

Pyrolysis and Molecular-Beam Mass Spectrum of Tetracarbonylnickel(0)¹

Steven M. Schildcrout,² George A. Pressley, Jr., and Fred E. Stafford

Contribution from the Department of Chemistry and The Materials Research Center, Northwestern University, Evanston, Illinois 60201. Received November 1, 1966

Abstract: A positive ion mass spectrum of Ni(CO)₄ was determined using a magnetic sector spectrometer capable of distinguishing the molecular-beam (zero ion-source contact) mass spectrum from possible contributions of pyrolysis intermediates which may be formed in the ion source. The mass spectrum is in fair agreement with a previous conventional mass spectrum. Evidence for gas-phase intermediates such as Ni(CO)₃ could not be found by sampling the contents of a low-pressure flow reactor. Previously unreported features of the mass spectrum include metastable ion peaks, each involving loss of one neutral CO group from a Ni(CO)_x^{+q} ion (*q* = 1, 2), and fragment ions resulting from C–O scission and from rearrangement. From appearance potential data, the ionization potential of Ni(CO)₄ is 8.35 ± 0.15 eV, and the mean Ni–C bond dissociation energy in Ni(CO)₄ is 39.3 ± 1.0 kcal/mole.

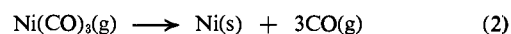
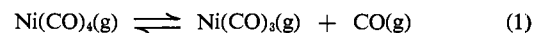
Metal carbonyls and their derivatives have been the subjects of recent mass spectrometric studies^{3–13} carried out for such purposes as determining molecular formulas, fragmentation mechanisms, and ion energetics and for testing theories of mass spectra.

Nickel carbonyl (tetracarbonylnickel(0)), the simplest of the known metal carbonyls, has been studied by Winters and Kiser^{3,7} with a time-of-flight mass spectrometer. They concluded from the clastogram that positive ion fragmentation occurs by stepwise loss of neutral CO groups. Similar mechanisms have been suggested for other carbonyls and derivatives.^{3–6,8,11–13}

In mass spectrometric work with diphosphine,¹⁴ tetraborane,^{15,16} and tetraborane carbonyl,¹⁷ it has been shown that a labile sample gas may pyrolyze on the hot ion-source filament or on nearby surfaces. Resulting gaseous products or intermediates may be present in large enough concentrations to contribute significantly to the mass spectrum and hence obscure that due to the molecule of interest. This effect is dif-

ficult or impossible to detect in conventional analytical spectrometers. It has been shown^{15–17} also that this problem may be avoided by measuring molecular-beam mass spectra, where contributions from only those molecules which have made no contact with the ion source are considered.

On the basis of kinetic evidence, the intermediate Ni(CO)₃ has been postulated in the homogeneous gas-phase pyrolysis of Ni(CO)₄ according to the mechanism^{18,19}



Evidence for the tricarbonyl has been reported also in other reactions of Ni(CO)₄ such as its photolysis,^{20,21} radiolysis,²² and CO exchange in solution.²³

The present study of Ni(CO)₄ was undertaken to (1) determine its molecular-beam mass spectrum and compare it to a spectrum taken with a conventional analytical instrument, (2) to search for metastable ion peaks which might confirm the proposed³ ion fragmentation scheme, (3) to seek mass spectrometric evidence for the existence of pyrolysis intermediates in the gas phase, (4) to obtain an electron-impact value of the ionization potential of Ni(CO)₄ for comparison with previous discrepant electron-impact⁸ and photoionization results,^{24,25} and (5) to obtain by electron impact an estimate of the average Ni–C bond-dissociation energy in nickel carbonyl and compare it to the previous calorimetric result.²⁶

Experimental Section

Commercially obtained Ni(CO)₄ (Delta Chemicals) was vacuum distilled trap to trap. During all runs, a Pyrex sample reservoir

(1) (a) Supported by the Northwestern University Materials Research Center (MRC) through a contract with the U. S. Advanced Research Projects Agency. Acquisition and maintenance of the mass spectrometer facility were made possible by support from the MRC, the U. S. Atomic Energy Commission, and the University. (b) Presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, paper V3.

(2) Recipient of Public Health Service Fellowship 1-F1-GM-33, 565-01 from the National Institute of General Medical Sciences, 1966–1967.

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attached to the inlet tube of the mass spectrometer was maintained at -78° (CO_2 -acetone bath), at which temperature the frozen sample has an equilibrium vapor pressure of about 1×10^{-1} torr.²⁷ Under these conditions, no sample impurities were detectable with the mass spectrometer.

The particular mass spectrometer²⁸ employed is described elsewhere,^{15,16} as is the method of obtaining molecular-beam spectra.²⁹

The more intense ion currents were detected simultaneously by a 50% transmission grid and a 16-stage Be-Cu secondary electron multiplier. This permitted measurement of multiplier gain, which was of the order of 3×10^5 but which varied by as much as a factor of 2, depending on the peak being measured. From those gains which could be measured, the gains for low-intensity peaks were estimated.

Appearance potentials (AP's) were measured by the vanishing current method, using ionization efficiency curves made automatically with an X-Y recorder.³⁰ Argon was leaked directly into the mass spectrometer and was used as the calibrant. Its AP was taken as 15.76 eV.³¹ An emission current regulated at 1.2 ma (corresponding to $\sim 10^{-5}$ amp trap current) was ordinarily used. Whether the emission current was 1.2 or 0.12 ma did not significantly affect AP results for the more intense peaks.

Ions and their neutral progenitors were identified by mass number, mass defect, isotope ratios, shutter effect, AP, and dependence of relative intensity on inlet valve setting, reactor temperature, and reactor orifice size. Metastable ions could be identified also by their peak shape, by agreement to ± 0.05 amu of observed and calculated apparent mass for at least two isotopes in each case, and by agreement of the AP with that of the corresponding stable daughter fragment.

Results and Discussion

Mass Spectrum. The observed molecular-beam mass spectrum of $\text{Ni}(\text{CO})_4$, including metastable ion peaks, is given in Table I. Relative ion currents are for a nominal 70-eV ionizing electron energy, with the reactor at about 20° . Appearance potentials for all observed species also are given in the table.

The instrument mass resolution ($M/\Delta M \sim 1000$) usually permitted peaks from ions containing nickel to be resolved from background peaks having the same mass number. Also Ar^+ and C_2O^+ , both at mass 40, could be resolved.

That Ni has five stable isotopes (58, 60, 61, 62, and 64) complicates the determination of ion current from a particular species. For example, at 70 eV, mass peak 74 has a "shutterable"²⁹ ion current of which 58% is due to $^{58}\text{Ni}^{16}\text{O}^+$, 37% is due to $^{62}\text{Ni}^{12}\text{C}^+$, and 5% is due to $^{64}\text{Ni}(^{12}\text{C}^{16}\text{O})_3^{2+}$. Also for this reason it was necessary to measure the AP of NiO^+ at m/e 78, corresponding to $^{62}\text{Ni}^{16}\text{O}^+$, rather than using the more abundant $^{58}\text{Ni}^{16}\text{O}^+$ or $^{60}\text{Ni}^{16}\text{O}^+$. The AP's of other Ni-containing fragments could be measured at masses corresponding to the ^{58}Ni isotope without interference from species with lower AP's.

All fragment peaks reported by Winters and Kiser³ are observed in the present case, and the relative inten-

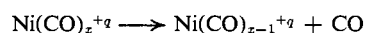
Table I. Room-Temperature Monoisotopic Molecular-Beam Mass Spectrum of $\text{Ni}(\text{CO})_4$

Ion or metastable	Relative ion current ^a		
	Multiplier output ^b	Corrected ^c	AP ^d
$\text{Ni}(\text{CO})_4^+$	31.0	23.8	8.35 ± 0.15
$\text{Ni}(\text{CO})_3^+$	43.8	34.8	8.89 ± 0.15
$\text{Ni}(\text{CO})_2^+$	42.2	36.4	10.21 ± 0.15
NiCO^+	100.0	100.0	12.17 ± 0.15
Ni^+	58.3	92.6	14.45 ± 0.15
$\text{Ni}(\text{CO})_4^{2+}$	0.29	0.26 ^e	25.1 ± 0.5
$\text{Ni}(\text{CO})_3^{2+}$	2.7	2.6 ^e	25.2 ± 0.5
$\text{Ni}(\text{CO})_2^{2+}$	5.8	5.9	27.2 ± 0.5
NiCO^{2+}	2.0	2.4 ^e	30.2 ± 0.5
NiC_3O_2^+	0.013	0.011 ^e	20.1 ± 0.5
NiC_2O^+	1.3	1.2	20.6 ± 0.3
$\text{NiC}_2\text{O}^{2+}$	0.19	0.20 ^e	38.5 ± 0.5
NiC_2^+	0.10	0.10 ^e	30.1 ± 1
NiC^+	6.1	7.3	22.1 ± 0.3
NiO^+	0.52	0.59 ^e	26.4 ± 1
C_2O_2^+	0.013	0.008 ^e	21.6 ± 0.5
C_2O^+	0.046	0.031 ^e	31.7 ± 1
C_2^+	0.043	0.032 ^e	39.9 ± 2
$\text{Ni}(\text{CO})_4^+ \rightarrow \text{Ni}(\text{CO})_3^+ + \text{CO}$	0.26	0.21 ^e	8.90 ± 0.15
$\text{Ni}(\text{CO})_3^+ \rightarrow \text{Ni}(\text{CO})_2^+ + \text{CO}$	0.070	0.061 ^e	10.6 ± 1
$\text{Ni}(\text{CO})_2^+ \rightarrow \text{NiCO}^+ + \text{CO}$	0.024	0.024 ^e	12.7 ± 1
$\text{NiCO}^+ \rightarrow \text{Ni}^+ + \text{CO}$	0.004	0.007 ^e	15.1 ± 2
$\text{Ni}(\text{CO})_4^{2+} \rightarrow \text{Ni}(\text{CO})_3^{2+} + \text{CO}$	0.011	0.010 ^e	26.9 ± 2
$\text{Ni}(\text{CO})_3^{2+} \rightarrow \text{Ni}(\text{CO})_2^{2+} + \text{CO}$	0.021	0.021 ^e	27.6 ± 0.5

^a Currents were measured at 70 eV and are given as percentages of the NiCO^+ current. ^b Analyzer entrance slit width 0.29 mm; exit slit 0.38 mm. ^c Corrected current is the multiplier output current divided by the multiplier gain. This should correspond to the product of the relative ion abundance and the ionic charge. ^d Appearance potential in eV with estimated 90% confidence limits. ^e Derived from estimated value of multiplier gain. Doubly charged ions A^{2+} are assumed to have a current gain 85% that of A^+ , as does $\text{Ni}(\text{CO})_2^{2+}$. Metastables are assumed to have the same gain as the corresponding daughter ion found at its true mass. C_2^+ and C_2O^+ are assumed to have the same gains as background CO^+ and CO_2^+ , respectively. Other unmeasured gains are estimated by assuming that gain is a simple function of mass for apparently structurally similar ions.

sities of these peaks are in fair agreement. An earlier mass spectrum³² was made at 25 eV, so the relative intensities are not directly comparable with the present results.

As shown in Table I, peaks due to metastable processes are now observed in the mass spectrum of $\text{Ni}(\text{CO})_4$. Each is of the type



This confirms the positive ion fragmentation mechanism proposed by Winters and Kiser.³ A sequence of four successive losses of neutral CO occurs from the singly charged parent ion. A similar sequence is indicated at least in part for the doubly charged ions, as Winters and Kiser have suggested also.³ Metastable processes forming NiCO^{2+} and Ni^{2+} may occur, but their peaks are apparently too weak to be detected with the present techniques. The fragment Ni^{2+} could not be detected, even at electron energies as high as 100

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(27) K. A. Walsh, U. S. Atomic Energy Commission, LA-1649, 1953 (declassified 1958); *Nucl. Sci. Abstr.*, **12**, Abstr. No. 4072 (1958).

(28) Built by Nuclide, Inc., State College, Pa. (type 12-in., 60° sector, HT); W. A. Chupka and M. G. Inghram, *J. Phys. Chem.*, **59**, 100 (1955).

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(31) C. E. Moore, "Atomic Energy Levels," Vol. 1, 2, National Bureau of Standards, Circular 467, U. S. Government Printing Office, Washington, D. C., 1949, 1952.

ev. An upper limit on its relative intensity is set at 0.15.

The present spectrum contains some previously unreported species which result from C-O bond cleavage. The existence of fragments of this type shows that while stepwise loss of CO is the predominant fragmentation route, an alternate route is followed to some extent. These fragments can be accounted for by loss of various numbers of CO and CO₂ groups. Such fragmentation steps have been suggested for the hexacarbonyls of chromium, molybdenum, and tungsten to account for C-O scission in those compounds.^{4,6}

Other novel fragments are NiO⁺ and C₂O_y⁺ (y = 0, 1, 2), which must be formed in unimolecular rearrangement processes since their relative intensities, like those of the other fragments, showed no pressure dependence. Very intense background signals prevented detection of possible Ni(CO)₄ fragments of the type CO_y⁺ (y = 0, 1, 2).

Metastable transitions involving loss of single neutral CO groups have been reported recently in the positive ion mass spectrum of Fe(CO)₅ by Winters and Collins.³³ They report also fragments involving C-O bond cleavage, including FeO⁺. These observations are analogous to the present results with Ni(CO)₄.

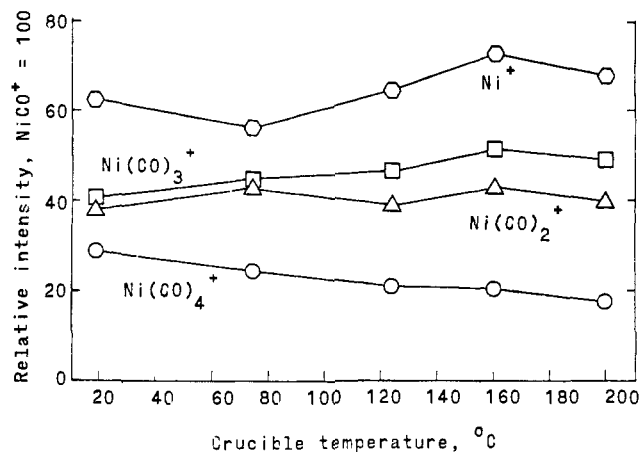
Since the present paper was originally submitted, Bidinosti and McIntyre³⁴ reported that they have measured the mass spectrum of Ni(CO)₄ under conditions similar to those presently employed. In their 50-ev spectrum they included most of the fragments detected in the present study, with the relative ion intensities in substantial agreement.

Pyrolysis Intermediates. Although the agreement of molecular-beam and conventional mass spectra of Ni(CO)₄ indicates that sample pyrolysis in the ion source does not produce significant quantities of gaseous intermediates, evidence for the existence of such intermediates was sought also by deliberate pyrolysis of the sample in the flow reactor of the mass spectrometer.

From its reported vapor pressure²⁷ and from the conductance³⁵ of the sample inlet system, the pressure of Ni(CO)₄ in the reactor is estimated to be 1 × 10⁻² torr when the inlet valves are fully opened with a 9 × 10⁻³ cm² effusion orifice in the reactor cap. This assumes negligible sample pyrolysis in the reactor and inlet system. The pressure could be lowered by closing the metering valve.

The molecular-beam intensity of a Ni(CO)₄ fragment was usually about 90% of the total ion intensity (*i.e.*, 90% "shutter effect"²⁹), indicating that Ni(CO)₄ is pumped rapidly by the vacuum-chamber walls. This fact helped distinguish Ni(CO)₄ fragments from ions arising from gases which form a stable background in the mass spectrometer. However, it precluded use of the percentage shutter effect as an aid in identifying reactive intermediates.

The intensities of the ions Ni(CO)_x⁺ (x = 0-4) were measured as a function of reactor temperature. As the temperature was raised from 19 to 200°, the absolute ion intensities decreased about 96%, and pressure

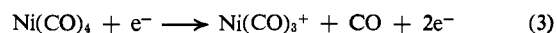


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Figure 1. Relative ion intensities of principal Ni(CO)₄ fragments as a function of reactor temperature. Intensities for ionizing electrons of 70 ev are given as percentages of the NiCO⁺ intensity and are not corrected for multiplier discrimination; estimated pressure of Ni(CO)₄ in the reactor at 19° is 1 × 10⁻⁴ torr. These data are from a single run and were reproduced in other runs to ±5% of a given relative intensity.

in the reactor and ion source regions increased, presumably because of CO. The decrease in absolute ion intensities shows that decomposition of the sample was nearly complete at 200°, but the relative ion intensities had changed only slightly as shown in Figure 1. The gradual decrease of Ni(CO)₄⁺ relative to Ni(CO)₃⁺ and lower ions is reproducible and might seem to indicate the presence of Ni(CO)₃. However, a temperature-induced change in the Ni(CO)₄ fragmentation pattern also could account for the result.

The process



must have a greater AP than



Assuming negligible excess energy in the products of these processes, the difference in AP's is $D[(\text{CO})_3\text{Ni}-\text{CO}]$. Ion-pair processes are not considered because the electron affinity of CO is expected to be very small. Therefore, at ionizing energies slightly above the AP of Ni(CO)₃⁺ process 4 should be more important relative to (3) than at 70 ev, if indeed Ni(CO)₃ is formed and (4) occurs. If Ni(CO)₃ is a pyrolysis intermediate, the intensity of Ni(CO)₃⁺ at low ionizing energy would be expected to increase as the reactor temperature is raised. Such an increase was not observed. Neither was an increase observed in similar experiments with the Ni(CO)₂⁺ and Ni⁺ peaks. These experiments were done at various pressures of Ni(CO)₄ and with effusion-orifice areas of either 9 × 10⁻³ or 0.14 cm². Enlarging the orifice decreases the residence time of the reactor contents, thereby decreasing the number of collisions a reactive molecule would have to survive before being detected.

Peaks which might correspond to a molecule of the type Ni₂(CO)_z were not detected.

Thus no evidence for the presence of gaseous intermediates in the Ni(CO)₄ pyrolysis has been found in this

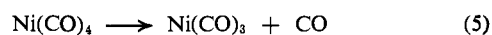
(33) R. E. Winters and J. H. Collins, *J. Phys. Chem.*, **70**, 2057 (1966).

(34) D. R. Bidinosti and N. S. McIntyre, submitted for publication.

(35) S. Dushman, "Scientific Foundations of Vacuum Technique," 2nd ed, revised by J. M. Lafferty, John Wiley and Sons, Inc., New York, N. Y., 1962.

investigation. The existence of such intermediates cannot, however, be precluded. Perhaps ready decomposition of an intermediate upon collision with the reactor walls permitted only a very small steady-state concentration which was not sufficient for detection by the present method. The importance of the heterogeneous pyrolysis¹⁹ under these conditions is not known. The large fragment ion intensities and the large per cent shutter effect of ions coming from neutral Ni(CO)₄ make this system less favorable for the detection of intermediates than the boron hydride systems in which the unstable species BH₃ and B₄H₈ have been successfully identified.^{15-17,29}

There may be some doubt about the validity of arguments which led to postulation of the Ni(CO)₃ intermediate. Chan and McIntosh¹⁹ have obtained $\Delta S^\ddagger = -16.2$ eu for the homogeneous gas-phase pyrolysis of Ni(CO)₄. This large negative value does not seem compatible with a mechanism whose rate-determining step



is a simple unimolecular dissociation.³⁶ Kangas, *et al.*,³⁷ have recently reconsidered an earlier study²³ of the rate of radioactive CO exchange of Ni(CO)₄ in solution. They obtained large negative entropies of activation for this first-order reaction in various solvents. The activation parameters for this reaction were found to be different from those for first-order substitution by phosphine derivatives. They concluded that CO exchange and ligand substitution proceed by different, non-competitive mechanisms and that previous assumptions that they are dissociative processes involving step 5 may be incorrect.

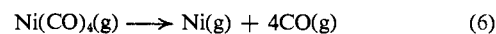
Electron-Impact Energetics. As given in Table I, the ionization potential of Ni(CO)₄ is 8.35 ± 0.15 ev. This is close to the photoionization values of 8.28 ± 0.03 ev²⁴ and 8.22 ± 0.02 ev²⁵ but is somewhat less than the electron-impact results of 8.64 ± 0.15 ev by Winters and Kiser³ and 8.57 ± 0.10 ev by Bidinosti and McIntyre.³⁴ The AP's of the Ni(CO)₄ fragment ions given by those investigators are consistently greater than those found in this study, and the results of Winters and Kiser are consistently greater than those of Bidinosti and

(36) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961.

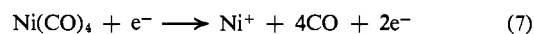
(37) L. R. Kangas, R. F. Heck, P. M. Henry, S. Breitschaft, E. M. Thorsteinson, and F. Basolo, *J. Am. Chem. Soc.*, **88**, 2334 (1966).

McIntyre. No explanation can be offered now for these differences, although in the present study the method of vanishing current was used with Ar⁺ calibrant while the others used the method of extrapolated voltage differences with Xe⁺.

The heat of the reaction



can be obtained by subtracting the spectroscopic ionization potential³¹ of Ni from the AP of Ni⁺ in the process



It is believed that (7) is responsible for formation of Ni⁺ from Ni(CO)₄ for reasons already mentioned. Using the AP in Table I, the heat of (6) is 6.82 ± 0.15 ev. Then the average dissociation energy of a Ni-C bond in Ni(CO)₄ is 1.71 ± 0.04 ev or 39.3 ± 1.0 kcal/mole. This is greater than the 35.2 ± 0.5 kcal/mole obtained by calorimetry,²⁶ but the formation of products with excess energy in the electron impact process may explain this difference.

Conclusions

A slight temperature dependence of the Ni(CO)₄ fragmentation pattern with 70-ev electrons is suggestive of the formation of a tricarbonyl reactive intermediate. No confirmative evidence, as from studies with low energy electrons, could be adduced, and it is likely that the change in fragmentation pattern is due to changes in the thermal population of the levels in the parent molecule; the pyrolysis remains a poorly understood reaction. While the detection of metastable ion peaks has confirmed stepwise loss of CO groups to be an important part of positive ion fragmentation in Ni(CO)₄, the detection of new fragments shows that the total fragmentation process at 70 ev is more complicated. Appearance potential measurements have given results for the ionization potential of Ni(CO)₄ and for $\bar{D}(\text{Ni-CO})$ in fair agreement with the results of photoionization and calorimetry, respectively.

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