propylmercapto-4-picoline (1.35 g), bp 83–84° (1.2 mm) [lit.[3] bp 67° (2 mm)], and then by benzene (500 ml), 3-propylmercapto-4-picoline (1.4 g), bp 78–79° (0.5 mm) [lit.[3] bp 139–140° (21 mm)].

2,5-Dimethyl-3-propylmercaptopyrazine.—A solution of 2,5-dimethylpyrazine 1-oxide[15] (3.1 g, 0.025 mole) and 1-propanethiol (5.7 g, 0.075 mole) in acetic anhydride (40 ml) was heated under reflux for 2 hr and then distilled. The fraction, bp 87–90° (0.1 mm) (2.7 g), was chromatographed on alumina (60 g), and the **sulfide** (1.23 g, 27%) was eluted by petroleum ether (350 ml) and benzene (200 ml), bp 73–75° (0.2 mm), $n^{25}\text{D}$ 1.5436. The nmr spectrum (neat) showed the pyrazine proton at δ 7.83, the two methyl groups as a singlet (δ 2.38, shoulder at δ 2.35), the propylmercapto group with the CH_2S at δ 3.10 (triplet), C–CH_2–C as a multiplet at δ 1.64, and the CH_3 at δ 1.02 (triplet).

Anal. Calcd for $C_9H_{14}N_2S$: C, 59.29; H, 7.74; N, 15.37. Found: C, 59.68; H, 7.81; N, 15.15.

2,5-Dimethyl-3,6-dipropylmercaptopyrazine.—A solution of 2,5-dimethylpyrazine 1,4-dioxide[16] (7.0 g, 0.05 mole) and 1-propanethiol (18 ml, 0.2 mole) in acetic anhydride (80 ml) was allowed to react as shown above for the mono-N-oxide to give a fraction (10 g), bp 121–126° (0.5 mm). Chromatography on 200 g of alumina gave the **sulfide** as the major fraction (2.50 g, 20%), mp 34°, being eluted by petroleum ether (400 ml), which could be crystallized from acetonitrile–ethanol (9:1), with poor recovery: mp 34–35°. Its nmr spectrum was devoid of aromatic protons and just exhibited resonances due to the aromatic CH_3 and S–$CH_2CH_2CH_3$ group.

Anal. Calcd for $C_{12}H_{20}N_2S_2$: C, 56.20; H, 7.86; N, 10.93. Found: C, 56.20; H, 8.08; N, 10.95.

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The Reactions of Metallocenes with Electron Acceptors[1a]

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The reaction products of ferrocene, cobaltocene, and bis(tetrahydroindenyl)iron with 2,3-dichloro-5,6-dicyanoquinone (DDQ) and tetracyanoethylene (TCNE) have been isolated and their physical properties, including infrared spectra, visible spectra, and electrical resistivities, have been determined. The equilibrium constants for the reaction, metallocene + TCNE = metallocinium + TCNE·⁻, have been measured in various solvents. The relationship between the oxidation–reduction potentials of the metallocenes and the properties of the products is discussed.

The recent interest in metallocene complexes has focused attention on the structure of these materials. In general, the structure has been formulated either in terms of π complexes or in terms of metallocinium salts. In the former case, the metallocene is considered to be a donor interacting with an acceptor, whereas in the second case the complete transfer of an electron from the donor to the acceptor gives rise to an ionic compound.[2]

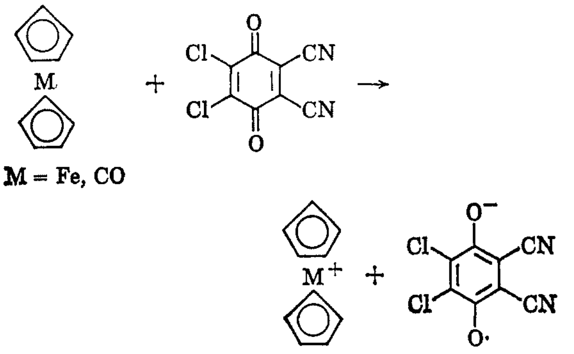
Our interest in the electrical properties of π complexes has prompted the synthesis of a number of metallocinium compounds by the reaction of ferrocene, cobaltocene, and bis(tetrahydroindenyl)iron[3] with tetracyanoethylene (TCNE) and 2,3-dichloro-5,6-dicyanoquinone (DDQ). We wish to report some of the physical properties of these compounds and some observations on their structure.

Results

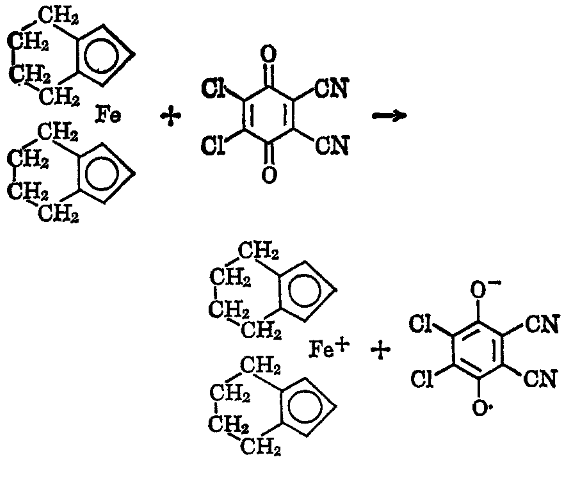
Complexes with 2,3-Dichloro-5,6-dicyanoquinone.—Ferrocene, bis(tetrahydroindenyl)iron, and cobaltocene react with DDQ in benzene to give black crystalline products which are essentially insoluble in nonpolar solvents, but which may be recrystallized from polar solvents such as acetonitrile. The products give satisfactory analyses for 1:1 ratios of metallocene and quinone.

The infrared spectra of the products are noticeably different from the spectra of the components. The carbonyl band of DDQ at 1680 cm^{-1} is absent as are characteristic bands of the metallocenes. Several similarities among the spectra of the three complexes are noted. In particular, the absorption at 2230 cm^{-1} owing to the nitrile group is greatly enhanced, and in all three compounds bands of similar intensity appear near 1600–1580, 1230, 1190, 1050, and 780 cm^{-1}.

These results suggest that the reaction should be formulated as indicated in eq 1 and 2. The pertinent



(1)



(2)

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[1] (a) This work was supported by Lockheed Independent Research Fund. (b) To whom inquiries should be sent.

[2] A complete theory of charge-transfer complexes has been proposed by R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

[3] J. H. Osiecki, C. J. Hoffman, and D. P. Hollis, *J. Organometal. Chem.* (Amsterdam), **3**, 107 (1965).

infrared data are the enhancement of the nitrile absorption which invariably occurs on conversion of DDQ to the hydroquinone form and the absorption in the region of the phenoxy radical[4] (1590 cm^{-1}). A number of complexes of the aromatic amine–quinone type has been studied by Matsunaga.[5] It was shown by comparison of the infrared spectra of the complex with the spectra of metal salts of the semiquinone that these materials could be identified as being ionic in character. The three products mentioned above have identical spectra, except for slight differences in extinction coefficients, from 300 to 700 mμ. These results are to be expected if the absorption is due to the semiquinone, since the observed extinction coefficients are an order of magnitude greater than those of the metallocinium ions.

When attempting to isolate a similar product from the reaction of nickelocene with DDQ, a brown amorphous solid is isolated. The analysis of this material indicates that a simple 1:1 product is not produced and the infrared spectrum shows no similarity to the previously described products.

The addition of silver perchlorate to an acetonitrile solution of the ferricinium 2,3-dichloro-5,6-dicyanoquinolate (M = Fe) results in a reduction in the intensity of the visible absorption and the appearance of a new band at 620 mμ. With a 40-mole excess of perchlorate only the 620-mμ absorption remains. The position and extinction coefficient identifies this absorption as being due to ferricinium perchlorate.[6] Similarly, the addition of a 40-mole excess of silver perchlorate to cobalticinium 2,3-dichloro-5,6-dicyanoquinolate (M = Co) causes the disappearance of the intense red color and replacement by the yellow color characteristic of the cobalticinium ion.

Complexes with Tetracyanoethylene.—The reaction of TCNE with cobaltocene in benzene gives a deep blue solid which dissolves in polar solvents to form a yellow solution. The analytical data indicate that the components combine in a 1:1 ratio. The product is quite stable when stored under nitrogen, but decomposes rapidly when exposed to air. TCNE undergoes a similar reaction with bis(tetrahydroindenyl)iron in ethyl acetate to give a black solid having a visible spectrum identical with that of the cobaltocene–TCNE product. It is more stable to air than the latter compound; however, it decomposes slowly when not stored under nitrogen. As with the cobaltocene–TCNE product, the components are present in a 1:1 ratio. The infrared spectra of both products are quite different from the spectra of the starting materials. The spectrum contains bands at 2190 and 1360 cm^{-1} characteristic of the tetracyanoethylene negative ion.[7] The properties of these materials are in marked contrast to those of the previously reported ferrocene–TCNE complex[7,8] which has an infrared spectrum almost identical with that of the superimposed spectra of the components. The products described above are best represented as the metallocinium salts, cobalticinium tetracyanoethylenide (I) and bis(tetrahydroindenyl)iron tetracyanoethylenide (II).

The visible spectra of I and II have a complex pattern centered around a maximum at 418 mμ and identical with the spectrum of TCNE$\cdot^-$.[8] The concentration of the radical ion is solvent dependent and the calculated equilibrium constants (K) for the reaction

$$\text{metallocene} + \text{TCNE} = \text{metallocinium} + \text{TCNE}\cdot^-$$

are summarized in Table I. The equilibrium constants were determined spectrophotometrically using the known value of the extinction coefficient of TCNE$\cdot^-$ to estimate the extent of the reaction.[7] Since some decomposition is noted even when carefully purified solvents are used, the values of K represent a lower limit when K is large ($>10^2$). Ferrocene–TCNE in dimethylformamide is particularly unstable and the spectrum of the decomposition product (a doublet at 410–390 mμ, possibly the pentacyanopropionide ion[8]) appears within a few minutes.

TABLE I

EQUILIBRIUM CONSTANTS FOR THE REACTION OF METALLOCENES WITH TCNE

	Equilibrium constant, K			
Metallocene	CH_2Cl_2	Acetone	CH_3CN	DMF[a]
Ferrocene	...	3×10^{-6}	8.6×10^{-4}	7×10^{-3}
Cobaltocene	10	90	7.0×10^{2}	...
Bis(tetrahydro-indenyl)iron	3.4×10^{-2}	0.38	$>10^2$	...
	Dielectric constant			
	9.08[b]	20.7[b]	37.5[b]	36.71[c]

[a] Dimethylformamide. [b] N. A. Lange, "Handbook of Chemistry," 10th ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1961. [c] G. R. Leader and J. F. Gormley, *J. Am. Chem. Soc.*, **73**, 5731 (1951).

The reaction of nickelocene with TCNE in benzene gives an immediate blue precipitate which rapidly decomposes to a brown solid. The blue product is only stable at Dry Ice temperature, but is too unstable at room temperature for further study.

Discussion

The formation of π complexes of metallocenes is complicated by the ease with which complete electron transfer occurs to give metallocinium compounds. We have described the preparation of several new compounds which have been demonstrated to be of the metallocinium type. This type of compound has been referred to as a charge-transfer complex of the dative type[5] or charge-transfer salt.[9] One should clearly differentiate between (a) π complexes, which have a neutral ground state and ionic excited states (giving rise to charge-transfer absorption) and (b) salts having an ionic ground state. Since the extent of electron transfer is related to the oxidation–reduction potentials of the donor and acceptor compounds, a comparison of oxidation–reduction potentials with the type of product is given in Table II. Ferrocene forms metallocinium compounds only with acceptors having very high oxidation–reduction potentials, while the easily oxidized cobaltocene gives metallocinium salts with all the acceptors tried. Since the cobaltocene–p-chloranil product has been described as a charge-transfer complex

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TABLE II

OXIDATION–REDUCTION POTENTIALS OF DONORS AND ACCEPTORS

Donor	$E°$, v	Acceptor	$E°$, v	Product type
Ferrocene	$+0.30^a$	*p*-Benzoquinone	-0.50^b	π complex
		Chloranil	$+0.01^b$	π complex
		TCNE	$+0.15^c$	π complex
		DDQ	$+0.51^b$	Ionic
Cobaltocene	-1.16^d	Chloranil	$+0.01$	Ionic
		TCNE	$+0.15$	Ionic
		DDQ	$+0.51$	Ionic
Bis(tetrahydro-indenyl)iron	...	TCNE	$+0.15$	Ionic
		DDQ	$+0.51$	Ionic

[a] In acetonitrile. J. Tirouflet, E. Laviran, R. Dabard, and J. Komenda, *Bull. Soc. Chim. France*, 857 (1963). [b] In acetonitrile. For the reaction quinone $+ e^- =$ semiquinone anion. M. E. Peover, *J. Chem. Soc.*, 4540 (1962). [c] In acetonitrile. See ref 7. [d] In 90% ethanol. J. A. Page and G. Wilkinson, *J. Am. Chem. Soc.*, **74**, 6149 (1952).

wherein there is only slight charge transfer in the solid state,[10] but should give a metallocinium compound, we have reinvestigated this reaction. The infrared spectrum of this 1:1 complex is found to be consistent with its formulation as a metallocinium salt. Of particular significance is the absence of carbonyl absorption and the presence of a number of absorption bands present in the chloranil semiquinone.[5]

Polarographic data are not available for the bis(tetrahydroindenyl)iron, but from data derived from alkyl-substituted ferrocenes[11] it is estimated that the oxidation potential is of the order of 0.07–0.02 v. Since this implies that oxidation should occur more readily than with ferrocene, the ionic nature of the TCNE product is expected.

The interaction of metallocenes with electron acceptors in solution shows a strong dependence on solvent polarity. As expected, solvents with high dielectric constants favor the formation of metallocinium compounds. However, if the oxidation–reduction potential of the acceptor is sufficiently high, the effect may be negligible. The extinction coefficients calculated for products with DDQ vary in the order cobaltocene > bis(tetrahydroindenyl)iron > ferrocene, but it is not clear if this represents a change in equilibrium constant or interference from the metallocinium ion. Only in the case of ferrocene–TCNE did the equilibrium favor the un-ionized components. This fact is consistent with the report that a true π complex of this material can be isolated.[8]

The measured equilibrium constant for bis(tetrahydroindenyl)iron correlates well with the observation that the product with TCNE is ionic in the solid state and with the estimated oxidation potential. The oxidation–reduction potentials of nickelocene[12] indicate that this compound should also give an ionic product when treated with TCNE, and our results suggest that this does occur. The instability of the product may be related to the ease with which a second electron can be removed to give nickelocene^{2+}.

Experimental Section[13]

Procedure.—The reactions were carried out in a dry box under an atmosphere of purified nitrogen. All the solvents were purified by distillation and/or chromatography and purged with argon or nitrogen. The visible and ultraviolet spectra were determined with a Cary Model 14 spectrophotometer. The infrared spectra were recorded by a Perkin-Elmer Infracord spectrophotometer with a NaCl prism and determined in potassium bromide pellets (0.5–1%). The infrared spectra of the complexes were also run in Nujol and no changes were observed in the regions of interest.

Ferrocene–DDQ Complex (1:1).—The ferrocene (0.372 g) purified by sublimation was dissolved at room temperature in benzene. A benzene solution of DDQ (0.445 g) purified by several recrystallizations from benzene was added to the above solution while stirring vigorously. A dark precipitate formed immediately. The yield was 0.795 g (97%). The product recrystallized from acetonitrile gave black crystals, stable in air, and melting at 178°. The infrared spectrum showed absorption at 3100 (m), 2230 (m), 1595 (s), 1550 (s), 1230 (m), 1190 (m), 1045 (m), 855 (s), and 785 (s) cm^{-1}. The visible and ultraviolet spectra in acetonitrile (0.034 g/l.) showed absorption at 590 mμ (ϵ 5200), 545 (4900), 457 (5500), and 345 (6000). Electrical measurements[14] on powder samples gave the bulk resistivity and thermal activation energy, respectively, as $\rho_{25} = 3 \times 10^{10}$ ohm cm and $E_a = 0.7$ ev. E_a was obtained from the equation $\rho = \rho_0 \exp(E_a/kT)$.

Anal. Calcd for $C_{10}H_{10}Fe \cdot C_8Cl_2N_2O_2$: C, 52.35; H, 2.44; Cl, 17.17; N, 6.78. Found: C, 52.41; H, 2.93; Cl, 16.90; N, 6.93.

Bis(tetrahydroindenyl)iron–DDQ Complex (1:1).—Bis(tetrahydroindenyl)iron was prepared by hydrogenating diindenyliron[3] with PtO_2 in ethanol. The hydrogenated diindenyliron (0.477 g) was diluted with a small amount of benzene and added to the benzene solution of DDQ (0.369 g) while stirring vigorously. A dark precipitate formed immediately. The yield was 0.842 g (quantitative) and the complex was recrystallized from acetonitrile. The black crystals melted at 108–109° and were stable in air. The infrared spectrum showed absorption at 3100 and 2950 (m), 2230 (s), 1580 (vs), 1540 and 1520 (s), 1230 (m), 1195 (s), 1055 (s), 885 (m), 780 (s), and 710 (m) cm^{-1}. The visible and ultraviolet spectra in acetonitrile (0.0311 g/l.) showed absorption at 590 mμ (ϵ 5500), 550 (4900), 457 (5200), 348 (7800); electrical resistivity, $\rho_{25} = 1 \times 10^8$ ohm cm.

Anal. Calcd for $C_{18}H_{22}Fe \cdot C_8Cl_2N_2O_2$: C, 59.90; H, 4.26; Cl, 13.61; N, 5.38. Found: C, 59.65; H, 4.55; Cl, 13.95; N, 5.62.

Cobaltocene–DDQ Complex (1:1).—The cobaltocene (obtained from Arapahoe Chemicals, Inc.) was purified by sublimation. A saturated benzene solution of cobaltocene (0.420 g) was prepared at room temperature. The benzene solution of DDQ (0.504 g) was added to it. A dark precipitate formed immediately; stirring was continued for 1 hr and the complex was filtered. The yield was 0.917 g (quantitative). The product was recrystallized from acetonitrile; the black crystals melted at 230–231° and were stable in air. The infrared spectrum showed absorption at 3130 (m), 2230 (s), 1580 (vs), 1520 (s), 1235 (m), 1195 (m), 1050 (m), 880 and 860 (m), and 785 (m) cm^{-1}. The visible and ultraviolet spectra in acetonitrile (0.0387 g/l.) showed absorption at 590 mμ (ϵ 6100), 550 (5600), 457 (5900), and 348 (7700); electrical resistivity, $\rho_{25} = 3 \times 10^{13}$ ohm cm; activation energy, E_a 0.9 ev.

Anal. Calcd for $C_{10}H_{10}Co \cdot C_8Cl_2N_2O_2$: C, 51.95; H, 2.43; Cl, 17.04; N, 6.73. Found: C, 51.98; H, 2.63; Cl, 17.33; N, 6.92.

Ferrocene–TCNE Complex (1:1).—Equimolar amounts of ferrocene and TCNE were dissolved separately at room temperature in a minimum volume of dry benzene. The two solutions were mixed and the resulting mixture was concentrated to dryness. Green crystals contaminated with the starting materials thus isolated were sublimed *in vacuo* (5 μ) at room temperature: mp 113–115° (lit.[8] mp 115–119°). The infrared

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[10] J. C. Goan, E. Berg, and H. E. Podall, *J. Org. Chem.*, **29**, 975 (1964).

[11] D. E. Bublitz, G. Hoh, and T. Kuwana, *Chem. Ind.* (London), 635 (1959).

[12] G. Wilkinson, P. L. Pauson, and F. A. Cotton, *J. Am. Chem. Soc.*, **76**, 1970 (1954).

[13] The microanalyses were run by the Berkeley Analytical Laboratory, Berkeley, Calif. All melting points reported are uncorrected.

[14] A. Ottenberg, C. J. Hoffmann, and J. Osiecki, *J. Chem. Phys.*, **38**, 1898 (1963).

spectrum showed absorption at 3100 (w), 2300 and 2280 (w), 1800–1650 (w, br), 1410 (m), 1160 (s), 1110 (vs), 1010 (s), 835 (vs), and 795 (w) cm^{-1}.

Several attempts to prepare the complex by irradiating cyclohexane solutions of the components, as described in the literature,[8] did not produce any of the ferrocene–TCNE complex: electrical resistivity, $\rho_{25} = 3 \times 10^{12}$ ohm cm, lit.[7] $\rho_{25} = 10^9$ ohm cm (single crystal).

Bis(tetrahydroindenyl)iron–TCNE Complex (1:1).—The hydrogenated diindenyliron (0.577 g), diluted with a minimum amount of dry ethyl acetate, was added to a saturated ethyl acetate solution of TCNE (0.256 g) at room temperature. A dark green color, together with a black precipitate, formed immediately: the yield was 82%, mp 77–80° (sealed tube). The infrared spectrum showed absorption at 3100 (m), 2950 (s), 2200 (s), 2160 (s), 1600 (s), 1470–1440 (s), 1360–1310 (m), 1030 (s), and 867 (s) cm^{-1}; electrical resistivity, $\rho_{25} \simeq 10^9$ ohm cm.

Anal. Calcd for $C_{18}H_{22}Fe \cdot C_6N_4$: C, 68.25; H, 5.25; N, 13.27. Found: C, 67.85; H, 5.12; N, 13.25.

Cobaltocene–TCNE Complex (1:1).—The cobaltocene (0.580 g) purified as described above was dissolved in benzene. The TCNE (0.390 g), recrystallized several times from benzene, was dissolved in a minimum amount of benzene and was added to the metallocene. A dark precipitate formed immediately. The dark blue complex was very sensitive to oxygen and melted at 165–167° (sealed tube). The infrared spectrum showed absorption at 3130 (m), 2190 (vs), 1600 (m), 1420 (s), 1370 (vs), 1020 (m), 865 (s), and 690 (s) cm^{-1}; electrical resistivity, $\rho_{25} = 10^{12}$ ohm cm; activation energy, $E_a = 2.6$ ev.

Anal. Calcd for $C_{10}H_{10}Co \cdot C_6N_4$: C, 60.58; H, 3.18; N, 17.67. Found: C, 60.50; H, 3.70; N, 16.16. (Difficulties were encountered in weighing the samples.)

Cobaltocene–*p*-Chloranil Complex (1:1).—Equimolar amounts of cobaltocene and *p*-chloranil were dissolved separately in a minimum amount of dry benzene. Upon mixing the solutions, a green precipitate formed immediately. The yield was quantitative and the bright green product decomposed around 105° to a yellow solid which upon cooling turned to olive green (sealed tube). The analytical data satisfied a 1:1 ratio. The bright green complex was found to decompose slowly in air to an olive green material. The infrared spectrum showed absorption at 3130 (m), 1550 (s), 1490 (s), 1420 (s), 1140 (m), 995 (ms), 913 (s), 870 (m), 720 (w), and 680 (m) cm^{-1}. This spectrum corresponds to the one reported for the 1:2 complex.[10] It appears that some confusion has taken place between the 1:1 (reported as olive green) and the 1:2 (reported as green) complexes.

Reactions of Thiols with Metals. I. Low-Temperature Oxidation by Metal Oxides[1]

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The oxidation of thiols by four transition metal oxides has been studied in xylene at 55° in the absence of oxygen. In all cases studied, oxidation of the thiol to its disulfide was observed. The most active metal oxide was manganese dioxide. Ferric oxide, cobaltic oxide, and cupric oxide displayed similar oxidizing capabilities. Product yields and rate studies indicate that thiol structure and acidity do not influence the rate of thiol conversion. The reactions are not influenced by the presence of amine catalysts but they are dependent on the rate of agitation. These facts suggest that the rate-determining step in these reactions is thiol adsorption on the surface of the metal oxide. Oxidation studies at various thiol–metal oxide ratios in the presence of an olefin resulted in the formation of sulfide. The latter apparently forms by a low-temperature, free-radical addition reaction in which the metal oxide functions as an initiator for the production of thiyl radicals. This finding represents the first unequivocal evidence for the production of intermediate free radicals in low-temperature oxidations by manganese dioxide and other transition metal oxides.

In previous studies, it was observed that thiols could be oxidized to disulfides by sulfoxides.[2-4] The rate of these reactions was markedly dependent on the acidity of the thiol[4] but, in the presence of acidic and basic catalysts,[5] reasonable reaction rates could be obtained with weakly acidic thiols ($pK_a = 12$–14). The ability of thiols to reduce sulfoxides under fairly mild conditions has prompted us to extend our studies in this area to inorganic oxidizing agents. Specifically, it was of interest to ascertain if metal oxides are capable of reacting in a manner analogous to sulfoxides. It appears that previous studies on thiol–metal oxide reactions have been limited to high-temperature and high-pressure reactions in the presence and absence of oxygen. Usually, the metallic oxides are dispersed on supports such as alumina, silica, and bauxite.[6] Under these reaction conditions, the thiol and its oxidation product(s) are oxidatively desulfurized to olefins and other products. Several factors suggested that metal oxides would be capable of oxidizing thiols under mild conditions. Manganese dioxide is capable of oxidizing alcohols and amines at low temperatures in nonpolar solvents.[7] Recently, it has been observed that cupric oxide, manganese dioxide, and chromic oxide are capable of initiating olefin autoxidations in the liquid phase. CuO as an initiator was five times more effective than cyclohexene hydroperoxide, twice as effective as benzoyl peroxide, and equivalent to azoisobutyronitrile.[8] Subsequently, it was established that Cr_2O_3 is capable of initiating the low-temperature, free-radical polymerization of styrene.[9]

The above results, coupled with our previous sulfoxide studies, suggested that transition metal oxides would be capable of oxidizing thiols at low temperatures in hydrocarbon media. This possibility was investigated and found to be true. Information on the nature of the reaction, *i.e.*, ionic *vs.* free radical, has also been obtained.

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(1) This is paper V in a series of studies on oxidation–reduction reactions in the presence of transition metal catalysts. For the previous paper in this series, see T. J. Wallace, R. M. Skomoroski, and P. J. Lucchesi, *Chem. Ind.* (London), 1764 (1965).

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