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ESR Examination of Ferrocene on Porous Silica*

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The effects of 2537 Å light, gamma radiation, oxygen and nitrogen on ferrocene adsorbed on porous silica in the form of porous Vycor glass rods have been investigated by ESR techniques. 2537 Å irradiation at 77°K results in the formation of atomic H, the C_5H_5 radical and possibly the $C_4H_4^-$ or the $C_5H_4^-$ radical anion. Gamma irradiation at 77°K gives an ESR spectrum characteristic of irradiated porous Vycor glass, with apparently no transfer of the excitation to the adsorbed ferrocene. Treatment with oxygen at room temperature produces an ESR signal of O_2^- with a hyperfine structure which indicates the association of the O_2^- with a hydrocarbon moiety containing five equivalent hydrogen atoms, and the anisotropy characteristics of the O_2^- signal suggest the presence of iron III in the complex. This complex may be typical of those present during oxidation of hydrocarbons on metal catalysts. The laser Raman spectrum of the adsorbed ferrocene is the same as that reported for crystalline ferrocene. Nitrogen gives no detectable effects.

INTRODUCTION

Organometallic complexes of transition metals are of increasing interest in biochemistry and catalysis. They are usually investigated in liquid systems as homogeneous catalysts. However, it is advantageous to develop means to use them in the adsorbed state on solid surfaces in heterogeneous catalytic systems. This would permit retention of the catalyst in the reacting system if the latter is a continuous process without the problem of separating the complex from the products. Furthermore, the treatment of the organometallic complex adsorbed on the surface with gases can be more easily controlled than when the complex is dissolved in a solvent for the latter case shows limited solubility of gases and a diffusion controlled interaction of the gas with the complex.

We have chosen ferrocene on porous Vycor glass as the system for study. Ferrocene was selected because it is a stable well-characterized and easily purified representative of a large class of π complex sandwich compounds. Miller, Tebboth and Tremaine (*1*) have reported that ferrocene on silicate glass may react with nitrogen. This is plausible on the basis that ferrocene has a low spin d^6 configuration similar to that found in the Ru(II) complexes of molecular N_2. Porous Vycor glass (PVG) is a suitable material to use as a support. It has a high surface area about 140 m^2/g and uniform size distribution of the 40 Å pores. On this support, Fujita and Turkevich (*2*) have stabilized methyl radicals at about 300°K (*3*).

The study of the surface properties of ferrocene in PVG is also part of the pro-

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gram of investigating the use of nuclear radiation for chemical purposes. It is envisaged that the nuclear radiation is to be absorbed in the solid support, degraded into smaller quanta which could migrate to the surface where they could activate a catalytic center. Ferrocene, because of its conjugated ring system and stability, seemed particularly appropriate for this purpose. The effects of gamma and ultraviolet radiation on this system were investigated. The effect of radiation on PVG (*3*), and on ferrocene (*4*), independently, have been reported previously.

Adsorption of nitrogen was studied in a static adsorption system in an attempt to confirm the report of Miller, Tebboth and Tremaine (*1*) that the ferrocene on glass adsorbs nitrogen. Furthermore the interaction of ferrocene on PVG and oxygen was studied. The ferrocene molecule has some similarity to biologically interesting metal containing systems. The investigation of oxygen adsorption by electron spin resonance techniques has been carried out on a number of systems (*5*), yet little work is reported on organometallics used in polymerization (*6*a) and hydrogenation (*6*b).

EXPERIMENTAL METHODS

Materials

Corning porous Vycor glass (749303-7930) rods $\frac{1}{16}$ in. in diameter were chemically cleaned in a boiling solution which was initially 10% H_2O_2, 20% HNO_3, and 20% $HClO_4$, followed by a minimum of three treatments with boiling, doubly distilled, water. These rods, while still wet, were placed in an acid-washed, water-rinsed quartz ESR tube, and sealed onto a vacuum system. The PVG rods were evacuated, treated for 12 hr at 525°C with 900 Torr oxygen, followed consecutively by 6 hr evacuation (525°C), 12 hr with hydrogen (800 Torr) at 525°C, and 12 hr evacuation to $<10^{-6}$ Torr. Rods so prepared gave no ESR signal before or after irradiation with 2537 Å light at 77°K, nor did their Raman spectra show any but the expected lines.

The ferrocene was obtained from Alpha Inorganics, and sublimed twice under vacuum. The oxygen used was Liquid Carbonic industrial grade purified by liquification. The hydrogen was Liquid Carbonic industrial grade purified by passage through an Englehard Industries "Deoxo" catalytic purifier, and thence through a previously degassed Linde x-13 molecular sieve and activated alumina trap at 77°K. The helium used was Liquid Carbonic grade A, purified by passage through a previously degassed Linde x-13 molecular sieve and activated alumina trap at 77°K. 2,2-Diphenyl-1-picryl hydrazyl (mp 136–138°C) (DPPH), "Baker grade" from J. T. Baker Chemicals was used as a *g* value standard.

Equipment

ESR spectra were taken on a Varian E-12 spectrometer using a Varian E-101 X-band microwave bridge and a 12 in. magnet with associated power supply. The magnetic field values for the hydrogen atom *g* value experiments were checked with a Nuclear Magnets Corp. M-12 precision gaussmeter, the RF frequency of which was monitored with a Hewlett Packard 5245L electronic counter in conjunction with a Boonton Radio Co. type 230A power amplifier.

The laser Raman spectra were obtained, using a Spex 1400 monochromator in conjunction with a Spectra Physics He–Ne laser.

A DuPont 310 curve resolver was used on the EPR spectrum of the cyclopentadienyl radical.

The vacuum system used was designed so that the samples would be isolated from all stopcocks by dry ice–acetone traps, and from mercury vapor by several liquid nitrogen traps with copper wool inserts. For gas treatment the system has a volume of 5 liters. Ultraviolet irradiation was carried out using a mercury argon resonance lamp forming a helix 5 cm in diameter and 20 cm long. This lamp emits predominantly at 2537 Å, with some emission at 1849 Å (primarily absorbed by air).

Procedure

Purified ferrocene was allowed to sublime through a break seal onto a number of clean PVG rods until the rods exhibited a pale lemon yellow color. The ferrocene supply was then sealed off and the samples were flushed twice with helium. The samples for ultraviolet irradiation were removed and the other samples were treated with 150 Torr oxygen at 25°C until the rods changed color to pale blue-green (≅1 hr). The samples were then twice helium flushed, evacuated and sealed after readmission of helium. At all times the samples were wrapped in aluminum foil to protect them from light. The visual checking when necessary was done as quickly as possible. The oxygen treated samples were stored in liquid nitrogen until spectra could be recorded. The ESR spectra of the ultraviolet irradiated samples were taken immediately after irradiation at 77°K. The ESR spectra of samples exposed to ^{60}Co gamma radiation at 77°K were taken within 24 hr of exposure. All ESR spectra were taken at 77°K. Samples for Raman investigation were similarly prepared in 4 mm o.d. quartz ESR sample tubes with a spherical bulb ≅8 mm o.d. blown on one end. These samples also had He pressure of about 400 Torr, except one series prepared under N_2.

RESULTS

Ultraviolet Irradiation

On ultraviolet radiation at 77°K, the ferrocene/PVG sample gave a fairly intense ESR spectrum (Fig. 1) consisting primarily of a well-defined six-line signal centered at $g = 2.0023 \pm 0.0005$, assigned to a C_5H_5 radical, and two lines of ≅20% the maximum central intensity at $g = 2.0021 \pm 0.0002$ (corrected) separated by 504.8 ± 0.2 G, assigned to hydrogen atoms.

The central signal at $g \approx 2$ shows a six-line hyperfine structure with an indication of an underlying spectrum. The separation between the outer lines is 6.0 ± 0.1 G while the two central lines have a separation of 5.6 G. The ratio of line heights was 5, 39, 93, 100, 36, 5 for the highest available power of 200 mW and 2, 21, 89, 100, 20, 3 for the lowest useful power of 0.3 mW. The theoretical ratio is 10, 50, 100, 100, 50, 10 for a six-line spectrum due to five equivalent spin = ½ nuclei. The main peak did not saturate up to maximum power level. At low power (5 mW) the second and the fifth lines show a poorly resolved structure suggesting the presence of other signals which affect the intensity ratios. The spectrum was resolved with a DuPont curve resolver into three components. The first had the main features of the unresolved spectrum: six lines $g' = 2.0028 \pm 0.0005$, A' of 6.2 ± 0.4 G. The second had

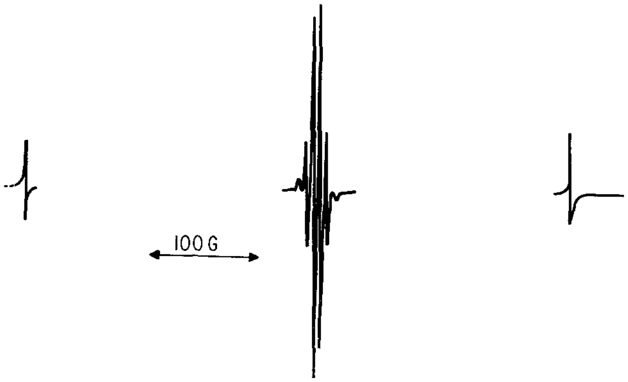

FIG. 1. ESR spectrum ferrocene/PVG at 77°K after 2537 Å irradiation.

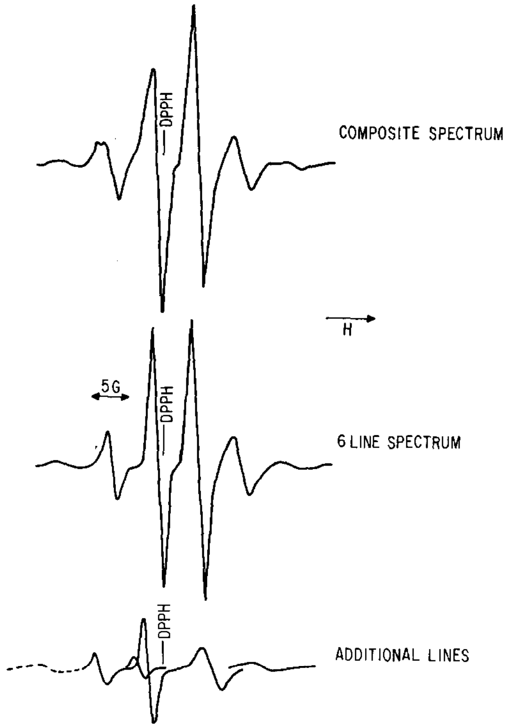

FIG. 2. Resolved ESR spectrum for 2537 Å irradiated ferrocene/PVG.

four visible lines which from examination suggested a five-line multiplet with $g'' = 2.0050 \pm 0.0005$ and $A'' = 7.5 \pm 1.0$ and the intensity ratio of (<3), 11, 34, 15, 3. The third was a weak signal at $g''' = 2.0056$ with line width of 1.5 ± 0.2 G and intensity of 7 on the scale previously used (Fig. 2). Warming the sample to 156°K produced a weak asymmetric signal (5% of the original) at $g'''' = 2.0000 \pm 0.0005$ and 2.2 G wide. This decreased in intensity on heat treatment, eventually disappearing at 373°K. The literature does not indicate any work on ESR signals produced by ultraviolet irradiation of ferrocene. Thrush (*8*) has reported detection by spectral means of cyclopentadienyl radicals and iron atoms in xenon flash photolysis of gaseous ferrocene (1 Torr and room temperature).

Gamma Irradiation

^{60}Co irradiation of ferrocene on PVG at 77°K produced a central signal (Fig. 3) and two widely separated signals assigned to H atoms. This ESR spectrum is essentially the same as gamma irradiated PVG alone (*3*). The central signal at $g = 2.010 \pm 0.005$ which is about 40 G wide, is identified as being principally due to OOH radicals with $g_z = 2.0140 \pm 0.0005$, $g_y = 2.0054 \pm 0.0005$ and $g_x = 2.0034 \pm 0.0005$ where $A_z = 8.5 \pm 0.1$, $A_y = 5.5 \pm 01$ and $A_x = 8.0 \pm 0.1$ G. The hydrogen atom signals have a g value of 2.0021 ± 0.0005 and an A value of 505 G. The intensity of these signals resulting from 3.5 megarads ^{60}Co gamma radiation is over an order of magnitude greater than those resulting from 10^{20} photons of 4 eV energy.

Saito (*4*) on gamma irradiation of polycrystalline ferrocene samples at 77°K reported a spectrum resulting from the superposition of two signals. The first with $g_\perp = 2.00$ and $g_\parallel = 2.032$ and the second with $g_1' = 2.00$, $g_2' = 2.098$ and $g_3' = 2.28$. The first signal was assigned to a straight ferrocenium ion and the second to a bent, protonated ferrocene radical. This spectrum extends well over 100 G with the strong sharp line in the $g \approx 2$ region about 20 G wide. On annealing the samples at 193°K for 20 hr, a five-line spectrum was found with $g = 2.00$ and an A value of 20 G with a line intensity ratio of 1:4:6:4:1, the theoretical ratio for a four component hyperfine signal. Saito assigned this to a ferrocene radical produced by the loss of hydrogen atom [$(C_5H_4)Fe(C_5H_5)$].

It is of interest to note that the ferrocenium ion produced by chemical oxidation in organic solvents gives at 4 and 20°K an asymmetric signal with $g_\parallel = 4.35$ and $g_\perp = 1.26$ with respective line widths of 140 and 250 G (*9*). This spectrum disappears at a temperature of 77°K and higher due to rapid spin lattice relaxation. Since our signals are almost identical with those produced by PVG alone we can conclude that the energy absorbed from the gamma rays by PVG is not transferred to the ferrocene to produce the ferrocene radicals (reported by Saito) but may produce the ferrocenium ion reported by Prins (*9*) but unobservable under our measurement conditions.

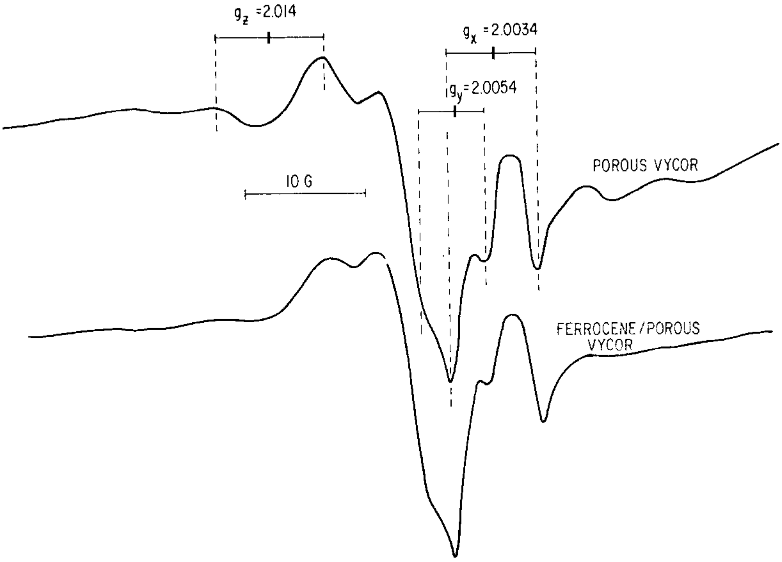

FIG. 3. ESR spectrum, ferrocene/PVG and PVG at 77°K after gamma irradiation.

Oxygen on Ferrocene/PVG

Samples of ferrocene adsorbed on PVG rods were exposed to 150 Torr O_2 at 25°C for 1 hr, then flushed twice with helium and evacuated. These exhibited a three-line asymmetric spectrum on ESR examination at 77°K (Fig. 4). Each of the three lines revealed unexpected hyperfine structure under appropriate modulation conditions (Fig. 5). Analysis shows that $g_{zz} = 2.0300 \pm 0.0002$, $g_{yy} = 2.0100 \pm 0.0002$ and $g_{xx} = 2.0020 \pm 0.0002$ (Fig. 6) while $A_{zz} = 16.5 \pm 0.5$ G, $A_{yy} = 3.3 \pm 0.2$ G and $A_{xx} = 4.0 \pm 0.2$ G. The observed spectrum was reversibly broadened by gaseous oxygen, and the samples were stable for days at room temperature.

PVG rods pretreated in the same manner but without ferrocene gave no ESR signals after the above oxygen treatment. Pretreatment conditions which reduced the hydroxyl concentration of the PVG re-

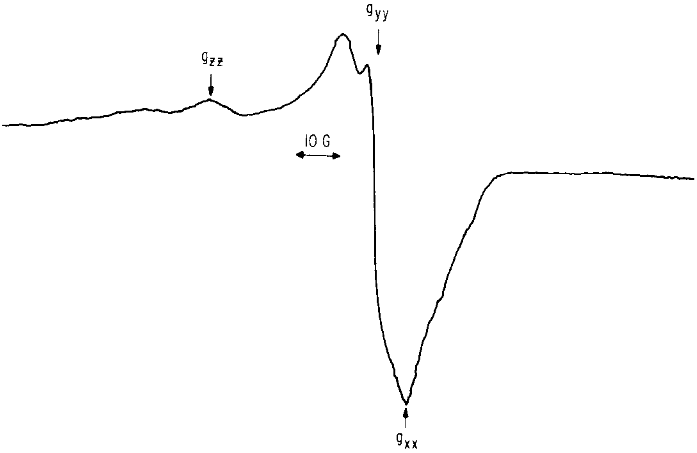

FIG. 4. ESR spectrum, O_2^- + ferrocene/PVG at 77°K. No irradiation.

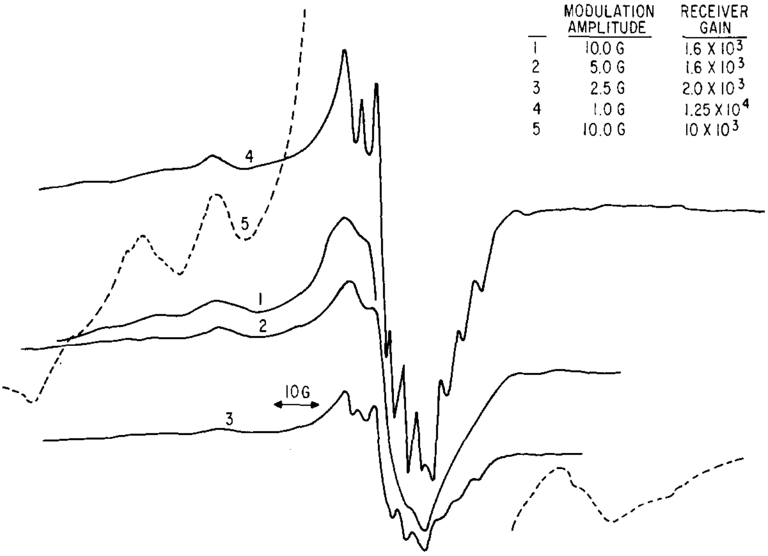

FIG. 5. ESR spectrum, O_2^- + ferrocene/PVG at 77°K under various gain and modulation conditions.

sulted in ferrocene/PVG sample which gave less intense and less clearly defined ESR signals after oxygen exposure.

We ascribe the signals obtained to O_2^- with a hyperfine structure due to five equivalent hydrogens. The g values and the overall shape of the signals are similar to those reported for O_2^-. Thus Iyengar *et al.* (*5*a,*5*b) gave for O_2^- on PVG the g values of 2.0302, 2.0144 and 2.0023, which are the same as those of Sato and Turkevich. PVG with a partial monolayer of palladium under 1 Torr of oxygen gives g values of 2.0321, 2.0118 and 2.006 (*10*).

Extensive work on O_2^- on metallic oxides (*5*), and γ-irradiated zeolites (*5*), has been reported. Känzig and Cohen (*5*c) in their work on O_2^- in alkali halides reported a

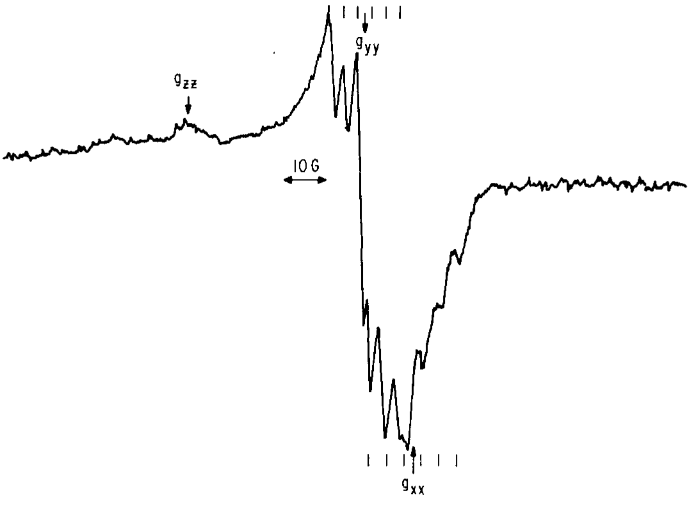

FIG. 6. ESR spectrum O_2^- + ferrocene/PVG at 77°K showing hyperfine structure of the g_{yy} and g_{xx} peaks.

partial resolution of the hyperfine structure due to K or Rb. Shvets, Sarichev and Kazansky (*5*d) have reported the hyperfine interaction of O_2^- with $^{51}V^{4+}$ in a tetrahedral surface site of V_2O_4/SiO_2. Their g values were $g_1 = 2.025$, $g_2 = 2.011$ and $g_3 = 2.005$ and the splitting constants were $A_1 = 13.2 \times 10^{-4}$ cm^{-1} (14.0 ± 0.5 G), $A_2 = 6.4 \times 10^{-4}$ cm^{-1} (6.8 ± 0.1 G) and $A_3 = 5.6 \times 10^{-4}$ cm^{-1} (6.0 ± 0.1 G). These hyperfine splitting values due to vanadium are similar to ours in that $A_z > A_y \cong A_x$. Wang and Lunsford (*5*e) have observed O_2^- with six-line hyperfine structure, $g_1 = 2.038$, $g_2 = 2.009$, $g_3 = 2.003$, with $A_1 = 6.5 \pm 0.5$ G, $A_2 = 4.7 \pm 0.5$ G and $A_3 = 5.7 \pm 0.5$ G, due to ^{27}Al in decationated NH_4^+-Y-zeolite. Our hyperfine structure is assigned to five hydrogens in the cyclopentadienyl ring of the ferrocene on which the O_2^- is adsorbed.

Raman Investigation

A Raman spectrum of the partial monolayer of ferrocene/PVG under 300 Torr He was taken, using the 5682 Å line of a He–Ne laser. Table 1 gives the observed lines assigned to ferrocene; the lines due to the PVG are not given. The data is in good agreement with the data of Long and Huege (*7*c) and Lippincott and Nelson (*7*a). Attempts to get a Raman spectrum of ferrocene with oxygen or with nitrogen were unsuccessful due to the strong fluorescence of the samples.

Ferrocene/PVG and Nitrogen

Data in the literature suggests that there may be an interaction of nitrogen and ferrocene. It should be recalled that in their discovery of ferrocene Miller, Tebboth and Tremaine (*1*) reported the production of a nitrogen–ferrocene precursor of ferrocene, formed on passage of cyclopentadiene in a stream of nitrogen over an iron ammonia synthesis catalyst. They further showed that ferrocene in glass showed adsorption of nitrogen at 100°C and 1 atm pressure. To check this we studied carefully the adsorption of nitrogen and argon at pressures from 0.5 to 1.5 atm at −40, 0, 25 and 100°C in a static system. No difference could be found in the absorption of the two gases. We must conclude that in the static system we used, which was sensitive to 0.1 ml (STP) of gas/g, that no adsorption could be detected. It is planned

TABLE 1

FERROCENE RAMAN SPECTRUM[a]

Ref. (*7*a)	Ref. (*7*b)	Ref. (*7*c)	This work	Assignment
3099	3110	3100 s[b]	3107 w	sym CH stretch
3085	3089	3085 w	—	CH stretch
3085	3045	3070 w	—	CH stretch
1408	1412	1412 m	—	sym CC stretch
1560	1527	1365 w	—	CC stretch
1178	1361	1175 w	—	CH(11) bend
1105	1390	1102 s	1106 s	sym, ring breathing
1050	1184	1059 m	1065 vw	CH(1) bend
1010	998	999 w	974 w	CH(11) bend
—	1054	892 w	—	ring distortion (11)
—	818	835 w	—	CH bend (1)
—	1105	812 w	Obscured	sym CH(1) bend
—	519	600 w	553 m	ring distortion (1)
388	390	390 s	Obscured	sym ring tilt
303	306	301 s	311 m	sym ring metal stretch

[a] Using the 5682 Å line of a He–Ne laser.

[b] Letters refer to line intensity.

to study this system using a dynamic pulse method.

DISCUSSION

Ultraviolet Radiation

The six-line spectrum found after ultraviolet radiation of ferrocene/PVG is assigned to the C_5H_5 radical on the surface of PVG. The spectrum resembles that for the C_5H_5 radical formed from *cyclopentadiene* as reported by other workers. Ohnishi and Nitta (*11*) obtained a six-line spectrum stable to 153°K with a separation of 5.6 G by bombardment of cyclopentadiene at 77°K with an electron beam. Liebling and McConnell (*12*) obtained six lines at $g = 2.0044$, a hyperfine splitting of 6.2 ± 0.1 G and an intensity ratio of 1:5:10:10:5:1.

The characteristics of the major portion of the signal that we observe in ultraviolet irradiated ferrocene on PVG are in agreement with the above, with $g = 2.0028 \pm 0.0005$ and $A = 6.0 \pm 0.4$ G. The intensity relationships are not those of the ideal free radical, but this is not uncommon for radicals adsorbed on surfaces.

The second component of the spectrum, the postulated quintet, is assigned on the basis of magnitude of the hyperfine splitting and this number of lines to a π system with four equivalent protons, either the $C_4H_4^-$ or the $C_5H_4^-$ radical anion. The first may be produced by the photo cleavage of $(C_4H_4)Fe(C_6H_6)$ which resulted from the photo-induced mutual C_5H_5 ring contraction and expansion of a ferrocene molecule. The second is due to the loss of a proton from a C_5H_5 radical.

There is some doubt as to the equivalence of the $C_5H_4^-$ protons. We have previously pointed out that Saito (*4*) has reported a five-line spectrum on gamma irradiation of ferrocene and ascribed it to the $(C_5H_4)Fe(C_5H_5)$ radical.

The third weak component, a small asymmetric signal at $g = 2.0056$ has not been identified with any species.

The large amount of hydrogen produced by irradiation of ferrocene on PVG compared to irradiation of PVG alone may be due to one or both of two causes. Ferrocene is a strong absorber of ultraviolet radiation and may act as a photosensitizer for the Si–OH groups which would then furnish H atoms. This is supported by the observation that the hydrogen atom production seems to decrease with dehydroxylation of the surface. On the other hand, the hydrogen atoms may be produced by dehydrogenation of the ferrocene or its decomposition products.

Gamma Irradiation

The gamma irradiation of ferrocene on PVG gives the same ESR spectrum as obtained for PVG alone. It is an order of magnitude more intense than that obtained by ultraviolet irradiation and the effect of ferrocene may be masked. There seems to be no preferred transfer of energy from the solid to the surface in contrast to the preceding case where absorption of light by the ferrocene seems to affect the silica hydroxyl groups in the PVG. The signals produced by gamma irradiation of PVG alone are dealt with in another communication (*3*a).

Oxygen Effect

The general shape, the g values, and the influence of excess oxygen on the signal obtained on treating ferrocene–PVG system with oxygen indicate the presence of O_2^- species. The novel finding is the discovery of the hyperfine structure of six lines which indicate that the O_2^- ion is closely associated with five protons, presumably those of the cyclopentadienyl ring. We thus have a new insight into the interaction of oxygen with a hydrocarbon. The iron atom has associated with it the hydrocarbon ring. The oxygen, on adsorption, receives an electron from this iron–hydrocarbon system, presumably from the iron, and the hydrocarbon situated between the O_2^- and the iron is in intimate contact with the oxygen, impressing the influence of its hydrogen nuclei on the ESR spectrum of the O_2^-. This may be a model system for the activated complex of hydrocarbon oxidation on metals.

Let us now consider the general shape of the O_2^- signal. The three distinct g tensor components would indicate that the O_2^- is situated in an orthorhombic crystalline field characterized by a Δ value—the separation of the normally degenerate π_x, π_y antibonding levels by the orthorhombic field, and an E value—the energy separation between the σ_z level and the higher of the split π_x and π_y levels. Känzig and Cohen (*5c*) have derived the following relationships which permit the calculation of Δ from the observed g values:

$$g_z = g_e + [2\lambda/(\Delta^2 + \lambda^2)^{1/2}]l,$$

$$g_x = g_e\Delta/(\Delta^2 + \lambda^2)^{1/2} + (\lambda/E)[(\Delta + \lambda)/(\Delta^2 + \lambda^2)^{1/2}] - \lambda/E,$$

$$g_y = g_e\Delta/(\Delta^2 + \lambda^2)^{1/2} + (\lambda/E)[(\Delta - \lambda)/(\Delta^2 + \lambda^2)^{1/2}] + \lambda/E,$$

where λ is the spin orbit coupling interaction, taken as 0.014 eV after Kasai (*5*f); l is the g_z angular momentum correction factor; and g_e is the g value for the free electron, 2.0023. Using an iterative calculation based on the above equations we obtain a value for Δ of 1.05 ± 0.1 eV. A semiempirical relationship (*13*) $0.33Z = \Delta$ where Z is the charge on the cation producing the orthorhombic crystal field gives us a value of Z of $+3$. This indicates an Fe^{3+} ion; hence ferrocenium is probably involved. The l value was found to be 1.04 which is close to that of the free ion value of 1.00. The E value is 3.5 ± 0.1 eV.

A charge transfer complex between ferrocene and oxygen is quite reasonable since the ferrocene ionization potential is 6–9 eV (*14*) compared to perylene (6.7 eV) which can be ionized by oxygen (*15*). Despite these favorable energetic considerations, ferrocene is *not* oxidized by molecular oxygen in the vapor, solution, nor in the solid, although it is easily oxidized by a variety of mild oxidizing agents (*15*). Adsorption of ferrocene on the PVG surface catalyzes the reaction possibly by perturbing the ferrocene permitting charge transfer from it to the oxygen. The orientation of the O_2^- with respect to the ferrocene is still open to question. The internuclear axis may be perpendicular, parallel or at an angle to the cyclopentadienyl plane. The hyperfine structure does reveal in a clear-cut way the interaction of the O_2^- with five equivalent hydrogens of a C_5H_5 ring of the adsorbed ferrocene. This, as mentioned above, is the first experimental indication of the close association of an oxygen with the material it will oxidize on a surface.

CONCLUSIONS

The ESR examination of the ferrocene on a PVG model system after ultraviolet irradiation shows that ferrocene dissociates producing primarily C_5H_5 radicals on the surface. A significant number of H atoms are also produced which may arise either from the surface hydroxyl groups and/or from ferrocene decomposition products. The ferrocene itself furnishes not only C_5H_5 radicals, but also lesser amounts of either the $C_4H_4^-$ or the $C_5H_4^-$ radical anion.

Gamma irradiation primarily gives results similar to those obtained from PVG alone. The nuclear radiation absorbed by PVG is not preferentially transferred to the ferrocene on the surface.

No evidence was obtained for the adsorption of nitrogen by ferrocene on PVG in the temperature interval between −40 and 100°C. On the other hand, oxygen adsorption at room temperature produced an O_2^- spectrum with a hyperfine structure due to the five hydrogens of a cyclopentadienyl ring of the ferrocene. This suggests a molecular model for the activated state involved in oxidation of hydrocarbons on metal catalysts, and the interaction of oxygen with biological metal systems.

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