Rate Studies of the Reaction of 1,1-Diphenyl-2-picrylhydrazyl Microcrystallites with Adsorbed Water on a Rutile Surface*

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Using an EPR spectrometer the rate of a novel solid state reaction of adsorbed microcrystallites of 1,1-diphenyl-2-picrylhydrazyl has been studied on a high area rutile sample in the absence of a solvent. The reaction is first order with respect to the radical concentration and the rate constants are inversely proportional to the initial concentrations of the radical. Diffusion-controlled kinetics seem to explain the experimental observations. The reaction apparently proceeds only on hydroxylated semiconducting surfaces. Theoretical evaluation of the molecular and electronic processes involved is not possible.

INTRODUCTION

It has been reported that 1,1-diphenyl-2-picrylhydrazyl (DPPH) undergoes a simultaneous intermolecular oxidation and reduction with adsorbed water on many substances (1). The coexistence of a solvent is not necessary for the occurrence of the reaction and the products are the same whether a solvent is present or not. It was found that the reaction is first order with respect to the radical concentration in presence of a solvent (2).

The adsorbed radical does not exist in a state of molecular dispersion on many surfaces after the removal of solvent. It is known from magnetic susceptibility studies of Kikuchi and co-workers (3) and electron paramagnetic resonance investigations of Golubev et al. (4) that, even for coverages as low as 0.02, physically adsorbed DPPH exists in a state of molecular aggregates or microcrystallites on silica gel and other oxidic surfaces. The nature of this aggregation may be explained if we consider the heterogeneous and essentially nonplanar structure of these surfaces. The radical molecule is most likely to be sitting in an edgewise position on the sites correspond-ing to the lowest energies or highest differential heats of adsorption. In this position the dispersion forces between the adsorbed molecules would be maximum and they would tend to form clusters or aggregates (5).

The present paper describes the direct measurement of the rate of reaction of the DPPH-microcrystallites with adsorbed water on the surface of a high area rutile sample. The results show that the reaction is first order with respect to the radical concentration and the rate constants are inversely proportional to the initial concentration. This is not a two-dimensional reaction like the dehydration of 1-phenyl-2-picrylhydrazine on similar surfaces (6).

A mechanistic interpretation of the reaction is not possible on the basis of the observed rate law since a diffusional process seems to control the kinetics. The surface hydroxyl groups and "F-centers"† must play a significant role in the evolution of such a mechanism. The thin-layer chromatographic separation and subsequent characterization show that the identical products are obtained on *n*-type oxidic surfaces such as TiO_2, ZnO, MgO, or on

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* The results of this investigation were verified using reflectance spectroscopy [see Ref. (6)].

† The term has been used in a very general sense and includes any free electrons available on semiconducting surfaces.

carbon black. On salts like KCl or pure silica gel no reaction takes place for long periods. The characteristic property, distinguishing the catalysts in whose presence the reaction occurs, seems to be the simultaneous existence of surface hydroxyl groups (7) and "F-centers." The reaction does occur very slowly on impure silica gel; probably other metal ions impart local semiconductor properties to the gel surface. Unfortunately, the rate studies yield only the relative values of the absolute reaction constants involved and, therefore, any theoretical evaluation of molecular and electronic processes is not possible.

EXPERIMENTAL METHODS

a. Rate determination. The rate of reaction of DPPH-microcrystallites adsorbed on an extremely pure rutile sample (63.8 m²/g) in the absence of a solvent was measured by the area under the line shape derivative curve obtained with a low frequency electron spin resonance apparatus (Alpha Scientific Laboratories, Model AL-340). A given quantity of the rutile sample was mixed with a benzene solution of DPPH for 3 min and filtered through a fritted-disc filter. The DPPH-coated rutile was pressed between sheets of filter paper to remove as much solution as possible. The powdered catalyst was then taken into an EPR-capsule and evacuated for 5 min to remove the traces of solvent. The capsule was exposed to air afterwards, and transferred to the EPR-coil kept at a temperature constant within 0.2°, using a specially constructed air thermostat. The decay of the resonance signal was monitored at regular intervals. The amount of the adsorbed DPPH for a given quantity of rutile was determined by comparing the area under the line shape derivative curve with that of a standard solution of DPPH.

The initial surface concentration of the radical was determined in the following manner. When the reaction was complete, the powder was taken out of the capsule, weighed, and refluxed with benzene in an extractor until the refluxing solution was colorless. Its absorbance, after appropriate dilution, was compared at 322 mμ with that of a standard solution which was obtained by reacting a known quantity of DPPH in benzene with a rutile sample.

b. Materials. The rutile sample was obtained from the Cabot Corporation and was prepared by flame hydrolysis of titanium tetrachloride. A conventional volumetric method was used to determine BET surface area by nitrogen adsorption. To determine the amount of adsorbed water on rutile, a weighed sample was evacuated at 100° for several hours and then weighed after dry air was introduced into the vessel. X-Ray analysis revealed that the sample is randomly oriented 100% rutile. The impurities as determined by atomic absorption spectroscopy were (ppm) Si < 10, Al < 10, Mg < 3, Cu < 3, Ca < 3, Sn < 3, Pb < 3, Fe < 3, Ni < 1, and Cr < 1. The rutile sample did not contain any detectable amount of chloride ion.

Reagent-grade 1,1-diphenyl-2-picrylhydrazyl was commercially available from Eastman Organic Chemicals and was used without further purification.

RESULTS AND DISCUSSION

Figure 1 shows the straight-line plots of the log of surface concentration of DPPH vs time for certain initial amounts at 20°. Apparently, the reaction is first order with respect to the radical concentration. There is a noticeable difference in the slopes for the different initial concentrations which indicates that this is not a true first order reaction. The apparent first order rate constants are obtained by multiplying the slopes by a factor 2.303 (Table 1, column 3). It is observed that the rate constants are inversely proportional to the initial concentrations of the radical (Table 1, column 4). No rate law based on a collisional process elucidates these facts. Any interpretation of these observations must be based on a diffusion-controlled kinetics, for the DPPH molecules must diffuse from the crystallite-sites to react with water at appropriate surface-sites. Indeed, such a diffusion-dependent process seems to explain certain salient experimental features and its concise mathematical formulation is given below.
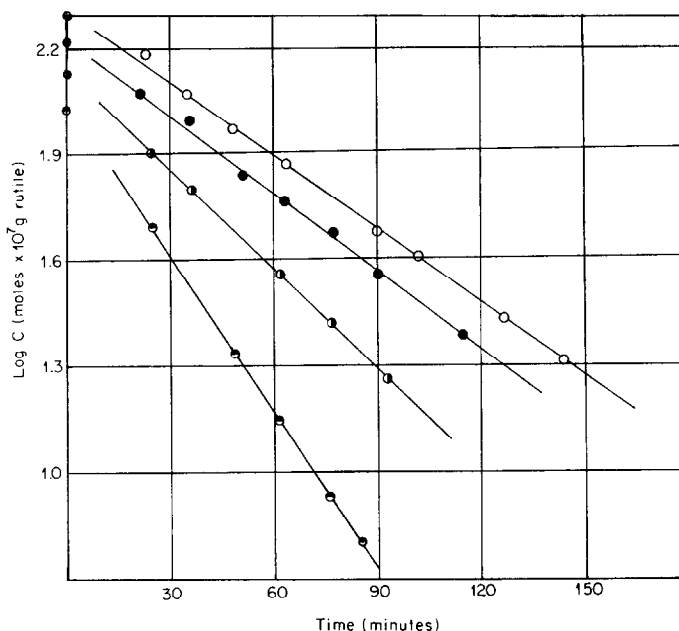
Fig. 1. Log concentration vs time for DPPH-microcrystallites at 20° on rutile (63.8 m²/g, 0.85 mmoles of H_2O/g): $\bigcirc$, 2.46 × 10⁻⁵ moles of DPPH/g; $\bullet$, 2.15 × 10⁻⁵ moles of DPPH/g; $\mathbb{O}$, 1.72 × 10⁻⁵ moles of DPPH/g; $\ominus$, 1.23 × 10⁻⁵ moles of DPPH/g.

It can be reasonably assumed that the low energy sites and hence the DPPH-microcrystallites are evenly distributed over the surface. Let h be the radius of the effective area at the disposal of a microcrystallite in which the DPPH molecules may diffuse and react. The DPPH-concentration at the periphery of the effective area will, therefore, be zero. Obviously, we are dealing here with a reactive system where the concentration and the concentration-gradient are changing with time, thus, our system may be considered to satisfy the following well-known differential equation

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2}\right), \qquad (1)$$

where D is the coefficient of diffusion. For the sake of simplicity, we shall consider the problem in one dimension only. This will in no way restrict the application of our results since the coordinates are isotropic. The solution of Eq. (1) is easily obtained by separation of variables and the most general solution in one dimension is (8)

TABLE 1

RATE CONSTANTS AND ACTIVATION ENERGY OF THE REACTION OF DPPH-MICROCRYSTALLITES ON RUTILE

DPPH conc[a] (moles/g rutile) (×10⁵)	Relative slopes from Fig. 1 (×10⁴)	Rate constants (sec⁻¹) at 20° (×10⁴)	Calculated rate constants (sec⁻¹) at 20° (×10⁴)	Rate constants (sec⁻¹) at 25° (×10⁴)	ΔE (kcal/mole)
2.46	1.14	2.61	2.61[b]	—	—
2.15	1.28	2.95	2.98	5.13	19.1
1.72	1.59	3.65	3.73	6.42	19.5
1.23	2.30	5.29	5.22	—	—

[a] The amount of DPPH (160 Å²) needed for a monolayer is 6.5 × 10⁻⁵ moles/g of rutile.
[b] This is taken to be the same as the experimental value.

$$c(x, t)$$

$$= \sum_{n=1}^{\infty} (A_n \sin \lambda_n x + B_n \cos \lambda_n x)$$

$$\times \exp(-\lambda_n^2 Dt),$$

where λ is a real number.

By imposing on the solution the following limiting conditions of our system

   (i) when $x = 0$, $\partial c / \partial x = 0$;

   (ii) when $t = t$, at $x = h$, $c = 0$;

and

   (iii) when $t = 0$, at $x = 0$, $c = c$;

we obtain

$$c(x, t) = \frac{4c_0}{\pi} \sum_{j=1}^{\infty} \frac{1}{(2j - 1)} \cos \frac{(2j - 1)\pi x}{2h}$$

$$\times \exp\left[-\left(\frac{(2j - 1)\pi}{2h}\right)^2 Dt \right],$$

where $j = 1, 2, 3. \ldots$ The average concentration $\bar{c}$ as a function of time may be obtained by the integration of the above equation:

$$\bar{c}(t) = \frac{1}{h} \int_0^h c(x, t)\, dx = \frac{8c_0}{\pi^2} \sum_{j=1}^{\infty} \frac{1}{(2j - 1)^2}$$

$$\times \exp\left[-\left(\frac{(2j - 1)\pi}{2h}\right)^2 Dt \right],$$

for $\bar{c} \leqslant 0.8\ c_0$, the first term is a good approximation to the solution. Thus,

$$\bar{c} = \frac{8c_0}{\pi^2} e^{-t/\tau} \qquad (2)$$

where $\tau \equiv 4h^2/\pi^2 D$ is called the relaxation time. We may consider the inverse of the relaxation time to be our first order rate constant. Clearly, Eq. (2) yields a linear relationship for the plot of the log of the surface concentration vs time. The inverse proportionality of the rate constants with the initial surface concentration of the radical is not explicitly involved in the above treatment and can only be explained from the above definition of rate constant if it is assumed that the coefficient of diffusion varies inversely with the initial surface concentration of the radical. How-

ever, any rigid justification of this assumption can not be offered because a molecular mechanistic picture is not available. The initial concentrations of the radical estimated from the intercepts ($= \log 8c_0/\pi^2$) compare quite favorably with the experimental values. It may be noticed that the values of rate constants give the relative values of the diffusion coefficient and in order to evaluate the absolute values we are required to determine the distance between the crystallites by some other independent method.

The temperature dependence of the diffusion coefficient may be expressed as (9)

$$D = D_0 \exp(-\Delta E/RT),$$

where ΔE is the activation energy for the process. The activation energies thus calculated are given in column 6 of Table 1. The absolute value of D_0 can not be evaluated since the value of diffusion coefficient are relative. Any rate law based on a diffusional process does not by itself throw any light on the mechanism of a reaction. We know that the reaction proceeds only on hydroxylated semiconducting surfaces and, therefore, the surface hydroxyl groups and "F-centers" must play a significant role in any mechanistic process. An attempt could have been made to develop a phenomenological theory of the reaction mechanism involving molecular and electronic processes only if the absolute values of the reaction constants had been available.

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