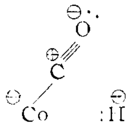
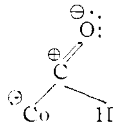
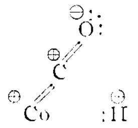
upon bond formation produces a charge on each atom of the sign which is circled. Only one CO group is shown. I is formed by putting the four CO groups tetrahedrally about the cobalt atom in its sp^3 orbitals. The negative charge on the cobalt atom is reduced by the transfer of the d electron to the hydrogen atom on the C_3 axis.


I


II


III

Structure II may be obtained from I by removing an electron pair from one CO π bond and placing it in the p orbital of the oxygen followed by bond formation between the p orbital of the carbon and the s orbital of the hydrogen using the electron pair previously on the hydrogen. Of course there are three resonating structures like II. Structure III enters into the resonance composite to counter-act the negative charge on the cobalt atom in structures I and II.

Comparison with Experiment.—The bonding found for the bridge model is in qualitative agreement with the substantiated experimental facts now known for $Co(CO)_4H$. It predicts a diamagnetic molecule. The weak covalent bonding of the hydrogen atom agrees with the ease of decomposition to form H_2 and $Co_2(CO)_8$. The large negative charge on the hydrogen atom calls for the large negative chemical shift found by Gutowsky and coworkers[11] in the proton magnetic resonance spectrum. And an interesting prediction may be made about the CO stretching vibration in $Co(CO)_4^-$, which may be described as having two electrons in ψ_V and two in ψ_{VI} followed by the delocalization of the charge. This latter process will not change the general character of the orbitals. Since ψ_{VI} is antibonding with regards to the CO bond, one expects the frequency of the CO stretching vibration in $Co(CO)_4^-$ to be less than those in $Co(CO)_4H$. The experimental values for $Co(CO)_4H$ are[6] 2122, 2043 and 2062 cm.$^{-1}$ while the value for $Co(CO)_4^-$ is[8] 1883 cm.$^{-1}$, in striking agreement with theory.

The question naturally arises as to how a molecule with a negative charged hydrogen can dissolve in water to form a strong acid. This process may be divided into the following steps

$$Co(CO)_4H(g) \longrightarrow Co(CO)_4{\mp}^{-}(g) + H^+(g) \quad +8.2 \text{ e.v.} \quad (1)$$
$$Co(CO)_4{\mp}^{-}(g) \longrightarrow Co(CO)_4^-(g) \quad -R \quad (2)$$
$$H^+(g) \longrightarrow H^+(aq) \quad -11.4 \quad (3)$$
$$Co(CO_4)^-(g) \longrightarrow Co(CO)_4^-(aq) \quad -1.7 \quad (4)$$
$$Co(CO)_4H(g) \longrightarrow Co(CO)_4^-(aq) + H^+(aq) \quad -4.9 - R \quad (5)$$

The value for the first step was taken from Fig. 5, that for the third is from a tabulation by Latimer[12] and that for the fourth was estimated from values for other negative ions by means of the Born equation for the hydration energy of ions. The second step releases the delocalization energy. Although this quantity is unknown, its exact value does not alter the conclusions. If it is taken as $R = 1$ e.v., the value for the energy released in the solution of $Co(CO)_4H$, step 5, is 5.9 e.v. Any process which releases 135 kcal. of energy has a strong motivation to take place.

Acknowledgment.—The authors gratefully acknowledge the financial support of this work by the Atomic Energy Commission under contract AT-(11-1)-164 with the Purdue Research Foundation.

LAFAYETTE, INDIANA

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[11] H. S. Gutowsky, private report.

[12] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, 1938, p. 22.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

The Raman Spectrum and Thermodynamic Properties of Iron Pentacarbonyl

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A sodium vapor source was used to obtain the Raman spectrum of iron pentacarbonyl. An assignment of frequencies consistent with the trigonal bipyramid structure of $Fe(CO)_5$ was made using this spectrum and the previously reported infrared spectrum. The thermodynamic functions C_p, $(H° - E_0°)/T$, $-(F° - E_0°)/T$, $S°$, $\Delta H_f°$, $\Delta F_f°$ and $\Delta S_f°$ were calculated at 100° temperature intervals from 298.16° to 1000°K. A comparison of the spectral and thermodynamic properties of $Fe(CO)_5$ with those of $Ni(CO)_4$ as well as a calculation of the metal–carbon bond energy shows that the Fe–C metal bonds are stronger than Ni–C bonds. The metal–carbon bonds in $Fe(CO)_5$ and $Ni(CO)_4$ are best regarded as single bonds with only a limited amount of double bond character.

Introduction

A considerable number of structural and spectroscopic studies of the transition metal carbonyls have been made in order to obtain a better understanding of the type of bonding involved.[1-7] The structure of iron pentacarbonyl, $Fe(CO)_5$, is interesting because of the rare occurrence of pentacoördinated compounds. The two possible structures for this compound are the trigonal bipyramid

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[1] For reviews of the metal carbonyls see: J. S. Anderson, *Quart. Rev.*, **1**, 331 (1947); A. A. Blanchard, *Chem. Revs.*, **21**, 3 (1937); W. E. Trout, *J. Chem. Ed.*, **14**, 453 (1937).

[2] R. K. Sheline and K. S. Pitzer, THIS JOURNAL, **72**, 1107 (1950).

[3] B. L. Crawford and P. C. Cross, *J. Chem. Phys.*, **6**, 525 (1938); B. L. Crawford and W. Horwitz, *ibid.*, **16**, 147 (1948).

[4] L. H. Long and A. D. Walsh, *Trans. Faraday Soc.*, **43**, 342 (1947).

[5] R. A. Friedel, I. Wender, S. L. Shufler and H. W. Sternberg, THIS JOURNAL, **77**, 3951 (1955).

[6] N. J. Hawkins, H. C. Mattraw, W. W. Sabol and D. R. Carpenter, *J. Chem. Phys.*, **23**, 2422 (1955).

[7] R. S. Nyholm and L. N. Short, *J. Chem. Soc.*, 2670 (1953).

(D_{3h} symmetry) and the tetragonal pyramid (C_{4v} symmetry). The former structure has been verified by electron diffraction studies.[8] It is consistent with an assignment of infrared fundamental frequencies[2] and with energy considerations from the general theory of directed valence.[9] The only evidence for the tetragonal pyramid structure is an interpretation of dipole moment studies which gives a value of 0.64 debyes for $Fe(CO)_5$ in solution.[10]

A calculation of the thermodynamic functions of $Fe(CO)_5$ as well as a complete interpretation of the infrared studies have not been made because of the failure to obtain a successful Raman spectrum. All previous attempts to obtain a spectrum failed because of the photochemical decomposition of the sample.[11]

We have recently obtained a Raman spectrum of liquid $Fe(CO)_5$ by using a sodium vapor lamp excitation source with solutions of optimum concentration which results in a maximum intensity of Raman scattering at a given wave length.[12] This latter condition is necessary because $Fe(CO)_5$ absorbs throughout most of the visible region of the spectrum. The results of our studies are consistent with the trigonal bipyramid structure and have been used in conjunction with the infrared studies of Sheline and Pitzer[2] to make an assignment of frequencies to the normal modes of vibration. The thermodynamic functions C_p, $-(F^\circ - E_0^\circ)/T$, $(H^\circ - E_0^\circ)/T$ and S° were calculated using this assignment. Such calculations are useful for the information which they furnish concerning the properties of $Fe(CO)_5$ in comparison to the other metal carbonyls.

Raman Spectrum.—Iron pentacarbonyl is extremely sensitive to blue and green light, undergoing decomposition to the iron enneacarbonyl, $Fe_2(CO)_9$. For this reason its Raman spectrum cannot be obtained with the conventional mercury sources using the 4358 or 5461 Å. Hg lines for excitation. Attempts by Duncan and Murray failed for this reason.[11] We had previously attempted, without success, to obtain a spectrum by using the 5770–5790 Å. Hg doublet. No results were obtained because a set of optical filters could not be found which would completely eliminate the blue and green mercury lines. Duncan and Murray were also unable to obtain a spectrum using a cadmium source.[11]

We had previously developed a technique for obtaining Raman spectra of colored compounds which partially absorb both the exciting and scattered radiation, provided that photo-decomposition does not occur.[12] The technique makes use of the fact that it is possible to reach a compromise between two effects: an increase in intensity of the scattered radiation due to an increase in concentration of the scattering compound, and a decrease in intensity resulting from an increase in the extent of absorption of the incident radiation as well as of the resulting Raman scattering. The optimum concentration for a given compound depends on a detailed knowledge of the absorption spectrum of the scattering substance. A more detailed discussion of this effect and the technique of using it will be given in a forthcoming publication.

To minimize the photodecomposition problem we have constructed an excitation source which utilizes the 5890–96 Å. doublet from sodium vapor lamps. The advantage of this source is that there are no strong lines below 5682 Å. This makes it possible to work with light sensitive compounds with a minimum of optical filtering. Using this source we found that significant decomposition of the $Fe(CO)_5$ did not occur except for the longest exposure times. Despite the minimization of the photo-decomposition problem, the only Raman lines which could be obtained for the pure liquid were the CO stretching frequencies at 1995 cm.$^{-1}$. To obtain the lower frequencies it was necessary to use dilutions of up to 4 to 1 in an inert solvent such as cyclohexane.

The Raman spectrum of $Fe(CO)_5$ is tabulated in Table I along with the Raman spectra of $Ni(CO)_4$ and $Mo(CO)_6$ which are the only other metal carbonyls whose Raman spectra have been studied. Although only four Raman lines of $Fe(CO)_5$ have been observed, the results compare favorably with the observed spectra of both $Ni(CO)_4$ and $Mo(CO)_6$, where four and two fundamental frequencies have been observed, respectively. The apparent simplicity of the spectra results from a piling up of characteristic group frequencies in these compounds. Thus the metal–carbon bending and the CO bending and stretching frequencies tend to appear in a narrow frequency range. The location of the low Fe–C bending frequencies is an important result necessary for the calculation of the thermodynamic functions of $Fe(CO)_5$.

TABLE I

RAMAN SPECTRA OF METAL CARBONYLS

Key: s = strong; m = medium and vw = very weak.

$Fe(CO)_5$		$Ni(CO)_4$[a]		$Cr(CO)_6$[b]	
Cm.$^{-1}$	I	Cm.$^{-1}$	I	Cm.$^{-1}$	I
110	s	82	(100)		
410	m	382	(20)	380	w
475[c]	vw	463	(8)		
1995	s	2043	(30)	2034	s

[a] Only the observed fundamental frequencies are listed here. Crawford and Cross (in ref. 3 in text) observed some additional overtone and combination bands. [b] See reference 6 in text. [c] This line was observed on only one plate and must be considered doubtful because of its low intensity.

Experimental

The sodium vapor source consisted of four General Electric type NA-9 sodium vapor lamps (10,000 lumens each), mounted in a cylindrical container which had been coated with magnesium oxide.

The Raman tube was mounted in a cylindrical, Pyrex, water-cooled jacket with two filter sections. The wave lengths below 5800 Å. were filtered out with a saturated solution of $K_2Cr_2O_7$. Considerable difficulty was experienced in finding a suitable filter to eliminate the weak lines in the region 5000 → 7000 Å. due to the presence of neon as a starter gas in the lamps. A 0.1 → 3% solution of the potassium salt of the tetrasulfonic acid of copper phthalo-

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[8] R. V. G. Ewen and M. W. Lister, *Trans. Faraday Soc.*, **35**, 681 (1949).

[9] R. Dandal and A. Bucher, *J. chim. phys.*, **42**, 6 (1945).

[10] E. Bergmann and L. Engel, *Z. physik. Chem.*, **B13**, 232 (1931).

[11] A. B. Duncan and J. W. Murray, *J. Chem. Phys.*, **2**, 636 (1934).

[12] E. R. Lippincott and R. D. Nelson, *ibid.*, **21**, 1307 (1953); R. D. Fisher and E. R. Lippincott, *Anal. Chem.*, **26**, 435 (1954).

cyanine in 90% H_2SO_4 was found adequate for this purpose.[13] The source was used with a Hilger 612 Raman spectrograph with glass optics. The spectra were obtained on Eastman 103-aE backed plates using exposure times up to 90 minutes. The pure liquid, or solutions in cyclohexane with dilutions up to 4 to 1, were distilled into conventional Raman tubes by standard methods. Extreme care was taken to prevent the sample from being exposed to any blue or green radiation. The $Fe(CO)_5$ was obtained from the General Aniline Corp., Easton, Pa. After purification by distillation it had a boiling point of 103°. The Raman spectra were read from the plates by standard methods, care being used to eliminate any cyclohexane lines from the final tabulation.

Since the 5890–5896 Å. sodium lines are separated by 17 cm.$^{-1}$, sharp Raman lines appear as doublets, while diffuse Raman lines appear as single broad lines due to the low dispersion of the instrument in the region 6000–7000 Å. Therefore, our instrument was incapable of distinguishing between Raman lines which were separated by less than 20 cm.$^{-1}$. Unresolved lines were read from the plates as being excited by the mean cm.$^{-1}$ value of the sodium doublet. Because of this we feel that some of our Raman lines represent more than one fundamental frequency.

Assignment of Frequencies.—The symmetry classes, selection rules and number of frequencies expected from a D_{3h} structure for $Fe(CO)_5$ are summarized in Table II. The numbering of the frequencies is the same as that used by Sheline and Pitzer.[2] The Raman active species consists of 13 fundamental frequencies (6E′, 4A′ and 3E″). These are 3 CO stretching, 3 Fe–C stretching, 4 CO bending and 3 Fe–C bending frequencies, respectively. The infrared active species consists of 10 fundamental vibrations ($4A_2''$ and 6E′) which are classified as 2 CO stretchings, 2 Fe–C stretchings, 3 CO bendings and 3 Fe–C bending frequencies, respectively. Sheline and Pitzer have assigned the infrared frequencies observed above 450 cm.$^{-1}$ but did not determine the frequencies of the Fe–C bending or all of the CO bending modes.[2] We have reviewed their infrared assignment and with one minor exception have found it to be consistent with our Raman studies. In addition we have been able to make a reasonable estimate of the low frequency, infrared active Fe–C bending modes from information obtained from the Raman spectrum of iron pentacarbonyl along with related spectral data from the $Ni(CO)_4$, $Cr(CO)_6$ and $Mo(CO)_6$ compounds.[2,3,6]

TABLE II

CLASSES, SELECTION RULES AND NUMBERS OF VIBRATIONS OF IRON PENTACARBONYL (D_{3h})

Class	Selection rule	Total vibrations
A_1'	Raman	4
A_1''	Inactive	0
A_2'	Inactive	1
A_2''	Infrared	4
E′	Infrared and Raman	6
E″	Raman	3

A_1' Fundamentals (Raman).—This species contains 2 CO and 2 Fe–C stretching frequencies, respectively, and is readily assigned from the observed Raman spectrum. The ω_1 and ω_2 CO stretching modes can be assigned to the 1995 cm.$^{-1}$ line. These frequencies are undoubtedly so close that they could not be resolved by our instrument. The ω_3 (equatorial) and ω_4 (axial) Fe–C stretching frequencies can be assigned to the 410 cm.$^{-1}$ line. Our instrument was again incapable of resolving these frequencies. This follows from the fact that one would not expect these frequencies to be separated by more than 20 cm.$^{-1}$. Support for this is obtained from the infrared spectrum[2] where the Fe–C stretching frequencies, ω_8 (639 cm.$^{-1}$) and ω_3 (614 cm.$^{-1}$) are separated by only 25 cm.$^{-1}$.

E′ Fundamentals (Raman and Infrared).—This species contains six frequencies. Three of them have been assigned[2]: ω_{10} (CO stretching) 2028 cm.$^{-1}$, ω_{12} (CO bending) 472 cm.$^{-1}$, and ω_{13} (Fe–C stretching) 614 cm.$^{-1}$. The Fe–C bending modes, ω_{14} and ω_{15}, can both be readily assigned to the Raman line at 110 cm.$^{-1}$ since it is broad and undoubtedly consists of a super-position of two or more lines. The other CO bending mode, ω_{11}, has not been observed but it should occur in the 350 to 450 cm.$^{-1}$ region by analogy with the other metal carbonyls. We have assigned ω_{11} at 375 cm.$^{-1}$.

E″ Fundamentals (Raman).—This species contains 1 Fe–C bending (ω_{18}) and 2 CO bending frequencies (ω_{16}, ω_{17}). The Fe–C bending (ω_{18}) has been assigned to the 110 cm.$^{-1}$ Raman line; ω_{16} and ω_{17} were not observed; however, by analogy with $Ni(CO)_4$, the frequency, ω_{12}, should be in the region 350 to 450 cm.$^{-1}$. We have assigned ω_{16} and ω_{17} to be 400 and 425 cm.$^{-1}$, respectively.

A_2'' Fundamentals (Infrared).—This species contains 1 CO stretching (ω_6), 1 Fe–C stretching (ω_8), 1 CO bending (ω_7) and one Fe–C bending (ω_9) frequencies, respectively. Sheline and Pitzer have assigned the infrared bands at 639 and 1994 cm.$^{-1}$ to ω_8 and ω_6, respectively.[2] Since there is one or more strong Raman lines at 1995 cm.$^{-1}$ an assignment more consistent with the selection rules would be to assign the infrared band at 1995 cm.$^{-1}$ to class E′, and the strong 2028 cm.$^{-1}$ infrared band to A_2''. Because ω_6 corresponds to a mode of vibration in which the motion of the CO group is along the C_3 axis, the assignment is consistent with the rule that antisymmetric stretching frequencies for a chain containing an odd number of atoms are higher than the corresponding symmetrical stretching frequencies, which in this case is ω_1. Accordingly our assignment of ω_6 and ω_{10} shown in Table III differs from that of Sheline and Pitzer. The ω_9 Fe–C bending mode is out of the range of infrared prism instruments but it can be assigned from the position of the analogous frequencies in the Raman spectrum. We assign a value of 100 cm.$^{-1}$ for ω_9. An infrared band has been observed recently at 425 cm.$^{-1}$ in $Fe(CO)_5$ by W. Wilson and W. Edgell (private communication). We have assigned this peak as ω_7.

A_2' Fundamentals (Inactive).—There is only one frequency in this class. It corresponds to the equatorial CO bending frequency (ω_5). Following the arguments of Hawkins, *et al.*,[6] we have assigned ω_5 as 500 cm.$^{-1}$.

The assignment of frequencies discussed above and presented in Table III is straight-forward with the exception of the CO bending frequencies. These must be considered as tentative. Nevertheless we feel the assignment is reliable enough to make a calculation of the thermodynamic functions of

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[13] We wish to thank O. Stallmann, of the du Pont Company, for furnishing us with a sample of this compound.

$Fe(CO)_5$, particularly since the uncertain frequencies assigned make a relatively minor contribution to the vibrational portion of the thermodynamic functions.

TABLE III

FREQUENCY ASSIGNMENTS FOR $Fe(CO)_5$

Number	Class	Cm.$^{-1}$	Description
1	A_1'	1995	CO stretching
2	A_1'	1995	CO stretching
3	A_1'	410	Fe–C stretching
4	A_1'	410	Fe–C stretching
5	A_2'	450	CO bending
6	A_2''	2028[a]	CO stretching
7	A_2''	425	CO bending
8	A_2''	639	Fe–C stretching
9	A_2''	100	Fe–C bending
10	E′	1994[a]	CO stretching
11	E′	375	CO bending
12	E′	472	CO bending
13	E′	614	Fe–C stretching
14	E′	110	Fe–C bending
15	E′	100	Fe–C bending
16	E″	400	CO bending
17	E″	425	CO bending
18	E″	110	Fe–C bending

[a] R. A. Friedel, *et al.* (ref. 5 in text) give 2033 cm.$^{-1}$ and 2012 cm.$^{-1}$ while Sheline and Pitzer earlier listed bands at 2028 cm.$^{-1}$ and 1994 cm.$^{-1}$.

Thermodynamic Functions.—The thermodynamic functions C_p°, S°, $(H^\circ - E_0^\circ)/T$ and $-(F^\circ - E_0^\circ)/T$ for one mole of perfect gas were calculated by standard methods using the harmonic oscillator, rigid rotator approximation. The bond distances (a Fe–C distance of 1.84 Å. and a C–O distance of 1.15 Å.) were obtained from the work of Ewen and Lister.[8] Using this information and a molecular symmetry of D_{3h} corresponding to a symmetry number of 6, the principal moments of inertia I_A and I_B are calculated to be 915×10^{-40} g. cm.^{2} and 1068×10^{-40} g. cm.^{2}, respectively. The vibrational contributions to the thermodynamic functions were calculated from the assignment given in Table III. The final results are tabulated in Table IV at 100° intervals from 298° to 1000°K.

TABLE IV

THERMODYNAMIC FUNCTIONS OF $Fe(CO)_5(g)$

T (°K.)	C_p°	$(H^\circ - E_0^\circ)/T$	$-(F^\circ - E_0^\circ)/T$	S°
298.16	41.6	26.9	79.4	106.2
300	41.7	27.0	79.6	106.5
400	45.7	31.2	87.9	119.2
500	48.5	34.4	95.2	129.6
600	50.6	37.0	101.8	138.8
700	52.3	39.0	107.6	146.6
800	53.7	40.8	112.9	153.7
900	54.8	42.3	117.9	160.1
1000	55.7	43.5	122.3	166.9

The thermodynamic functions of formation of $Fe(CO)_5(g)$ from the elements in their standard states corresponding to the reaction

$$Fe(s) + 5C(s) + 5/2O_2(g) \longrightarrow Fe(CO)_5(g)$$

are tabulated in Table V. These calculations were made by using the heats of formation and vaporization of $Fe(CO)_5$; the thermodynamic functions of iron given by Kelley[14]; and the heats of formation, free energies of formation, and entropies of formation given in the N.B.S. tables.[15] The calculated value for the standard heat of formation (ΔE_0°) at 0°K., for $Fe(CO)_5(g)$ was −177.3 kcal./mole.

TABLE V

THERMODYNAMIC FUNCTIONS OF FORMATION OF $Fe(CO)_5(g)$

T(°K.)	ΔF_f°	ΔH_f° kcal.	ΔS_f°, cal./deg.
298.16	−168.3	−178.7	35
300	−168.2	−178.7	35
400	−166.6	−179.5	33
500	−164.7	−180.1	31
600	−163.3	−180.5	29.5
700	−161.4	−180.7	28
800	−159.9	−180.9	26
900	−158.6	−180.8	24
1000	−158.3	−180.6	22

Since the thermodynamic functions for the reaction

$$Fe(s) + 5(CO)(g) \longrightarrow Fe(CO)_5(g)$$

are of interest, we have calculated ΔH, ΔS and ΔF for this reaction at 100° intervals (Table VI).

TABLE VI

THERMODYNAMIC FUNCTIONS FOR THE REACTION $Fe(s) + 5CO(g) \rightarrow Fe(CO)_5(g)$

T(°K.)	ΔH°	ΔF°	ΔS°
298.16	−46.5	−4.5	142
300	−46.5	−3.8	142
400	−47.9	8.3	141
500	−48.6	20.8	139
600	−48.9	33.1	137
700	−48.7	45.9	135
800	−48.3	58.0	133
900	−47.7	69.1	130
1000	−46.8	81.3	128

The thermodynamic functions of $Ni(CO)_4$ have been calculated from spectroscopic data by Crawford and Cross.[3] Recently Hawkins, *et al.*,[6] have given the calculated thermodynamic functions for $Cr(CO)_6$ and $Mo(CO)_6$. In Table VII we have compared the calculated S° and C_p° for these four compounds. The S° value at 298°K. for $Fe(CO)_5$ is somewhat closer to that of $Ni(CO)_4$ than it is to the value for $Cr(CO)_6$. The reason for this is found in the assignment of the low frequencies. In $Ni(CO)_4$ the metal-C bending frequencies are near 80 cm.$^{-1}$ while in $Fe(CO)_5$ they are near 110 cm.$^{-1}$. Thus the tighter skeletal structure of $Fe(CO)_5$ results in a relatively small vibrational contribution

TABLE VII

COMPARISON OF S° AND C_p° VALUES FOR THE METAL CARBONYLS

	$Ni(CO)_4$[a]	$Fe(CO)_5$	$Cr(CO)_6$[b]	$Mo(CO)_6$[b]
C_p°	34.8	41.6	51.0	52.3
S°	97.0	106.3	116.5	121.0

[a] See reference 4 in text. [b] See reference 6 in text.

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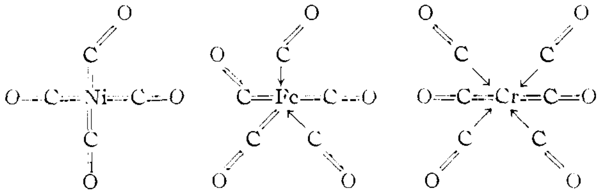
[14] K. K. Kelley, *U. S. Bur. Mines Bull.*, 371 (1934); 383 (1935) and 476 (1949).

[15] Circular 500 "Selected Values of Chemical Thermodynamic Properties," U. S. Government Printing Office, Washington, D. C. (1952); N. B. S. American Petroleum Institute Research Project 44, "Selected Values of Properties of Hydrocarbons."

compared to the contribution of $Ni(CO)_4$. Since the metal-bending frequencies in $Cr(CO)_6$ and $Mo(CO)_6$ were assigned by analogy with $Ni(CO)_4$ near 80–90 cm.$^{-1}$, these modes also give a relatively large contribution to the vibrational entropy for $Cr(CO)_6$ and $Mo(CO)_6$. In view of the fact that the Cr–C and Mo–C bonds are probably stronger than Ni–C bonds it would appear that the assignment of the metal-bending modes near 80–90 cm.$^{-1}$ is not justified. Evidence that these metal–C bonds are about as strong as the Fe–C bonds is obtained from their infrared spectra.[6] The infrared active asymmetric metal–C stretching frequency appears in the 600–700 cm.$^{-1}$ region in agreement with the corresponding frequencies in $Fe(CO)_5$.[2]

Comparison of the Bond Properties of $Fe(CO)_5$ and $Ni(CO)_4$.—There has been considerable discussion as to whether the metal–carbon bonds in $Fe(CO)_5$ are stronger or weaker than those of $Ni(CO)_4$.[2,4,7,16] If the linkage is better represented as a single bond then the theory of directed valence predicts that the Fe–C bond is the stronger, since Pauling's scale of bond strengths gives relative values of 2 and 2.72 for sp^3 and dsp^3 hybridization, respectively. For the same reason $Cr(CO)_6$ should have stronger metal–carbon bonds than either $Fe(CO)_5$ or $Ni(CO)_4$ since d^2sp^3 octahedral hybridization gives a relative strength of 2.92. On the other hand, if the metal–carbon linkages are best described in terms of double bonds, the strength of the bonds should decrease in the order Ni–C > Fe–C > Cr–C. This may be seen readily from a consideration of the structures



where the M–carbon bonds are of order 2, 1.6, 1.33, respectively.

Infrared studies[2] have indicated that the Fe–C bond is stronger than the Ni–C bond. However, Cable and Sheline have recently[16] indicated from thermochemical data that the Ni–C bond is the stronger of the two.

Our studies indicate that the Fe–C bond is the stronger. Both the Fe–C skeletal stretching (410 cm.$^{-1}$) and bending (110 cm.$^{-1}$) frequencies are higher than the corresponding frequencies in $Ni(CO)_4$ (382 and 80 cm.$^{-1}$, respectively). Consistent with this is the observation that the symmetric CO stretching frequency is lower in $Fe(CO)_5$ than in $Ni(CO)_4$, indicating a smaller CO bond energy which corresponds to a larger Fe–C bond energy. A calculation of the Fe–C bond stretching force constant from a simple valence force model gives $k_{Fe-C} = 2.77 \times 10^5$ dynes/cm., in comparison with a $k_{Ni-C} = 2.42 \times 10^5$ dynes/cm. (a detailed normal coördinate analysis by Crawford and Cross[3] gives $k_{Ni-C} = 2.52 \times 10^5$ dynes/cm.). The difference between the first two values is 15%. The major part of the difference is certainly associated with a larger Fe–C bond energy.

Sufficient thermodynamic data[14] are available to calculate the heat of atomization corresponding to the following reactions at 298°K.

$$Fe(CO)_5(g) \longrightarrow Fe(g) + 5C(g) + 5O_2(g)$$

$$Ni(CO)_4(g) \longrightarrow Ni(g) + 4C(g) + 4O_2(g)$$

To calculate the metal–carbon bond energy from these heats of atomization one needs to know the CO bond energy in these compounds. To estimate the difference in CO bond energy for $Fe(CO)_5$ and $Ni(CO)_4$ we will make use of the relation $kr = nD$ where k = bond stretching force constant, r = bond length, and D = bond dissociation energy. n is a parameter which has the same value for all CO bonds. We have previously used this relation to correlate successfully a large number of bond properties in both diatomic and polyatomic molecules.[17] The relation will be used here to set up a proportion from which one can predict the CO bond energy in $Fe(CO)_5$ and $Ni(CO)_4$ using the carbon monoxide frequency and bond energy as reference quantities. The distinction between bond energy and bond dissociation energy need not concern us in this calculation, since the difference is effectively cancelled out in the proportion. The results of the calculation are given in Table VIII. Since there are two proposed bond energies for carbon monoxide (257 and 224 kcal./mole) corresponding to the two controversial values for the heat of sublimation of carbon (172 and 140 kcal./mole, respectively), we give two sets of predicted bond energies. The CO bond energies may be combined with the heat of atomization of $Fe(CO)_5$ and $Ni(CO)_4$ to give the Fe–C and Ni–C bond energies, respectively. The results are given in Table VIII. The Fe–C bond energy is 6 kcal./mole larger than the Ni–C bond energy. Cable and Sheline[16] have made a similar calculation whereby they obtained bond energies of

TABLE VIII

PROPERTIES OF METAL–CARBON BONDS

Compound	Bond	Force constant (dynes/cm.) × 10^{-5}	Bond energy (kcal./mole)
CO	CO	18.55	257^e 224^f
$Fe(CO)_5$	CO	$(15.1)^a$	225^e 196^f
$Fe(CO)_5$	Fe–C	2.8	59^e 53^f
$Ni(CO)_4$	CO	15.9^b	237^e 207^f
$Ni(CO)_4$	Ni–C	2.52^b	53^e 48^f
$Sn(CH_3)_4$	Sn–C	2.37^c	51^d
$Pb(CH_3)_4$	Pb–C	1.94^c	49^d
$Zn(CH_3)_2$	Zn–C	2.39^c	39^d
$Cd(CH_3)_2$	Cd–C	2.05^c	31^d
$Hg(CH_3)_2$	Hg–C	2.45^c	24^d

[a] Calculated from the CO force constant in $Ni(CO)_4$ and the CO frequency of 1995 cm.$^{-1}$ in $Fe(CO)_5$. [b] See reference 3 in text. [c] See reference 17 in text. [d] See reference 16 in text. [e] L_c = 172 kcal./mole. [f] L_c = kcal./mole.

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(16) J. W. Cable and R. K. Sheline, "Bond Hybridization and Structure in the Metal Carbonyls," *Chem. Revs.*, **56**, 1 (1956).

(17) E. R. Lippincott and R. Schroeder, *J. Chem. Phys.*, **23**, 1131 (1955).

95 and 89 kcal./mole, respectively. Their calculation was based on the incorrect assumption that the CO bond energy is the same in $Fe(CO)_5$ as in $Ni(CO)_4$. The Raman spectrum of $Fe(CO)_5$ indicates that this assumption is not justified. Also, they had no effective means of estimating the CO bond energy from that of carbon monoxide. The Fe–C and Ni–C bond energies calculated here are of the same order of magnitude as bond energies calculated for Sn–C and Pb–C, indicating that the Fe–C and Ni–C bonds must have a bond order only slightly larger than 1.[16] This result is consistent with the values for the Sn–C, Pb–C, Zn–C and Cd–C bond stretching force constants which have values of 2.37, 1.94, 2.39 and 2.05 × 10^7 dynes/cm., respectively.[18]

NOTE ADDED IN PROOF.—We have recently made detailed calculations of the valence force symmetry coördinates (VFSC) and valence force coördinates (VFC) for $Fe(CO)_5$ using the Wilson FG technique and the above assignment of frequencies. We calculate for the axial and equatorial Fe–C bond stretching VFC the values 3.06 × 10^5 and 3.29 × 10^5 dynes/cm, respectively.

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Dipole Moment Measurements of Tetrazole Derivatives

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Dipole moments have been measured for a variety of tetrazole derivatives. It has been established that such measurements are not suitable for recognizing "meso-ionic" compounds.

Introduction

Henry, Finnegan and Lieber[1] recently reported the preparation of 1,3-dimethyl-5-iminotetrazole, a cyclic "meso-ionic" compound. It was anticipated[2] that the reaction of 2-methyl-5-aminotetrazole with methyl benzenesulfonate, according to the procedure of Herbst, Roberts and Harvill,[3] would result in the formation of the 1,2-dimethyl derivative. However, a preliminary X-ray analysis of the hydrobromide salt of the resultant compound[2] and a modified three-dimensional Fourier synthesis by Bryden[4] demonstrated unambiguously that the compound was the cyclic "meso-ionic" 1,3-dimethyl-5-iminotetrazole.

A complete X-ray analysis will lead to an accurate structure; however, it is not generally applicable to all compounds. The purpose of this investigation was to see what information about the structure of tetrazoles could be obtained from dipole moment measurements and whether it was possible to recognize "meso-ionic" compounds by such measurements.

Experimental

Materials and Methods.—Mallinckrodt, analytical reagent grade benzene was purified by crystallizing twice and then fractionally distilling after standing several days over freshly cut and ribboned sodium. All was rejected but the center cut which was redistilled in the same manner before use. The specific volume parameter for the solvent was obtained for each run from a least-squares examination of the specific volume, weight fraction data and was found to be constant to ±0.02%.

Tetrazoles.—These were obtained, fairly pure, from Drs. R. A. Henry and W. G. Finnegan. The solids were sublimed once immediately prior to each run. The liquids, small quantities of which were available, were distilled through a Vigreux column before use.

Dielectric Constants.—These were measured with a Leeds and Northrup Company capacitance and conductance bridge using No. 1553 shielded ratio box. The dielectric constant cell consisting of three concentric cylinders of brass tubing was similar in design to the measuring condenser of Smyth and Morgan.[5] The assembly was sealed into an annular "Pyrex" glass cylindrical vessel. The annular space reduced the quantity of solution required and aided in the circulation of the thermostated kerosene. The apparatus was calibrated with benzene, the dielectric constant of which was taken to be 2.2750 at 25°.[6]

Specific volumes were determined with a 25-ml. "Weld" specific gravity bottle with which specific gravities can be determined to within 0.001%.

Refractive indices were measured with a "Spencer Abbe" refractometer. The pure benzene was taken to have a standard refractive index of 1.5002.

Calculation of Moment.—The following nomenclature has been used throughout this paper. W_2 is the weight fraction of the solute, ϵ the dielectric constant of the solution, V its specific volume. P_∞ is the solute polarization at infinite dilution, R_2 is the molar refraction of the solute for the D-sodium line. ϵ_1 and V_1, the dielectric constant and the specific volume of the solvent, respectively, are the intercepts while α and β are the slopes of the straight lines obtained by plotting ϵ and V against W_2, respectively.[7]

$$\epsilon = \epsilon_1 + \alpha W_2 \qquad (1)$$

$$V = V_1 + \beta W_2 \qquad (2)$$

The derived data, obtained from the experimental data by the method of least squares, are presented in Table I with the slopes of the above lines, along with solute polarizations at infinite dilution calculated from the Halverstadt and Kumler[8] relationship.

$$P_\infty = \frac{3\alpha V_1 M_2}{(\epsilon_1 + 2)^2} + M_2(V_1 + \beta)\frac{(\epsilon_1 - 1)}{(\epsilon_1 + 2)} \qquad (3)$$

Included also in Table I is the molar refraction of the solute for the D-sodium line calculated from

$$R_2 = \frac{R_{1,2} - R_1}{X_2} + R_1 \qquad (4)$$

where R is molar refraction, X is mole fraction and subscripts 1, 2, 1,2 indicate solvent, solute, solution, respec-

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