Excess Oxygen of Chromia

II. Reaction with Diphenylpicrylhydrazine

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Oxidation of diphenylpicrylhydrazine (DPPH.H) to diphenylpicrylhydrazyl (DPPH) is effected by mesoporous chromias with excess oxygen but not by their microporous equivalents, the pores of which are too small to permit entrance and egress of DPPH.H and DPPH. Of the iodometric oxidizing capacity of the macroporous chromias, 30–40% forms DPPH, 10% remains unused and the remainder is consumed in oxidizing DPPH to diamagnetic products. The reaction is nearly complete in one day at 25°C. Addition of oxygen at this point leads to a substantial rate of catalytic oxidation which continues for days. The catalytic site is probably Cr(V) which is difficultly reducible because of some special structural feature. Mesoporous chromias devoid of excess oxygen upon which oxygen has been adsorbed at −78°C oxidize DPPH.H to DPPH but they provide little catalytic oxidation.

CrO₃ on wide-pore silica also oxidizes DPPH.H to DPPH but its catalytic activity is small and dies rapidly. The lower catalytic activity is probably associated with the much higher dispersion of the CrO₃/SiO₂. Studies by EPR of CrO₃/SiO₂ gave results consistent with Cr(V) being the catalytic site. In the reduction of Cr(VI) by DPPH₂, Cr(V) is an intermediate which reaches a maximum concentration of at least 9% and then declines.

INTRODUCTION

This paper reports the results of a study of the oxidation of diphenylpicrylhydrazine (DPPH.H) dissolved in benzene to diphenylpicrylhydrazyl (DPPH) by the excess oxygen of chromia. The reaction is an unusually simple one which involves merely the abstraction of a hydrogen atom from DPPH.H as shown in Fig. 1. The oxidation is known to be effected by several solid oxidizing agents such as lead dioxide (*1*) and manganese dioxide (*2*). However, the stimulation for our investigation came from reports that platinum covered with adsorbed oxygen also effected the oxidation, Garnett and coworkers (*3,4*), extended by Moyes *et al.* (*5*). In this work, platinum surfaces were exposed to oxygen, the oxygen pumped off, and a benzene solution of DPPH.H added. Formation of DPPH was monitored either by epr or by optical spectroscopy. The first group of workers reported that subsequent introduction of oxygen led to further reaction of DPPH.H, i.e., that platinum would catalyze reaction between DPPH.H and oxygen. The second group reported that platinum metal powder would not act as a catalyst but that DPPH.H was oxidized only by a preformed, adsorbed layer of oxygen on platinum. As will appear, certain chromias are catalysts for reaction between DPPH.H and oxygen.

DPPH.H is a large reductant with a diameter of about 1.4 nm. We have investigated the effect which the texture of a solid oxidant may have upon its reactivity with DPPH.H by examining reaction between DPPH.H and chromias of
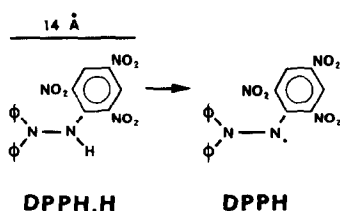
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FIG. 1. Diphenylpicrylhydrazine (DPPH.H) and diphenylpicrylhydrazyl (DPPH).

various textures and of oxidized chromium species in 13X molecular sieves and on wide-pore silica gels.

EXPERIMENTAL

Technique. The chromia (usually about 0.1 g, computed as are all weights in this paper on the basis of fully dehydrated Cr_2O_3) was placed in 7 mm tubing at C upon a plug of Pyrex glass wool as shown in Fig. 2. The reaction vessel was attached to the gas-vacuum line by means of a Swagelock union with Teflon ferrules connected to the 0.25 in. o.d. tubing at A. The chromia was then activated in flowing gases as desired. The code for the chromia and for its treatment is that of paper I. After activation, the capillary below the catalyst was sealed by fusing and the Rotoflo 6/13 value was closed.

The reaction vessel was then connected to the DPPH.H supply system by the Swagelock union. The supply system consisted of a 55.3 cm^3 delivery bulb located between Fisher and Porter Teflon needle valves. The delivery bulb could be filled from a 5 liter storage bulb via the upper valve and the contents delivered to the reaction vessel via the lower valve which terminated in a section of 0.25 in. tubing. Appropriate leads to helium, vacuum and vent permitted the reaction vessel to be filled with a benzene solution of DPPH.H without atmospheric contamination.

Benzene was degassed by bubbling a stream of dry nitrogen through it and benzophenone and sodium wire were added. The mixture was refluxed and, after a blue

color appeared, the benzene was distilled into a vessel containing DPPH.H (Eastman Kodak Company). The resulting solution was transferred to the 5 liter storage bulb and degassed with flowing argon. Molecular sieve 5A was added to eliminate any adventitious water and the bulb was pressurized and kept under argon. The concentration of the DPPH.H was 2.5×10^{-2} M by optical spectroscopy. There was no DPPH background in ESR.

After receiving the solution of DPPH.H, the reaction vessel was shaken at room temperature in a mechanical shaker. During shaking the chromia was in the bulb of the reaction vessel. By suitable manipulation one could transfer solution free of chromia to the ESR probe shown in Fig. 2. It was of 3 mm o.d. fused silica attached to the reaction vessel by a Pyrex-Vycor graded seal. Analyses for DPPH by ESR were performed at 25°C on a Varian E-4 spectrometer. When present, oxygen was first removed by flushing with argon. Signal heights were compared to those of a 0.1% pitch standard. The procedure was calibrated with solutions of DPPH of known concentration. Signal heights were linear with concentration to 0.6×10^{-3} M.

We endeavored at all stages to avoid introduction of oxygen or water. The system
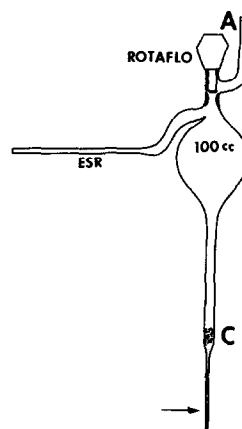

FIG. 2. The reaction vessel for ESR measurements.

was regularly checked for leaks with a helium mass spectrometer leak tester. The helium used in the activation was 99.995% grade purified by passage through activated charcoal at $-196°C$.

Oxidation of DPPH.H to DPPH. Figure 3 exhibits yields in the oxidation by **85** of DPPH.H to DPPH as a function of the conditions of activation. Some of the scatter in the data may result from the temperature of activation being uncertain to about 5°. Swirls of DPPH could be seen arising from the more active chromias immediately following introduction of the benzene solution of DPPH.H. The rate of production of DPPH gradually declined and usually became very slow after about one day. After a few weeks, the content in DPPH slowly declined. Yields of DPPH given are usually those after about one day. Runs in which chromia was omitted gave no DPPH.

Reactions of DPPH. Solutions of DPPH in benzene, usually about 25 cm³ of 0.001 M, were added to various samples of chromia. Upon adding DPPH to **85**,
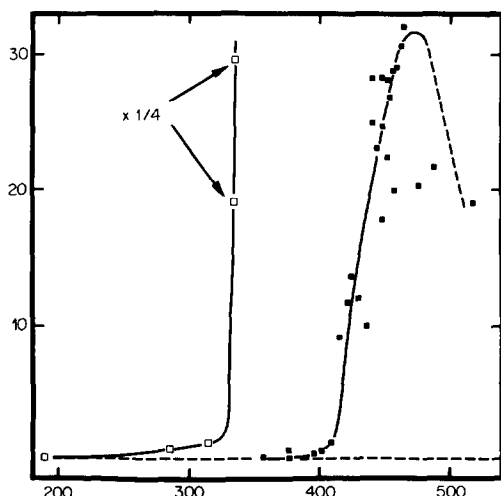

FIG. 3. Oxidation of DPPH.H by **85**; yield of DPPH as a function of the temperature of activation of **85** in helium (filled squares) and in oxygen (open squares). The amount of **85** used was 0.06 g. *y*-axis, mmole DPPH/mole Cr; *x*-axis, temperature of activation in °C.

He446, the content in DPPH decreased with time and another batch of solution was added. Over one day, 11 mmole/mole Cr disappeared from solution. Extraction of the chromia by acetone gave an orange solution which was evaporated to dryness and the residue was dissolved in benzene. This solution was devoid of an ESR signal. Chromatography on Whatman no. 1 chromatography paper using cyclohexane plus a small amount of carbon tetrachloride as solvent established the absence of DPPH and DPPH.H and the presence of two compounds of much lower R_f values, one yellow and one magenta, the latter being the faster moving. Even chromia devoid of excess oxygen led to the disappearance of DPPH provided it was mesoporous, for example, **85**, H_2496 and **85W135**, vac470, H_2300.

Catalytic oxidation of DPPH.H to DPPH. The following experiment is typical of those with a number of X–Cr(VI)'s activated in helium to between 437 and 518°C. Sample **85,He518** initially generated 19 mmole of DPPH/mole Cr during a period of one day. After adding O_2 at 1.2 atm and shaking for 12 hr, 23 mmole more DPPH was formed. The benzene solution was replaced with a fresh one. This was repeated twice. The yields were 30, 46, and 20 mmole. Thus an initial yield of DPPH of 19 was followed by one of 119 mmole/mole Cr. Oxygen at a pressure of 1.8 atm gave increased yields and rates. Addition of a few drops of water to the reaction vessel after several oxygen cycles reduced the catalytic yields of DPPH to one quarter to one-half of the previous yields. Exposure of the chromia sample to water vapor at 25°C before the initial reaction cut the initial and the catalytic yield substantially but not completely.

Cr(VI)/silica gel. Chromium compounds were deposited on the internal surface of 60–80 mesh wide-pore silica gel (average pore diameter, 14 nm) by two methods. In one, a dilute solution of sodium hydroxide

was added to Davison silica gel grade 59 to a pH of about 9.5 and the gel was washed five times with water. Addition of a small amount of dilute solution of chromium nitrate led to deposition of chromia on the surface of the gel (6). The gel was washed thrice with water and dried in an oven at 125°C. The gel becomes orange upon heating in flowing oxygen at 525°C. Iodometric titration of the orange gel gave the %Cr (by wt) as 0.35. The material is designated Cr^{3+}/SiO_2.

In the other method, wide-pore silica gel was impregnated with CrO_3 aq and dried at 125°C. Iodometric analysis of a sample on Davison grade 59 without activation gave %Cr as 0.28. It is designated $CrO_3(0.28)/SiO_2$. A similar preparation on Davison grade 62 is designated $CrO_3(2.38)/SiO_2$ to indicate its chromium content.

The scatter of iodometric titrations of these materials and also that of potassium dichromate was much smaller than those of titrations of chromias. The titrations were reproducible to ±3%. Activation of samples of CrO_3/SiO_2 in oxygen to about 450°C reduced the iodometric titer but only about 4% in agreement with Hogan (7).

The dispersion of reduced CrO_3/SiO_2 was probably greater than that of Cr^{3+}/SiO_2 since CrO_3/SiO_2, H_2300 was more rapidly oxidized to Cr(VI) by oxygen at 450°C than was Cr^{3+}/SiO_2.

Most experiments with these materials involved preliminary activation to about 450°C in oxygen. Such samples as well as unactivated samples of CrO_3/SiO_2 oxidized DPPH.H to DPPH in yields of 31–47% of the iodometric titer. Several experiments with acetone and acetic anhydride rather than benzene as solvents gave yields in this range but dioxane gave only 9%. Chromic anhydride dissolved in acetone gave about 11%.

The EPR of chromia/silica could be determined by transferring it to the side tube

of the reaction vessel (Fig. 2). The sample contained the silica plus inter- and intraparticular solution amounting to about 2% of the total benzene solution. Signals were integrated by the Varian Analog Chopper Stabilized Operational Amplifier, Model 232-3.

If DPPH.H dissolved in benzene is added to $CrO_3(0.28)/SiO_2$, the appearance of a signal from adsorbed DPPH is accompanied by one from Cr(V) which maximizes in a few minutes and then decays slowly. After 5 days, one-half of the signal intensity has been lost. In a similar experiment, the EPR probe was immersed in liquid nitrogen 30 sec after exposure to DPPH.H in benzene and the EPR run at −196°C. Integration of the Cr(V) signal indicated that 5% of the chromium was present as Cr(V). The sample was then thawed at 25°C and refrozen after 10 min. The Cr(V) then amounted to 9%. A further thaw with refreezing after twenty min led to a weaker Cr(V) signal. Exposure of chromium/silicas containing Cr(V) to a solution of DPPH in benzene did not change the shape of the Cr(V) signal.

Cr^{3+}/SiO_2, H_2320 gave no initial yield of DPPH. Subsequent addition of oxygen led to formation of DPPH but only to DPPH/Cr = 0.03. If the oxygen was added before the DPPH.H, and evacuated after a few min, a small signal of Cr(V) was formed. Introduction of DPPH.H caused the signal to decay in the same fashion as that of Cr(V) generated from Cr(VI). If oxygen was added for the second time, no new Cr(V) was formed.

Addition of oxygen to the system CrO_3/SiO_2 plus DPPH.H broadens the DPPH and the Cr(V) signals, the latter so seriously as nearly to disappear. Flushing with argon restores the DPPH signal but reappearance of the Cr(V) signal varies with the time of exposure to oxygen. Thus, if after an exposure of a few minutes, the benzene solution is withdrawn, the chromium/silica rinsed with benzene and dried

by evacuation, the Cr(V) signal reappears unchanged. However, if the period of exposure is 20 min, the signal reappears with only 50% of its former intensity. Addition of DPPH.H in benzene to this sample causes an increase in the DPPH signal but not in that of the Cr(V) signal. If, after about one day, systems which were initially CrO_3/SiO_2 plus DPPH.H in benzene were exposed to oxygen for 12 hr, the Cr(V) signal was permanently eliminated.

DISCUSSION

Oxidation of diphenylpicrylhydrazine DPPH.H. Table 1 presents the results of agitating various types of chromias with a solution of DPPH.H in benzene at 25°C. Formation of dissolved DPPH was observed only with *mesoporous* chromias containing excess oxygen. Either type of excess oxygen, surface chromate or ox-

ygen adsorbed at −78 or 25°C, was effective. The *microporous* chromias containing excess oxygen, A–Cr(VI), A–Cr(x), and A–Cr(III)O_2ads, gave negligible yields of DPPH. In accord with these observations, CrO_3 on wide pore silica gel oxidized DPPH.H to DPPH whereas CrO_3 in the pores of molecular sieve 13× did not.

After activation, both A–Cr(III) and X–Cr(III) catalyze the hydrogenation of ethylene at −78°C and of 1-hexene at 60°C (8). However, it is understandable that the 1 nm pores of microporous chromia (paper I) should fail to admit the much larger substrate DPPH.H and that entrance and egress of DPPH.H and DPPH should be easy with mesoporous chromias and wide pore silica gel.

As shown in Fig. 3, **85,** activated in helium produces little DPPH unless the

TABLE 1

REACTION OF DPPH.H WITH CHROMIAS AND RELATED MATERIALS AT 25°C[a]

	Oxidation to DPPH	No oxidation to DPPH
No excess oxygen	No examples	A–Cr(III): **25,**He460 **85,**H$_2$350,He460 X–Cr(III): **85**W135,vac470,H$_2$300 **85,**O$_2$351,CO390
Excess oxygen	X–Cr(VI): **85,**He450 **85,**O$_2$335 **85**W135,He440[b] **85,**H$_2$285,vac300,[c] O$_2$25,He455 X–Cr(III):O$_2$ads: X–Cr(III) plus O$_2$[d] at −78 or 25°C CrO_3/SiO_2[e]	A–Cr(VI): **135,**He360 **85,**He400 A–Cr(x): **85**W135,He200 A–Cr(III)O$_2$ads: A–Cr(III) plus O$_2$ at −78 or 25°C CrO_3 in 13X[f]

[a] For code to chromias (such as A–Cr(III)) see Table 1 of paper I. The code to treatments (such as **85,**H$_2$350, He460) is also in paper I.

[b] 21 mmole DPPH/mole Cr.

[c] 12 mmole DPPH/mole Cr. **85,**H$_2$320,He320,O$_2$25,He444 gave 25.

[d] **85**W135,vac465,H$_2$330,O$_2$−78 and **85,**H$_2$450,O$_2$25,H$_2$320,vac460,O$_2$−78 both gave 15–16 mmole DPPH/mole Cr.

[e] CrO_3 on wide pore silica gel, average pore diameter = 14 nm.

[f] Cr(VI) in molecular sieve 13X made by ion exchange of Cr^{3+} followed by oxidation in O_2 at 450°C or by impregnating 13X with a solution of chromic acid followed by drying. By iodometric analysis (paper I) both contained about one mequivalent of oxidizing capacity per gram.

temperature of activation exceeds 400°C. The yield then rises rapidly with increasing temperature of activation and probably declines beyond about 460°C. Activation *in vacuo* gave similar results. The temperature interval for the development of activity for forming DPPH is exactly that for conversion of microporous A–Cr(VI) to mesoporous X–Cr(VI) as shown in paper I. Thus, the process leading to development of activity is pore enlargement perhaps accompanied by migration of oxidized chromium species to the surface. This phenomenon is shown in an extreme form during activation in oxygen (Fig. 3). There is a nearly sharp break between activation at 315°C giving little oxidation and activation at 335°C giving large amounts of oxidation. The break coincides with transition from microporous, amorphous to mesoporous, crystalline chromia.

The maximum yields of DPPH for the chromias and the CrO_3/SiO_2 in the lower left corner of Table 1, were in general in the range of 30–40% of the iodometric titer. Addition of a fresh solution of DPPH.H generated negligible further DPPH. Where is the residual oxidizing capacity? Since considerable DPPH might remain adsorbed on the chromia, a number of experiments were made in which agents which might displace any adsorbed DPPH were added about one day after initial addition of DPPH.H. Addition of ammonia, pyridine or trimethylamine led to visible and immediate evolution of DPPH. The total amount of DPPH was rapidly increased by 10–15%. The newly formed DPPH may have been present as adsorbate on the chromia but it may have resulted from uncovering Cr(VI) by removal of oxidized DPPH or from generation of Cr(VI) by disproportionation of Cr(V) or Cr(IV). Carbon dioxide, nitrous oxide carbon monoxide, and ethylene led to the liberation of no additional DPPH.

In another attempt to locate the missing oxidizing titer, the chromia was titrated iodometrically after exposure to the benzene solution of DPPH.H for one day. This required a solvent which would remove benzene and then dissolve in the aqueous iodide solution and not interfere chemically. Glacial acetic acid or acetone appeared to function satisfactorily. Several experiments of this nature were run of which the following was typical. A sample 85, He438 initially generated 19 meq DPPH/mole Cr. Iodometric titer after washing with acetic acid gave a titer of 9 meq/mole Cr. This unused oxidizing titer might be in addition to the desorbed DPPH, or, as mentioned, it might represent the same titer. In any case, about 50% of the iodometric titer remains unidentified.

Reaction of DPPH with chromia. Exposure of a solution of DPPH in benzene to microporous chromias, A–Cr(III), A–Cr(VI), A–Cr(x), and A–Cr(III)O_2ads, resulted in no loss in DPPH but X–Cr(VI) caused a decline in the concentration of DPPH. Pyridine liberated very little of the lost DPPH but acetone extracted an orange material which was devoid of an ESR signal. The orange material was separated into magenta and yellow components by paper chromatography. X–Cr(VI) of large oxidizing capacity (85, $O_2$360, vac25) rapidly destroyed DPPH and only the yellow component could be isolated from the product.

X–Cr(VI) prepared from 85 destroyed DPPH at an augmented rate if the sample was exposed to water vapor before addition of DPPH and even A–Cr(VI) so treated [for example, 25, He456, $H_2O(v)(0.33)(25)$] led to some loss of DPPH. Pyridine and ammonia desorbed no DPPH from the water-treated samples. This effect of water vapor may explain the observation that treating a sample like 85, He448 with water vapor followed by evacuation for 12 hr before addition of the benzene solution of DPPH.H led to a faster initial formation of DPPH but to a max-

imum yield which was only about one-half of normal.

The acetone extracts of a number of samples of X–Cr(VI), which had been used in runs with DPPH.H, contained large quantities of the magenta and sometimes also of the yellow component.

It thus appears that treatment of X–Cr(VI) with DPPH.H leaves about 10% of the oxidizing capacity unused, about 35% is used to form DPPH and the remaining oxidizing capacity is consumed in oxidizing DPPH first to a magenta compound and that to a yellow material.

There have been several studies of the decomposition of DPPH on the surfaces of solids (9–11). It has been proposed that the rather complicated processes which occur on the surfaces of rutile, anatase, zinc oxide, kaolin and charcoal in the presence of adsorbed water involve various reactions of DPPH with adsorbed water and which lead to disproportionation to DPPH.H and oxidized products. In addition, it is likely that X–Cr(VI) can oxidize DPPH. We found that an acetone solution of chromic anhydride oxidized DPPH to the magenta compound.

Salomon and Hawthorne (11) had reported that extraction by benzene and then ethyl acetate of samples of kaolin and titania which had been used for the decomposition of DPPH contained a magenta compound characterized by $\lambda_{max} = 525$ nm and by peaks at 154, 182-3, and 228 in the mass spectrum. They proposed the following formula for it:
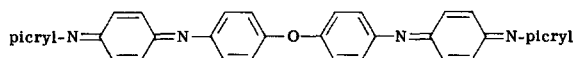
reaction has become very small and if oxygen is now added, formation of DPPH recommences immediately. In the most protracted experiment in which three replacements with fresh solutions of DPPH.H were made, an initial yield of 19 mmole/g Cr was followed by the formation of 119. Water must be formed during oxidation of DPPH.H to DPPH but it is clearly not a strong poison. Addition of larger quantities of water cuts the catalytic yields substantially but it does not eliminate the reaction. However, interpretation of such experiments is difficult because the water may fill pores in the chromia and block the reaction of DPPH mechanically and water promotes further reaction of DPPH. Nitrous oxide gives only a small catalytic yield when substituted for oxygen in reactions which had started with X–Cr(VI).

Microporous A–Cr(III) and A–Cr(VI) and mesoporous X–Cr(III) give no initial yield and no catalysis. However, if X–Cr(III) is treated with oxygen at −78°C and then exposed to DPPH.H there is a substantial initial yield but the catalytic yield is only a few % of that obtained in starting with X–Cr(VI). Sites capable of acting catalytically are produced in much larger quantities starting with X–Cr(VI) than with X–Cr(III)O₂ads. Apparently DPPH.H blocks Cr³⁺(cus) and prevents reaction with oxygen; otherwise X–Cr(III) would give a catalytic yield since X–Cr(III)O₂ads gives an initial yield.

Since DPPH.H is a one electron ox-

picryl-N=⟨ ⟩=N–⟨ ⟩–O–⟨ ⟩–N=⟨ ⟩=N-picryl

The optical spectrum and the mass spectrum of our magenta compound coincided with those reported by Salomon and Hawthorne. In addition, NMR indicated the absence of N–H and O–H groups.

Catalytic oxidation of DPPH.H by chromia. If DPPH.H is allowed to react with X–Cr(VI) for one day until the rate of

idizing agent, it must reduce Cr(VI) via the sequence Cr(VI) → Cr(V) → Cr(IV) → Cr(III). The sites capable of acting catalytically are not Cr³⁺(cus) since these would be strongly blocked by water. Since X–Cr(III)O₂ads is not X–Cr(VI) but probably some form of Cr(V) (paper I), X–Cr(III)O₂ads should generate Cr(IV) and

$Cr^{3+} \cdot H_2O$ when it acts as an oxidizing agent. It appears likely, then, that the catalytic sites are Cr(V) and the absence of much catalytic oxidation when nitrous oxide is substituted for oxygen is consistent with this since nitrous oxide must be a two electron oxidizing agent if one rejects $Cr(VI)O^-$ as unlikely. Whatever the oxidation number of the catalytic sites, they have a special feature; they do not directly oxidize DPPH.H but they react with oxygen to form surface species which do and which in so doing revert to the catalytic sites.

The reduction of X–Cr(VI) would be expected to involve various reactions similar to the following examples:

$$Cr(VI)O^{2-} + H.DPPH \rightarrow$$
$$Cr(V)OH^- + DPPH$$
$$Cr(IV)OH^- + H.DPPH \rightarrow$$
$$Cr^{3+}OH_2 + DPPH$$
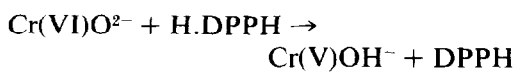
We have not established the nature of the special structural features which lead certain Cr(V) sites to act catalytically but not directly oxidatively. Perhaps the Cr(V) sites lack the neighboring O^{2-} ions needed for a reaction of the form of the upper equation above but are still capable of reacting with oxygen to form $Cr(VI)O_2^-$. Or, perhaps, two adjacent such Cr(V) sites form Cr(VI)–O–O–Cr(VI). Both of these species should be capable of oxidizing DDPH.H. Water formed during the reaction could desorb or migrate from Cr(VI) and probably Cr(V) but not from Cr(III).

Reactions of CrO₃/SiO₂. We deposited two types of chromium compounds on wide pore (average pore diameter = 14 nm) silica gel, Cr_2O_3/SiO_2. Since before use samples were usually heated in oxygen at 460°C and since Cr_2O_3/SiO_2 is completely oxidized to CrO_3/SiO_2 upon heating in oxygen (6), the oxidation state of samples of both types was usually Cr(VI). All gels in the Cr(VI) form oxidized DPPH.H to DPPH and the ratio

(DPPH formed)/(iodometric titer)

was about the same as for samples of X–Cr(VI).

The CrO_3/SiO_2's were originally examined in connection with the role of the texture of the oxidant in the oxidation of DPPH.H. However, another aspect of Cr/SiO_2 also proved useful. Because of the spin exchange with the paramagnetic surface, the only visible EPR signal from chromia is the very broad signal of Cr(III) (12). The much more highly dispersed chromia/silica also exhibits signals from adsorbed DPPH and from Cr(V). The latter species has been studied by several groups on chromia/silica and related materials particularly in connection with the polymerization of ethylene on CrO_3/SiO_2 (13–16). Cr(V) appears both during oxidation of Cr_2O_3/SiO_2 and during reduction of CrO_3/SiO_2.

Adsorption of DPPH on chromia/silica is small. Thus, addition of pyridine to the solution after oxidation of DPPH.H with $CrO_3(0.28)/SiO_2$, O_2472 led to an increase in the concentration of DPPH in the benzene solution which was barely within the limits of detectability, and which corresponded to the desorption of about one molecule of DPPH/60 nm² of total area. However, if the reacted CrO_3/SiO_2 was transferred to the ESR tube, we could examine a system consisting of the silica with only about 2% of the solution. The signal observed was a broadened one characteristic of adsorbed DPPH. Addition of pyridine led to the immediate conversion of the ESR signal to the sharper one characteristic of DPPH in benzene. Addition of pyridine to the system, DPPH adsorbed on silica gel alone, gave results indistinguishable from those just described. Probably, then, the DPPH is primarily adsorbed on the silica rather than on the chromia fraction of the surface of chromia/silica.

Content in Cr(V) was also assayed by examining the Cr/SiO_2 transferred to the EPR tube. Cr^{3+}/SiO_2, vac450, O_2225 exhibited a substantial signal from Cr(V). The

signal was removed by hydrogen at 300°C, rapidly initially but completely only in hours. Exposure of this reduced sample to oxygen at 25°C followed by evacuation generated a small signal of Cr(V) which increased tenfold upon continued evacuation at 140°C for a few minutes and tenfold again at 500°C for a few minutes. In our view, the exposure to oxygen led to conversion of Cr^{3+}(cus) to $Cr(IV)O_2^-$ which on heating was partially converted to Cr(V). We could detect no signal from O_2^-, but, because of spin exchange, such a signal would not necessarily be expected.

CrO_3/SiO_2, vac450 gave a small signal of Cr(V) which was eliminated by oxygen at 450°C. Treatment with ammonia at 25°C changed the color of $Cr(VI)/SiO_2$ from orange to brown, it led to the appearance of a large signal of Cr(V), and after several hours it led to about a 30% loss in iodometric titer. We had been unable to establish the occurrence of reduction of X–Cr(VI) by ammonia by heterogeneous iodometry (paper I) but scatter in those experiments was much more serious than in those with CrO_3/SiO_2.

A signal from Cr(V) appears immediately upon addition of DPPH.H to $Cr(VI)/SiO_2$. The signal maximizes in about 10 min and then declines slowly. The maximum amount of Cr(V) which we could detect was 9% of total chromium.

CrO_3/SiO_2 gave catalytic conversion of DPPH.H to to DPPH upon the addition of oxygen but the catalytic yields were smaller, only one-half to one-quarter those of X–Cr(VI). Further, the catalytic activity decayed much more rapidly with CrO_3/SiO_2. This may be associated with the fact that oxygen eliminates Cr(V) (or at least its EPR signal) in an exposure of about 12 hr. This difference between the catalytic behavior of X–Cr(VI) and CrO_3/SiO_2 may indicate that Cr(V) can exist at the surface of chromias in positions stabilized against reduction by DPPH.H and destruction by oxygen in ways impossible on the highly dispersed chromia/silica. This suggestion is tentative since we had no independent way to assay the content of the unsupported chromias in Cr(V).

ACKNOWLEDGMENTS

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