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]

Thomas J. Wallace

*The Esso Research and Engineering Company, Process Research Division, Exploratory Research Section, Linden, New Jersey*

*Received October 4, 1965*

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.

---

(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).

(2) T. J. Wallace, *ibid.*, 501 (1964).

(3) T. J. Wallace, *J. Am. Chem. Soc.*, **86**, 2018 (1964).

(4) T. J. Wallace and J. J. Mahon, *ibid.*, **86**, 4099 (1964).

(5) T. J. Wallace and J. J. Mahon, *J. Org. Chem.*, **30**, 1502 (1965).

(6) For a review, see E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. I, Chemical Publishing Co., New York, N. Y., 1958, Chapter 2.

(7) For the most recent review, see R. M. Evans, *Quart. Rev.* (London), **13**, 61 (1959).

(8) J. Berger, C. Meyer, G. Clement, and J. C. Balaceanu, *Compt. Rend.*, **251**, 2235 (1961).

(9) C. Meyer, G. Clement, and J. C. Balaceanu, *Bull. Soc. Chim. France*, 2591 (1963).

TABLE I

SUMMARY OF THIOL COUPLING REACTIONS PROMOTED BY MANGANESE DIOXIDE

20 ml of Degassed Xylene

55°, $N_2$, 1000 rpm

| Thiol[a] (mole) | $MnO_2$, moles | Time, hr | Disulfide Mp, °C | Lit. mp,[b] °C | Mole % yield[c] |
|---|---|---|---|---|---|
| 1-Hexadecane- (0.05) | 0.05 | 22 | 53 | 53–55 | ~100 |
| 1-Dodecane- (0.05) | 0.05 | 24 | 32 | 32–34 | 73 |
| α-Toluene-[d] (0.05) | 0.05 | 19 | 70 | 71 | 84 |
| Benzene- (0.05) | 0.05 | 22 | 60 | 61 | 89 |
| 1,4-Butanedi-[e] (0.10) | 0.10 | 70 | 32 | 32 | 74 |

[a] Gc indicated 90–100% thiol conversion for the reaction times listed. [b] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. III, Chemical Publishing Co., New York, N. Y., 1960, Chapter 7, p 362 ff; G. Claeson, G. Androes, and M. Caliva, *J. Am. Chem. Soc.*, **83**, 4360 (1961). [c] (Moles of RSSR isolated/theoretical moles) × 100. [d] Gc analysis indicated that benzaldehyde, thiobenzaldehyde, and benzoic acid were not present. [e] Initially, this reaction was exothermic by 20–30°.

TABLE II

THIOL COUPLING REACTIONS PROMOTED BY OTHER METAL OXIDES

20 ml of Degassed Xylene

55°, $N_2$, 1000 rpm

| Thiol (mole) | Metal oxide (mole) | Time, hr | Disulfide Mp, °C | Mole % yield[a] |
|---|---|---|---|---|
| 1-Hexadecane- (0.05) | $Fe_2O_3$ (0.05) | 23 | 53 | 37 |
| 1-Hexadecane- (0.05) | $CO_2O_3$ (0.05) | 68 | 53 | 29 |
| 1-Dodecane- (0.05) | $Fe_2O_3$ (0.05) | 22 | 32 | 30 |
| 1-Dodecane- (0.05) | $CO_2O_3$ (0.05) | 22 | 32 | 48 |
| 1-Dodecane-[b] (0.05) | CuO (0.05) | 22.5 | 32 | 14 |
| 1,4-Butanedi-[c] (0.10) | CuO (0.10) | 144 | 32 | ~10 |

[a] (Moles of RSSR isolated/theoretical moles) × 100. [b] An equivalent yield of dodecyl sulfide was detected by gc analysis. [c] Polymeric material was also observed. This is consistent with the extent of thiol conversion (52%).

## Results

The ability of manganese dioxide ($MnO_2$), ferric oxide ($Fe_2O_3$), cobaltic oxide ($Co_2O_3$), and cupric oxide (CuO) to oxide thiols was studied in xylene at 55 ± 0.1°. The solvent was degassed and stored in a nitrogen drybox, all reaction mixtures were prepared in a nitrogen drybox, and the reaction vessel was thoroughly sealed to prevent contact with oxygen during the course of reaction. Since the systems are heterogeneous in nature, most reactions were carried out at the same stirring speed (1000 rpm). Initially, the ability of $MnO_2$ to promote the oxidative coupling of a series of thiols was determined. The reaction conditions employed and the results obtained are summarized in Table I. 1-Dodecanethiol, 1-hexadecanethiol, α-toluenethiol, and benzenethiol were converted to their corresponding disulfides in yields of 73–100% over reaction periods of 19–24 hr. The structure of each disulfide was substantiated by its melting point and mixture melting point with an authentic sample. It was also possible to oxidize 1,4-butanedithiol to 1,2-dithiacyclohexane with $MnO_2$. This disulfide was obtained in 74% yield after 70 hr of reaction. In all cases, disulfide yields were based on the amount of isolated product. The results suggest that the yield of product is not influenced by the structure nor the acidity of the thiol. A similar study on the oxidation of 1-hexadecanethiol and 1-dodecanethiol by $Fe_2O_3$, $Co_2O_3$, and CuO was also carried out and these results are summarized in Table II. The yields of the acyclic disulfides varied from 14 to 48%. In the case of CuO, equivalent yields of the disulfide and monosulfide were obtained. An attempt to oxidize 1,4-butanedithiol with CuO was only slightly successful. A 10% yield of the dithiane was obtained along with other unidentified polymeric material. These results suggest that there is little difference in the oxidizing capabilities of $Fe_2O_3$, $Co_2O_3$, and CuO. However, these three metal oxides are definitely not so active as $MnO_2$.

Obviously, the above oxidation reactions involve a corresponding reduction of the metal oxides. Two questions then arise. What is the nature of the reduction step, *i.e.*, ionic or free radical, and what is the rate-determining step? Experiments designed to answer these questions have been carried out. The oxidation of 1-dodecanethiol in the presence of excess 1-dodecene was carried out at 55° using each metal oxide. The results of our 1-dodecanethiol addition studies in the presence of $MnO_2$ are summarized in Table III. As the mole ratio of thiol/$MnO_2$ was varied from 1 to 200 a gradual decrease in thiol conversion was observed and a corresponding increase in per cent selectivity to sulfide was observed. Thus, when $MnO_2$ is employed in catalytic amounts, a free-radical olefin addition reaction competes successfully with the dimerization reaction. Similar results, though more pronounced, were obtained with $Fe_2O_3$ and $Co_2O_3$. These results are summarized in Table IV. At a thiol/metal oxide ratio of 1, disulfide formation competed successfully with sulfide formation. At ratios of 2 to 20, sulfide was formed in 90–100% selectivity. Thiol conversion again decreased as the thiol/metal oxide ratio increased but at sufficiently long reaction times; *e.g.*, for $Co_2O_3$, 71 and 163 hr, reasonable conversions of 1-dodecanethiol were obtained. In the case of CuO, sulfide formation was observed in the presence and absence of olefin.

Rate studies were next carried out at 55° and 1000 rpm in 75 ml of xylene using 5 × $10^{-3}$ mole of thiol and metal oxide. Under these conditions, the rate of thiol disappearance did not adhere to either first- or

TABLE III

1-DODECANETHIOL ADDITION REACTIONS TO 1-DODECENE CATALYZED BY $MnO_2$

1-Dodecene/1-Dodecanethiol = 10

55°, $N_2$, 1000 rpm

| $1\text{-}C_{12}H_{25}SH$, mole | $MnO_2$, mole | RSH/$MnO_2$ | Time, hr | % conversion of $1\text{-}C_{12}H_{25}SH$ | RSSR, mole | RSR, mole | % selectivity[a] of RSR |
|---|---|---|---|---|---|---|---|
| 0.01 | 0.01 | 1 | 18 | 100 | $4.96 \times 10^{-3}$ | $0.13 \times 10^{-3}$ | 2.5 |
| 0.01 | 0.001 | 10 | 20 | 100 | $4.81 \times 10^{-3}$ | $0.17 \times 10^{-3}$ | 6.3 |
| 0.01 | 0.0005 | 20 | 22 | 45 | $0.96 \times 10^{-3}$ | $0.13 \times 10^{-3}$ | 11.9 |
| 0.01 | 0.0005 | 20 | 18 | 41 | $1.53 \times 10^{-3}$ | $0.18 \times 10^{-3}$ | 10.5 |
| 0.01 | $5 \times 10^{-5}$ | 200 | 27 | ... | $1.84 \times 10^{-3}$ | $1.80 \times 10^{-3}$ | 49 |

[a] [Mole of RSR/(mole of RSR + mole of RSSR)] × 100.

TABLE IV

1-DODECANETHIOL ADDITION REACTIONS TO 1-DODECENE CATALYZED BY OTHER METAL OXIDES

1-Dodecene/1-Dodecanethiol = 10

55°, $N_2$, 1000 rpm

| $1\text{-}C_{12}H_{25}SH$, mole | Oxide (mole) | RSH/metal oxide | Time, hr | % conversion of $1\text{-}C_{12}H_{25}SH$ | RSSR, mole | RSR, mole | % selectivity[a] of RSR |
|---|---|---|---|---|---|---|---|
| 0.01 | $Fe_2O_3$ (0.01) | 1 | 22 | ... | $1.74 \times 10^{-3}$ | $1.54 \times 10^{-3}$ | 47 |
| 0.01 | $Fe_2O_3$ (0.005) | 2 | 26 | 100 | Trace | $5.42 \times 10^{-3}$ | 100 |
| 0.01 | $Fe_2O_3$ (0.001) | 10 | 20 | 70 | $0.05 \times 10^{-3}$ | $3.73 \times 10^{-3}$ | 98 |
| 0.01 | $Fe_2O_3$ (0.0005) | 20 | 25 | 40 | $0.17 \times 10^{-3}$ | $2.23 \times 10^{-3}$ | 93 |
| 0.01 | $Co_2O_3$ (0.01) | 1 | 24 | 87 | $1.20 \times 10^{-3}$ | $1.54 \times 10^{-3}$ | 56 |
| 0.01 | $Co_2O_3$ (0.005) | 2 | 18 | 10 | Trace | $0.44 \times 10^{-3}$ | 100 |
| 0.01 | $Co_2O_3$ (0.005) | 2 | 163 | 100 | Trace | $5.10 \times 10^{-3}$ | 100 |
| 0.01 | $Co_2O_3$ (0.0005) | 20 | 71 | 30 | $0.20 \times 10^{-3}$ | $1.40 \times 10^{-3}$ | 90 |
| 0.01 | CuO (0.01) | 1 | 23 | 100 | $1.70 \times 10^{-3}$ | $3.50 \times 10^{-3}$[b] | 67 |

[a] [Mole of RSR/(mole of RSSR + mole of RSR)] × 100. [b] Based on blank, no olefin, only 50% of the sulfide arises by olefin addition.

second-order kinetics. The effect of stirring speed on the rate was next determined. As indicated in Table V, the per cent conversion of 1-dodecanethiol in the presence of $Fe_2O_3$ was stirring dependent. As the stirring speed was increased from 1000 to 3000 rpm the per cent thiol converted per hour increased from 0.6 to 2.8. A similar study with $MnO_2$ indicated that the per cent thiol converted after 30 min varied from 15 to 35% between 1000 and 3000 rpm. The effect of thiol acidity and amine catalysis on the rate of thiol disappearance was next determined in xylene. These results are summarized in Table VI. As shown, the per cent thiol converted per hour was not influenced by thiol acidity and 1-dodecylamine had essentially no effect on the rate of 1-dodecanethiol disappearance. The above rate dependence on agitation and rate independence of thiol acidity and amine catalysis is consistent with a diffusion-controlled process.

TABLE V

EFFECT OF STIRRING SPEED ON REACTION RATE

$5 \times 10^{-3}$ mole of $1\text{-}C_{12}H_{25}SH$

$5 \times 10^{-3}$ mole of $Fe_2O_3$

75 ml of Degassed Xylene

| % RSH converted/hr | Rpm |
|---|---|
| 0.6 | 1000 |
| 2.2 | 2000 |
| 2.8 | 3000 |

TABLE VI

EFFECT OF THIOL ACIDITY AND 1-DODECYLAMINE ON REACTION RATE

$5 \times 10^{-2}$ mole of Thiol

$5 \times 10^{-2}$ mole of $Fe_2O_3$

75 ml of Xylene

55°, $N_2$, 1000 rpm

| Thiol | % RSH converted/hr | $pK_a$ |
|---|---|---|
| $1\text{-}C_{12}H_{25}SH$ | 0.60 | 14 |
| $C_6H_5CH_2SH$ | 0.40 | 10.5 |
| $C_6H_5SH$ | 0.31 | ~6–7 |
| $1\text{-}C_{12}H_{25}SH$[a] | 0.95 | |

[a] A 10/1 ratio of $1\text{-}C_{12}H_{25}SH/1\text{-}C_{12}H_{25}NH_2$ was used.

Finally, the stability of some typical disulfides was determined in the presence of $MnO_2$ and $Fe_2O_3$. Benzyl disulfide, *n*-butyl disulfide, and *sec*-butyl disulfide were stirred with a 5-mole excess of $MnO_2$ and $Fe_2O_3$ in xylene for 14 days. Gas chromatographic analyses indicated that essentially all of the disulfide was unreacted. Hence, it can be concluded that disulfides are not oxidized by metal oxides under these mild conditions.

## Discussion

The results of the present study have established that metal oxides are capable of oxidizing thiols to disulfides in nonpolar media under mild conditions. This is consistent with the previously mentioned catalysis effects of metal oxides in liquid phase autoxidation and polymerization reactions.[8,9] The results obtained with $MnO_2$ (see Table I) indicate that, for thiols, this oxidizing agent is as efficient as hydrogen peroxide and dimethyl sulfoxide. The dioxide definitely gives higher disulfide yields than those usually observed with iodine in aqueous sodium hydroxide.[10] Thus the present technique may also be considered as a new synthetic tool. The rate studies in Tables V and VI are indicative of a diffusion-controlled process since thiol structure and acidity usually exert a large influence on chemically controlled ionic and free-radical reactions.[11] The latter is also true for the

---

(10) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1959.

(11) A. A. Oswald and T. J. Wallace, "The Base-Catalyzed Oxidation of Thiols and the Co-Oxidation of Thiols with Olefins," Part II, Organic Sulfur Compounds, N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., 1965, Chapter 8.

catalysis of thiol oxidations by amines and other organic bases.[5,11,12] Hence, the greater rate of oxidation observed with $MnO_2$ in comparison with the other metal oxides is most likely due to surface effects and different rates of thiol adsorption. This would seem reasonable since a 20–30° temperature rise was observed when 1,4-butanedithiol and $MnO_2$ were brought into reaction. No noticeable amount of heat was given off when the dithiol and CuO were brought into reaction.

The olefin addition studies summarized in Tables III and IV are indicative of a radical reaction. Obviously, disulfides arise by the dimerization of thiyl radicals (RS·) and sulfide must arise by a low-temperature, free-radical addition reaction. The reaction scheme shown below with $MnO_2$ would seem to be most consistent with the observed results. At low thiol/metal oxide ratios, steps 1–3 are probably the predominant reaction path. At high thiol–metal oxide ratios, the oxide apparently functions like other conventional radical initiators and the product arises primarily by the sequence shown in steps 4 and 5. Under the latter conditions, the dimerization step could also contribute to chain termination. The results in Tables III and IV also indicate that the olefin addition reaction is least favorable in the presence of $MnO_2$. This is apparently due to the greater initial concentration of thiyl radicals produced in the presence of this metal oxide. This in turn decreases the amount of thiol available for the chain-transfer step. Thus, the above sequence is probably an oversimplification of the true nature of the reaction.

$$RSH + Mn^{IV}O_2 \longrightarrow RS\cdot + HOMn^{III}O \qquad (1)$$

$$RSH + HOMn^{III}O \longrightarrow RS\cdot + Mn^{II}O + H_2O \qquad (2)$$

$$2RS\cdot \longrightarrow RSSR \qquad (3)$$

$$RCH{=}CH_2 + RS\cdot \longrightarrow R\dot{C}HCH_2SR \qquad (4)$$

$$RSH + R\dot{C}HCH_2SR \longrightarrow RS\cdot + RCH_2CH_2SR \qquad (5)$$

Steps 1–3 in the above reaction scheme are similar to those proposed to explain the high-temperature oxidation of diarylmethanes to tetraarylethanes and phenylcarbinols to aldehydes and ketones by $MnO_2$,[13] the oxidation of *para*-substituted anilines to azobenzenes in refluxing benzene,[14] and substituted benzyl alcohols to benzaldehydes.[15] Undoubtedly, radical intermediates are involved in these reactions since it is well known that metal oxides such as $WO_3$ and $MnO_2$ are capable of scavenging hydrogen atoms.[16] However, the present study is the first in which the proposed radical intermediate has been trapped (isolated) by a known radical reaction. The ready oxidation of thiols by metal oxides under these mild conditions is also consistent with the ease of phenol oxidations by $MnO_2$ in ether at room temperature.[17] Phenols, like thiols, form fairly stable free radicals. Hence, it would seem that the stability of the resulting free radical is involved to some extent in the rate of hydrogen atom transfer to the surface of the metal oxide.

As indicated in Tables II and IV, dodecyl sulfide is produced from the reaction of 1-dodecanethiol with CuO even in the absence of olefin. CuO appears to be unique in this respect. In addition to the mechanism which is suggested above, a competing reaction may take place in which intermediate cupric thiolates are produced. The latter could decompose to sulfide and presumably cupric sulfide. Such species are formed when copper metal and thiols are exposed to oxygen[18] and they are reported to be unstable.[19] This possibility has not been investigated as yet. However, the result observed suggests that certain thiol–metal oxide reactions may be more complex than those reported in the present study.

$$Cu(SR)_2 \longrightarrow CuS + RSR \qquad (6)$$

## Experimental Section

**Reagents.**—1-Dodecanethiol and 1-hexadecanethiol were obtained from Columbia Organic Chemicals; benzenethiol and $\alpha$-toluenethiol were obtained from Evans Chemetics Inc. Temperature-programmed gas chromatographic analyses (F and M Model No. 609) on a 2-ft silicone rubber column (30 wt % silicone rubber on Chromosorb W) between 75 and 250° indicated that each thiol was at least 98% pure. 1,4-Butanedithiol was obtained as the ultrapure reagent from the Wateree Chemical Co. All thiols were stored in a nitrogen drybox on a continuous basis. Cobaltic oxide, cupric oxide, and ferric oxide were purchased from Ace Scientific Supply Co. as reagent grade materials. Manganese dioxide was prepared according to the method of Attenburrow, *et al.*[20]

**Synthesis of Authentic Disulfides.**—All authentic disulfides were synthesized from their corresponding thiols using the oxidation technique recently described by Wallace.[3] The thiol was added to an excess of dimethyl sulfoxide (DMSO) and the reaction mixture was heated at 100–160° overnight. The sulfoxide reduction product, dimethyl disulfide, easily distilled from the reaction mixture as the reaction progressed because of its low boiling point (34°). On standing, the disulfides precipitated and could easily be purified by recrystallization from ethanol or acetone. The melting point of each disulfide synthesized by this technique agreed with that tabulated in Reid.[21] In the case of 1,2-dithiacyclohexane, a slight modification of the above procedure was used. The dithiol was added to a hot, stirred solution of DMSO over an extended time period. This minimized the formation of polymeric disulfide. The disulfide was isolated by the above technique and identified by its boiling point, 87–88° at 34 mm (lit.[22] bp 87–88° at 34 mm), and its melting point, 32° (lit.[22] mp 32°).

**General Procedure for Thiol–Metal Oxide Coupling Reactions.**—A general procedure was employed for the thiol–metal oxide reactions listed in Tables I and II. The desired quantity of metal oxide and degassed solvent were placed in either a 50- or 100-ml four-necked flask in a nitrogen drybox. The flask was equipped with a sealed paddle stirrer. A tight-fitting, self-sealing Neoprene diaphragm was inserted into each neck of the flask. The diaphragm extended down from the neck of the flask and further sealing was accomplished by wrapping a heavy piece of copper wire around the outside of the diaphragm. This arrangement provided double protection against contamination by air. The sealed flask was then removed from the nitrogen drybox and transferred to a constant-temperature bath (usually 55 ± 0.1°). When thermal equilibrium was reached,

---

[12] T. J. Wallace, N. Jacobson, and A. Schriesheim, *Nature*, **201**, 608 (1964).

[13] (a) E. F. Pratt and S. P. Suskind, *J. Org. Chem.*, **28**, 638 (1963); (b) E. F. Pratt and J. F. Van DeCastle, *ibid.*, **26**, 2973 (1961).

[14] O. H. Wheeler and D. Gonzalez, *Tetrahedron*, **20**, 189 (1964).

[15] R. J. Gritter, G. D. Dupré, and T. J. Wallace, *Nature*, **202**, 179 (1964).

[16] H. W. Melville and J. C. Robb, *Proc. Roy. Soc.* (London), **A196**, 445 (1956).

[17] D. H. Hey, J. A. Leonard, and C. W. Rees, *J. Chem. Soc.*, 5963 (1963).

[18] (a) E. Dittrich, *Brennstoff-Chem.*, **14**, 283 (1933); (b) *ibid.*, **15**, 148 (1934); (c) *ibid.*, **20**, 348 (1939).

[19] E. P. Kohler, *Am. Chem. J.*, **22**, 67 (1899).

[20] J. Attenburrow, *et al.*, *J. Chem. Soc.*, 1094 (1952).

[21] E. E. Reid, "Organic Chemistry of Bivalent Sulfur Compounds," Vol. III, Chemical Publishing Co., New York, N. Y., 1960, pp 395–399.

[22] G. Claeson, G. Androes, and M. Calvin, *J. Am. Chem. Soc.*, **83**, 4360 (1961).

prethermostated thiol was injected into the reaction flask through the self-sealing Neoprene diaphragm by a syringe. The reaction was then initiated by stirring (usually 1000 rpm) the heterogeneous mixture. Completeness of reaction or extent of reaction was determined by gc analysis using an internal hydrocarbon standard and predetermined molar response factors.[23] Upon termination of the reaction, the reaction flask was transferred to the nitrogen drybox, the mixture was filtered to remove the hydrocarbon layer, the inorganic phase was washed with xylene (three volume excess) to remove any adsorbed or occluded product, and the filtrates were combined. Subsequent dilution with ethanol and storage in a coldbox (0°) precipitated the disulfides which were collected by filtration and dried to a constant weight. The structure of each disulfide was confirmed by its melting point and mixture melting point with the authentic disulfides prepared above. One exception to this procedure was 1,2-dithiacyclohexane. This disulfide was isolated by fractional distillation on a 16-in. silvered column equipped with a tantalum-wire spiral. Its boiling point (86–88° at 35 mm) and melting point (30–32°) agreed with reported values[22] and a mixture melting point with an authentic sample was not depressed. It should be noted that all disulfide yields were based on the amount of isolated product. Hence, the yields shown in Tables I and II represent minimum values.

**Thiol Addition Reactions to 1-Dodecene.**—Reaction mixtures in the 1-dodecanethiol addition reactions to 1-dodecene were prepared in the manner described above. In these studies, a 10/1 mole ratio of olefin/thiol was employed and the mole ratio of thiol/metal oxide was varied as shown in Tables III and IV. Cetane (0.01 mole) was added at the beginning of each reaction as an internal standard for gc analysis. Using predetermined molar response factors, it was then possible to compute the amount of thiol converted and the amount of sulfide and disulfide formed from each peak on the gas chromatograph at the end of the reaction. The glpc unit employed in these analyses was an F and M Model No. 609 flame-ionization gas chromatograph equipped with a Minneapolis Honeywell recorder and a disk integrator (Model No. 201). The injection port of the unit was maintained at 305° and the inlet pressure of helium was 36 psig. The block of the detector was maintained at a constant temperature of 245°. The helium flow through the column was 100 cc/min when measured at room temperature with a flowmeter. All quantitative data was obtained on a 3 ft, 20 wt % Carbowax (20 MM) on Chromosorb W column (0.25-in. stainless steel tubing). This column gave excellent separation of all mixtures used in the present study.[24]

**Related Gas Chromatography Data.**—In the above studies and in the rate studies listed in Tables V and VI, a series of molar response factors between the compound(s) of interest and its corresponding internal standard were computed. These values are summarized in Table VII. The competition studies on coupling and olefin addition reactions were carried out with 1-dodecanethiol because of the thermal stability of the resulting disulfide. Aromatic disulfides dissociate at fairly low temperatures and benzyl disulfide undergoes thermal decomposition (above 200°) to stilbene and presumably hydrogen sulfide and sulfur.[25] Occasionally, higher boiling compounds were detected in the gas chromatographs from the olefin addition reactions. Presumably, these were telomers which are frequently observed in free-radical olefin addition reactions.

Table VII

Summary of Gas Chromatographic Conditions

| Reactant measured | Internal standard | Response factor | Preferred column temp, °C |
|---|---|---|---|
| 1-Dodecanethiol | Cetane | 1.41 | 185 |
| Dodecyl sulfide | Cetane | 1.20 | 225 |
| Dodecyl disulfide | Cetane | 1.82 | 290 |
| Toluenethiol | Diphenylmethane | 1.87 | 200 |
| Benzenethiol | Toluene | 1.15 | 200 |

**Acknowledgment.**—The author is indebted to Mr. John J. Mahon who performed all of the experimental work and to the Esso Research and Engineering Company especially the Process Research Division for the privilege of publishing this research.

---

[23] For a discussion on the significance of molar response factors, see A. E. Messner, D. M. Rosie, and P. A. Argabright, *Anal. Chem.*, **31**, 230 (1959).

[24] For other applications, see T. J. Wallace and J. J. Mahon, *Nature*, **201**, 816 (1964).

[25] E. Fromm, *Ber.*, **36**, 538 (1903).

---

# The Metalation of 1-Methoxynaphthalene with *n*-Butyllithium

Bruce M. Graybill[1] and D. A. Shirley[2]

*The University of Tennessee, Knoxville, Tennessee*

*Received November 5, 1965*

The metalation of 1-methoxynaphthalene by *n*-butyllithium has been reinvestigated. Evidence from the metalation of 1-methoxynaphthalene-8-*d* indicates that metalation occurs concurrently at the 2 and 8 positions, and no rearrangement of the lithium from carbon 8 to carbon 2 is involved as proposed earlier. Attack at position 2 is favored, but the relative amounts of isomers formed seem to be influenced by the source of the *n*-butyllithium and how it is produced. Evidence from nmr proton spectra is presented for a coordination complex between the methoxy group and *n*-butyllithium.

The metalation of 1-methoxynaphthalene by *n*-butyllithium was first studied by Sunthanker and Gilman,[3] who reported that metalation followed by carbonation gave 1-methoxy-2-naphthoic acid in 25% yield.

More recently, Barnes and Nehmsmann[4] repeated this experiment and found a mixture of 1-methoxy-2-naphthoic acid and 8-methoxy-1-naphthoic acid. The latter results were interpreted in terms of the reaction sequence shown in Scheme I.

Acid III appeared to be formed in larger yield early in the reaction, but the amount decreased and the amount of acid IV increased as the reaction proceeded. This apparent change in acid content with reaction time was explained by postulating the equilibrium between the 8-lithio (I) and 2-lithio (II) compounds. Barnes[4] also calculated the electron densities of the ring carbon atoms in 1-methoxynaphthalene and came to the conclusion that position 8 contains the most acidic proton. Because of the experimental results and the electron-density calculations, Barnes concluded that metalation by *n*-butyllithium must take place first at the more acidic 8 proton followed by equilibrium with the thermodynamically more stable 2 isomer.

---

[1] National Science Foundation summer participant, 1965, from Graceland College, Lamoni, Iowa.

[2] To whom inquiries concerning this publication should be sent.

[3] S. V. Sunthanker and H. Gilman, *J. Org. Chem.*, **16**, 8 (1951).

[4] R. Barnes and L. Nehmsmann, *ibid.*, **27**, 1939 (1962).