this out and, on the basis of the assumption made, give estimates of the rate constants for steps 1b and 2 for both cases of excess reagent.

With amine in large excess, both the formation of the ion pair, $RNH_2^+Cl^-$, by step 1b at the end of the induction period, and the decomposition of that substance by step 2, are more rapid than in the systems containing excess CCl_4. The more rapid formation of the ion pair in the amine-rich solutions would be predicted by the greater polarity of these solutions[24] and the greater rate of step 2 by the large concentration of free amine. On the other hand, the CCl_4-rich solutions contain very low concentrations of free amine, so that the ion pair, although formed more slowly, will also decompose only slowly in those solutions. Thus, the average value of the second-order velocity constants given in Table III, $1.45 \times 10^{-3} M^{-1} \sec^{-1}$, can be taken as the rate constant for step 2 in the amine-rich media. Similarly, the rate constant for step 1b in the CCl_4-rich systems can be taken as the value, $4.3 \times 10^{-4} \sec^{-1}$, found at all CCl_4 concentrations for those systems.

The value of the induction time can be used to obtain a rough estimate of the rate constant of step 1b in the amine-rich solutions. Assuming that the excited particles, $(RNH_2)^+(CCl_4)^-$, formed in step 1a are forming without appreciable decomposition during the induction period and that they reach a steady state concentration by the end of that period, it can be shown that the rate constant for step 1b is equal to the reciprocal of that induction time. In that way, the induction time of 16 min observed for the amine-rich solutions corresponds to a rate constant of $1 \times 10^{-3} \sec^{-1}$ for formation of the ion pair.

The rates of Cl^- ion formation are also consistent with the proposed mechanism. With amine in large excess, the rate is high as expected from the high rate of step 2, but the high rate of step 2 also causes sufficient chain reaction to produce additional Cl^- ion, which accounts for the lack of a limiting value. With the CCl_4 in excess, step 2 is extremely slow as is also the Cl^- formation.

Photodecomposition of Gas-Phase Transition Metal Carbonyl Anions

Robert C. Dunbar*[1a] and Bennett B. Hutchinson[1b]

Contribution from the Departments of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, and Abilene Christian College, Abilene, Texas 79601. Received February 27, 1974

Abstract: Photodisappearance spectra have been obtained by ion cyclotron resonance technique for ten transition metal carbonyl anions. The ion disappearance mechanism is believed to be photodissociation, although electron photodetachment was not ruled out. The spectra are interpreted on the assumption that the photodisappearance curves reflect optical absorption peaks of the gas-phase ions. Comparison of the spectra indicates that the optical absorption of the species $M(CO)_n^-$ shifts in regular fashion toward the blue either on increasing n or on moving to a metal of higher atomic number. The only exceptional case, $Ni(CO)_3^-$, is predicted to be anomalous by theory. Arguments are presented for assigning the optical transition involved as arising from a charge transfer process carrying a metal 3d-type electron into a higher ligand orbital. The results for $Co(CO)_4^-$ are compared with solution properties of the ion and are found to be entirely consistent.

Photodisappearance investigation of gas-phase ions using trapped-ion techniques and ion cyclotron resonance (icr) detection of ion disappearance has been a successful approach to obtaining optical absorption information about a number of ionic species.[2-7] The optical properties of gas-phase transition metal containing ions are of particular interest for comparison with the large body of spectroscopic knowledge about condensed-phase transition metal species. Early investigation showed that several transition metal carbonyl anions in the gas phase have observable photodisappearance rates, and the photodisappearance rates were observed to be strongly wavelength dependent.[8] Recent careful investigation by Richardson and Brauman[9] of the $Fe(CO)_4^-$ system yielded convincing evidence that the photodisappearance process in this case is photodissociation, rather than electron photodetachment; in agreement with earlier work,[8] a weak peak was observed near 700 nm, and a much more intense region of photodissociation commencing near 500 nm.

(1) (a) Alfred P. Sloan Fellow, 1973–1975; Case Western Reserve University; (b) Abilene Christian College.

(2) (a) R. C. Dunbar, *J. Amer. Chem. Soc.*, **93**, 4354 (1971); (b) *ibid.*, **95**, 472 (1973).

(3) J. M. Kramer and R. C. Dunbar, *J. Chem. Phys.*, **59**, 3092 (1973).

(4) R. C. Dunbar and E. Fu, *J. Amer. Chem. Soc.*, **95**, 2716 (1973).

(5) R. C. Dunbar, *J. Amer. Chem. Soc.*, **95**, 6191 (1973).

(6) K. C. Smyth and J. I. Brauman, *J. Chem. Phys.*, **56**, 1132 (1972). This article contains an extensive set of references to recent experimental photodetachment work.

(7) K. C. Smyth and J. I. Brauman, *J. Chem. Phys.*, **56**, 4620, 5993 (1972), and references therein.

(8) R. C. Dunbar, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 9–14, 1972.

(9) J. H. Richardson and J. I. Brauman, *J. Amer. Chem. Soc.*, submitted for publication.

Anions are readily obtained for a variety of metal carbonyls,[10,11] and we have extended the investigation of metal carbonyl optical properties to an extensive series of gas-phase anions. Sufficient data were obtained to permit some limited generalizations and to suggest some relevance of the gas-phase results to known condensed-phase phenomena.

Experimental Section

The icr spectrometer, xenon-arc light source, narrow-band interference filters, and monochromator used in this work have been described previously in detail.[2-5]

The anions were obtained by electron bombardment of the neutral metal carbonyls $V(CO)_6$, $Cr(CO)_6$, $Mn_2(CO)_{10}$, and $Fe_2(CO)_9$ or $Fe(CO)_5$, $Co_2(CO)_8$, and $Ni(CO)_4$. Neutral gas pressures were normally near 10^{-6} Torr (lower pressures were found to increase greatly the problems of space-charge peak shifts and thermal peak shifts). Sample decomposition in the inlet was found to be a problem only for $Co_2(CO)_8$, and for this species a flowing-inlet configuration was used in which the sample vapor was continuously pumped through the inlet manifold and out to the roughing pump. Ionizing electron energy was not found to be a significant variable except for those ions ($Cr(CO)_4^-$ and $Co(CO)_3^-$) having a resonance dissociative-attachment peak and was normally kept as low as possible consistent with good ion intensity.

Ions were trapped with the usual conditions of high-trapping voltage (several volts) and low-drift voltages. Despite the relatively high pressures, ion trapping times were typically many seconds, and a typical ion in all these systems is thermalized by hundreds or thousands of collisions with neutral molecules.

To counter recurrent problems with space-charge-related peak shifts, the ion densities were kept low (well below the point of marginal-oscillator saturation), and great care was exercised to keep the observing radiofrequency field centered on the peak during irradiation.

The ions $Cr(CO)_5^-$, $Cr(CO)_4^-$, $Ni(CO)_3^-$, and $V(CO)_5^-$ were studied using interference-filter wavelength selection (100-Å bandpass spaced 200 Å apart, with 150-Å filters at 7000, 7500, and 8100 Å). $Fe(CO)_4^-$ and $Co(CO)_4^-$ (below 3400 Å) were irradiated with the monochromator with 4-mm slits (140 Å fwhm), while $Co(CO)_3^-$, $Mn(CO)_4^-$, and $Co(CO)_4^-$ (above 3400 Å) were irradiated with the monochromator without slits (fwhm ~300–400 Å).

Ion cyclotron resonance ejection[2] with an ejecting field of ~0.1 V/cm was employed in the following cases: $Cr(CO)_5^-$ was ejected in examining $Cr(CO)_4^-$; $Mn(CO)_5^-$ was ejected in observing $Mn(CO)_4^-$; $Co(CO)_3^-$ was ejected in observing $Co(CO)_4^-$; $Co(CO)_4^-$ was ejected in observing $Co(CO)_3^-$. In the $Co(CO)_4^-$ case some residual interference from $Co(CO)_3^-$ remained even with ejection, and the data were corrected for this according to the observed $Co(CO)_3^-$ disappearance spectrum. For $Mn(CO)_4^-$, in addition to cyclotron ejection of $Mn(CO)_5^-$, trapping ejection[12] with a 0.5 V applied radiofrequency field was used to eject all the species in the $Mn_2(CO)_n^-$ region, of which several were observed. Dinuclear anions were present in all of the carbonyls[13] but were not found to interfere except in manganese.

Results

Photodisappearance was studied in the ten anions examined by trapping the anions in the trapping icr cell, irradiating the ions, and monitoring the decrease in the anion icr signal, corresponding to destruction of the anion, as a function of wavelength. Fuller discussions of principles and methods of icr photodecomposition experiments may be found in ref 1–7. Two serious potential sources of systematic error must be considered.

First, disappearance of the anion may occur not only by photodissociation but also by photodetachment or
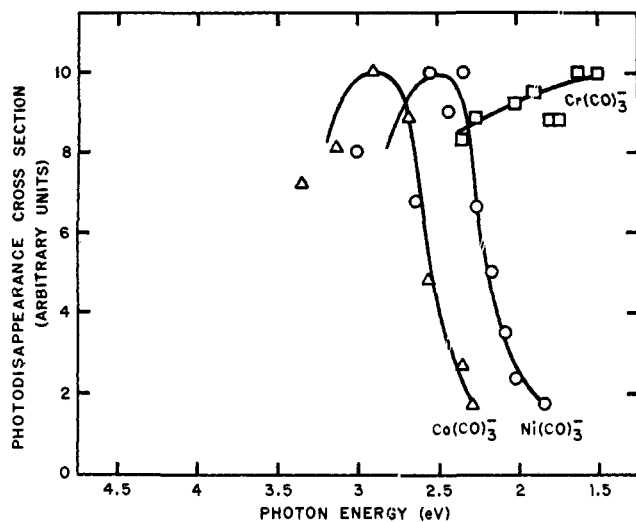
(10) S. Pignataro, A. Foffani, F. Grasso, and B. Cantone, *Z. Phys. Chem. (Frankfurt am Main)*, **47**, 106 (1965).

(11) R. E. Winters and R. W. Kiser, *J. Chem. Phys.*, **44**, 1964 (1966).

(12) D. P. Ridge and J. L. Beauchamp, *J. Chem. Phys.*, **51**, 470 (1969).

(13) See R. C. Dunbar, J. F. Ennever, and J. P. Fackler, *Inorg. Chem.*, **12**, 2734 (1973).

photon-induced ion–molecule reaction.[14] The question whether the observed photodisappearance is due to photodissociation or, alternatively, to electron photodetachment is obviously important in the interpretation but unfortunately an unambiguous answer could not be obtained with available techniques. A direct search for the icr peaks corresponding to photodissociation products was made in most cases, and at least for $Cr(CO)_5^-$, $Cr(CO)_4^-$, and $Fe(CO)_4^-$ small increases in the ion minus carbonyl peaks were observed under irradiation. However, apparently because of the high reactivity of the product ions toward parent neutral, nothing approaching a reasonable mass balance was achieved in any system, and the failure to observe dissociation products for $Cr(CO)_3^-$ and $Ni(CO)_3^-$, for instance, cannot be considered significant. The situation is complicated by the likelihood that the probable photodissociation product ions are themselves rapidly photodissociated in the wavelength regions of interest.

Electron-scavenging experiments[12] using CCl_4 with $Ni(CO)_3^-$, $Cr(CO)_4^-$, and $Cr(CO)_5^-$ appeared to indicate the production of some free electrons in the ion photodisappearance wavelength regions, and some photodetachment might be suspected in these systems. However, reaction of photodissociation products with CCl_4 to produce Cl^- is a plausible alternative explanation of these observations.

Using experimental conditions which we are unable to duplicate, Richardson and Brauman[9] have obtained convincing evidence that the photodisappearance of $Fe(CO)_4^-$ is essentially entirely due to photodissociation. In our spectrometer the behavior of $Fe(CO)_4^-$ was entirely similar in the above described control experiments to that of the other carbonyl anions. Since the results to be described are suggestive of a similar photochemical process being involved for all the anions, and since we consider Richardson and Brauman's evidence for $Fe(CO)_4^-$ to be strong, it seems a reasonable presumption that our photodisappearance results should all be interpreted as reflecting a photodissociation process, pending the ultimate resolution of this question with more refined experimental approaches.

The possibility that the observed photodisappearance is due to photon-induced reactions is in no way ruled out by our data in any case, since there were always several ionic species present in the cell which showed intensity variations under irradiation. However, since such processes must initiate with photon absorption by the ion of interest and thus indicate optical absorption by the ion, the possibility that the excited ion is depleted by reaction rather than by dissociation is of little importance in the interpretation.

A very small and not always reproducible peak in the $Fe(CO)_4^-$ disappearance curve was also observed at about 700 nm. The sharp peaking of this spectral feature (as opposed to step-function behavior) did not suggest electron detachment, and it appears most likely to be a photodissociation peak as previously hypothesized.[8] Richardson and Brauman[9] have observed this peak with better intensity.

The other serious source of systematic error arises from the fact that under the conditions of these experiments the cell always trapped a mixture of several

(14) J. M. Kramer and R. C. Dunbar, *J. Amer. Chem. Soc.*, **94**, 4346 (1972).

Figure 1. Photodisappearance results for the metal tricarbonyl anions. Note that the photodisappearance cross sections (presumed to be photodissociation cross sections) are separately normalized for each ion, so that comparison of absolute values between ions is not possible. The solid curves are estimated best fits.
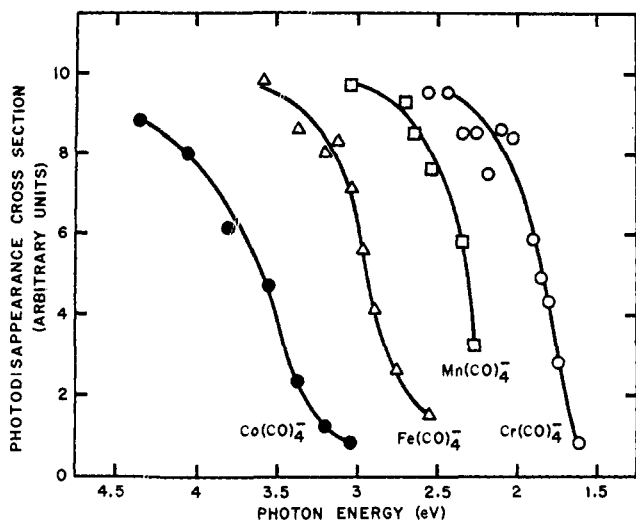
Figure 2. Photodisappearance results for metal tetracarbonyl anions.

anion species, including both primary electron-impact products and ion–molecule reaction products.[13] In the study of the photodisappearance of any particular anion, photochemical pathways involving other anions may result in production of the ion of interest, with a corresponding rise in its icr signal; this rise may mask the desired photodisappearance process, giving erroneous apparent thresholds and spurious structure in the photodetachment spectra. To the extent possible these effects were identified and minimized (1) by working at electron energies chosen to maximize production of the ion of interest and minimize production of interfering ions and (2) by efficient cyclotron resonance[2] and/or trapping-field resonance ejection[15] from the cell of one or more of the interfering ions. The specific application of these techniques is described in the Experimental Section.

(15) J. L. Beauchamp and J. T. Armstrong, *Rev. Sci. Instrum.*, **40**, 123 (1969).
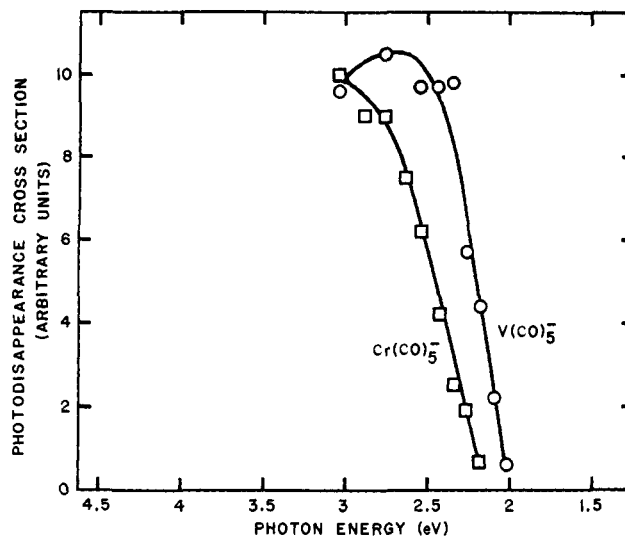
Figure 3. Photodisappearance results for metal pentacarbonyl anions.

The photodisappearance spectra of all the anions were similar, showing a well-defined threshold followed by a more or less well-defined peak. The relative rate of a photodecomposition process was shown to be obtainable from the observed icr signal decrease by[5]

$$k \propto (I_0 - I)/I$$

where k is the rate constant, I is the light-on signal, and I_0 is the light-off signal. The k values are converted to relative cross sections by dividing by the measured photon flux. In these experiments the relative cross sections for each ion were measured over a series of wavelengths, but no attempt was made to determine absolute cross sections or to relate the cross sections for one ion to those for another. Accordingly, the photodisappearance spectra for the anions observed have been normalized so that the peak cross sections for all the ions have roughly the same value, and these spectra are plotted in Figures 1–3. Photodisappearance was not reproducibly observed for $Mn(CO)_5^-$ between 800 and 300 nm, and it appears that over this wavelength region this ion may not have a photodisappearance cross section comparable in magnitude with the other ions studied.

Discussion

Within each series of anions containing a given number of carbonyls, the regular shift of the photodisappearance onset to higher energy on going toward metals of higher atomic number is the most striking feature of the data. As discussed above, the data will be interpreted on the assumption that the effect observed is photodissociation. By analogy with neutral metal carbonyls,[16] it seems reasonable to suppose that the energy required to dissociate a carbonyl group from a typical metal carbonyl anion would be in the vicinity of 1–1.5 eV. Since (with the exception of $Cr(CO)_3^-$)

(16) D. R. Lloyd and E. W. Schlag, *Inorg. Chem.*, **8**, 2544 (1969); F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Chapter 7; metal–carbonyl bond strengths of 1 to 1.5 eV may also be calculated for several metal carbonyl cations using appearance potential data in J. L. Franklin, F. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. **26** (1969).
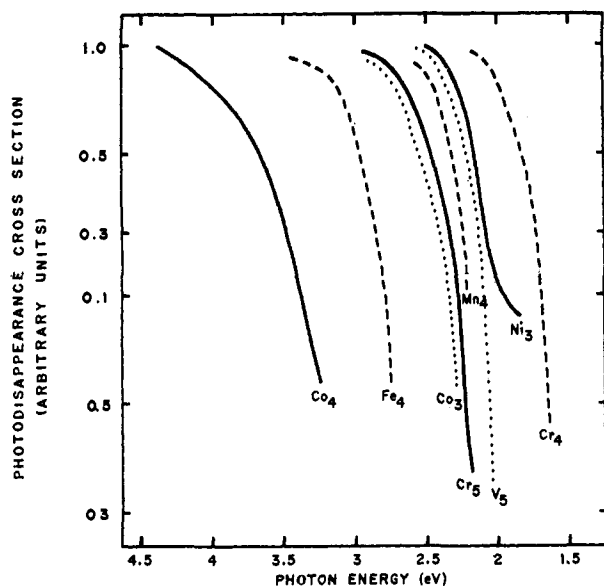
Figure 4. Logarithmic plot of the threshold curves obtained from Figures 1-3. The notation M_n denotes the curve for the anion $M(CO)_n^-$.

Figure 5. Plot of optical absorption peak energy derived from threshold photodetachment curves. Tricarbonyl anions (▲), tetracarbonyl anions (■), and pentacarbonyl anions (●) are indicated, and the dashed lines represent a guess as to the trend in each series.

all of the ions studied showed onsets at substantially greater energies than this, it may be assumed that the observed spectra are determined by the optical absorption properties of the anions, rather than reflecting the energetics of the dissociation process. Accordingly, the spectra may be considered to give optical absorption spectral information about these anions.

For many of the anions, experimental considerations limited the wavelength region of investigation to the low-wavelength side of the photodissociation peak, so that the peak wavelength was not directly observable. Assuming that the curve shapes are approximately similar in all cases, however, a reasonable comparison of the various species is possible. To facilitate this, the data are all plotted together in logarithmic form in Figure 4, in which the similarity of curve shapes is evident. The optical absorption peak energies obtained in this way are given in Table I. It should be

Table I. Optical Absorption Peak Energy of Metal Carbonyl Anions (eV)

$Mn(CO)_5$	(>4?)	$Mn(CO)_4$	2.9
$Co(CO)_4$	3.8	$V(CO)_5$	2.7
$Fe(CO)_4$	3.3	$Ni(CO)_3$	2.5
$Co(CO)_3$	3.0	$Cr(CO)_4$	2.2
$Cr(CO)_5$	3.0	$Cr(CO)_3$	<1.5

noted that while the absolute energies of these transitions are uncertain by several tenths of an electron volt (several thousand wave numbers), the comparison of the optical peak positions between two of the anions is much more precise. The curve for $Cr(CO)_3^-$ dropped off steadily for wavelength decreasing from the instrumental cut off at 810 nm, indicating a peak near or below 1.5 eV. The failure to observe $Mn(CO)_5^-$ photodisappearance suggests, but certainly does not prove, that any peak lies above 4 eV.

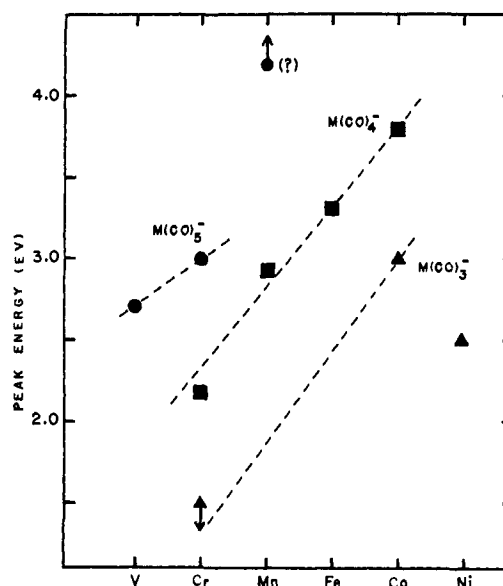The two consistent trends in the data are evident: a shift of the optical absorption of $M(CO)_n^-$ to higher

energy either on an increase in n or on moving to a metal of higher Z (except for $Ni(CO)_3^-$) (see Figure 5).

It is commonly assumed that whereas the free metal atoms for these elements have $3d^{n-2}\,4s^2$ (or $3d^{n-1}\,4s$) configuration, the neutral carbonyl molecule has $3d^n$ configuration, where the metal 3d orbitals mix with π^* ligand antibonding orbitals (among others) to some extent.[17] It would be difficult to rationalize the regular trends of the observed results in terms of d–d type transitions. Recent molecular orbital calculations[18] indicate that in $Ni(CO)_4$ and $Cr(CO)_6$, at least, the low optical transitions are all metal to ligand in character, and an interpretation of the present results in terms of metal-to-ligand charge-transfer transitions seems most reasonable. The energies of the low-lying ligand-type orbitals are probably not greatly affected by either the number of ligands or the nature of the metal atom. However, the metal 3d-type orbitals are probably greatly stabilized by an increase in the number of carbonyls (the $3d^{n+1}$ configuration of the bare metal anion is believed to be quite strongly unbound,[19] so that the ligands clearly play a large role in stabilizing the 3d orbitals) or by moving to a metal of higher atomic number (this is, at least, true for the neutral carbonyls[20]). Since any change which stabilizes the 3d electrons more than the ligand orbitals shifts the optical absorption to higher energy, the trends observed in the present data are entirely consistent with this qualitative interpretation assigning them as charge-transfer transitions. More quantitative or elaborate analysis hardly seems warranted at present for species whose structures are not known.

(17) (a) N. A. Beach and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 5713 (1968); (b) I. H. Hillier and V. R. Saunders, *Mol. Phys.*, **22**, 1025 (1971).
(18) A. F. Schreiner and T. L. Brown, *J. Amer. Chem. Soc.*, **90**, 3366 (1968).
(19) O. P. Charkin and M. E. Dyatkina, *J. Struct. Chem. (USSR)*, **6**, 397 (1965).
(20) D. R. Lloyd and E. W. Schlag, *Inorg. Chem.*, **8**, 2544 (1969).

The failure of $Ni(CO)_3^-$ to follow the general trend is readily accounted for in this interpretation. Since the 3d orbitals are filled in the neutral carbonyl, the extra electron in the anion must occupy a higher orbital, presumably a ligand orbital. The lowest optical transitions of the anion would presumably involve this higher energy electron, so that this anion should not be compared with any of the others, in which the lowest transition involves a 3d-type electron.

It may be pointed out that the interpretation presented above in terms of metal-to-ligand charge-transfer transitions is readily carried over essentially unchanged to photodetachment thresholds. The qualitative analysis is identical, with the role of the ligand acceptor orbitals simply being taken instead by the free-electron continuum states. Accordingly, the question of whether the process observed was photodissociation or photodetachment is seen in fact to be of small importance for a first qualitative interpretation of these results.

It may be noted, finally, that for one anion, $Cr(CO)_4^-$, direct comparison with condensed phase results is possible. While the solution spectrum of $Cr(CO)_4^-$ is not available to us, the ion is reported to be light yellow.[21] This is entirely consistent with the gas-phase spectrum, which has a weak tail extending just into the blue end of the visible spectrum. The gas-phase result indicates that the near-uv absorption of $Cr(CO)_4^-$ results in destruction of the ion, and this is in accord with the observation that the ion in solution is light sensitive to blue light.[21] While stabilization of the other anions studied here in condensed phase may be difficult, it would be of considerable interest to determine whether the visible region absorption peaks observed in gas phase are also observed in condensed phase, where the ion structures might be characterized.

(21) H. Stammreich, K. Kawai, Y. Tavares, P. Krumholz, J. Behmoiras, and S. Bril, *J. Chem. Phys.*, **32**, 1482 (1960).

Trigonal Bipyramidal Chromium Pentacarbonyl and Its Implications to Structure and Bonding Considerations of Pentacarbonyls and Pentacarbonyl Anions

Ernst P. Kündig and Geoffrey A. Ozin*

Contribution from the Lash Miller Chemistry Laboratories and Erindale College, University of Toronto, Toronto, Ontario, Canada. Received November 19, 1973

Abstract: The reactions of Cr atoms with CO at 4.2–10°K are investigated by matrix isolation infrared spectroscopy. Examination of the reaction products in $^{12}C^{16}O/Ar$ and $^{12}C^{16}O/^{13}C^{16}O/Ar$ matrices establishes the existence of a $Cr(CO)_5$ species having a D_{3h} trigonal bipyramidal stereochemistry. The data obtained using pure $^{12}C^{16}O$ are quite different from those in $^{12}C^{16}O/Ar$ matrices and exhibit a number of features which strongly suggest that square pyramidal $Cr(CO)_5$, originally thought to be the primary product of $Cr(CO)_6/Ar$ matrix photolyses, is actually $Cr(CO)_5S$, where S is either an O-bonded isocarbonyl or a sideways-bonded carbonyl ligand. The spectral and bonding properties of 15-, 16-, 17-, and 18-electron valence shell pentacarbonyls and pentacarbonyl anions are compared and a theory is presented which rationalizes the observed stereochemical changes on passing from the 16- and 18-electron trigonal bipyramidal pentacarbonyls to the 15- and 17-electron square pyramidal pentacarbonyls.

Recently Turner and coworkers[1] have reported infrared spectroscopic evidence for $Cr(CO)_5$ formed in the 228.8-nm matrix photolysis of $Cr(CO)_6/Ar$ mixtures at 15°K. Apart from the intense carbonyl absorption belonging to $Cr(CO)_6$, *three* new CO stretching modes were observed at 2093.4 (vw), 1965.4 (s), and 1936.1 (m) cm^{-1} and were assigned to a C_{4v} square pyramidal form of $Cr(CO)_5$. These deductions were based in part on the number, frequencies, and relative intensities of the observed CO stretching modes and by comparison with the results of Sheline and coworkers[2] for $Cr(CO)_5$ formed by photolysis of $Cr(CO)_6$ in frozen hydrocarbon glasses at 77°K.

Further investigations by Turner and coworkers[3] led them to suggest that the primary photolysis products of $Cr(CO)_6$ in weakly interacting matrices such as methane, or argon matrices doped with nitrogen, were $Cr(CO)_5S$, where S = CH_4 or N_2. As expected, the $Cr(CO)_5S$ complexes so formed had very similar infrared spectra to the proposed C_{4v} $Cr(CO)_5$ in Ar. On the basis of these results and the solution photolysis experiments of others,[4] it was proposed[1,3] that the primary photolysis product of $Cr(CO)_6$ in solution at room temperature was $Cr(CO)_5S$, where S = solvent.

An intuitively disconcerting aspect of Turner's results

(1) M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc. A*, 2939 (1971).
(2) I. W. Stolz, G. R. Dobson, and R. K. Sheline, *J. Amer. Chem. Soc.*, **84**, 3589 (1962); **85**, 1013 (1963).

(3) M. A. Graham, R. N. Perutz, M. Poliakoff, and J. J. Turner, *J. Organometal. Chem.*, C34, 34 (1972).
(4) M. A. El-Sayed, *J. Phys. Chem.*, **68**, 433 (1964); G. R. Dobson, *ibid.*, **69**, 678 (1965); J. Nasielski, P. Kirsch, and L. Wilputte-Steinert, *J. Organometal. Chem.*, **29**, 269 (1971).