggest that a permanent Jahn–Teller distortion does not adequately explain the experimental observations.

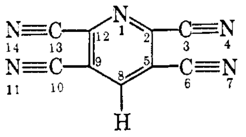
The isotropic nitrogen hyperfine splittings in radical systems continue to be of interest[2,3] as is the rationalization of such splittings in terms of the relationship between π-electron spin densities and ^{14}N coupling constants based on the Karplus–Fraenkel[4] treatment of ^{13}C. The anion radicals of tetracyanopyridine and pentacyanopyridine have been studied by esr techniques for these reasons and as an aid in determining whether the radical observed upon reduction of tricyano-*s*-triazine is a manifestation of a permanent Jahn–Teller distortion.[5]

Experimental Details

The anion radicals were prepared by reduction of tetra- and pentacyanopyridine with potassium metal mirrors in 1,2-dimethoxyethane under vacuum by standard techniques. The esr spectrometer was a Varian V-4502 equipped with a dual cavity, a 12-in. electromagnet, and a flux stabilizer to scan the magnetic field.

The spectra were recorded at room temperature. However, a few low-temperature experiments indicated possible ion-pairing phenomena. The anion radicals of both tetra- and pentacyanopyridine were stable for long periods of time under the experimental conditions.

The following numbering system was used in reporting hyperfine splittings and in the calculations.



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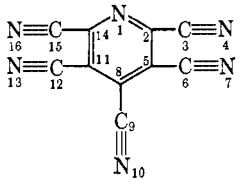

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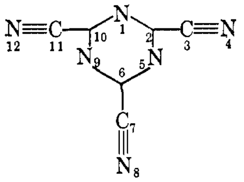

iii

The two compounds 2,3,5,6-tetracyanopyridine (mp 203–204°) and pentacyanopyridine (280–300° dec) were synthesized by Wallenfels and Neuman.[6]

Experimental Results

The esr spectra of $\sim 3 \times 10^{-4}$ *M* solutions of tetra- and pentacyanopyridine anion radicals consist of 13 and 11 lines, respectively. The line widths are rather large, ~0.3 oersted. The assignments of the hyperfine splittings, which are given in Table I, are unambiguous. However, it is gratifying and significant for later discussion regarding triacyano-*s*-triazine that these assignments are in reasonable agreement with the McLachlan[7]-modified MO calculations. The results of the calculations, which will be discussed later, are shown in Tables II and III.

Results of the Cyanopyridine Calculations

A. MO Calculations. Both simple Hückel and McLachlan[7] MO-SCF type calculations of π-spin den-

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(1) (a) Presented in part at the 152nd National Meeting of the American Chemical Society Meeting, New York, N. Y., Sept 11–16, 1966; (b) Department of Chemistry, St. Louis University, St. Louis, Mo.

(2) M. T. Jones, *J. Am. Chem. Soc.*, **88**, 227 (1966).

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(5) A. Carrington, H. C. Longuet-Higgins, and P. F. Todd, *Mol. Phys.*, **9**, 211 (1965).

(6) K. Wallenfels and P. Neuman, *Tetrahedron*, in press.

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