

## Two-Dimensional Dehydration of Phenylpicrylhydrazine on Titanium Dioxide

### Catalytic Activity of F Centers

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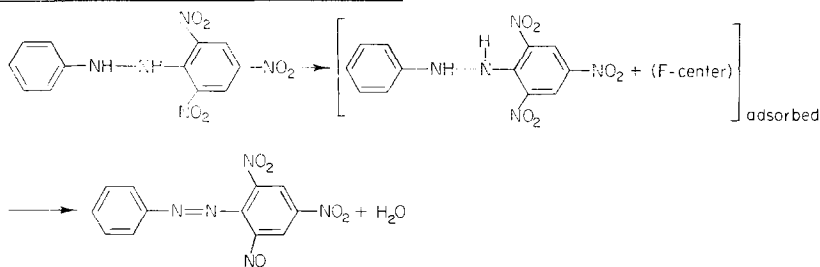
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The rate of dehydration of phenylpicrylhydrazine in the adsorbed state has been studied on an anatase surface. The reaction is two-dimensional in the sense that no phase equilibria are involved. At less than a monolayer coverage, the reaction seems to be zero order with respect to the surface concentration of the hydrazine and the rate of reaction remains constant at constant temperature. A reaction mechanism employing the F centers of the adsorbent is discussed. The transition state theory, analogous to a heterogeneous catalytic reaction involving a strongly adsorbed reacting gas, apparently satisfies the experimental observations. To check the validity of the experimental method, the rates of the reaction of DPPH on the rutile surface as determined with reflectance measurements were compared with those obtained previously by ESR measurements. The two sets of values are in excellent agreement.

#### INTRODUCTION

It has been found that  $\alpha$ -phenyl- $\beta$ -picrylhydrazine (HPPH) undergoes a dehydration reaction on *n*-type oxidic surfaces (1). The adsorbed HPPH molecules

developing on the surface (1). The color eventually fades and the final product 2-nitroso-4,6-dinitroazobenzene is obtained in almost theoretical yield (>95%). The overall reaction is depicted as follows:



impart a deep purple color to the adsorbent surface, in contrast to the pale yellow color of the hydrazine solution. A faint electron spin resonance signal characteristic of the free radical, phenylpicrylhydrazyl, is also detected. It appears more reasonable, however, to attribute the color to the excited state of the adsorbed HPPH molecules, rather than to a very few free radicals

The present paper describes direct measurements of the rates of reaction of the adsorbed HPPH on an anatase surface in the absence of solvent using reflectance technique. The results show that the reaction is zero order with respect to the surface concentration of the HPPH up to a monolayer and the rates remain constant with coverage at constant temperature. The reactants and products remain on the surface without any phase equilibria being

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involved. In this sense, the reaction is truly two-dimensional. Controlled experiments showed that the amount of adsorbed water affects the amount of adsorbed HPPH but not the rate of its reaction.

The proposed mechanism involves the catalytic activity of the substrate F centers which are presumably mobile. Considering that the number of F centers on the surface remains constant with time and is insignificant compared to the number of the adsorbed HPPH molecules and that the F centers are always associated with the reactant, a zero order rate law immediately follows. All other feasible mechanisms seem to give a first order rate law. To check the validity of the experimental method, the rate of the reaction of  $\alpha,\alpha$ -diphenyl- $\beta$  picrylhydrazyl (DPPH) on the previously used rutile sample (2) was determined. This reaction is first order with respect to the surface concentration of the radical, as was found before by employing ESR measurements. The rate constants and the energy of activation are in good agreement and it turns out that the present reflectance technique is much more sensitive than the ESR method for the rate determination of the adsorbed DPPH.

#### EXPERIMENTAL

**a. Preparation of compounds.**  $\alpha$ -Phenyl- $\beta$ -picrylhydrazine (HPPH) was prepared by the method described by Fisher (3) by treating an alcoholic solution of 1 mole of picryl chloride with 2 moles of phenylhydrazine. The resulting lustrous red flaky crystals were washed with water and then with alcohol. They were twice recrystallized from alcoholic solution. The melting point was 181° as reported and the elemental analysis agreed with the values calculated for HPPH.

2-Nitroso-4,6-dinitroazobenzene was prepared by dissolving  $\alpha$ -phenyl- $\beta$ -picrylhydrazine in hot glacial acetic acid by the procedure of Freund (4). The precipitated yellow flakes of the compound were recrystallized from glacial acetic acid and washed thoroughly with distilled water [mp 247° (dec.), lit. 248°]. The elemental

analysis was in agreement with the calculated values.

**b. Determination of surface area and the amount of adsorbed water on the catalysts.** The surface area of anatase was determined by nitrogen adsorption on Englehard Isorpta Analyzer. To determine the amount of adsorbed water on the catalysts, the samples were evacuated at 100° for several hours and then weighed after dry air was introduced into the vessel.

**c. Kinetic studies.** The rate of disappearance of the purple color due to HPPH adsorbed on an extremely pure anatase sample (52.1 m<sup>2</sup>/g) in the absence of a solvent was determined on a Beckman Model DK-1 Spectrophotometer with diffuse reflectance attachment using magnesium oxide as a reference.

A given quantity of anatase was thoroughly mixed in an acetone solution of HPPH and filtered through a fritted-disc filter. The HPPH-coated anatase was pressed between the sheets of filter papers to remove as much solution as possible. The pellet obtained was broken into pieces and sifted with a spatula until the powder became dry. The coated anatase powder was then placed onto the reflectance plate, covered with a quartz slide, and quickly introduced into the spectrophotometer. The whole preparatory operation took about 5 min. The absorbance curve was repeated at regular time intervals between 350  $\mu$  and 700  $m\mu$  until no change was observed. Figure 1 shows typical absorbance vs. wavelength plots for various time intervals. After the reaction was complete, the powder was scraped off the reflectance plate, weighed, and refluxed with benzene in an extractor until the refluxing solution was colorless. After appropriate dilutions, its absorbance was compared at 430  $m\mu$  with that of a standard solution which was obtained by reacting in solution a known quantity of HPPH in benzene with an anatase sample. The reaction is exactly the same whether a solvent is present or not. This was determined by the yields of the nitroso compound and by thin-layer chromatographic analysis. The resulting solution, which contains mainly the nitroso com-

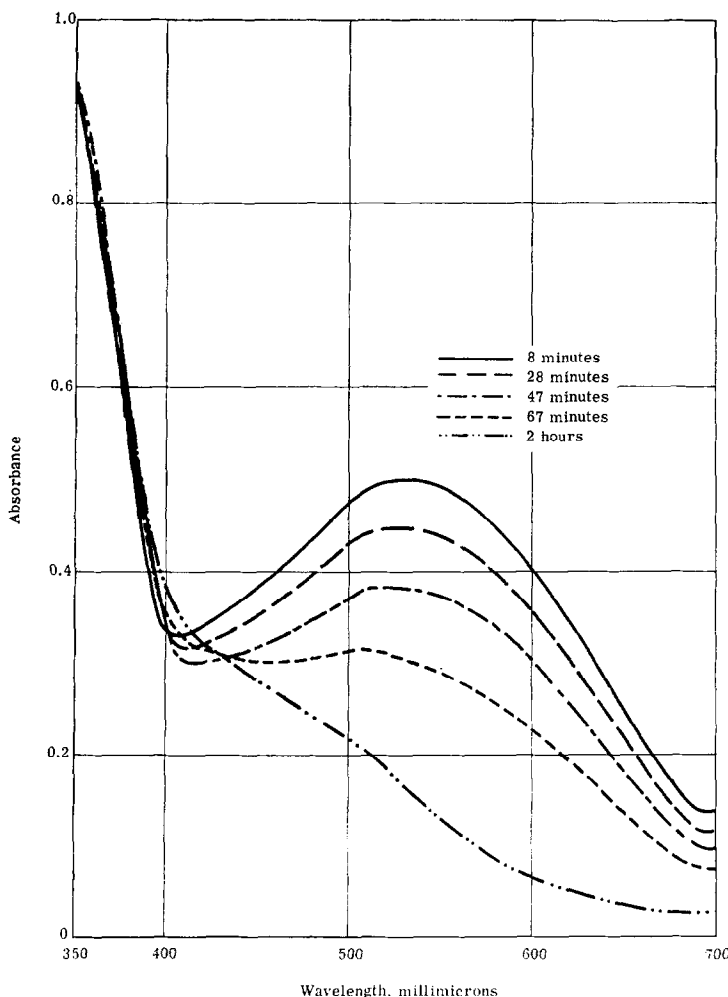


Fig. 1. Absorbance vs. wavelength for HPPH (6.98 mg/g  $\text{TiO}_2$ ) at  $22^\circ$  on anatase for certain time intervals.

pound, follows Beer's Law. Thus, the amount of HPPH initially absorbed on anatase was determined.

The initial absorbance values of HPPH on anatase were obtained by extrapolation at 535 and 690  $m\mu$ . The final values for the nitroso compound were obtained when no change in the absorbance curve was observed with time. The solution of the following simultaneous equations gives the concentration of HPPH on the surface at a given time provided that the amount of HPPH does not exceed a monolayer:

$$\begin{aligned} a_{11}x + a_{12}y &= A_1 \\ a_{21}x + a_{22}y &= A_2 \end{aligned}$$

where  $a_{11}$  and  $a_{21}$  are the initial absorbances of HPPH and  $a_{12}$  and  $a_{22}$  are the final ab-

sorbances of the nitroso compound at 690 and 535  $m\mu$ , respectively.  $A_1$  and  $A_2$  are the measured absorbances at the two wavelengths for the mixture of the two substances, whereas  $x$  and  $y$  represent the amounts of HPPH and the nitroso compound on the surface at a given time. This method is not applicable if the amount of HPPH exceeds a monolayer on the surface since in that case some HPPH, not directly adsorbed on the surface, will also be present and its absorbance is not accounted for. The concentration of the nitroso compound on the surface was found to follow Beer's Law. The concentration of HPPH is reliable to within 5% to 10%.

The kinetic studies of the rate of reaction of DPPH on the rutile surface (63.8

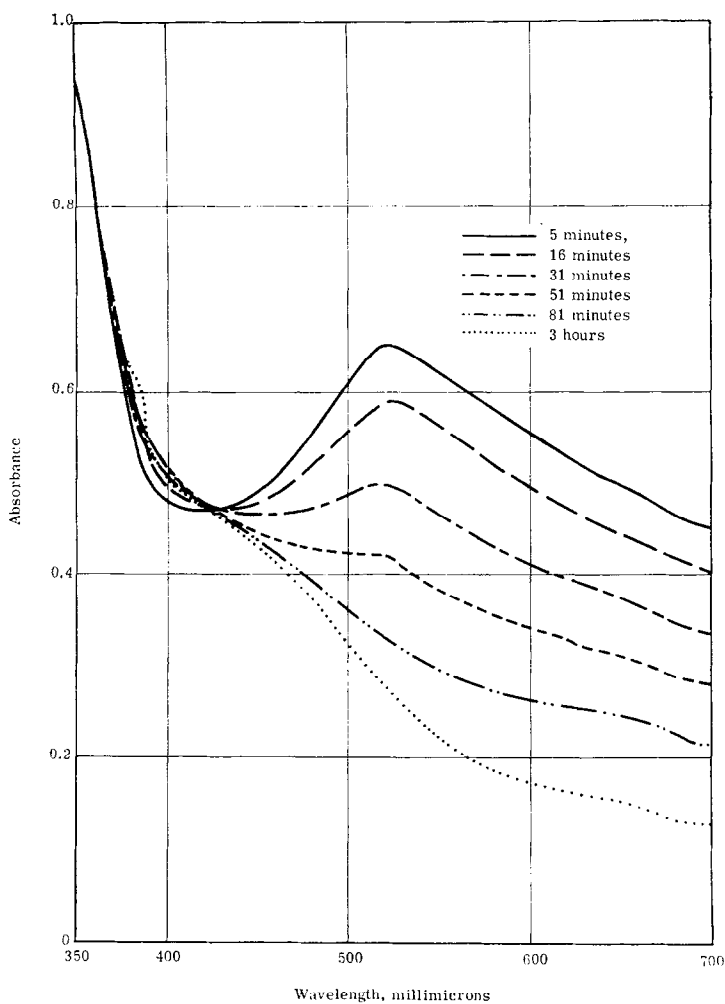


FIG. 2. Absorbance vs. wavelength for DPPH (4.77 mg/g  $\text{TiO}_2$ ) at  $20^\circ$  on rutile ( $63.8 \text{ m}^2/\text{g}$ , 0.85 millimoles  $\text{H}_2\text{O}/\text{g}$ ) for certain time intervals.

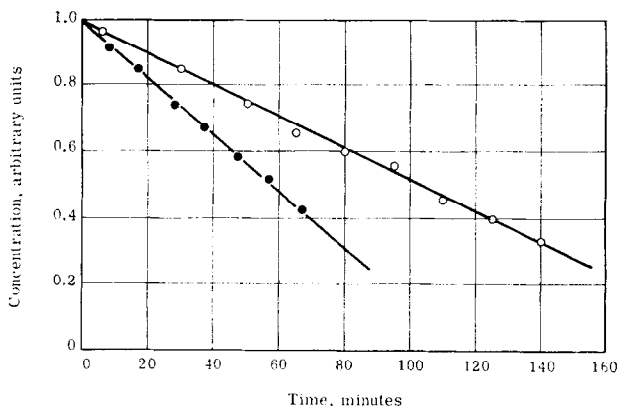


FIG. 3. Concentration vs. time for HPPH at  $22^\circ$  on anatase ( $52.1 \text{ m}^2/\text{g}$ , 0.13 millimoles  $\text{H}_2\text{O}/\text{g}$ ): O, 12.61 mg HPPH/g  $\text{TiO}_2$ ; ●, 6.98 mg HPPH/g  $\text{TiO}_2$ .

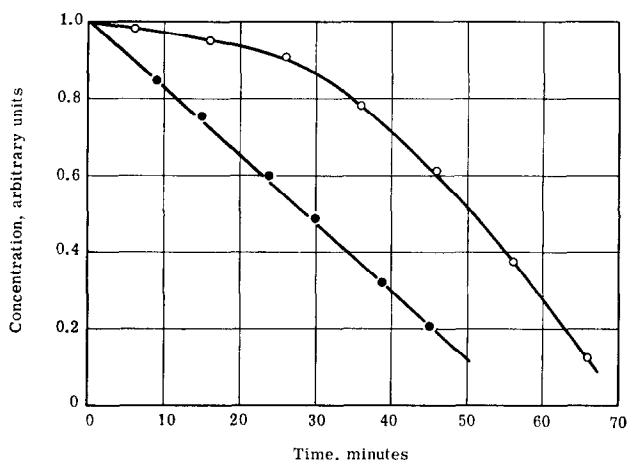


FIG. 4. Concentration vs. time for HPPH on anatase: O, 27.19 mg HPPH/g TiO<sub>2</sub> ( $\theta > 1$ ) at 22°; ●, 8.98 mg HPPH/g TiO<sub>2</sub> at 31°.

m<sup>2</sup>/g) in the absence of solvent were conducted as described above for HPPH on anatase. Figure 2 shows typical absorbance vs. wavelength plots for the disappearance of DPPH adsorbed on rutile surface for various time intervals.

In all the above studies, the temperature remained constant within 0.5°. No impurities in concentrations greater than 10 ppm were listed in the analyses for anatase as well as rutile except that 200 ppm SiO<sub>2</sub> and 50 ppm Sn were listed for both samples.

### RESULTS

Figure 3 shows two plots of concentration vs. time for adsorbed HPPH on anatase at 22° at two different initial concentrations. Figure 4 is a similar graph for different coverages and temperatures. Clearly, the three plots for which there was less than a monolayer coverage of HPPH show that the reaction in each case is zero order. In the fourth plot, for more than a monolayer coverage ( $\theta > 1$ ), the data do not show a zero order reaction. But, the experimental method in this case fails to give the correct HPPH concentration which is directly in contact with the surface, as has been explained before.

The amount of HPPH which gives a monomolecular layer on a certain quantity of anatase can be reasonably determined. Considering the planarity of the adsorbed HPPH molecules and the solid packing of

spheres on the surface, the effective area of a molecule will be the same as that of a DPPH molecule (5), that is, 160 Å<sup>2</sup>. However, unlike DPPH,\* the adsorbed HPPH molecule must lie flat on the anatase surface for dehydration via the F-center mechanism to take place. The saturation amount of HPPH to give a monolayer on 1 g of the anatase is 17.19 mg. This was calculated by using the surface area of anatase (52.1 m<sup>2</sup>/g) and the effective area of an adsorbed HPPH molecule (160 Å<sup>2</sup>).

The zero order rate constant,  $k_0$ , is obtained by multiplying the slopes of the relative concentration vs. time plots with the amount of HPPH initially adsorbed on the anatase. The two  $k_0$  values at two different HPPH concentrations for the two-dimensional reaction at 22° are nearly

\*It is known from magnetic susceptibility studies of Aston and co-workers (6) and ESR investigations of Kirecnko *et al.* (7) that, even for coverages as low as 0.02, physically adsorbed DPPH exists in a state of molecular aggregates or crystallites on silica gel and other oxidic surfaces. This behavior of adsorbed DPPH is reflected in the shape of the adsorption isotherms obtained on these materials (D. N. Misra, unpublished results). This phenomenon becomes evident when it is considered that in the edge-wise position, the dispersion forces between the adsorbed DPPH molecules will be maximum. The molecules, then, tend to form clusters or aggregates.

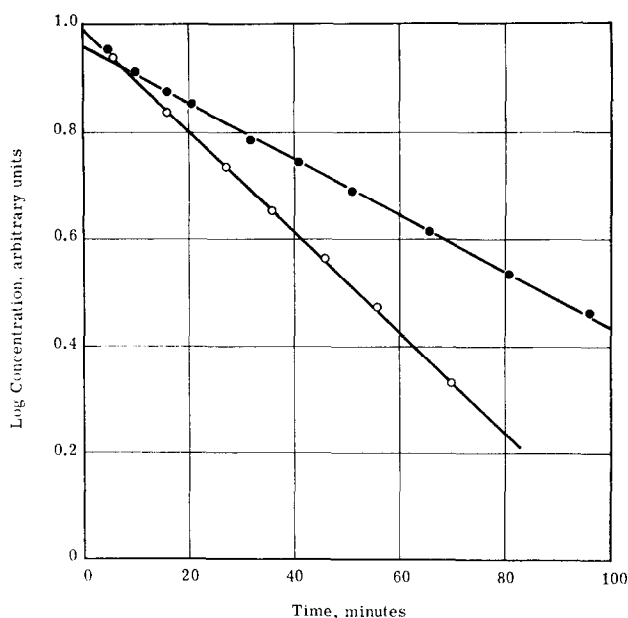


Fig. 5. Log concentration vs. time for DPPH on rutile: O, 4.85 mg DPPH/g TiO<sub>2</sub> at 25°; ●, 4.77 mg DPPH/g TiO<sub>2</sub> at 20°.

identical (see Table 1). This shows that the rate constant at a given temperature is not dependent on the surface coverage (for  $\theta > 1$ ). The plot of the values of  $\log k_0$  vs.  $1/T$  for the reaction at 10°, 22°, and 31° is linear and the energy of activation obtained is approximately 20 kcal/mole.

Figure 5 gives two straight-line plots of the log of the surface concentration of DPPH vs. time. Both plots have about the

same initial DPPH coverage, but at two different temperatures (20° and 25°). The reaction is, therefore, first order with respect to the radical concentration. In the present studies, the coated sample was not evacuated and the traces of solvent may have adhered to the adsorbent. This tends to give a lower rate constant than the one obtained previously when the sample was evacuated thoroughly. The  $k_1$

TABLE 1  
RATE CONSTANTS AND ACTIVATION ENERGIES OF THE TWO-DIMENSIONAL REACTIONS

Reaction conditions	HPPH conc. (mg/g TiO <sub>2</sub> )	Relative slopes from figures $\times 10^4$	Rate constants $\times 10^4$	$\Delta E$ (kcal/mole)
HPPH on:			$k_0$ (mg sec <sup>-1</sup> )	
Anatase, 22° (Fig. 2)	6.98 <sup>a</sup>	1.41	9.84 <sup>b</sup>	20
Anatase, 22° (Fig. 2)	12.61	0.78	9.84	
Anatase, 31° (Fig. 3)	8.98	2.95	26.49	
Anatase, 10°	5.12	0.45	2.30	
DPPH on:			$k_1$ (sec <sup>-1</sup> )	
Rutile, 20° (Fig. 5)	4.77 (4.89) <sup>c</sup>	0.88 (1.21)	2.03 (2.78)	20 (15)
Rutile, 25° (Fig. 5)	4.85 (4.89)	1.56 (1.87)	3.62 (4.31)	

<sup>a</sup> This is equivalent to  $2.53 \times 10^{13}$  molecules/cm<sup>2</sup>.

<sup>b</sup> This may be expressed as  $3.57 \times 10^9$  molecules/cm<sup>2</sup> sec.

<sup>c</sup> The values given in parentheses were obtained by ESR measurements (ref. 2).

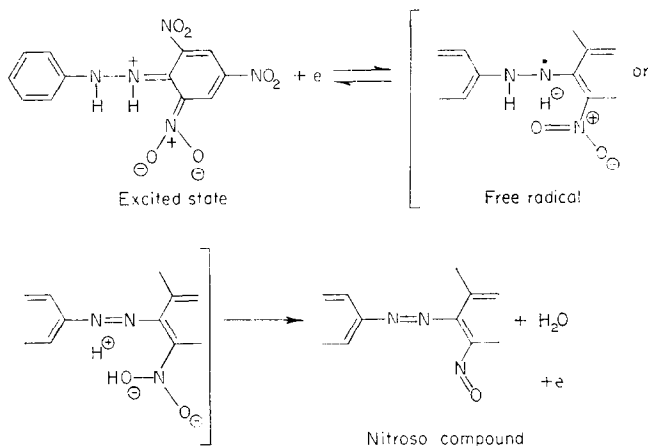
values obtained by the two methods compare favorably (see Table 1) when we also consider the difference in the experimental techniques. The difference in the activation energies as obtained from the two methods lies within experimental errors.

### DISCUSSION

Many organic substances with peripheral dipoles when adsorbed on oxidic surfaces or on salt layers show absorption spectra which are shifted appreciably to the red side of the spectrum (8-10). In benzene solution HPPH has a maximum of light absorption at  $325\text{ m}\mu$ ; when adsorbed on anatase it shows an absorption maximum at  $517\text{ m}\mu$  (same as that of DPPH). The anion of HPPH (11) which is generated in basic or pyridine solution (dark green)

of the oxidic surface. The act of adsorption, of course, decreases the energy difference between the ground level and the excited level or, equivalently, between the nonpolar and polar forms (12). We can not characterize this species specifically, at present.

Thus, the species existing on the surface is either the excited state of the HPPH molecule or its surface-induced polar form and its dehydration on the surface of anatase follows a zero order rate law. It is a well-known fact that both rutile and anatase are *n*-type oxides and have a stoichiometric excess of electrons which manifest themselves as F centers. These color centers play a very significant role in many chemical processes (13-15). We may visualize the dehydration process involving the F centers as follows:

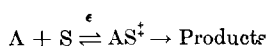


has maximum absorption at  $410\text{ m}\mu$  (same as that of DPPH in  $\text{H}_2\text{SO}_4$ ). It is, therefore, hard to assign the shift of the absorption spectrum to the ion or salt formation. The shift could not be attributed to the generation of the free radical, phenylpicrylhydrazyl, because the amount of the free radical estimated from the ESR signal intensity is extremely small. Thus, it appears reasonable that the shift in the maximum absorption may result either from the fact that the excited state of the molecule is adsorbed more strongly than the ground state (9) or from the induction of a higher relative contribution of the polar form of the molecule by the polarity

of the oxidic surface. There could be several resonance structures for each of the above species, of course. The number of F centers on the surface of a rutile crystal is of the order of  $10^{11}$  electrons/ $\text{cm}^2$ .\* It is, perhaps, for this reason that the number of free radicals detected by ESR measurements is exceedingly small.

The reaction between an excited HPPH molecule (A) on the surface and an F-center (S) may be represented as

\*This number was obtained by Dr. F. G. Wakim at Itek Corporation by studying the decay in dark conductivity of a rutile single crystal which was evacuated in an ultra-high vacuum system prior to introduction of oxygen.



where  $AS^\ddagger$  is the activated complex and  $\epsilon$  stands for the energy of activation at absolute zero. The semiconductor behavior of titanium dioxide implies that the F centers must be mobile. The active surface, comprised of F centers, remains completely covered with HPPH molecules. If the activated complex decomposes at one site, it is created elsewhere on the surface because of the mobility of the F centers. The concentration of the molecules adsorbed on the active surface may be taken as constant if the number of active sites (i.e., F centers) is significantly smaller than the total concentration of the adsorbed molecules. This condition is apparently met in the present case, therefore, the rate becomes independent of the concentration of the adsorbed molecules and the zero order rate law follows.

A little reflection shows that this catalytic reaction, where phase equilibria are not involved, is completely analogous to a heterogeneous catalytic reaction involving a strongly adsorbed reacting gas. A similar treatment according to transition state theory (16) gives the velocity constant as

$$v = c_s(kT/h) \exp(-\epsilon/RT)$$

where  $c_s$  is the concentration (number per unit area) of F centers and other symbols have usual designations. Taking the value of the frequency factor  $kT/h$  as  $10^{12}$  per second,  $c_s$  as  $10^{11}$ , and  $\epsilon$  as 20 kcal/mole, the value of the calculated rate constant turns out to be  $1.91 \times 10^8$ , as compared to the observed value of  $3.57 \times 10^9$ . The agreement may be considered as satisfactory in view of the fact that many experimental and theoretical parameters are only approximate and the number of F centers on anatase powder has been taken as equal to that of a rutile single crystal.

The effect of adsorbed water on the rate of the reaction was not exhaustively explored; however, several control experiments did establish that the amount of adsorbed water only affects the amount of adsorbed HPPH but not the rate of its

reaction. This seems to be in accord with our discussion.

The uniqueness of the above treatment is difficult to establish. Any rate law based on molecular collisions leads to higher order rate laws and must be ruled out. The planar configuration of the adsorbate molecule, consisting of  $\pi$ -electron systems, imparts to it considerable dispersion energy of interaction with the surface; therefore, its mobility will be very restricted. Thus, the chemical reaction that is observed here is an individual molecular process not a collective one. Also, the reaction rates signify the intrinsic property of the isolated molecules as modified by the semiconductor surface and not the property of molecules in an ensemble. If the role of the F centers is completely ignored, we will have to attribute some characteristic half-life to any activated complex that may develop and the rate law will be a first order one. When a diffusional rate law involving a phenylpicrylhydrazyl radical and a hydrogen atom is considered, a first order rate law is again obtained. Therefore, it appears that our treatment may also be unique.

#### ACKNOWLEDGMENTS

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