$$V^* = V_p^*$$

$$K^* = K_p + \frac{k_6(k_2 + k_3 + k_4p)}{k_1(k_3 + k_5 + k_4p)}[P_2] \qquad (20)$$

where V_p^*, K_p^* are the V^*, K^* obtained when $[P_1] = p$, $[P_2] = 0$. Equation 20 is of the same form as eq. 19.

Acknowledgments.—This work was supported by funds of the National Institutes of Health. One of us (A. J. A.) wishes to thank the National Science Foundation for fellowships awarded to her during this research.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN, NEW YORK]

Photochemical Reactions of Thiobenzophenones[1]

BY GERALD OSTER, LOUIS CITAREL[2] AND MURRAY GOODMAN

RECEIVED JULY 5, 1961

Irradiation of thioketones with visible light transforms them quantitatively to their oxygen analogs. The quantum yield of the reaction is less the greater the dark stability of the compound in air. For thiobenzophenone the dependence of quantum yield on oxygen concentration indicates that the reactive excited species has a lifetime of at least 1.5×10^{-7} sec. Near ultraviolet light transforms thiobenzophenone in the absence of oxygen into benzhydryl mercaptan, benzhydryl disulfide and tribenzhydryl tetrasulfide. This reaction takes place best with solvents which have easily extractable hydrogens and is inhibited by oxygen. Photolysis of thioketones proceeds in saturated hydrocarbon solvents if far ultraviolet light is employed. The absorption bands of thiobenzophenone in ethanol at 315 mμ and 595 mμ are further separated for thiobenzophenones with electron releasing substituents. The position of the two bands is influenced by the nature of the solvent.

Introduction

Thioketones differ strikingly from their oxygen analogs in that they are colored (usually blue) and highly reactive. Their ultraviolet spectra also offer some interesting differences from their oxygen counterparts. The photochemistry of benzophenone recently has been described in detail.[3] One purpose of the present work is to compare the photochemical reactions of thiobenzophenone with those of benzophenone. The thio compounds have widely separated absorption bands and hence allow the selective excitation of a single band without interference from other overlapping bands. As a consequence, one might expect differences in photochemical behavior depending on the wave length region used for excitation. The second purpose of the present work is to describe the effect of substituents on both the visible and ultraviolet spectra of substituted aromatic thiones.

Experimental

Materials.—The thioketones were prepared by treatment of an ethanolic solution of the corresponding ketone with H_2S in the presence of HCl.[4] The ketones were obtained either from Eastman or synthesized and purified by well known procedures. The thioketones were purified by chromatography over Florisil (Floridin Co., Tallahassee, Florida).[5] Nitrogen–oxygen gas mixtures were supplied by Matheson Company.

Benzhydryl disulfide was prepared by the procedure of Staudinger and Freudenberger[6] in 63% yield. The synthesis of benzhydryl mercaptan was accomplished by two different procedures. In the first method thiobenzophenone (5.0 g., 0.025 mole) was dissolved in anhydrous ether and reduced *via* the usual lithium aluminum hydride reduction. During the reaction the solution color turned from a deep blue to a pink. The complex was decomposed by the slow addition of water and the aqueous phase separated from the organic phase. The aqueous phase was extracted further with two 50 ml. portions of ether and the ether phases combined. The ether was removed by distillation leaving an oily residue which was dried over magnesium sulfate. The oily material was distilled under reduced pressure to yield 3.5 g. (70%) of a colorless oil, b.p. 138° at 2.5 mm., n^{25}D 1.6159 (reported n^{25}D 1.6159[7]). In the second method, this compound was prepared by the procedure described by Suter.[7]

Procedures.—Visible and ultraviolet spectra were determined in absolute ethanol at room temperature using a DU spectrophotometer which was modified to be automatically recording (Process Instruments, Inc.).

For the visible light photochemistry the solutions were irradiated with nearly monochromatic light of 588 mμ achieved by an interference filter (Bausch and Lomb) placed in front of a 500 watt tungsten lamp projector (Bell and Howell, type TDC). The change in transmission was followed by the use of a red-sensitive RCA 1P22 photomultiplier tube whose output was amplified with an Aminco photometer instrument and recorded as a function of time on a Leeds and Northrup Speedomax recorder. Gases previously equilibrated with ethanol were bubbled through the solutions. The concentrations of the thioketones were adjusted to give an optical density of unity at 588 mμ. The reaction also was followed by determining the ultraviolet spectrum of a 100-fold dilution of a 1 ml. aliquot drawn at intervals from the solution being irradiated. The intensity of the light falling on the solution was determined with a calibrated thermopile (Eppley Laboratories, Newport, R. I.).

For the near ultraviolet light photochemistry two lamps were employed. To follow the reaction, we used an AH-4 (General Electric) high pressure mercury lamp with a Wood's glass filter to isolate the 365 mμ line and a $CuSO_4$ filter[8] to remove the deep red component. The change in transmission at 365 mμ was followed on the recorder as described above but now a RCA 1P28 photomultiplier was used. In order to obtain large amounts of products produced by near ultraviolet light a Hanovia S-100 intermediate pressure mercury lamp was employed. This lamp in the form of a straight tube was inserted in a water-cooled (de-ionized water cooled externally) quartz jacket fitted with a flint glass filter to absorb ultraviolet radiation below 300 mμ. The lamp and quartz jacket were incorporated in an apparatus designed to allow for the irradiation of a sample under inert atmosphere and with facilities to draw off samples at any desired time interval. The reaction chamber can contain 700 ml. of solution. If desired one can isolate any particular spectral line by circulating the appropriate light

---

[1] Presented at the 135th National Meeting of the American Chemical Society, Boston, April 1959. Taken in part from the Ph.D. thesis of Louis Citarel, Polytechnic Institute of Brooklyn, June 1960.

[2] Thiokol Research Fellow 1958–1959.

[3] J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald and R. B. Martin, *J. Am. Chem. Soc.*, **81**, 1068 (1959).

[4] H. Staudinger and H. Freudenberger, *Ber.*, **61**, 1576 (1928).

[5] R. H. Abeles, R. F. Hutton and F. H. Westheimer, *J. Am. Chem. Soc.*, **79**, 712 (1957).

[6] H. Staudinger and H. Freudenberger, *Organic Syntheses*, **11**, 94 (1931).

[7] M. M. Klenk, C. M. Suter and S. Archer, *J. Am. Chem. Soc.*, **70**, 3846 (1948).

[8] E. J. Bowen, "Chemical Aspects of Light," 2nd Ed., Oxford, 1947, Appendix II.

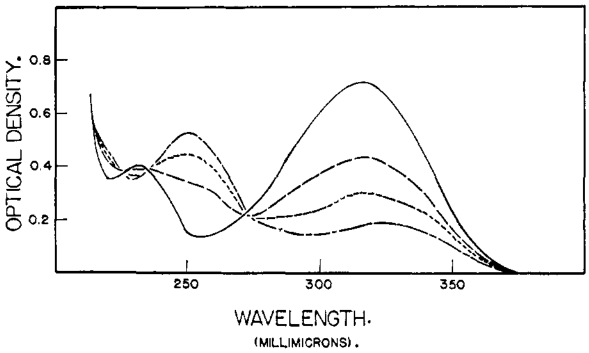


Fig. 1.—Changes in the ultraviolet spectra of thiobenzophenone while being photooxidized under the action of yellow light. Time, in minutes, of illumination: ——— 0, — — — 15, - - - - 30, — - — 60.

filter solution[8] through the quartz jacket. The filter solution also acts as a coolant.

The quantum yield for the near ultraviolet light reaction was determined by using the S-100 lamp and isolating the 313 mμ line with the appropriate light filter solution.[8] The sample was placed in a quartz container. The radiation dosage was measured with a ferri-oxalate actinometer.[9]

For the far ultraviolet light photochemistry a 35 watt Hanovia mercury lamp producing mainly (about 90%) 254 mμ was employed. The lamp was in the form of a helix which surrounded a 100 ml. quartz test-tube containing 30% acetic acid to remove ultraviolet light below 240 mμ. The sample was placed in a 10-ml. 1-cm. diameter test-tube which was positioned along the axis of the large test-tube. The concentration of the thioketone (in cyclohexane) was adjusted to give an optical density of 0.77 at 254 mμ. Samples of the solution were removed at 5 min. intervals and their spectra measured.

Isolation of Products.—The irradiation of thiobenzophenone in the apparatus described above was performed using ethanol as solvent and in a similar experiment using 2-propanol as solvent. The irradiation was carried out to completion by the observation of the complete decolorization of the solution. In both cases a white material was formed and deposited on the walls of the apparatus and was recovered by filtration. More of the same material was recovered on further cooling of the solvent. This material was recrystallized from aqueous acetone and gave a m.p. of 167–168° decomposing to a blue material. Further evaporation of the solvent in both cases produced another white material having a m.p. of 151–152° and melting to a clear yellow liquid. The remainder of the photolysis products after complete removal of the solvent consisted of a yellow oil which could be purified by vacuum distillation. By this procedure a colorless oil was recovered with a boiling point of 138° at 2.5 mm., n^{25}_{D} 1.6148. The residue from the distillation was insoluble in ordinary organic solvents but soluble in carbon disulfide. Based on 5 g. of starting material 3.4 g. (68%) of material melting at 151–152° (dibenzhydryl disulfide), 0.8 g. (16%) of the oil (benzhydryl mercaptan) and 0.45 g. (9%) of material m.p. 167–168° were recovered. Similar proportions were observed for both solvent systems. In some cases lower yields of materials were observed due to decomposition of the products to reproduce the starting material. Molecular weight determinations were carried out on the material melting from 167–168° by cryoscopy using cyclohexane as solvent. The value obtained was 585 (calculated for the tetrasulfide 570).

Results and Discussion

Spectra.—The spectral maxima of the thioketones and their oxygen counterparts are summarized in Table I. The maxima are classified according to the terminology used by Burawoy[10] into K(Konjugiert) and R(Radicalartig) bands, the former being those of high molecular extinction coefficient (*ca.* 10^4). In more modern assignments the K and R bands often are referred to as $\pi \rightarrow \pi^*$ and $N \rightarrow \pi^*$ transitions, respectively. The R bands for ketones lie in the near ultraviolet region, whereas for thioketones the R bands lie in the visible region. Mulliken[11] attributes this effect to the lower ionization potential of the non-bonding p-electrons of sulfur as compared with those of oxygen.

TABLE I

SPECTRAL CHARACTERISTICS (IN ETHANOL) OF SOME KETONES AND THIOKETONES

Compound	K Band λ_{max} (mμ)	ϵ_{max}	R-Band λ_{max} (mμ)	ϵ_{max}
Benzophenone	250	18,200	333	170
Thiobenzophenone	315	15,100	595	177
p,*p*′-Dimethoxybenzophenone	290	22,500	330	146
p,*p*′-Dimethoxythiobenzophenone	350	26,100	570	277
p-Methoxybenzophenone	250	8,890	..	..
	285	15,580		
p-Methoxythiobenzophenone	320	11,030	585	252
	360	15,800		
p-Nitrobenzophenone	265	19,880	..	..
p-Nitrothiobenzophenone	300	12,930	610	133
	310	12,450		

In agreement with Burawoy's observations[10] with the spectra of other compounds electron releasing substituents (*e.g.*, *p*,*p*′-dimethoxy) on both the ketones and the thioketones shift the K bands to longer wave lengths and the R bands to shorter wave lengths. Electron attracting substituents (*e.g.*, *p*-nitro) on the other hand have a lesser effect on the K band shift but shift the R band to longer wave lengths, at least for the sulfur compound. The R band in *p*-nitrobenzophenone is difficult to observe, since it probably is masked on the K band.

The effect of polarity of the solvent on the position of the K and R bands has been considered,[10,12] and it was noted that a highly polar solvent shifts the R band to shorter wave length regions. We find a similar effect for the thioketones. For example, the R band maximum for thiobenzophenone in benzene appears at 12 mμ longer wave length than that in ethanol. The K band, on the other hand, is shifted in an opposite manner.

The qualitative results of the irradiation of thiobenzophenone under various conditions are summarized in Table II.

When thiobenzophenone is irradiated in the presence of oxygen with visible light, the product is benzophenone.[13] As seen from Fig. 1 benzophenone is the only product of the reaction, since there is a constant isosbestic point (at 272 mμ) as the reaction proceeds. Using sunlight as the radiant source,[13] one obtains a trisulfide as a byproduct which probably arises from the mixed reaction effect of both visible and ultraviolet light. The quantum yield for the photooxidation of the thio-

---

(9) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **235**, 518 (1956).

(10) A. Burawoy, *J. Chem. Soc.*, 1177 (1939). See also P. Brockelhurst and A. Burawoy, *Tetrahedron*, **10**, 118 (1960).

(11) R. S. Mulliken, *J. Chem. Phys.*, **7**, 121 (1939).

(12) G. J. Brealy and M. Kasha, *J. Am. Chem. Soc.*, **77**, 4462 (1955).

(13) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 275 (1943).

TABLE II

IRRADIATION OF THIOBENZOPHENONE UNDER VARIOUS CONDITIONS

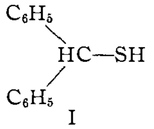
Wave length (mμ)	Solvent	Atmosphere	Result
588	Ethanol	Oxygen	Photooxidation
588	Ethanol	Helium	No reaction
365	Ethanol	Oxygen	No reaction
365	Ethanol	Helium	Photoreduction
365	2-Propanol	Helium	Photoreduction
365	Cyclohexane	Helium	No reaction
365	Carbon tetrachloride	Helium	No reaction
254	Cyclohexane	Helium	Photolysis

benzophenone using 588 mμ is 5.6×10^{-2}. The quantum yield of photooxidation of the *p,p'*-dimethoxy derivative was slightly lower, namely, 4.8×10^{-2}, and of the *p*-nitro derivative was much higher, namely, 18.1×10^{-2}. It may be of interest to note that the nitro derivative is also the least stable of these compounds in the dark.

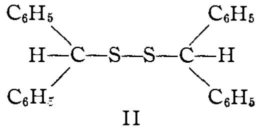
The dependence of rate of photooxidation on oxygen concentration is given empirically by the relation rel. rate $= (O_2)/\alpha + (O_2)$, where (O_2) is the oxygen concentration (mole/liter) in the solution and α is an empirical constant having the value 1.0×10^{-3} mole/liter.

These results are consistent with the scheme that an excited species can either fall to the ground state or react with oxygen to give product. According to this reaction scheme α is the reciprocal of the product of the lifetime of the excited species and the bimolecular rate constant of the reaction of the excited species with oxygen. If every diffusional encounter leads to a reaction, then the rate is given by the number of encounters per unit time which for the case of a medium viscosity of alcohol at room temperature is 6×10^9 sec.$^{-1}$ mole^{-1} liter. Hence the lifetime cannot be smaller than 1.5×10^{-7} sec. This result is compatible with the lifetime computed from the Ladenberg formula relating lifetime and area under the absorption band.[14] Here the area under the R band $\int \epsilon \, d(1/\lambda)$ is approximately 3.5×10^5 cm.$^{-2}$ mole^{-1} liter and the upper limit of the natural lifetime is computed to be 1.7×10^{-6} sec.

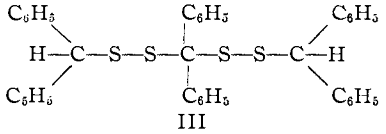
Thiobenzophenone under the action of near ultraviolet light does not undergo any over-all reaction if oxygen is present. This is also the case with benzophenone.[3] In the absence of oxygen, however, thiobenzophenone is photoreduced to yield the compounds



I



II



III

in the approximate ratio 3:4:0.5. Compounds I and II were identified by unequivocal synthesis and from their physical constants reported in the literature.[6,7] The structure of compound III (compare ref. 15) is based on a combination of elemental analysis, molecular weight and proton magnetic resonance spectra.[16]

The nuclear magnetic resonance spectral data for benzhydryl mercaptan, dibenzhydryl disulfide and the presumed tetrasulfide (III) are presented in Table III. The areas under each band for all the compounds are in conformity with structures given. The assignments for compound III, however, present some difficulties in that the 2.44 band takes the form of a highly spin-coupled pattern. Furthermore, the 6.20 band is displaced relative to the bands for benzyl protons in compounds I and II.

TABLE III

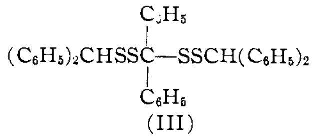
N.M.R. SPECTRAL DATA OF THE SULFUR-CONTAINING COMPOUNDS

Compound	τ Values (p.p.m.)[a]	Assignment of protons
Benzhydryl mercaptan (compound I)	2.62	Aromatic
	4.50	Benzyl
	4.58	
	7.70	Mercaptan
	7.78	
Dibenzhydryl disulfide (compound II)	2.65	Aromatic
	5.11	Benzyl
Tetrasulfide (presumed to be compound III)	2.44	Aromatic
	2.79	
	6.20	Benzyl

[a] Relative to benzene.

With benzophenone under these conditions of ultraviolet irradiation, the prominent product is dibenzopinacol.[3] No sulfur analog of the pinacol is observed with thiobenzophenone, however. The pinacol formation is believed to arise from combination of two benzhydrol radicals, the hydrogens being abstracted from the solvent. With thiobenzophenone, on the other hand, the major product compound II (dibenzhydryl disulfide) may arise from the combination of two benzhydrylthiyl radicals ($(C_6H_5)_2CHS\cdot$) made through the abstraction of hydrogen from the solvent. Alternatively, this radical could further abstract a hydrogen atom from the solvent to yield the other important product, compound I (dibenzhydryl mercaptan). The tetrasulfide (compound III) may arise from the scheme

1. $(C_6H_5)_2CS^* + (C_6H_5)_2CHSSCH(C_6H_5)_2 \longrightarrow (C_6H_5)_2CHS\cdot + (C_6H_5)_2\dot{C}SSCH(C_6H_5)_2$
(II)
2. $(C_6H_5)_2CHS\cdot \longrightarrow (C_6H_5)_2CH\cdot + S$
3. $(C_6H_5)_2CHS\cdot + S \longrightarrow (C_6H_5)_2CHSS\cdot$
4. $(C_6H_5)_2CHSS\cdot + (C_6H_5)_2\dot{C}SSCH(C_6H_5)_2 \longrightarrow$



$$(C_6H_5)_2CHSS\overset{C_6H_5}{\underset{C_6H_5}{C}}—SSCH(C_6H_5)_2$$

(III)

The ultraviolet spectra of the products which are formed by the action of near ultraviolet light show that absorption of these compounds is only

---

[14] R. Ladenburg and F. Reiche, *Naturwissenschaften*, **11**, 584 (1923).

[15] J. Tsuragi and T. Nakabayashi, *J. Org. Chem.*, **25**, 1744 (1960).

[16] We wish to thank Dr. Nelson Trenner of Merck, Sharp and Dohme Laboratories for the n.m.r. studies which were carried out using a 60 megacycle high resolution Varian instrument.

appreciable below 300 mμ. The quantum yield of photoreduction of thiobenzophenone is 4.74 × 10^{-3}, only about half as large as that for benzophenone.

The far ultraviolet is sufficiently energetic to affect thiobenzophenone even in a relatively inert solvent such as cyclohexane. Products could not be isolated since they absorb light and are subsequently photolyzed bylig ht of this wave length region. All one observes as irradiation proceeds is a decrease in absorption in the K band and an increase in end absorption below 210 mμ.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY, LAFAYETTE, INDIANA]

Kinetics of 1,10-Phenanthroline Chelation. III. Effect of Cyanide and Azide Ions on the Dissociation Rate of Tris-(1,10-phenanthroline)-iron(II)

BY D. W. MARGERUM AND L. P. MORGENTHALER[1,2]

RECEIVED MAY 20, 1961

Cyanide and azide ions as well as hydroxide ion greatly increase the rate of displacement of 1,10-phenanthroline from the tris-(1,10-phenanthroline)-iron(II) complex. A mechanism is proposed based on the interaction of the nucleophile with the Fe(II) at its octahedral face within the pockets formed between the 1,10-phenanthroline molecules in the tris complex.

Introduction

A pronounced hydroxide ion effect on the rate of dissociation of tris-(1,10-phenanthroline)-iron(II) was reported previously.[3] This effect is of particular interest because an SN1CB mechanism is not feasible with 1,10-phenanthroline as a ligand. In view of the efforts to prove the SN1CB mechanism[4,5] or the SN2 mechanism[6] for Co(III) reactions, it is worthwhile to examine other nucleophiles with this Fe(II) system which is isoelectronic with Co(III). The present work shows that the hydroxide ion behavior was not a specific effect and that cyanide ion and azide ion also greatly accelerate the dissociation of $\mathrm{FePh_3^{+2}}$. As a subsequent paper[7] shows, this is in striking contrast to the behavior of $\mathrm{NiPh_3^{+2}}$ substitution reactions.

Experimental

$\mathrm{FePh_3(ClO_4)_2}$ was prepared by the reaction of stoichiometric quantities of ferrous ammonium sulfate and 1,10-phenanthroline monohydrate in water and precipitation of the perchlorate salt with sodium perchlorate. The solid was twice recrystallized from aqueous sodium perchlorate solutions.

$\mathrm{FePh_2(CN)_2 \cdot 2H_2O \cdot CHCl_3}$ was prepared by the method proposed by Schilt[8,9] for the preparation of $\mathrm{FePh_2(CN)_2}$. After recrystallization from chloroform in a Soxhlet extractor, shiny dark purple crystals were obtained which were washed with a small quantity of chloroform and dried over magnesium perchlorate.

Anal. Calcd. for $\mathrm{FePh_2(CN)_2 \cdot 2H_2O \cdot CHCl_3}$: C, 51.89; H, 3.39; N, 13.45; Cl, 17.02; Fe, 8.94. Found: C, 52.15; H, 3.48; N, 13.37; Cl, 17.50; Fe, 9.06.

Part of the chloroform containing product was recrystallized from sulfuric acid. The solid was dried *in vacuo* over sulfuric acid and stored over magnesium perchlorate.

Anal. Calcd. for $\mathrm{FePh_2(CN)_2 \cdot H_2O}$: C, 64.21; H, 3.73; N, 17.28. Found: C, 62.98; H, 3.75; N, 17.61.

Sodium azide was recrystallized from hot water and standardized by oxidation with permanganate ion.[10]

Spectra were measured on a Cary 14 spectrophotometer and kinetic studies were followed with a thermostated Beckman DU spectrophotometer. All *p*H measurements were made on a Beckman Model G *p*H meter. All kinetic studies were made at constant ionic strength maintained with $\mathrm{Na_2SO_4}$ or KCl. The precision of rates was 5% or better.

Results and Conclusions

Cyanide System.—In his original paper describing the properties of the $\mathrm{FePh_2(CN)_2}$ and $\mathrm{FePh(CN)_4^{-2}}$ complexes,[8] Schilt proposed the rapid and complete disproportionation of the neutral complex in water

$$2\mathrm{FePh_2(CN)_2} \rightleftharpoons \mathrm{FePh_3^{+2}} + \mathrm{FePh(CN)_4^{-2}} \quad (1)$$

This was based on spectrophotometric analyses of aqueous solutions of $\mathrm{FePh_2(CN)_2}$. However, he reported the concentration of the tetracyano complex as twice the concentration of $\mathrm{FePh_3^{+2}}$, which is impossible in the disproportionation reaction.

In this Laboratory it was found that aqueous mixtures of $\mathrm{FePh_3^{+2}}$ and $\mathrm{FePh(CN)_4^{-2}}$ would not form sufficient quantities of $\mathrm{FePh_2(CN)_2}$ to be extracted by chloroform for several days. On the other hand all the 1,10-phenanthroline containing species could be extracted into chloroform from solutions of $\mathrm{FePh_2(CN)_2}$ which were one week old. Neither of these facts is consistent with the disproportionation reaction. If an equilibrium such as (1) occurs, it must be very slow in both directions.

The aqueous spectrum of $\mathrm{FePh_2(CN)_2}$ has an $\epsilon_{\max}$ at 510 mμ, about 2/3 that for $\mathrm{FePh_3^{+2}}$, but the former spectrum is broader and is distinguishable from the latter. If the ratio of $\mathrm{FePh(CN)_4^{-2}}$ to $\mathrm{FePh_3^{+2}}$ is calculated from the spectrum assuming the disproportionation in equation 1, the inconsistent value of 2.0 is found. Furthermore, the total iron content is 17% too high when calculated in this manner.

---

[1] Abstracted from a thesis submitted by L. P. Morgenthaler to the Graduate School of Purdue University, June 1961, in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

[2] Western Electric Engineering Research Center, Princeton, New Jersey.

(3) D. W. Margerum, *J. Am. Chem. Soc.*, **79**, 2728 (1957).

(4) F. Basolo, H. H. Schmidtke and R. G. Pearson, *ibid.*, **82**, 4434 (1960).

(5) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y.

(6) C. K. Ingold, R. S. Nyholm and M. L. Tobe, *Nature*, **187**, 477 (1960); D. D. Brown, C. K. Ingold and R. S. Nyholm, *J. Chem. Soc.*, 2678 (1953); C. K. Ingold, Fifth Weizmann Memorial Lecture Series, the Weizmann Science Press of Israel, 1959.

(7) L. P. Morgenthaler and D. W. Margerum, *J. Am. Chem. Soc.*, **84**, 710 (1962).

(8) A. A. Schilt, *ibid.*, **79**, 5421 (1957).

(9) A. A. Schilt, *ibid.*, **82**, 3000 (1960).

(10) J. H. van der Meulen, *Rec. trav. chim.*, **67**, 600 (1948).