Chemiluminescent Reactions of Nickel, Iron, and Cobalt Carbonyls with Ozone

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INTRODUCTION

Metal carbonyls have been historically used for metal purification but are becoming increasingly used in chemical vapor deposition and preparation of nanomaterials.[1] Metal carbonyls are toxic and therefore, when used industrially, the area in which they are used must be monitored in case of unintended leakage.[2] Nickel and iron carbonyls were first reported to chemiluminesce with ozone by Morris and Niki and the emission spectra reported by Groth et al.[3,4] A fast, sensitive, and portable chemiluminescent monitor for nickel carbonyl was developed by Stedman et al. based on these initial observations.[5] The detectors are configured either with a broad band pass filter to monitor both nickel and iron carbonyls, or with selective optical filters and a pre-reactor to monitor only one. The selective optical filters are based on the published spectra.[5] The system was later adapted by Houpt et al. to remove the interference of iron carbonyl by making use of the difference in chemiluminescent lifetimes from the two metal carbonyls.[6]

Cobalt carbonyl and cobalt nitrosyl carbonyl have been shown to induce a signal in commercial filter-based detectors.[7] The cobalt carbonyls may be an impurity in nickel carbonyl detection or a detector specific to cobalt may be needed. Therefore, the chemiluminescence spectra from these cobalt compounds needed to be determined. Charge-coupled device (CCD) technology now provides the ability to monitor all wavelengths at once and thus preserve accurate relative intensities. This feature also allows pressure dependence studies to be conducted relatively easily in order to observe the extent to which the intensity distributions change with reaction pressure. New monitoring instruments for metal carbonyls would be simpler and less expensive if inexpensive vacuum pumps and thus higher pressures could be used in the reactor. Therefore, a study concerning intensity as a function of pressure was also carried out.

EXPERIMENTAL

Materials. Gaseous mixtures were made with purified CO and the metal carbonyls in 5 L gas sampling bags obtained from Calibrated Instruments Inc. (Ardsley, NY). The CO was purified by passing through a trap containing a few upstream iodine crystals and activated charcoal.[5] The nickel carbonyl bag contained 0.1 mL of liquid nickel tetracarbonyl syringed directly from the sample container and 5 L of purified CO. The iron pentacarbonyl was purchased from Aldrich (St. Louis, MO) and 1 mL was syringed directly from the bottle into the sampling bag containing 5 L of purified CO. The cobalt tricarbonyl nitrosyl and the dicobalt octacarbonyl were obtained from Strem Chemical (Newburyport, MA). A sampling bag was made with 0.5 mL cobalt tricarbonyl nitrosyl in 5 L of purified CO. Dicobalt octacarbonyl is a solid at room temperature. A bottle containing the crystals was fit with a septum and a line supplying purified CO was introduced through a syringe needle into the septum. The vaporized $Co_2(CO)_8$, along with the CO carrier gas slightly above the vacuum system pressure, left through a second syringe needle and continued to the flow system. Ozone dilute in oxygen was produced by means of a silent discharge in an ozone generator manufactured by Triple-O-International Systems (Model RF, Nirim, IN).

Instrumentation. The chemiluminescence spectra were detected by a scientific-grade, high quantum efficiency Ocean Optics (Dunedin, FL) QE65000 spectrometer. The spectrometer has a 25 μm entrance slit and a high resolution composite grating (#HC 1), allowing a spectral window of 200–925 nm. The instrument has a spectral resolution of about 1.9 nm. Wavelength accuracy was verified by using an atomic sodium lamp. The system uses a 1000 μm single fiber optic to direct light into the instrument. The fiber was clamped in front of the Pyrex window of the flow cell and no focusing optics were used. The spectrometer was connected by a USB cable to a laptop computer. The spectrometer was not calibrated for absolute intensities across the spectral window and all spectra are therefore reported uncorrected. Intensity versus pressure curves were determined using a photomultiplier tube (PMT) (RCA 1P28) observing through a 579 ± 20 nm optical filter (Baird-Atomic). Current from the PMT was displayed on a picoammeter.
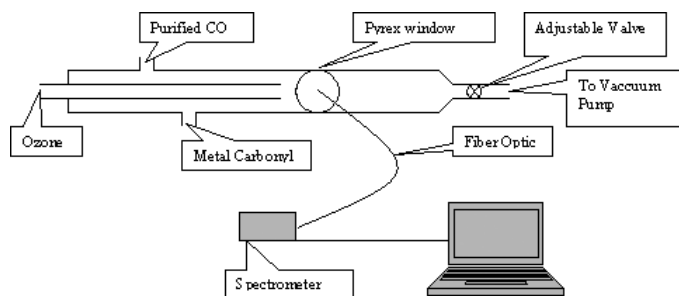
FIG. 1. Setup of the flow system and spectrometer.

Procedure. The setup for the chemiluminescent spectroscopy is illustrated in Fig. 1. An ozone oxygen mixture is generated and passing through a needle valve enters the vacuum flow system through a sliding inner adjustable flow tube. Purified CO enters the system through a side port. Except for the $Co_2(CO)_8$, the metal carbonyls entered through another side port and mixed with the purified CO before reacting with the ozone. The $Co_2(CO)_8$ bottle was put in line with the purified CO and thus entered through the same port. The metal carbonyl/CO mixture reacted with the ozone at the end of the adjustable flow tube, which was slid in and out to achieve the greatest light intensity in front of the Pyrex window.

In order to avoid the effects of background light, all of the chemiluminescent measurements were made in darkness. The system was first evacuated with a vacuum pump and the system would usually reach 0.054 torr. The reactants are admitted to the system and the flows were on average 400 mL min^{-1} purified CO, 600 mL min^{-1} O_2/O_3 mixture, and 100 mL min^{-1} metal carbonyl mixture. The O_2/O_3 mixture was measured at 0.45% O_3 by ultraviolet (UV) absorption at 254 nm. The flow velocity for the experiments was typically 2400 cm s^{-1} at a pressure of 0.7 torr, and chemiluminescence would occur within milliseconds of reactant mixing. Once the flow system was evacuated, the purified CO was introduced to the system followed by the O_2/O_3. When the pressure was stabilized, the ozone generator was turned on and flow from the metal carbonyl/CO bag was introduced to the system. At this point

the chemiluminescent glow was apparent and measurements were made. For each metal carbonyl, an optimum integration time was determined to find the greatest signal-to-noise ratio for the spectra. These times were typically either 30 s or 60 s with a dark background subtracted. Shorter integration times lacked intensity and longer integration times suffered from stray light and the eventual coating of opaque material, apparently metal oxides, on the windows. Once the spectra of the metal carbonyl chemiluminescence were taken, the main valve to the vacuum pump was slowly closed. This provided for an increased total pressure in the system, and measurements at these higher pressures were made with both the Ocean Optics spectrometer and the PMT to determine the effect of higher pressures on the observed emission.

RESULTS AND DISCUSSION

Spectral Features. This work, with the use of the Ocean Optics QE65000, provided more spectral structures and accurate wavelengths than previously reported. Figure 2 represents the reaction of ozone with $Ni(CO)_4$ and shows more spectral structure in the 600–800 nm range than previously reported.[4,5] These bands correspond to the red degraded bands of NiO listed as System II by Malet and Rosen.[8] Spectra reproduced in Groth et al. show little structure for wavelengths longer than 620 nm, while Stedman et al.'s spectra show little information beyond 700 nm.[4,5] Emission peak wavelength assignment from this work corresponds well to peaks from the previously reported wavelength regions.

Figure 2 shows the intensity distribution from the reaction between Fe(CO)$_5$ and ozone. The intensity distribution and spectral features match those of Groth et al. and Stedman et al.[4,5] Peak wavelength assignments agree with Groth et al. and lead to the conclusion that Stedman et al. reported wavelengths shifted by 20 nm to the red.

For the first time, chemiluminescence spectra from the reaction between ozone and $Co_2(CO)_8$ and $Co(CO)_3NO$ are reported. Figure 3 shows the intensity distribution from both reactions. As was noted in the Introduction, it can be seen that the reactions of cobalt carbonyls with ozone emit light in the same spectral window as the nickel and iron carbonyls. This
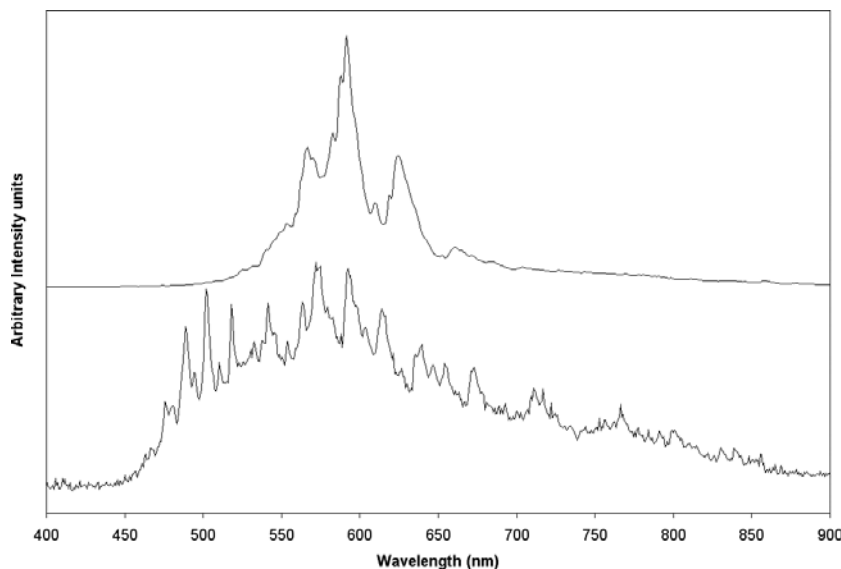

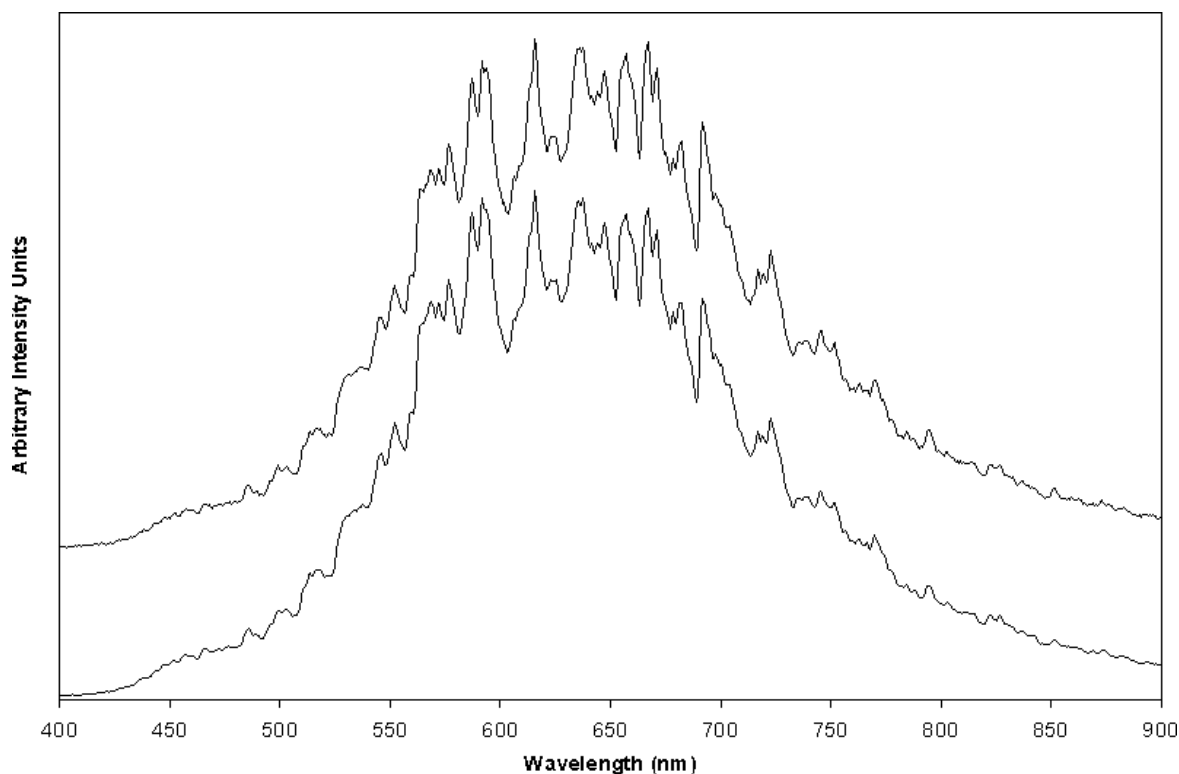FIG. 2. Uncorrected chemiluminescent emission intensity spectra for (*top*) FeO* and (*bottom*) NiO*; offset for clarity.
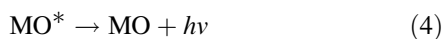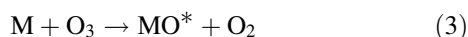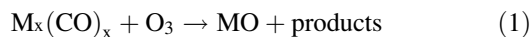
Fɪɢ. 3. Uncorrected chemiluminescent emission intensity spectra from (**top**) dicobalt octacarbonyl and (**bottom**) cobalt tricarbonyl nitrosyl when reacted with ozone and purified carbon monoxide; offset for clarity.

accounts for their detection in the commercial $Ni(CO)_4$ detector.

Mechanism. Morris and Niki suggested the generalized mechanism below based on several observations:[3]

$$M_x(CO)_x + O_3 \rightarrow MO + products \qquad (1)$$

$$MO + CO \rightarrow M + CO_2 \qquad (2)$$

$$M + O_3 \rightarrow MO^* + O_2 \qquad (3)$$

$$MO^* \rightarrow MO + hv \qquad (4)$$

The first reaction is only schematic. The last three constitute a chain reaction in which M and MO catalyze the oxidation of CO by O_3 together with the emission of a chemiluminescent photon. There is a marked enhancement in emission intensity when excess CO is added. Groth confirms the CO + O_3 catalytic oxidation in the presence of Fe and Ni carbonyls.[4] Table I shows that the obvious reaction with adequate exothermicity to provide MO* is that shown in Eq. 3. The

fact that the reaction in Eq. 4 produces the observed emission has been verified by comparison to band heads from various studies of NiO and FeO laser excitation analysis.[11–13] The mechanism proceeding through vapor-phase metal atoms and ozone in Eq. 3 is confirmed by spectral comparisons with direct studies in the cases of the reactions of Fe and Ni.[11,14]

TABLE II. CoO bands matched to references and their assignments (nm).

Our bands	Reference bands	Assignments[c]
793	793.5[a]	
769	768.5[a]	
751	750.0[a]	
743	744.0[a]	
721	722.0[a]	
716	716.5[c]	C-X (0,0)
690	690.0[b], 690.6[c]	C-X (1,0)
665	665.0[b], 666.3[c]	C-X (2,0)
653	655.8[c]	E-X (0,0)
643	643.6[c]	C-X (3,0)
631	632.0[b], 633.8[c]	E-X (1,0)
622	622.1[c]	C-X (4,0)
614	615.2[c]	E-X (2,0)
607	608.1[c]	C-X (4,0)
591	592.0[b], 593.7[c]	E-X (3,0)
575	575.6[c]	E-X (4,0)
557	558.7[c]	E-X (5,0)
542	541.9[c]	E-X (6,0)
526	526.7[c]	E-X (7,0)
512	512.2[c], 511.8[c]	E-X (8,0)
498	497.7[c]	E-X (9,0)
484	484.5[c]	E-X (10,0)

TABLE I. ΔH for $M + O_3 \rightarrow MO^* + O_2$. The exothermicities have been converted into minimum calculated wavelengths to compare with those observed.

Metal	ΔH_{rxn} (kcal/mol)	λ min calculated (nm)	λ min observed (nm)
Ni	76[a]	381	465
Fe	75[b]	376	524
Co	130[c]	220	440

[a] See Ref. 3.
[b] See Ref. 9.
[c] See Ref. 10.

[a] See Ref. 15.
[b] See Ref. 16.
[c] See Ref. 17.

Table I also shows that the reaction in Eq. 3 is sufficiently exothermic to produce excited CoO^*, which then can emit a photon in the visible region shown in Eq. 4. Table II shows very good evidence that the observed low resolution spectra actually match the CoO^* band heads obtained at much higher resolution by other methods. The intensity enhancement upon adding excess CO is visually comparable to that for iron carbonyl. The evidence above, while not conclusive, certainly points to the newly observed cobalt carbonyl chemiluminescence operating by the same mechanism.

Pressure Dependence. The overall pressure in the flow system was varied from 1 torr to 10 torr by adjusting the main valve from the flow system to the vacuum pump. An attempt was made with the CCD spectrometer to determine whether the relative spectral intensities of the various bands changed with increasing pressure. When normalized, the spectra taken at these varied pressures practically overlaid each other within the noise limitations, and thus the intensity distributions do not seem to be pressure dependent. Interestingly for the $Ni(CO)_4$ reaction, the 10 torr spectra were almost an order of magnitude more intense overall than any of the lower pressures, while the iron and cobalt carbonyls sharply decreased in intensity with increasing pressure. To investigate further, the CCD spectrometer was removed and the system was fitted with a PMT and an optical bandpass filter centered on 579 nm. These studies were carried out at much lower carbonyl flow rates in order to avoid the formation of opaque deposits on the walls and windows of the flow system. The main pump valve was again adjusted to increase the total pressure of the system from 0.8 torr to 83 torr for each metal carbonyl reaction with ozone. Nanoamp currents were recorded from the PMT as the pressure was increased incrementally to 83 torr and decreased back to 0.8 torr. The optimum pressures for maximum intensity for each reaction were found for nickel, iron, and cobalt carbonyls and were 9.4 torr, 0.88 torr, and 1.0 torr, respectively. The chemiluminescence from nickel carbonyl remained detectable at the system's measurable limit of 83 torr. This has useful implications for monitoring purposes since a larger, cheaper, and easier to achieve pressure might produce an adequate signal for $Ni(CO)_4$ and may improve the instrumental ability to detect this toxic compound specifically and at low cost.

CONCLUSION

The chemiluminescence spectra from the reaction of ozone with nickel tetracarbonyl, iron pentacarbonyl, dicobalt octacar-bonyl, and cobalt tricarbonyl nitrosyl in excess carbon monoxide were investigated. The use of Ocean Optics' new QE65000 high quantum efficiency spectrometer provided relative spectral intensities for these reactions. The reaction with the nickel compound produced more bands than previously reported and the iron pentacarbonyl spectrum shows that one previous study's wavelength assignments were incorrect. The chemiluminescent reaction of cobalt carbonyl compounds with ozone has been studied for the first time and appears to proceed through the same reaction mechanism as described for nickel and iron carbonyl. Spectral relative intensities do not appear to change with increasing pressure for any of the four metal carbonyls studied but peak intensity for $Ni(CO)_4$ actually increases with increasing pressure up to almost 10 torr.

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