CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
KANSAS STATE UNIVERSITY, MANHATTAN, KANSAS

# A Mass Spectrometric Investigation of Nickel Tetracarbonyl and Iron Pentacarbonyl[1]

BY ROBERT E. WINTERS AND ROBERT W. KISER

*Received October 8, 1963*

Electron impact data are presented for nickel tetracarbonyl and iron pentacarbonyl. Assignments of the probable processes of ionization and dissociation are made consistent with the observed energetics, and heats of formation of the various ions are given. From appearance potential data (i) the ionization potentials of nickel tetracarbonyl and iron pentacarbonyl are 8.64 ± 0.15 and 8.53 ± 0.2 e.v., respectively, and (ii) the calculated second ionization potentials for $Ni(CO)_2$ and FeCO are 17.6 and 16.2 e.v., respectively. The apparent stepwise loss of CO groups from $M(CO)_x^+$ in the kinetic breakdown scheme is discussed.

## Introduction

Metal carbonyls occupy a position of peculiar interest in the chemistry of the transition elements. Various metal carbonyl compounds have been found to have excellent catalytic and complexing characteristics. We believe that electron impact studies of these molecules can provide significant information concerning these compounds and their gaseous ions. Therefore, we have undertaken investigations of these carbonyls using mass spectrometric techniques.

J. J. Thomson was unable to study $Ni(CO)_4$ in the discharge bulb of his parabola mass spectrograph,[2] but many others have since used the carbonyl of nickel in mass spectrographic determinations of the nuclidic masses of the nickel isotopes. Vilesov and Kurbatov[3] recently have reported ionization potentials determined by photoionization methods for a number of transition metal carbonyls. However, no detailed investigation of the appearance potentials and heats of formation of the various ionic products of the ionization and dissociation processes has been made.

Because of the interest in these carbonyl compounds, we have commenced our mass spectrometric study of a number of transition metal carbonyl compounds by examining the carbonyls of two group VIII elements, iron and nickel. We have determined mass spectral cracking patterns for these compounds along with ionization and appearance potential data for the principal ions formed from these two carbonyls. From the experimental data, the second ionization potentials of $Ni(CO)_2$ and FeCO are calculated. The observation is made that the dissociation processes subsequent to ionization apparently involve successive losses of CO groups. This is a novel situation and, as discussed below, dictates further study of other carbonyl compounds by mass spectrometric methods.

## Experimental

The mass spectra and appearance potentials which we report were obtained with a Bendix Model 12-100 time-of-flight mass spectrometer with an analog output system consisting of a monitor and scanner. The instrumentation has been described previously.[4]

Mass spectra for each of the compounds were obtained at nominal electron energies of 70 e.v. Appearance potentials were determined using the method of extrapolated voltage differences, described by Warren.[5] Ionization efficiency curves were plotted for each determination and the linear portions of the curves forced parallel. The voltage differences at given currents were plotted as a function of the current, and the value of $\Delta E$ obtained upon extrapolation to zero current was added algebraically to the ionization potential of the calibration gas employed. Xenon mixed with the compound being investigated was used to calibrate the ionizing voltage. The known spectroscopic value (12.13 e.v.) for the ionization potential of xenon was used.[6] Ionization potentials also were determined using the technique of Lossing, Tickner, and Bryce[7] and were checked by means of the energy compensation method.[8] The measurements of appearance potentials were made using the iron and nickel isotopes of 56 and 58 a.m.u., respectively, to achieve greater detection sensitivity.

TABLE I
ISOTOPIC ABUNDANCES OF IRON AND NICKEL

| Element | Mass, a.m.u. | % abundance This work | % abundance Accepted (1961) |
|---|---|---|---|
| Iron | 54 | 5.1 ± 0.3 | 5.82 |
| | 56 | 91.5 ± 0.3 | 91.66 |
| | 57 | 3.0 ± 0.4 | 2.19 |
| | 58 | 0.4 ± 0.2 | 0.33 |
| Nickel | 58 | 68.4 ± 0.8 | 67.77 |
| | 60 | 26.3 ± 0.5 | 26.16 |
| | 61 | 1.3 ± 0.4 | 1.25 |
| | 62 | 3.2 ± 0.4 | 3.66 |
| | 64 | 0.8 ± 0.4 | 1.16 |

The samples of nickel tetracarbonyl and iron pentacarbonyl were obtained from commercial sources. No significant impurities were noted in the mass spectra after several vacuum distillation steps. In particular, $Fe(CO)_5$ was noted to be

---

[1] This work was supported in part by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-751 with Kansas State University. A portion of a dissertation to be presented by R. E. Winters to the Graduate School of Kansas State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] F. W. Aston, "Mass Spectra and Isotopes," 2nd Ed., Edward Arnold and Co., London, 1942, p. 150.

[3] F. I. Vilesov and B. L. Kurbatov, *Dokl. Akad. Nauk SSSR*, **140**, 1364 (1961).

[4] E. J. Gallegos and R. W. Kiser, *J. Am. Chem. Soc.*, **83**, 773 (1961); *J. Phys. Chem.*, **65**, 1177 (1961).

[5] J. W. Warren, *Nature*, **165**, 811 (1950).

[6] C. E. Moore, National Bureau of Standards Circular 467, Volume 3, Washington, D. C., 1958.

[7] F. P. Lossing, A. W. Tickner, and W. A. Bryce, *J. Chem. Phys.*, **19**, 1254 (1951).

[8] R. W. Kiser and E. J. Gallegos, *J. Phys. Chem.*, **66**, 947 (1962).

Table II

Appearance Potentials and Heats of Formation of the Principal Ions of Nickel Tetracarbonyl

| Ion | 70 e.v. relative abundance | Appearance potential, e.v. | Process | $\Delta H_f$ (ion), kcal./mole |
|---|---|---|---|---|
| $NiCO^{2+}$ | 1.7 | . . . | $Ni(CO)_4 \rightarrow NiCO^{2+} + ?$ | . . . |
| $Ni(CO)_2^{2+}$ | 4.5 | 28.3 ± 1 | $\rightarrow Ni(CO)_2^{2+} + 2CO$ | 560 |
| $Ni^+$ | 72.0 | 16.0 ± 0.3 | $\rightarrow Ni^+ + 4CO$ | 330 |
| $NiCO^+$ | 100.0 | 13.5 ± 0.2 | $\rightarrow NiCO^+ + 3CO$ | 246 |
| $Ni(CO)_2^+$ | 36.7 | 10.7 ± 0.2 | $\rightarrow Ni(CO)_2^+ + 2CO$ | 155 |
| $Ni(CO)_3^+$ | 33.1 | 9.36 ± 0.15 | $\rightarrow Ni(CO)_3^+ + CO$ | 97 |
| $Ni(CO)_4^+$ | 19.6 | 8.64 ± 0.15 | $\rightarrow Ni(CO)_4^+$ | 54 |

Table III

Appearance Potentials and Heats of Formation of the Principal Ions of Iron Pentacarbonyl

| Ion | 70 e.v. relative abundance | Appearance potential, e.v. | Process | $\Delta H_f$ (ion), kcal./mole |
|---|---|---|---|---|
| $FeCO^{2+}$ | 6.6 | 30.2 ± 2 | $Fe(CO)_5 \rightarrow FeCO^{2+} + 4CO$ | 629 |
| $Fe^+$ | 100.0 | 16.1 ± 0.2 | $\rightarrow Fe^+ + 5CO$ | 330 |
| $FeCO^+$ | 92.2 | 14.0 ± 0.2 | $\rightarrow FeCO^+ + 4CO$ | 255 |
| $Fe(CO)_2^+$ | 17.2 | 11.8 ± 0.2 | $\rightarrow Fe(CO)_2^+ + 3CO$ | 178 |
| $Fe(CO)_3^+$ | 2.7 | 10.3 ± 0.3 | $\rightarrow Fe(CO)_3^+ + 2CO$ | 117 |
| $Fe(CO)_4^+$ | 9.1 | 10.0 ± 0.2 | $\rightarrow Fe(CO)_4^+ + CO$ | 83 |
| $Fe(CO)_5^+$ | 11.1 | 8.53 ± 0.2 | $\rightarrow Fe(CO)_5^+$ | 23 |

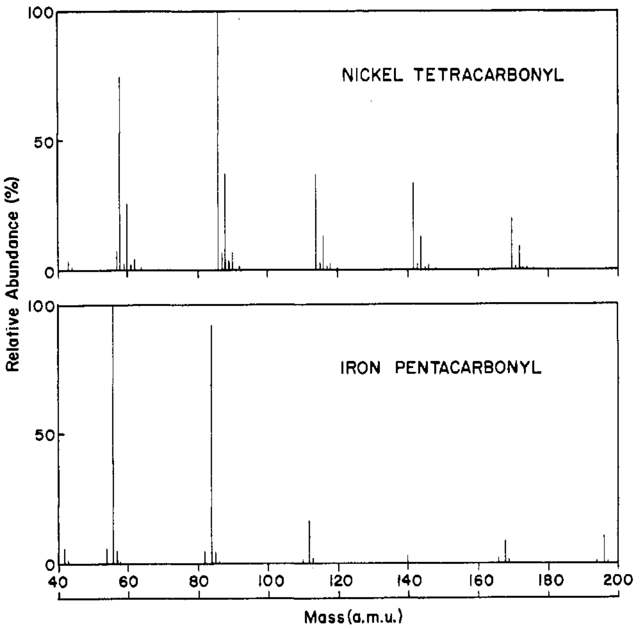

Fig. 1.—Mass spectral cracking patterns of nickel tetracarbonyl and iron pentacarbonyl.

absent from the $Ni(CO)_4$ sample. Kel-F grease was used on all stopcocks and joints with which the carbonyl compounds came into contact.

No deleterious effects were observed in introducing the samples to the ion source. However, replacements of the tungsten filament were necessary several times during the course of the study. Ionization and appearance potentials were reproducible within the quoted errors with the different filaments.

## Results

The nickel and iron isotopic abundances found experimentally in this study are listed in Table I along with the presently accepted values. The agreement in both cases is well within the experimental error.

The appearance potential data for the two compounds investigated are given in Tables II and III. The relative abundance for the most abundant isotope of the principal ions formed at 70 e.v. is given in column 2. The measured appearance potentials are summarized in column 3 and the probable processes for the formation of the ions are given in column 4. The heats of formation consistent with the proposed processes for the various ions are given in the last column.

The heats of formation of both transition metal carbonyls were determined by Fischer, Cotton, and Wilkinson.[9,10] The values for nickel tetracarbonyl[9] and iron pentacarbonyl[10] are −145.1 and −173.7 kcal./mole, respectively These were employed in all of the thermochemical calculations. The heat of formation of carbon monoxide was taken to be −26.4 kcal./mole.[11]

## Discussion

**Mass Spectra.**—The 70-e.v. mass spectra of these compounds are shown in Fig. 1 (background contributions have been removed). The mass spectra of the two transition metal carbonyls exhibit many similar characteristics. The most abundant species are the metal ion and the monocarbonylmetal ion. However, in the mass spectrum of nickel tetracarbonyl, the dominant species is the $NiCO^+$ and in the iron pentacarbonyl spectrum, the $Fe^+$ is of greatest intensity. Similar trends were reported by Baldock and Sites[12] at slightly different electron energies. Figure 2 shows the manner in which the ion abundance varies as a function of the electron energy for the singly-charged metal-containing ions in each of the compounds studied.

---

[9] A. K. Fischer, F. A. Cotton, and G. Wilkinson, *J. Am. Chem. Soc.*, **79**, 2044 (1957).

[10] F. A. Cotton, A. K. Fischer, and G. Wilkinson, *ibid.*, **81**, 800 (1959).

[11] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, Washington, D. C., Feb. 1, 1952.

[12] R. Baldock and J. R. Sites, U. S. Atomic Energy Commission V-761, Technical Information Services, Oak Ridge, Tenn., 1951.

All isotopes were utilized in determining the fraction of the total ion current for each species at any particular energy. These curves are quite different from other commonly-encountered clastograms. At low energies the parent ion dominates, and as the energy is increased, the fragment ions "grow in" and "peak out" in order of their appearance potentials. This "peaking-out" tendency probably is due to further fragmentation of the respective ions to still smaller fragment ions. This appears to be a characteristic of the metal carbonyls and leads us to believe that the respective ions are formed by successive losses of CO groups.

**Ionization and Appearance Potentials.**—The ionization potentials determined for the two compounds in this study are somewhat higher than the reported literature values. The value of 8.64 e.v. for $I$ [$Ni(CO)_4$] is somewhat larger than 8.28 e.v. determined by Vilesov and Kurbatov[3] by photoionization. Using our experimentally determined ionization potential, the heat of formation of the parent ion is calculated to be 54 kcal./mole. For iron pentacarbonyl, our value of the ionization potential (8.53 e.v.) is significantly greater than the 7.95 e.v. reported by Vilesov and Kurbatov.[3] Our experimental value leads to a heat of formation of $Fe(CO)_5^+$ of 23 kcal./mole.

The doubly-charged species, $NiCO^{2+}$ and $Ni(CO)_2^{2+}$, were detected in the mass spectrum of nickel tetracarbonyl. One might also expect a detectable amount of $Ni^{2+}$; however, the most abundant isotope of nickel (58 a.m.u.) would cause this doubly-charged ion to occur at $m/e = 29$, for which a background peak was found to occur. This background eliminated further experimental investigation of any $Ni^{2+}$ species. Additionally, we were unable to detect any peaks above background at $m/e = 30.5$ or 31 which would be due to isotopic species of $Ni^{2+}$.

The heats of formation of $Ni(CO)_2^+$ and $Ni(CO)_2^{2+}$, 155 and 560 kcal./mole, respectively, derived from the appearance potentials, allow one to calculate the second ionization potential of $Ni(CO)_2$ from the process

$$Ni(CO)_2^+ \longrightarrow Ni(CO)_2^{2+} + e \qquad (1)$$

17.6 e.v. is calculated for the second ionization potential from the data presented in Table II.

The heat of formation of the nickel ion is 330 kcal./mole, as calculated from its appearance potential (16.0 e.v.). This result is much higher than the 278 kcal./mole determined spectroscopically.[13] Based on energetic considerations, however, the process assigned is the most reasonable one for the formation of this ion from nickel tetracarbonyl.

One doubly-charged species, $FeCO^{2+}$, was observed in the mass spectrum of iron pentacarbonyl. Because of the large abundance of the iron isotope at $m/e = 56$ (see Table I), an investigation for the occurrence of $Fe(CO)_2^{2+}$ could not be made. When we used the naturally-occurring carbon-13 isotope peak (at $m/e = 56.5$) to search for the $Fe(CO)_2^{2+}$ ion, we found that we would be able to detect it only if the $m/e = 56$ peak was due to 10% or more of $Fe(CO)_2.^{2+}$ We did not observe any $m/e = 56.5$ peak, and therefore conclude that $Fe(CO)_2^{2+}$ is less than 10% of the $Fe^+$ ion intensity, if, in fact, it even is formed in this system. Similarly, no study could be made of $Fe^{2+}$ because of the large intensity at $m/e = 28$ due to $CO^+$.

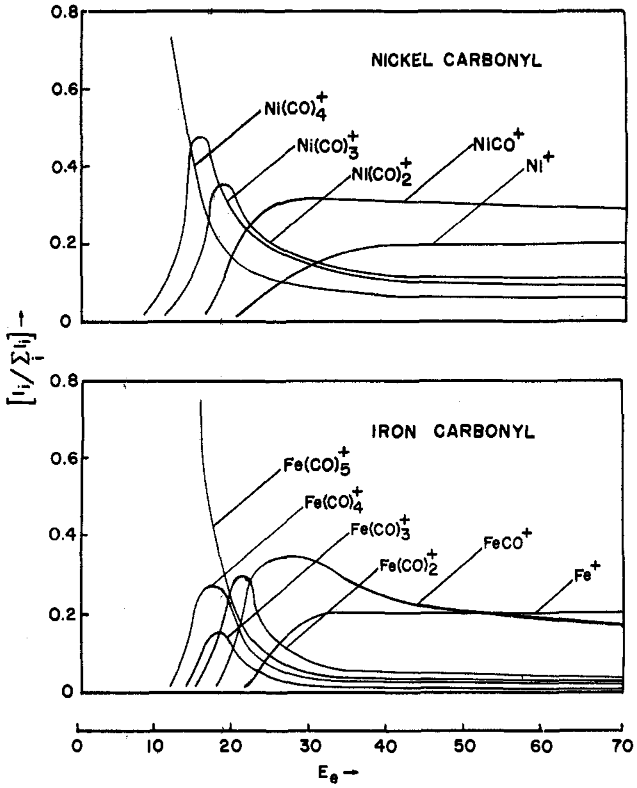

Fig. 2.—Clastograms for nickel tetracarbonyl and iron pentacarbonyl.

From the calculated heats of formation of $FeCO^+$ and $FeCO^{2+}$, using the assigned processes, we calculate the second ionization potential of FeCO to be 16.2 e.v., in accordance with the process

$$FeCO^+ \longrightarrow FeCO^{2+} + e \qquad (2)$$

Energetic considerations lead us to conclude that the various ions observed in the iron pentacarbonyl spectrum are formed by the successive removal of neutral CO groups, even as in the $Ni(CO)_4$ molecule.[14] The heat of formation of $Fe^+$, equal to 330 kcal./mole based on our experimental data, is greater than the value of 277 kcal./mole determined spectroscopically.[13] However, removal of five neutral CO fragments again best satisfies the energetic requirements, and we therefore have assigned the process as shown in Table III.

Many other ions were also investigated; however, no further comments will be made concerning the thermochemical properties of these ions here since these data are conveniently summarized in Tables II and III.

---

(13) C. E. Moore, "Atomic Energy Levels," Volume 1, National Bureau of Standards Circular 467, Washington, D. C., 1949.

(14) The steps $Ni(CO)_4 \rightarrow Ni(CO)_3 + CO$ and $Ni(CO)_3 \rightarrow Ni + 3CO$ (and similar steps for $Fe(CO)_5$) are proposed by C. E. H. Bawn, *Trans. Faraday Soc.*, **31**, 440 (1935), and by A. P. Garratt and H. W. Thompson, *J. Chem. Soc.*, 524, 1817, 1822 (1934).

## Conclusions

On the basis of the experimental data obtained in this study, we have proposed that the fragmentation of these transition metal carbonyl ions occurs by successive removal of neutral CO groups. The clastograms for both the iron and nickel carbonyls are very similar, and, as mentioned above, the peculiar nature of these clastograms appears to be characteristic of these metal carbonyls.

Significantly, no ions of the type which would result from the cleavage of the C–O bonds in these carbonyls were observed, *i.e.*, $NiC^+$ and $NiO^+$ were not observed. This further supports the contention that CO groups as such are removed in the successive steps of the fragmentation processes.

We are currently performing the appropriate calculations based on the improved quasi-equilibrium theory[15] in order to test further the proposal concerning the successive loss of CO groups in the anticipation that this approach will either give additional strength to these ideas or show up any fallacy in these contentions.

---

(15) M. Vestal, A. L. Wahrhaftig, and W. H. Johnston, *J. Chem. Phys.*, **37**, 1276 (1962).

---

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASSACHUSETTS

# Vibrational Spectra and Bonding in Metal Carbonyls. III. Force Constants and Assignments of CO Stretching Modes in Various Molecules; Evaluation of CO Bond Orders[1a]

BY F. A. COTTON[1b]

*Received December 11, 1963*

Data from the literature for a large number of substituted group VI carbonyls and for some manganese carbonyl halides and their derivatives are treated by the methods described in earlier papers in this series. It is shown how the method can eliminate incorrect assignments in certain cases. A relationship between CO bond orders and CO force constants is delineated and used to deduce, from differences in the calculated CO stretching constants, the changes in CO bond orders. It is also shown that absolute values of the bond orders may be estimated. The relative $\pi$ acceptor strengths of various ligands are discussed semiquantitatively and it is shown, *inter alia*, that $PF_3$ is a stronger $\pi$-accepting ligand than CO, while ligands such as dimethylformamide and methylformamide are actually $\pi$-donors. The relationship of the CO stretching force constants used in this series of papers to more rigorous values is discussed.

## I. Introduction

In earlier papers in this series,[2,3] a method for analyzing and assigning the spectra of CO stretching vibrations in octahedral metal carbonyls has been proposed, tested, and applied to a limited number of substituted group VI carbonyls. The present paper extends the study in the following ways:

(1) Using the method, data from the literature for a large number of diverse compounds are treated. It is shown how the method can eliminate incorrect assignments in certain cases.

(2) A relationship between CO bond orders and CO force constants is delineated and used to deduce, from differences in the calculated CO stretching constants, the changes in CO bond orders. It is also shown that absolute values of the bond orders may be estimated.

(3) The relative $\pi$-acceptor strengths of various ligands are discussed semiquantitatively and it is shown, *inter alia*, that $PF_3$ is a stronger $\pi$-accepting ligand than CO, while ligands such as dimethylformamide and methylformamide are actually $\pi$-donors.

(4) The relationship of the CO stretching force constants used in this series of papers to more rigorous values is discussed.

## II. Group VI Carbonyls

**Sources of Data.**—Poilblanc and Bigorgne[4] have reported data for a great many substituted molybdenum carbonyls in which the substituents are phosphorus(III) compounds. Schmutzler[5] has prepared, in small quantities, *cis*-$Mo(PF_3)_3(CO)_3$ and recorded its CO stretching frequencies in KBr. Data for still other compounds containing P(III) compounds as ligands have been reported by Magee, *et al.*,[6] Chatt and Watson,[7] Abel, Bennett, and Wilkinson,[8] and in part I of this series. Data for molecules with sulfur(II) molecules as substituents have been reported by

---

(1) (a) Supported by the U. S. Atomic Energy Commission; (b) Fellow of the Alfred P. Sloan Foundation.

(2) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

(3) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).

(4) R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. France*, 1301 (1962).

(5) R. Schmutzler, Explosives Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington 98, Del., private communication.

(6) T. A. Magee, C. N. Matthews, T. S. Wang, and J. H. Wotiz, *J. Am. Chem. Soc.*, **83**, 3200 (1961).

(7) J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961).

(8) E. W. Abel, M. A. Bennett, and G. Wilkinson, *ibid.*, 2323 (1959).