

of k_d/k_c for certain pairs of radicals.²¹ An alternative basis of correlation was inferred from a plot of $\log k_d/k_c$ vs. $S_d^\circ - S_c^\circ$, the difference in entropies of the products of disproportionation and combination. Most of the experimental points fall quite close to the straight line $\log k_d/k_c = 0.131(S_d^\circ - S_c^\circ) - 5.47$, confirming the general validity of the relationship. However, certain difficulties attend the application of this equation to the reactions of the cyclohexadienyl radical. First, $k_e/k_c = 0$ for both $(C_2H_5\cdot + C_6H_7\cdot)$ and $(C_3H_7\cdot + C_6H_7\cdot)$; even with realistic limits of error the deviation is likely to remain large. Second, the detailed application of the equation to the calculation of k_d/k_c for secondary radicals is no more successful than the use of $0.067n_d'$. Indeed, the greatest deviation is obtained with the only cyclic radical included in the correlation, the cyclopentyl radical, whereas $0.067n_d'$ predicts exactly the observed value of k_d/k_c for this radical. Third, the electron spin density distribution of the cyclohexadienyl radical differs fundamentally from that of any of the radicals included in the correlation, and presumably this difference should be represented in the equation by an additional term which normally vanishes. For these reasons we have concluded that the behavior of the system is described with least uncertainty by the expression $n_c k_d/n_d k_c$.

The ratio of the adducts is given by $k_c^I/k_c^{II} = 0.85 \pm 0.09$, significantly less than unity; on purely statistical grounds we should expect a value of 2. This ratio indicates the nature of the transition state. If the activated complex were to resemble the resultants rather than the reactants, then the course of the reaction should be strongly influenced by the electron localization energy of the cyclohexadienyl radical. Since this is least at the *ortho* positions, the formation of the conjugated adduct I would be favored and the

(21) R. A. Holroyd and G. W. Klein, *J. Phys. Chem.*, **67**, 2273 (1963).

ratio should exceed 2. This is not the case. On the other hand, if the activated complex were to resemble the reactants closely, then the course of reaction should be dominated by free valence. The highest free valence on the cyclohexadienyl radical is found at the *para* position, and addition there would form the unconjugated adduct II. The predominance of II therefore indicates a loosely bonded transition state in which the electronic structure of the cyclohexadienyl radical has not been greatly perturbed. Free valence also appears to dominate the course of mutual disproportionation of cyclohexadienyl radicals in benzene solution,²² which yields cyclohexadiene-1,3 and cyclohexadiene-1,4 in the ratio of 1:2.7.

Conclusions

The interaction of the cyclohexadienyl radical with the isopropyl radical is described by the quotient $n_c k_d/n_d k_c \geq 0.26 \pm 0.04$. This value is unusually high for secondary radicals, and demonstrates that the course of the interaction may favor the formation of a product possessing a particularly high delocalization energy such as benzene. The value $k_c^I/k_c^{II} = 0.85 \pm 0.09$ indicates that the activated complex is loosely bonded and shows that the relatively small delocalization energy of a conjugated cyclohexadienyl ring is inadequate to influence the ratio of the adducts appreciably. The high reactivity of cyclohexadiene-1,4 toward metathesis is attributed to the favorable conjunction of a major increase in electron delocalization with a minor change in the geometry of the carbon skeleton.

Acknowledgment.—We wish to thank the National Research Council of Canada for financial support of this work and for a studentship to R. D. S.

(22) M. K. Eberhardt, *ibid.*, **67**, 2856 (1963).

[CONTRIBUTION FROM THE UNION CARBIDE RESEARCH INSTITUTE, TARRYTOWN, NEW YORK]

The Crystal and Molecular Structure of Tropone Iron Tricarbonyl

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The crystal structure of one form of $(C_6H_6CO)Fe(CO)_3$ has been determined by X-ray diffraction. The structure is found to be a π -complex with the iron atom bonded to four carbon atoms of the seven-membered ring.

Introduction

It has been shown that the reaction of iron dodecarbonyl with acetylene in inert solvent yields a number of organo iron carbonyls.¹ Among these is $(C_6H_6CO)Fe(CO)_3$, which is found to exist in at least two crystalline modifications. The compound can also be directly synthesized from tropone and $Fe_3(CO)_{12}$. It follows that $(C_6H_6CO)Fe(CO)_3$ is a complex made up of tropone bonded to an $Fe(CO)_3$ group by π -electrons.

One opinion arising in discussions of the bonding in this molecule is that the metal atom should overlap with the π -orbitals of all seven carbon atoms in the free

tropone ring. For example, in treating the bonding from a molecular orbital point of view, Brown² assumed that the iron atom is centrally located with respect to the double bonds of a planar tropone ring. On the other hand, Weiss and Hübel³ concluded that there is a localized double bond in the tropone ring. This they inferred from the fact that hydrogenation with H_2 under pressure and Pd at 40–70° produced cycloheptadienone-iron tricarbonyl.

This structure determination, along with the work on a triphenyl derivative by Smith and Dahl,⁴ clears up this

(2) D. A. Brown, *J. Inorg. Nucl. Chem.*, **13**, 212 (1960).

(3) E. Weiss and W. Hübel, *Chem. Ber.*, **95**, 1179 (1962).

(4) D. L. Smith and L. F. Dahl, *J. Am. Chem. Soc.*, **84**, 1743 (1962).

(1) W. Hübel and E. Weiss, *Chem. Ind. (London)*, 703 (1959).

TABLE I
PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	x	σ_x	y	σ_y	z	σ_z	B	σ_B
Fe	0.2355	0.0002	0.1414	0.0001	0.1594	0.0001	3.12	0.027
O ₁	-0.1890	0.0011	0.0811	0.0006	0.1778	0.0006	6.43	0.186
O ₂	0.3797	0.0011	-0.0667	0.0006	0.0865	0.0006	5.90	0.167
O ₃	0.4574	0.0012	0.0846	0.0007	0.3716	0.0007	7.34	0.205
O ₄	-0.1093	0.0010	0.3825	0.0006	0.2287	0.0005	6.00	0.170
C ₁	-0.0193	0.0015	0.1023	0.0007	0.1697	0.0007	4.22	0.202
C ₂	0.3230	0.0015	0.0152	0.0009	0.1132	0.0008	4.41	0.210
C ₃	0.3712	0.0015	0.1080	0.0008	0.2862	0.0008	5.00	0.227
C ₄	-0.0060	0.0014	0.3516	0.0009	0.1622	0.0007	4.64	0.195
C ₅	0.2067	0.0014	0.3073	0.0007	0.2065	0.0007	4.06	0.193
C ₆	0.3784	0.0015	0.2931	0.0008	0.1522	0.0007	4.15	0.204
C ₇	0.3477	0.0014	0.2398	0.0008	0.0544	0.0007	4.44	0.208
C ₈	0.1436	0.0015	0.2048	0.0008	0.0016	0.0008	4.52	0.215
C ₉	-0.0349	0.0015	0.2805	0.0009	-0.0188	0.0008	4.86	0.223
C ₁₀	-0.0963	0.0014	0.3499	0.0010	0.0505	0.0007	4.98	0.207

apparent discrepancy between theoretical assumptions and the conclusions drawn from chemical evidence. It is now clear that the iron atom bonds to only four atoms of the tropone ring and causes the shape of the ring to be far from planar.

Experimental

No untwinned crystals could be found in the first sample of tropone iron tricarbonyl, m.p. 83–84°, submitted to this laboratory by Dr. Hübel. A second modification (m.p. 63.5–64.5°), which he later obtained by recrystallization from benzene, yielded readily to a structure determination. Because of a relatively high vapor pressure at room temperature, a crystal (0.2 mm. in length and 0.1 mm. diameter) was sealed in a very small glass tube. The observed X-ray extinctions correspond to the space group $P2_1/c$, with $a = 6.52 \text{ \AA.}$, $b = 12.08 \text{ \AA.}$, $c = 12.90 \text{ \AA.}$, and $\beta = 101.2^\circ$. The calculated density is then 1.64 g./cm.³ for four molecules per cell. The observed density of the higher melting form is 1.65 g./cm.³.

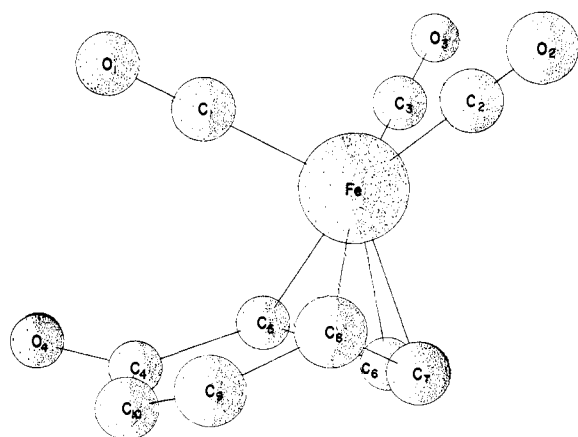


Fig. 1.— $(C_6H_6CO)Fe(CO)_3$.

The stationary-crystal, stationary-counter technique⁵ was used with a General Electric XRD-5 single-crystal orienter and Zr-filtered Mo radiation to survey a total of 1753 reflections. Of these, 1465 gave counts higher than the background, which was estimated for each reflection at two neighboring points, at greater and smaller 2θ values, along the white radiation (2θ) streak. This method was found to be satisfactory for the few reflections that are overlapped by one or more large nearby peaks. For example, a reflection hkl can be affected by the scattering of radia-

(5) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Company, Milwaukee 1, Wis., 1957, p. 81.

tion of wave length 2λ ($K\alpha$) from a reflection $h/2, k/2, l/2$.⁶ However, most of the intensities are unaffected by this error, and additional counting actually results in larger statistical error than is necessary. The method of a general background survey is faster and is usually accurate for the large body of data that is free of overlap error. The intensities were all counted for a constant time interval, which results in poorly determined weak intensities.

Structure Determination and Refinement

A three-dimensional Patterson function was calculated on an IBM-7090 using a general Fourier program of A. Zalkin. The position and orientation of the $Fe(CO)_3$ group was easily seen in the vector map. An electron density map was then calculated, and the rest of the structure made its appearance.

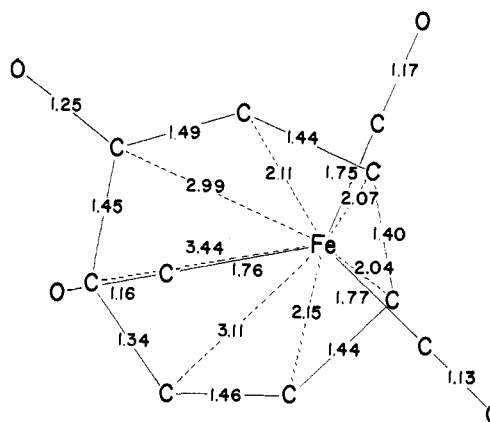


Fig. 2.—Bond distances in $(C_6H_6CO)Fe(CO)_3$.

The resulting structure was refined by three-dimensional full-matrix least-squares using a program written by Trueblood, Sparks, and Gantzel. Individual isotropic thermal parameters were used throughout the refinement. Since the first counting decade is omitted from the G.E. equipment, the variance of a count from the scaler is equal to one-tenth of the count. After measuring the count C under a Bragg peak and taking the sum B of the background counts from two observations, the weight w and the variance σ_F^2 were estimated for each F value from the relation

(6) L. Alexander and G. Smith, *Acta Cryst.*, **15**, 983 (1962).

$$\frac{1}{w} = \sigma_p^2 = 0.025 \left(\frac{C + (B/4)}{C - (B/2)} \right)$$

For counts C not greater than $B/2$, the weight was taken to be zero.

Although counting statistics is of course not the only source of error to be feared, all other sources such as absorption, extinction, and variations in primary beam intensity were ignored in this assignment of weights.

TABLE II

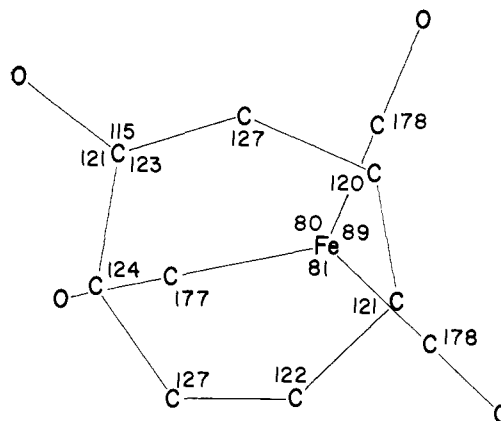
BOND DISTANCES AND ANGLES

Bond	Distance, Å.	σ	Angle	Degrees	σ
Fe-C ₁	1.757	0.009	Fe-C ₁ -O ₁	177.1	0.8
Fe-C ₂	1.771	0.010	Fe-C ₂ -O ₂	178.1	0.9
Fe-C ₃	1.749	0.010	Fe-C ₃ -O ₃	178.3	0.9
Fe-C ₅	2.114	0.009	O ₄ -C ₄ -C ₅	115.5	0.8
Fe-C ₆	2.067	0.010	O ₄ -C ₄ -C ₁₀	121.3	0.9
Fe-C ₇	2.042	0.010	C ₅ -C ₄ -C ₁₀	123.0	0.9
Fe-C ₈	2.149	0.010	C ₄ -C ₅ -C ₆	127.4	0.8
O ₁ -C ₁	1.160	0.012	C ₅ -C ₆ -C ₇	120.4	0.9
O ₂ -C ₂	1.134	0.012	C ₆ -C ₇ -C ₈	121.4	0.9
O ₃ -C ₃	1.170	0.013	C ₇ -C ₈ -C ₉	122.2	0.9
O ₄ -C ₄	1.248	0.012	C ₈ -C ₉ -C ₁₀	126.9	0.9
C ₄ -C ₅	1.492	0.013	C ₄ -C ₁₀ -C ₉	123.8	0.9
C ₄ -C ₁₀	1.447	0.014			
C ₅ -C ₆	1.442	0.013			
C ₆ -C ₇	1.396	0.013			
C ₇ -C ₈	1.435	0.014			
C ₈ -C ₉	1.463	0.014			
C ₉ -C ₁₀	1.343	0.014			

After several cycles of least-squares refinement, the R factor is 0.116 for the 1465 observed reflections and 0.065 for the stronger half of these reflections. The final atomic positions and temperature factor along with their estimated standard deviations are listed in Table I.

The view of the molecule given in Fig. 1 clearly shows that the iron atom is bonded to the π -system of

just four of the carbon atoms. The tropone molecule is nonplanar, but can be referred to two planes that intersect at a dihedral angle of about 47°. The C₄-O₄ group is displaced from the mean plane of C₅-C₈-C₉-C₁₀ so that O₄ is actually 0.76 Å. out of this plane. This may arise from the packing arrangement, which finds the C₄-O₄ group cradled by a nearby Fe(CO)₃ group.

Fig. 3.—Bond angles in (C₆H₆CO)Fe(CO)₃.

The important bond distances and angles (Table II, Fig. 2 and 3) are all in good agreement with those of Smith and Dahl. It is noteworthy that the shorter distance of 1.396 Å. for C₆-C₇ is likely to be significant in that this shortening is also observed by Smith and Dahl. Likewise, the same effect is observed in the butadiene unit of the cyclooctatetraene complexes of iron tricarbonyl.⁷

Acknowledgment.—The author wishes to thank the authors of the several computer programs for making their efforts generally available, Dr. Walter Hübel of Union Carbide European Research Associates for supplying the samples, and Dr. V. Schomaker for many helpful discussions.

(7) B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2084 (1962).

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Bisamine Complexes of Boronium Ions. The Reaction of Amine Boranes with Iodine¹

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The reaction of amine boranes with iodine in the presence of excess amine is found to be a convenient, general method for the synthesis of bisamine complexes of boronium ions, R₂B(amine)₂⁺.

It is now well established that very stable tetravalent boron cations of the type R₂BL₂⁺ can be formed in a number of ways and may conveniently be considered as ligand- (L) stabilized boronium ions. The recent reports of Miller and Muettterties² and of Nöth and co-workers³ clearly delineate the possibilities of formation of unsubstituted cations (H₂BL₂⁺). Davidson

and French⁴ and Mikhailov and co-workers,⁵ in particular, have described a number of amine-stabilized organoboronium ions of the type R₂B(amine)₂⁺, where R is either alkyl, cycloalkyl, or aryl. Numer-

(4) J. M. Davidson and C. M. French, *J. Chem. Soc.*, 3364 (1962).

(1) Supported in part by a grant from the National Science Foundation.
(2) N. E. Miller and E. L. Muettterties, *J. Am. Chem. Soc.*, **86**, 1033 (1964).

(3) H. Nöth, H. Beyer, and H.-J. Vetter, *Ber.*, **97**, 110 (1964).

(5) B. M. Mikhailov and T. K. Kosminskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1703 (1963); B. M. Mikhailov, V. D. Sheludyakov, and T. A. Shchegoleva, *ibid.*, 1698 (1962); B. M. Mikhailov and N. S. Fedotov, *ibid.*, 1590 (1960); 1482 (1959); B. M. Mikhailov, N. S. Fedotov, T. A. Shchegoleva, and V. D. Sheludyakov, *Dokl. Akad. Nauk SSSR*, **145**, 340 (1962).