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## The Reaction of 2,2-Diphenyl-1-picrylhydrazyl with Minerals

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### SUMMARY

2,2-Diphenyl-1-picrylhydrazyl (DPPH) is reversibly adsorbed at acidic centers on the surfaces of a variety of common mineral pigments and fillers, and undergoes a subsequent irreversible reaction with adsorbed water or surface hydroxy groups to yield 1,1-diphenyl-2-picrylhydrazine, 1-(4'-nitrophenyl)-1-phenyl-2-picrylhydrazine, and 4,4'-oxybis[N-(4-picryliminocyclohexa-2,5-dienylidene)aniline] as the major products. The rate of the irreversible reaction on kaolinite is second-order with respect to DPPH and probably depends on the disproportionation between a DPPH and a protonated DPPH molecule. The possible use of DPPH as a probe for the activity of mineral fillers in polymer chemistry, and some implications on its use as a diagnostic test for radical species are discussed.

### INTRODUCTION

In other papers [1-4] the surface acidity of "neutral" aluminum-silicate fillers, such as kaolinite or bentonite, is shown to profoundly affect the chemistry of monomer or polymer systems. For example, these minerals can initiate the cationic polymerization of monomers, or they

can retard radical polymerization and cross-linking by trapping the intermediate propagating radical species or by promoting the ionic decomposition of peroxide initiators [4].

In this paper we report the use of DPPH (2,2-diphenyl-1-picrylhydrazyl) for the possible measurement of the surface acidity, and the activity of a variety of clay mineral fillers towards free radicals. The reaction of DPPH with kaolinite and with anatase has been studied in detail because of the important mechanistic aspects of these reactions in the present context. The results are of general interest in relation to the use of DPPH as a diagnostic probe for the detection of free radicals.

## EXPERIMENTAL AND RESULTS

The reactions using DPPH were conducted in darkness under a nitrogen atmosphere at 20°C unless otherwise specified. Thin-layer chromatography (TLC) of the products was performed on Silica Gel G Merck with benzene as elutant, and column chromatography on silica gel with benzene or 5% ethyl acetate-benzene as elutants. IR spectra of dispersions in KBr were recorded using a Beckman DK-2, and NMR spectra in  $\text{CDCl}_3$  using Varian H-60 and H-100 instruments. The ESR spectra at 20°C were recorded using a Varian V-4501 Instrument. DPPH concentrations were determined from peak-heights of the first-derivative presentation of the ESR signals; concordant DPPH assays were also obtained by titration with 2-mercapto-benzoic acid [5]. Mass spectra were obtained using a Hitachi-Perkin Elmer RMU-6D instrument; samples were examined by direct evaporation at chamber temperatures of 50 and 150°C; perfluorokerosine was used as a calibration standard. Microanalyses were performed by the Australian Microanalytical Service, Melbourne.

### Reagents

Malone kaolin from Egerton, Victoria, was supplied by Rodda Pty. Ltd., Melbourne. This was a dry-processed natural kaolinite with BET specific surface of  $9.3 \text{ m}^2 \text{ g}^{-1}$ , cation-exchange capacity of  $56 \mu\text{equiv g}^{-1}$  and containing approximately  $20 \mu\text{equiv g}^{-1}$  of exchangeable aluminum species. The kaolinite was dried in air at 110°C and, where indicated, rehydrated by exposure to water vapor; the water content was determined from the weight loss at 110°C. Its surface acidity was determined with Hammett indicators [6]. Aqueous colloidal anatase with a BET specific surface of  $300 \text{ m}^2 \text{ g}^{-1}$

was treated with sulfuric acid (7.5% w/w anatase), evaporated in vacuo, and then heated in air at 110°C. Diphenylpicrylhydrazyl was recrystallized from 2:1 benzene-hexane, and dried at 80°C/10<sup>-2</sup> mm for 16 hr; TLC showed the material to be pure. Solvents were of analytical quality and dried over molecular sieve 4A before use.

### Reaction of DPPH with Anatase

Anatase (1 g) was reacted with a nitrogen-purged solution of DPPH (100 mg) in benzene (30 ml) for 18 hr. The mixture was filtered under nitrogen and the residue washed repeatedly with benzene and then with ethyl acetate. The benzene and ethyl acetate solutions were examined separately by TLC, then fractionated by column chromatography, the composition of the fractions being checked using TLC. A "tetrabase" spray was used for detection of any benzoquinone, and a "ferric ferri-cyanide" spray for phenolic and arylamino-derivatives. The volatile components of the benzene and ethyl acetate solutions were also examined by gas chromatography. The yields of products are given in Table 1.

### Reaction of DPPH with Malone Kaolin

The procedure used for anatase was also applied to the reaction of DPPH with kaolinite; the results are summarized in Table 1. The rate of disappearance of DPPH from a  $1.3 \times 10^{-3}$  M solution in benzene (100 ml) on reaction with samples of kaolinite (5 g) at 30°C was monitored by the ESR signal intensities from the supernatant liquid; these results are shown on Fig. 1.

### Products of the Reactions

The reaction products of DPPH with anatase and kaolinite were similar and yielded four fractions on chromatography. These contained 1,1-diphenyl-2-picrylhydrazine (DPPH.H; TLC R<sub>F</sub> 0.57), found principally in the benzene extract; recovered DPPH (R<sub>F</sub> 0.55) liberated from its mineral complex on extraction with ethyl acetate; an orange colored compound (R<sub>F</sub> 0.24) found in both the benzene and ethyl acetate extracts; and a magenta-colored compound (R<sub>F</sub> 0.04) also liberated from its mineral complex on extraction with ethyl acetate. Some highly-colored material was also retained on the mineral surface (anatase), and as a nonelutable fraction on chromatography of the reaction products. No benzoquinone, other DPPH-derived fragments, or solvent-derived species were detected. The

Table 1. Reaction of DPPH with Kaolinite and with Anatase

Substrate	Water content of mineral	Solvent	Initial DPPH (% w/w mineral)	Recovered DPPH (% w/w initial DPPH)	Mole proportion of products per mole DPPH reacted			Magenta <sup>e</sup> compound
					DPPH.Hc	DPPH.NO <sub>2</sub> d		
Anatase	Dry	Benzene	10	9	0.69	0.06		0.07
Kaolinite	5.6%	Benzene	1.1	56 <sup>b</sup>	0.71	0.03		0.09
	0.7% <sup>a</sup>	Benzene	1.0	13	0.68	0.08		0.08
	Dry	Benzene	1.1	11	0.65	0.10		0.08
	Dry	Benzene	2.0	17	0.71	0.12		0.07
	Dry	CCl <sub>4</sub>	1.0	10	0.62	0.12		0.10

<sup>a</sup> Corresponds to the water content of the commercial kaolin.

<sup>b</sup> Includes 12% isolated from benzene extract.

<sup>c</sup> 1,1-Diphenyl-2-picrylhydrazine (R<sub>F</sub> 0.57).

<sup>d</sup> 1-(4'-Nitrophenyl)-1-phenyl-2-picrylhydrazine (R<sub>F</sub> 0.24).

<sup>e</sup> 4,4'-Oxybis [N-(4-picryliminocyclohexa-2,5-dienylidene) aniline] (R<sub>F</sub> 0.04).

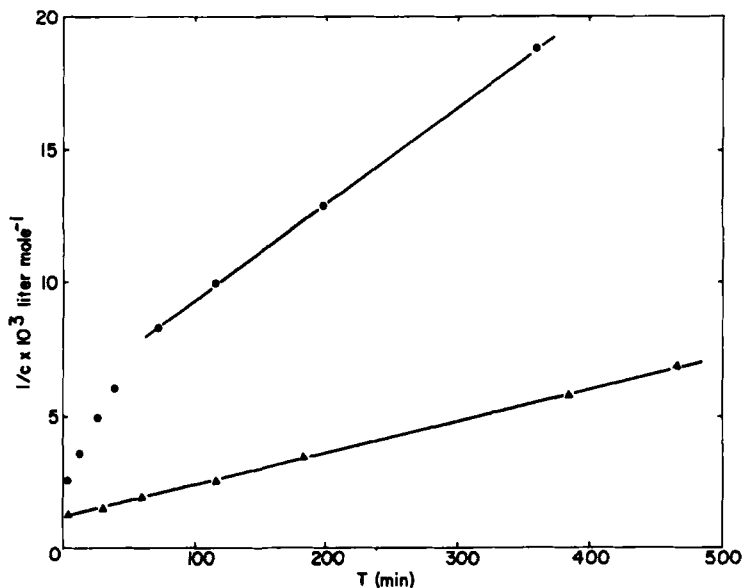


Fig. 1. Second-order rate plots for the reaction of DPPH with kaolinite; (●) with dry kaolinite; (▲) with kaolinite containing 1.2% water.

major products appeared to be formed simultaneously; prolonged reaction times only resulted in increased yields of unresolved highly-colored materials. TLC showed that the same four major products were also formed in the reaction of benzene solutions of DPPH with the other minerals listed in Table 2, and with 2 N aqueous sulfuric acid.

The DPPH.H was identified by analysis (found: C, 54.5%; H, 3.2%; N, 17.4%;  $C_{18}H_{12}N_5O_6$  requires: C, 54.7%; H, 3.3%; N, 17.7%) and by mass and IR spectroscopic comparison with an authentic sample. The orange-colored fraction was similarly identified as 1-(4'-nitrophenyl)-1-phenyl-2-picrylhydrazine (DPPH.NO<sub>2</sub>; mp, 148°C) [7, 8]. The magenta-colored fraction was recrystallized from CCl<sub>4</sub> as a tenaciously-solvated blue-black powder, mp, 168°C (found, after drying at 80°C/0.1 mm for 16 hr: C, 47.7%; H, 2.3%; N, 15.5%; Cl, 12.1%;  $[C_{36}H_{20}N_{10}O_{11} \cdot 0.85CCl_4]$  requires: C, 47.8%; H, 2.2%; N, 15.2%; Cl, 12.1%),  $\lambda_{max}$  (EtOH) 525 m $\mu$  (log  $\epsilon$ , 4.61). Its IR spectrum showed a strong band at 1600 cm<sup>-1</sup> (conj. C=N), and an absence of -NH-, -OH, or monosubstituted phenyl groups; the absence of these groups was also indicated by the NMR spectrum. Its mass spectrum showed strong ion peaks ascribed to a picrylamino fragment (m/e 228; C<sub>6</sub>H<sub>3</sub>N<sub>4</sub>O<sub>6</sub> + H), an oxydiphenylimino fragment (m/e 182, 183; C<sub>12</sub>H<sub>8</sub>NO + H) and

Table 2. Comparative Activity of Minerals

Mineral	BET specific surface ( $\text{m}^2 \text{g}^{-1}$ )	(M) moist (D) dried <sup>b</sup>	Surface acidity ( $\text{H}_0$ range)	Reactivity		
				DPPHC	CHPd	Styrene <sup>c</sup>
Malone kaolin	9.3	M	ca. -3.0	20.3	3.6	-
		D	8.2	45	41.0	++
Cornish kaolin	21	M	1.5 to -3.0	8.8	1.0	-
		D	-5.6 to -8.2	17.2	1.0	+
Hydrite 10 <sup>a</sup>	10.4	M	-3.0 to -5.6	5.5	9.4	-
		D	-8.2	45	33.5	++
Hydrite 10S <sup>a</sup>	—	M	1.5 to -3.0	5.5	3.4	-
		D	1.5 to -3.0	6.3	1.3	-

Talc	—	M	2.8 to 1.5	3.1	1.0	—
		D	1.5 to -3.0	3.6	1.0	—
Bentonite	ca. 15	M	1.5 to -3.0	8.0	1.0	—
		D	-8.2	16.0	40.1	+
Attapulgite	ca. 13	M	1.5 to -3.0	7.2	1.5	—
		D	ca. -3.0	45	45	++
Rutile titania	7.2	M	6.8 to 4.0	3.0	1.0	—
		D	6.8 to 4.0	3.0	1.0	—

<sup>a</sup> Hydrite 10 is an acid-flocced kaolin; Hydrite 10S is Calgon-treated Hydrite 10; both are supplied by the Georgia Kaolin Company, New Jersey.

<sup>b</sup> Moist (M) refers to minerals equilibrated with atmospheric moisture; dried (D) refers to mineral samples dried in air at 110°C.

<sup>c</sup> Amount of DPPH ( $\mu$ mole) removed from solution by mineral (1 g) under conditions described in the text.

<sup>d</sup> Amount of cumyl hydroperoxide ( $\times 10 \mu$ mole) decomposed by mineral (1 g) under conditions described in the text.

<sup>e</sup> Catalytic activity for polymerization of styrene; (—) inactive; (+) active; (++) strongly active.



its decarbonylation ion ( $m/e$  154), together with weak ion peaks at  $m/e$  317 ( $C_{12}H_6N_5O_6 + H$ ) and  $m/e$  408 ( $C_{18}H_{10}N_5O_7$ ). It could be readily reduced with sodium borohydride to yield an orange-colored derivative having an IR spectrum similar to that of 4-picrylamino-diphenylamine, and which could be readily reoxidized to the magenta-colored compound. We propose that the magenta compound is 4,4'-oxybis[N-(4-picrylimino-cyclohexa-2,5-dienylidene) aniline] (IV, Fig. 2).

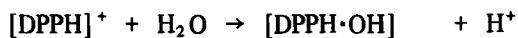
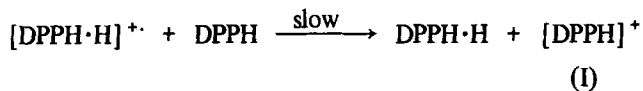
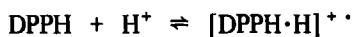
### Comparative Activity of Malone Kaolin and Other Minerals

A selection of commercially available mineral fillers and pigments was tested for activity towards DPPH, cumyl hydroperoxide, and styrene: 1) a mineral sample (1 g) was reacted with a  $10^{-3}$  M solution of DPPH in benzene (10 ml) for 15 min, the mixture centrifuged, and the DPPH content of an aliquot (2 ml) of the supernatant solution determined by titration with  $10^{-3}$  M ethanolic 2-mercaptobenzoic acid; 2) a mineral sample (1 g) was reacted at 20°C with a 0.04 M solution of cumyl hydroperoxide in benzene (10 ml) for 30 min and the residual hydroperoxide determined by iodometric titration [9]; 3) a mineral sample (1 g) was mixed with styrene (5 ml) in benzene (5 ml) and stood for 60 min at 20°C; the polymerization activity was gauged from the yield of polymer precipitated on addition of the mineral-free products to methanol. The results are summarized in Table 2.

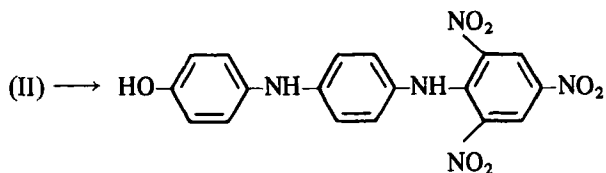
### DISCUSSION

DPPH reacts faster with minerals which are dry, and this observation is consistent with the increase in surface acidity which accompanies the removal of adsorbed water [1, 2]. In addition to Brønsted acidity, the dried kaolinite possesses Lewis acid centers [2], and on inorganic surfaces these are known to complex radical species, including DPPH, which can be reversibly adsorbed at these centers [10]. However, the appearance of these Lewis centers does not cause any major variation in the products of the irreversible reaction of DPPH with kaolinite (Table 1), and the dried minerals are mainly distinguishable from those with adsorbed moisture by the larger amount of DPPH adsorbed initially, and by the greatly increased rate at which the adsorbed DPPH undergoes a subsequent irreversible reaction which appears to primarily involve the surface Brønsted acid centers.

The use of the DPPH titer to predict the activity of the minerals in other reactions is complicated. For example, in chain reactions, such as



(II)



(III)

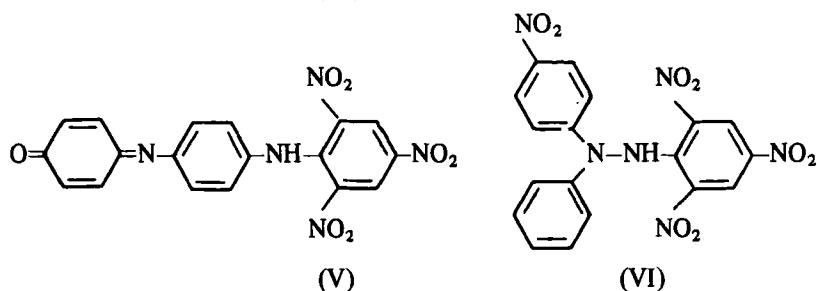
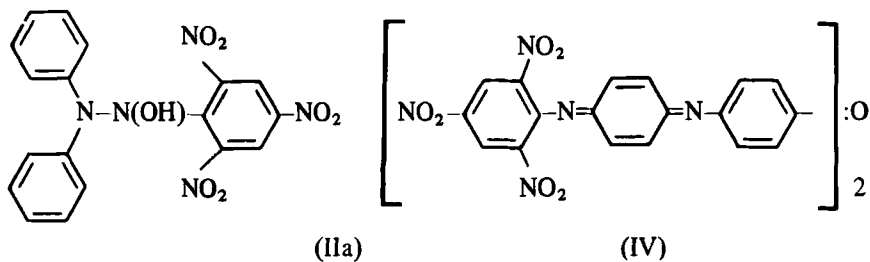


Fig. 2. Mechanism of initiation, and products of the acid-catalyzed reaction between DPPH and water adsorbed on mineral surfaces.

the cationic polymerization of styrene, only a few, strongly acidic sites are required, whereas the ionic decomposition of cumyl hydroperoxide requires a larger number of acidic sites which need not be as strong as those required to initiate the styrene polymerization. The DPPH titer does not readily distinguish between surfaces containing a few strong or many weak sites.

The mechanism and kinetics of the DPPH reaction, however, are of interest because of the widespread use of DPPH as a specific reagent for the detection of organic free-radicals. Many workers still accept that the loss of the characteristic color and ESR signal of DPPH is unequivocal evidence for the presence of these radical species. The formation of DPPH.H is also often regarded as conclusive proof of hydrogen abstraction via a free-radical mechanism. The reaction of DPPH with minerals bears a strong similarity with those known to involve ionic mechanisms, viz., the heterolytic decomposition of peroxides [4], the cationic polymerization of styrene [3, 11], and the protonation of Hammett indicators. An ionic mechanism is further supported by the findings of Imai and co-workers [10] on the reaction of DPPH with the related silica-alumina cracking catalysts. With the dried kaolinite and anatase we find that the adsorbed DPPH loses its characteristic color and ESR signal, but that addition of a base, such as ethyl acetate, early in the reaction regenerates most of the original DPPH, suggesting that the DPPH is present on the surface as an acid-base complex.

Following an initial rapid adsorption, the decrease in concentration of a DPPH solution in equilibrium with undried kaolinite follows second-order kinetics (Fig. 1). The kinetics of the reaction with dried kaolinite are more complex as there is also a decrease in rate as some of the reactive sites are poisoned by the adsorbed reaction products. However, the reaction appears to approach second-order kinetics with time. Assuming that the adsorption isotherm is linear, the rate of the irreversible reaction of DPPH with the Bronsted centers on undried kaolinite, i.e., kaolinite partially poisoned by adsorbed water, is therefore second-order with respect to DPPH. To account for this observation and for the products of the reaction, we propose a reaction sequence utilizing adsorbed water molecules or surface hydroxyl groups (Fig. 2). Note that if the kaolinite retained even only a monolayer of adsorbed water, equivalent to  $0.2 \text{ mmole g}^{-1}$ , or 0.3% by weight, this amount would be in excess of the amount of DPPH contained in the initial solution, and more than 20 times the requirements of the reaction sequence.

It is not known whether the hypothetical intermediate p-semidine

derivative (III) is formed from the cation (I) by a concerted process or via an oxyderivative (II); the N-hydroxy-diphenylpicrylhydrazine (IIa) is unknown, and substances previously assigned this structure have been shown to be DPPH.NO<sub>2</sub> (VI) [8].

The p-semidine derivative (III) is presumably oxidized by further DPPH to yield additional DPPH.H and either the picrylindoaniline (V) or the related enolic ether (IV) which we isolated. The DPPH.NO<sub>2</sub> (VI) is believed to be a by-product arising from the alternative o-semidine rearrangement of species (I) or (II). We have shown that 2-picrylaminodiphenylamine reacts with DPPH to yield DPPH.NO<sub>2</sub> together with highly-colored condensation products presumably derived from the phenazine species which would be formed by cyclization of the imino-radical intermediate with elimination of NO<sub>2</sub> from the picryl group; a similar reaction has been reported in the photolysis of DPPH [7]. Neither DPPH.NO<sub>2</sub> nor condensed species were produced in the reaction of 4-picrylaminodiphenylamine with DPPH.

Aston and co-workers [12] have reported that the reactions of DPPH with an acidified anatase of high moisture content, with silica gel, and with a sulfuric acid-benzene mixture yield DPPH.H, together with p-benzoquinone and "N-picryl-p-phenylenediamine," the presumed hydrolysis products of the indoaniline (V). The rates were reported to follow first-order kinetics, and a different reaction sequence involving one-electron transfer processes with reactive centers on the solid surfaces was proposed. However, the present reactions followed different kinetics, and we were unable to detect either the indoaniline (V) or its hydrolysis products in the reaction products.

The products described for the reaction of DPPH were not peculiar to the particular kaolin or anatase samples used; they were formed in the reactions with other minerals (Table 2), and were even formed in some homogeneous acidic systems to be reported elsewhere. We therefore suggest that there is a general, irreversible, acid-catalyzed reaction of DPPH with water or inorganic surface hydroxyl groups, which is probably initiated by the reaction between a DPPH and a protonated DPPH molecule. The disappearance of the characteristic color and ESR signal of DPPH therefore is not an unambiguous test for the presence of other radical or electron-deficient species.

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