species in this mixture are the chelate, the monodentate, and the hexaaquo in *ca.* 65, 15, and 20% yield. Over a short time period the changes in extinction can be accounted for entirely by ring closure for the monodentate form, and at low acid with, in addition, a small amount of dissociation, and therefore the spectrophotometric measurements were made without separating the monodentate form.

The results obtained in the spectrophotometric studies are summarized in Table I.

TABLE I

CHELATION STUDIES ON $(H_2O)_5Cr{-}O_2CCH_2CO_2H^{2+}$ (25°, μ = 1.0 *M*)

Concn. of complex, *M*	H^+, *M*	% chelation[a]	$k_{\text{chelation}}$, sec.$^{-1}$
0.00140[b]	0.1	74	6.2×10^{-6}
0.00185[c]	0.2	88	8.0×10^{-6}
0.00174	0.5	100	1.58×10^{-5}
0.00140	1.0	100	2.60×10^{-5}

[a] The hydrolysis to the aquo complex accounts for the remainder. [b] Prepared from Pb^{2+}–Cr^{2+}–malonic acid reaction. [c] Prepared from Fe^{3+}–Cr^{2+}–malonic acid reaction.

Discussion

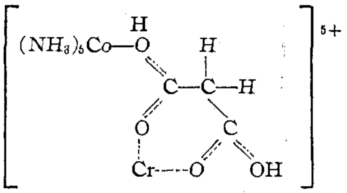
The data of Table I show that the rate of chelation increases with the concentration of acid. When the values of the specific rate *k* in Table I are plotted against (H^+), they are found to conform well to the relation

$$k = 4.0 \times 10^{-6} + 2.2 \times 10^{-7}(H^+) \text{ (units: } M \text{ and sec.)}$$

The existence of the second term in the rate law, though at first surprising, becomes less so if the possibility of ring closure by substitution at carbon rather than at chromium is entertained. For substitution at carbon, a rate term first order in (H^+) is to be expected as in ester hydrolysis or oxygen exchange between a carboxylic acid and solvent. The rate corresponding to the first term of the rate law is several times slower than is the rate of water exchange between $Cr(H_2O)_6^{3+}$ and the solvent, and this term may correspond to substitution at Cr(III); in any case, the specific rate for the term sets an upper limit on the rate of substitution at Cr(III). It is interesting to note that the substitution is as slow as it is, particularly because the local concentration of the free carboxylate end is high. The observation suggests that the displacement of water is not greatly assisted by the incoming carboxyl which, it must be remembered, is protonated. At low (H^+), a term inverse in this variable is expected but our measurements were not extended enough to reveal this effect.

The aquation is less sensitive to (H^+) in the range we investigated than is the rate of ring closure. This may mean that for aquation the acid-independent term relative to the acid-dependent one is greater than is the case for ring closure, or it may mean that the term inverse in (H^+) is to some extent featured in the rate law for aquation under the conditions of our experiments.

Comparison of the work described here with that reported by Svatos and Taube[1] shows that, at ordinary concentrations, the oxidation–reduction reaction of Cr^{2+}(aq) with malonatopentaamminecobalt(III) is much more rapid than ring closure of the chelate. This being so, important features of the mechanism can be settled by examining the nature of the Cr(III) product formed by the reaction. Experiments were done making up two reaction mixtures, each at $\mu \sim 2.5$ *M*, but the first at 0.2 *M* H^+ and the second at 2.4 *M* H^+. For the first solution, more than 90% of the reaction proceeds by the path which is inverse in (H^+) (corresponding to reaction of the complexed dinegative anion); for the second, approximately 75% by the path first order in (H^+). Analysis of the reaction mixture using the ion-exchange technique showed that well in excess of 85% of the product by each path is the chelate. This observation together with our present observations on rate of ring closure proves that by each path the chelate ring is formed before Cr^{2+}(aq) is oxidized and requires a re-examination of the mechanism for the path corresponding to the term first order in (H^+). Specifically the conclusion[1] that this path corresponds to remote attack is incorrect. An activated complex along the following lines is indicated rather than one in which chromium attacks only the remote carboxyl group.



The conclusion[1] that a methylene proton is lost in the activation process is neither proven nor disproven by the current findings.

Since the chelate is formed directly by the reaction of Cr^{2+}(aq) by the path inverse in (H^+), it is reasonable to attribute the high second-order specific rate observed by this path compared to that for the acid malonato complex to the chelation, rather than simply to a decrease in electrostatic repulsion. This conclusion was by no means clear on the basis of the earlier work.

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π Bonding in the $M(CO)_3$ Group

BY S. F. A. KETTLE

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It is generally accepted that an important feature of the bonding of terminal carbonyl groups to a metal atom in the transition metal carbonyls is its synergic aspect. That is, the polarity which is a consequence of C→M σ-electron donation is offset, and the donation assisted, by the presence of M→C back donation. The acceptor orbitals on the carbonyl group are antibonding orbitals of π symmetry so that the electron distribution between the metal and carbon atoms is pictured as a dipolar core surrounded by a cylindrical electron cloud of opposite polarity. It is the purpose of this communication to demonstrate that important modifications of this bonding occur in the majority of metal carbonyl complexes.[1]

A characteristic of the metal carbonyls and their substituted derivatives is the frequent occurrence of a $M(CO)_3$ group. We shall discuss the π bonding within this group and show that the commonly observed nonlinearity of the M–C–O fragments is a consequence of bonding and not solely a result of crystal packing forces.

The π^* orbitals of the carbon monoxide molecules in $M(CO)_3$ may be conveniently divided into two sets: (a) those which, when viewed along the threefold axis, diverge radially from the axis, and (b) those which are orthogonal to the first set. These two sets are shown in Figure 1. Under the operations of the C_{3v} point group each set of orbitals forms the basis for a reducible representation, that from set a having A_1 and E components and that from set b having A_2 and E components. Metal orbitals of A_1 symmetry are s, p_z, and d_{z^2}; those of E symmetry are p_x, p_y; d_{yz}, d_{zx}; and $d_{x^2-y^2}$ and d_{xy}. Because the two sets of carbon monoxide π^* orbitals transform independently there is no symmetry requirement that they interact equally with the metal orbitals. That is, the π^* electron density of each CO group will show twofold rotational symmetry rather than full cylindrical symmetry.

It follows, from arguments closely analogous to those used by Ingold and King[2] for the case of π^* occupation in acetylene, that the M–C–O fragments will be bent. The only important difference from the acetylene case is that the bending will be a function of the *difference* in occupation of the two π^* orbitals. Consequently, a linear M–C–O structure will only occur by accident. The reason for different M–C–O angles within one $M(CO)_3$ group (often they are equal to within experimental error) must lie either in crystal forces or, more probably, in the influence of other groups within the molecule which result in the symmetry of the $M(CO)_3$ group being lower than C_{3v}.[3]

The nonequivalence of the two π^* orbital sets is also shown by the overlap integrals between the metal and carbon monoxide group orbitals given in Table I. There are no metal orbitals of A_2 symmetry; the metal p and s orbitals are, to a first approximation, empty and therefore unable to participate in the back-donation process (the s orbital is also orthogonal to the carbon monoxide π^* orbitals) and so we do not include them in our discussion. The overlap integrals between the metal d orbitals and the carbon monoxide orbitals are a product of two factors. The first is a geometric factor which is a function of the angle between the threefold rotation axis and a M–C bond axis. This angle has been taken as 54° 44′, corresponding to a CMC angle of 90°. The second factor is the π overlap integral in a linear M–CO system, S_π. This we leave as an algebraic factor; its precise value depends on the metal.

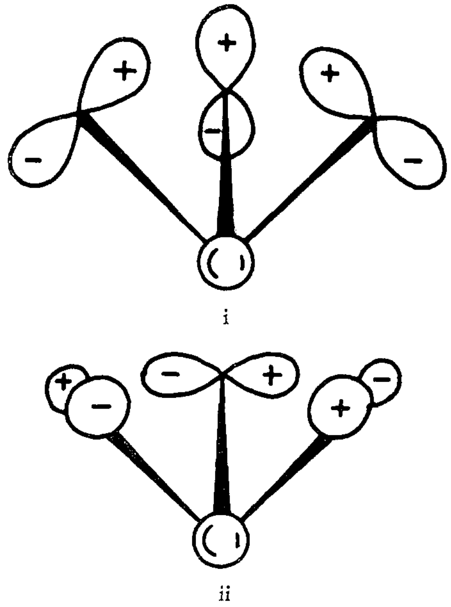

Figure 1.—(i) Diagramatic representation of the A_1 combination of type a orbitals. (ii) Diagramatic representation of the A_2 combination of type b orbitals.

TABLE I

GROUP OVERLAP INTEGRALS[a]

CO π^* orbitals		Metal orbitals		
		d_{z^2}	d_{yz}, d_{zx}	d_{xy}, $d_{x^2-y^2}$
a	A_1	$\sqrt{2}S_\pi$	0	0
	E	0	$\sqrt{\frac{1}{6}}\,S_\pi$	$\sqrt{\frac{1}{3}}\,S_\pi$
b	E	0	$\sqrt{\frac{1}{2}}\,S_\pi$	S_π

[a] These integrals are obtained by setting $\vartheta = 54° 44'$ ($\vartheta = \tan^{-1}\sqrt{2}$) in the formulas we have given elsewhere: S. F. A. Kettle, *Inorg. Chem.*, in press.

It is evident that all of the metal d orbitals are involved in back donation. If it is assumed that overlap is a measure of back-bonding participation, then one obtains the order E (d_{xy}, $d_{x^2-y^2}$) > E (d_{yz}, d_{zx}) > A_1 (d_{z^2}), or, in terms of individual orbitals, $d_{xy} = d_{x^2-y^2} > d_{z^2} > d_{yz} = d_{zx}$. It is dangerous to generalize these results but, in a compound like π-$(C_5H_5)Mn(CO)_3$, where the principal contribution to the π-(C_5H_5)–Mn bonding probably involves d_{zx} and d_{yz}, it seems likely

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[1] The simple bonding scheme is frequently proposed in the context of a discussion of nickel carbonyl, one carbonyl group being arbitrarily oriented along the z axis. Since the other carbonyl groups in the molecule do not then lie on coordinate axes it follows that the bonding mechanism proposed for the unique carbonyl group cannot be applicable to the other three!

[2] C. K. Ingold and G. W. King, *J. Chem. Soc.*, 2702 (1953).

[3] Entirely analogous arguments show that bending of the M–C–O chain is to be expected in $M(CO)_2$ and $M(CO)_4$ groups. Only for the M(CO) case is linearity to be expected; structures containing this fragment should, then, provide the best opportunity for the study of crystal forces and the effect of other coordinated groups.

that back bonding to the carbonyls occurs largely through d_{xy} and $d_{x^2-y^2}$.

In Table II we give a representative selection of those M–C–O bond angles which have been reported —there is too much data available to be comprehensive. It is seen that these bonds are almost invariably bent, the average deviation from linearity being *ca.* 5°.

TABLE II

REPRESENTATIVE MCO BOND ANGLES[a]

Compound	M–C–O angles, deg.	Ref.
$[C_2H_5SFe(CO)_3]_2$	168, 175, 175, 169, 169, 178 (±4°)	*b*
π-$(C_5H_5)Mn(CO)_3$	178, 180, 176	*c*
$Co_2(CO)_8$	176, 175, 177	*d*
$Fe_5(CO)_{15}C$	172, 168, 176, 175, 175, 180, 176, 170, 174, 179, 173, 174, 169, 177, 172 (±4°)	*e*
$(C_6H_5)_2C_2Co_2(CO)_6$	178, 176, 178, 179, 176, 174	*f*
$C_4H_6Fe(CO)_3$	179, 178, 178	*g*
$C_8H_8Fe(CO)_3$	173, 178, 178 (±1°)	*h*
$C_8H_8Fe_2(CO)_6$	173, 177, 176, 178, 177, 176 (±3°)	*h*

[a] Average errors are quoted where these data are available. [b] L. F. Dahl and C. H. Wei, *Inorg. Chem.*, **2**, 328 (1963). [c] A. F. Berndt and R. E. March, *Acta Cryst.*, **16**, 119 (1963). [d] G. G. Sumner, H. P. Klug, and L. E. Alexander, *ibid.*, **17**, 732 (1964). [e] E. H. Braye, L. F. Dahl, W. Hübel, and D. L. Wampler, *J. Am. Chem. Soc.*, **84**, 4633 (1962). [f] W. G. Sly, *ibid.*, **81**, 18 (1959). [g] O. S. Mills and G. Robinson, *Acta Cryst.*, **16**, 758 (1963). [h] B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2084 (1962).

In conclusion, it should be noted that the discussion in this paper is also applicable to other MR_3 groups, of which $M(CN)_3$ and $M(NO)_3$ are perhaps the most important.

CONTRIBUTION FROM THE MELLON INSTITUTE,
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Organosulfur Derivatives of the Metal Carbonyls. VIII. New Aspects of the Chemistry of Methylthio Derivatives of Iron Carbonyl[1]

BY R. B. KING AND M. B. BISNETTE

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The reactions between dodecacarbonyltriiron and various sulfides, mercaptans, and disulfides to give the stable red $[RSFe(CO)_3]_2$ compounds were first discovered by Hieber and Spacu[2] in 1937 and subsequently studied further by various research groups.[3-7] Even the earliest workers with these compounds noted that the more reactive dodecacarbonyltriiron was necessary for the formation of reasonable quantities of $[RSFe(CO)_3]_2$ compounds in thermal reactions with organic sulfur compounds; the more readily available but less reactive pentacarbonyliron gave little or no $[RSFe(CO)_3]_2$ compounds when allowed to react with similar organic sulfur compounds. Only in 1963 were discovered certain fairly unusual chelate-type organosulfur compounds, notably bis(trifluoromethyl)dithietene[7] and 3,4-toluenedithiol,[7] which gave appreciable quantities of $[RSFe(CO)_3]_2$ compounds on treatment with pentacarbonyliron at atmospheric pressure. However, aliphatic disulfides and mercaptans, even chelating ones such as 1,2-ethanedithiol, gave very low yields of $[RSFe(CO)_3]_2$ compounds on treatment with pentacarbonyliron at atmospheric pressure.

We have now found that $[CH_3SFe(CO)_3]_2$ can be synthesized very easily and efficiently in 60% yield by heating pentacarbonyliron with dimethyl disulfide in an autoclave in the presence of carbon monoxide under pressure. The proton n.m.r. spectrum of the product obtained from this reaction indicated it to contain 70 to 80% of *anti*-$[CH_3SFe(CO)_3]_2$ (previously[6] designated as "isomer A") and 20 to 30% of *syn*-$[CH_3SFe(CO)_3]_2$ (previously[6] designated as "isomer B").[8]

In a further study of this reaction pentacarbonyliron and dimethyl disulfide were heated in a sealed autoclave in the *absence* of any additional carbon monoxide. Some $[CH_3SFe(CO)_3]_2$ was also formed in this reaction; however the major product was a red solid completely insoluble in all organic solvents tried including even acetone and dichloromethane, which dissolve most metal carbonyl derivatives. Analyses indicated this red material to be $[(CH_3S)_2Fe(CO)_2]_n$. The insolubility of this compound suggests it to be a polymer analogous to the closely related polymeric carbonyl halides $[M(CO)_2I_2]_n$ (M = Fe[9] or Ru[10]) and to the recently reported[11] nitrosyl halides $[M(NO)_2Cl_2]_n$ (M = Mo or W). In the case of $[(CH_3S)_2Fe(CO)_2]_n$ the iron atoms in the polymer would be linked by sulfur bridges as depicted in I. Each iron atom is bonded to four sulfur atoms and two carbonyl groups and is thus hexacoordinate. The presence of two strong infrared carbonyl stretching frequencies at 2010 and 1956 cm.$^{-1}$ indicates that the two carbonyl groups occupy *cis* positions as indicated in I. This region of the infrared spectrum resembles entirely that of the related carbonyl and nitrosyl halides cited above. An attempt to obtain $[(CH_3S)_2Fe(CO)_2]_n$ from $[CH_3SFe(CO)_3]_2$ and excess dimethyl disulfide in boiling toluene resulted instead in a brown insoluble pyrophoric solid with complete destruction of the red $[CH_3SFe(CO)_3]_2$. This ability of $[CH_3SFe(CO)_3]_2$ to react further with excess dimethyl disulfide in an open system suggests a reason for the failure to obtain appreciable quantities of $[CH_3$-

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[1] For part VII of this series see R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 486 (1965).

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[6] R. B. King, *J. Am. Chem. Soc.*, **84**, 2460 (1962).

[7] R. B. King, *ibid.*, **85**, 1584 (1963).

[8] For X-ray crystallographic evidence for assignment of the *anti*- and *syn*- configurations to isomers A and B, respectively, see L. F. Dahl and C. W. Wei, *Inorg. Chem.*, **2**, 328 (1963).

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[11] F. A. Cotton and B. F. G. Johnson, *Inorg. Chem.*, **3**, 1609 (1964).