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THE ROLE OF HYDROXYLATED SEMICONDUCTING SURFACES IN THE REACTION OF 1,1-DIPHENYL-2-PICRYLHYDRAZYL WITH ADSORBED WATER*

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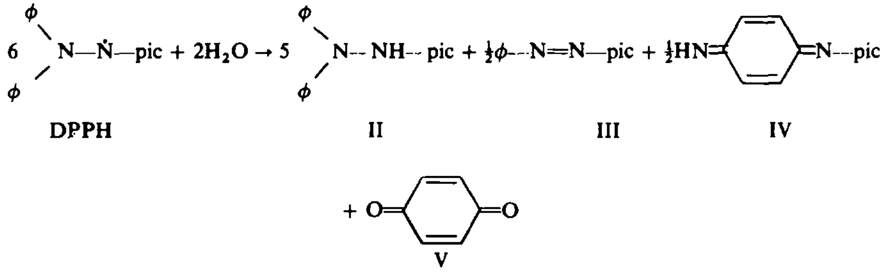
AbstractThe role of hydroxylated semiconducting surfaces in the intermolecular oxidation and reduction reaction of 1,1-diphenyl-2-picrylhydrazyl with adsorbed water has been explored. Major products were isolated on various catalysts, characterized and their yields determined. The reaction is the same whether a solvent is present or not. It appears that a simultaneous presence of surface OH groups and 'F-centers' is necessary on the surface of a catalyst for the reaction to occur. Considering the mode of catalysis a mechanism for the reaction is proposed on stoichiometric basis.

IT WAS reported in a preliminary communication[1] that 1,1-diphenyl-2-picrylhydrazyl (DPPH) reacts with adsorbed water on many substances and undergoes an intermolecular oxidation and reduction process. The general characteristics of the reaction with respect to the role of surface OH groups in concurrence with 'F-centers'‡ of the substrate was not fully recognized in our previous communique. Also, the known oxidation product was falsely characterized as 2.4,6-trinitro-4'-aminodiphenylamine. It has since been unequivocally shown to be 2,4,6-trinitroazobenzene (III). The unknown product is unstable under ambient conditions and yields a resinous substance along with picramide. It has been tentatively characterized as 2,4,6-trinitrophenyl-*p*-benzoquinonediimine (IV). The overall catalytic reaction may, therefore, be represented as

(1)



The yield is essentially quantitative for 1,1-diphenyl-2-picrylhydrazine (II) and around 80% for each of the other products as shown in Table 1. It is observed that a simultaneous presence of OH groups and 'F-centers' on catalytic surface is necessary for

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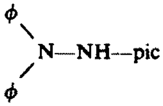
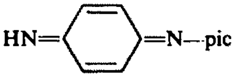
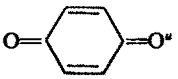
‡ The term has been used in a very general sense and includes any free electrons available on semiconducting surfaces.

TABLE 1. YIELDS OF PRODUCTS FROM THE REACTION OF DPPH (5 g) IN BENZENE (1000 ml) WITH ADSORBED WATER ON ANATASE (100 g)

Product	Found, g	Calcd (Eq. 1), g	% Yield
	4·10	4·18	98
ϕ—N=N—pic	0·27	0·33	82
	0·26	0·33	79
	0·19	0·23	83

[a] The yield was determined spectroscopically. A flash sublimation of the products on another run gave a yield of 36%.

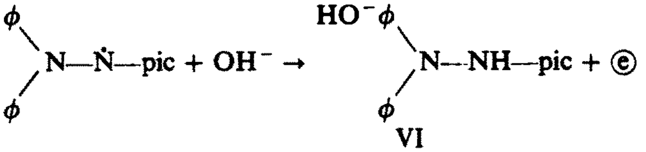
the reaction to take place. The significance of this catalytic effect for biological and other organic reactions can only be stipulated. For a certain other reaction,[2,3] we have reported that the n-type oxidic surfaces may serve as general catalysts for electron transfer processes. Air was, generally, excluded from the reaction system, however, its presence does not seem to affect the reaction perceptively.

Characteristics of the catalysts. Identical products are obtained on n-type oxidic surfaces such as TiO_2, MgO, ZnO or on carbon black as shown by TLC separation of products and their subsequent characterization. On salts like NaCl or KCl and 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 presence of surface OH groups[4] and 'F-centers'. The reaction, however, does occur very slowly on impure silica gel, other metal ions probably impart local semiconductor properties to the gel surface.

Mechanistic interpretation. In the light of above observations about the nature of the catalytic surface, the following mechanism may be proposed for the reaction which coordinates all the known facts. The free-radical, DPPH, may initially interact specifically with the surface OH group* and the following reaction may be represented as:

$$\text{DPPH} + \rightarrow\text{TiOH} + ⓔ \rightarrow \text{II} + \rightarrow\text{TiO}^- \qquad \text{(Reduction)}$$

$$\rightarrow\text{TiO}^- + \text{H}_2\text{O} \rightarrow \text{TiOH} + \text{OH}^- \qquad \text{(Surface hydrogenation)}$$



VI

$$\phi_2\text{N—}\dot{\text{N}}\text{—pic} + \text{OH}^- \rightarrow (\text{HO}^-\phi)(\phi)\text{N—NH—pic} + ⓔ \qquad \text{(Oxidation)}$$

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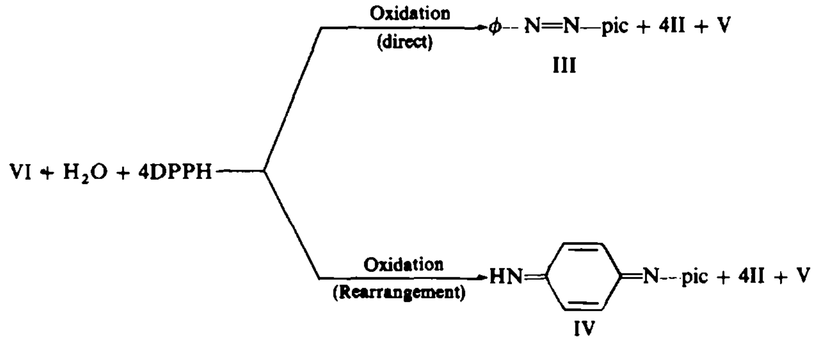
* Kiselev *et al.*[5] have shown in an extensive study that the molecules possessing π-bonds, lone electron pairs, and functional groups like ₋OH or ₋NH specifically interact with surface hydroxyls.

where ⓔ symbolizes a surface 'F-center'. The compound VI may in turn get oxidized directly or via rearrangement. The oxidation is preceded by hydrolysis of VI and followed by further reduction of four DPPH molecules:



All the above reaction steps add up to give an overall balance of Eq 1. Obviously, the first two steps of the mechanism may be generalized for any catalyst possessing surface OH groups and 'F-centers'. It may be accidental that the yields of III and IV are about equal. On the basis of the proposed mechanism, we may expect that the first step, the reduction of the radical, to be relatively slow because it is likely to be diffusion-controlled. The second and third steps involving the surface hydrogenation and the oxidation of the radical are likely to be fast and the last two steps should be fast.[*]

Rate studies. The apparent rate of the reaction is first order with respect to the radical concentration whether a solvent is present[6] or not.[7] In the absence of a solvent the reaction is essentially a solid state surface reaction and the DPPH molecules prefer to aggregate on oxidic surfaces as microcrystallites[8,9] and the observed kinetics on rutile surface is, naturally, diffusion controlled.[7] Therefore, the rate studies do not elucidate the reaction mechanism very much.

It is observed that in the absence of a solvent the reaction is extremely fast on carbon black (Cabot Carbolac-2, 800 m^2/g) and anatase (7·55 wt. per cent H_2SO_4, 263 m^2/g; no acid is consumed in the reaction) and is complete before the solvent can be removed from the system. In the case of carbon black the reason for this unusual reactivity may be the fact that on carbon surface the radical exists in a molecularly dispersed state without any aggregation.[10] The plausible cause for the unusual reactivity in other case may be that the anatase surface is covered with almost a monolayer of sulfuric acid which is possibly ester-linked to the surface[11] and, therefore, a much stronger reducing agent than any surface OH group. The radical could react completely before any aggregation on anatase surface occurs.

EXPERIMENTAL

The amount stated at the head of Table 1 were shaken together overnight at room temp after which the characteristic color of the radical was no longer evident. The catalyst was filtered off and the benzene distilled off. For the spectroscopic determination of V the benzene was condensed and further benzene added to the distillation flask until no quinone came over in the distillate. The determination of quinone was also

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[*] The reactions of DPPH with hydroquinone phenylpicrylhydrazine and 2,4,6-trinitro-4'-aminodiphenylamine are almost instantaneous.

carried out gravimetrically for another run by removing as much of the benzene as possible through a fractionating column which retained the quinone. After a flash evaporation of the remaining benzene at − 77°, the quinone was vacuum sublimed at 40° from the residue on to a cold liquid N_2 finger.

The hydrazine was crystallized out of the remaining solid (minus quinone). The residue from this crystallisation was separated by TLC. The small amount of II separated was added to the main batch.

Thin layer chromatography. The plates were conventionally prepared by using Adsorbosil-1 (Applied Science Laboratories, State College, Pa.). The developing soln was a 15% mixture of light petroleum in benzene. The plates used for testing purposes were 1¾ in. by 8 in. and for quantitative separation of products, 8 in. by 8 in. Three visible spots were obtained on the plates which in order of their decreasing R_f values are corresponding to III, II and IV. To isolate a constituent, the TLC band was scraped off the plates and the colored powder refluxed with chloroform in an extractor until the refluxing soln was colorless. The soln was filtered through a fritted-disc, the solvent evaporated off, and the remaining solid weighed after evacuation at 100°.

Identification of products. The m.ps of the following products and their mixed m.ps with authentic samples were: 1,1-diphenyl-2-picrylhydrazine, m.p. 169°, mixed m.p. 169°; 2,4,6-trinitroazobenzene, m.p. 149°, mixed m.p. 149°; *p*-benzoquinone, m.p. 114–115°, mixed m.p. 114–115°. For the first two compounds elemental and mass-spectral analyses exactly agreed with the calculated values. The characteristic odor and IR spectra definitely established the identity of quinone.

The identification of the compound characterized as IV is only tentative. When freshly chromatogrammed this compound appears yellowish on the plate and becomes brownish preceded by a pale yellow halo after a few hr. The brownish product extracted from the TLC band could not be crystallized even after repeated chromatogramming and under microscope it appeared resinous and gummy. No tractable derivatives could be prepared. It gave a variable elemental analyses ($C_{12}H_{7-10}N_{3-4}O_{4-5}$) and m.p. ranges. The associated yellow product obtained from a number of plates, after purification, gave yellow needles from the benzene soln. The elemental and mass-spectral analyses as well as m.p. and mixed m.p. determinations established this product as *picramide*.

The reaction of 2.4,6-trinitro-4′-aminodiphenylamine with DPPH was studied with a view that the dehydrogenation product may be IV. This, instead, appears to be a complex reaction involving polymerized products; the fraction of products soluble in chloroform, however, gives only two TLC spots characteristic of II and IV. Under ambient conditions IV is likely to yield picramide and the compounds originating from *p*-benzoquinonimine which are not easily isolable. The material balance of Eq 1 and the proposed mechanism of the reaction seem to support our characterization of IV.

Preparation of compounds for identification

1-*Phenyl-2-picrylhydrazine.* The method of its preparation has been described elsewhere.[3]

2.4,6-*Trinitroazobenzene.* This compound was prepared by the method described by Fisher[12] by treating a hot alcoholic solution of 1-phenyl-2-picrylhydrazine with an excess of yellow oxide of mercury. The compound precinitated out of the filtrate upon cooling and was further purified by TLC. The m.p. was 149°, not 142° as reported, and the elemental analysis was in agreement with the calculated values.

2,4,6-*Trinitro-4′-aminodiphenylamine.* This compound was prepared by the method suggested by Morgan and Micklethwait[13] by heating together for a few hr in dry toluene a mixture of *p*-phenylenediamine (9 g), picrylchloride (13 g) and anhyd NaOAc (6 g). After evaporating off toluene, the crystalline product was washed with warm alcohol and recrystallized from EtOAc in the form of lustrous black prisms. The m.p. was 187° as reported and the elemental analysis was in agreement with the calculated values.

All other chemicals used in this research were commercially available in reagent grades.

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