# Production of Carbonyl Anions by the Vacuum Ultraviolet Photolysis of Matrix Isolated Metal Carbonyls

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*Summary* I.r. spectroscopic evidence is presented for the formation of $Ni(CO)_3^-$ from the vacuum u.v. photolysis of $Ni(CO)_4$ in low temperature matrices; photolysis of $Cr(CO)_6$ under similar conditions gives bands previously assigned to $Cr(CO)_5^-$, and of $Fe(CO)_5$ two new bands probably due to $Fe(CO)_4^-$.

CHARGED species have recently been generated in low temperature matrices by a variety of techniques. Co-condensation of alkali-metal atoms with $B_2H_6$ has led to the observation of the e.s.r. spectrum of $B_2H_6^-$ on visible photolysis,[1] and vacuum u.v. photolysis of matrix isolated $HCCl_3$ has led to the identification[2] of $CCl_3^+$. Most recently, co-condensation of alkali-metal atoms with $Cr(CO)_6$ and $Co(CO)_3NO$, diluted with Ar and CO, respectively, at 12K has resulted in i.r. spectra attributable to $Cr(CO)_5^-$ and $Co(CO)_4^-$ on u.v. photolysis.[3]

Preliminary experiments reporting the application of vacuum u.v. photolysis to carbonyl chemistry with special reference to nickel carbonyl are now described. $Ni(CO)_4$, matrix isolated in argon at 12K with a dilution of 1:8000 gives rise to three i.r. absorptions in the carbonyl region: 2052·2vs, 2048·1sh, and 2013·1w $cm^{-1}$.

The strong absorption is due to the $t_2$ carbonyl stretching mode of the $Ni(CO)_4$ tetrahedron, the weaker shoulder arising through a slight distortion from this geometry and the weak band due to $Ni(^{12}CO)_3{}^{13}CO$ in natural abundance. After 5 min photolysis using a microwave powered hydrogen discharge lamp (to be described in detail in a later publication) fitted with a LiF window, three new i.r. absorptions are produced, at 2016·3, 2177·9, and 1857·9 $cm^{-1}$. The first of these is readily identified as arising from the $Ni(CO)_3$ fragment which may be generated[4] by the u.v. photolysis of matrix isolated $Ni(CO)_4$. We were unable to detect the associated production of CO due to a weak absorption of 2138·1 $cm^{-1}$ caused by CO impurity in the matrix. The second absorption lies 39·8 $cm^{-1}$ to higher frequency than CO. This shift is similar to that observed (40·6 $cm^{-1}$) in the gas phase between $CO^+$ and $CO^5$. The third band lies to lower frequency than the carbonyl vibrations of any known binary nickel carbonyl (see Table).

TABLE. Carbonyl i.r. frequencies ($cm^{-1}$) of nickel carbonyls in Ar matrices

| | |
|---|---|
| $Ni(CO)_4$ | 2052 |
| $Ni(CO)_3$ | 2016 |
| $Ni(CO)_2$ | 1967[a] |
| Ni(CO) | 1996[a] |
| $Ni(CO)_3^-$ | 1858 |

[a] R. L. DeKock, *Inorg. Chem.*, 1971, **10**, 1205.

In order to identify the absorber responsible for the third band a sample of $Ni(CO)_4$ isotopically enriched with $^{13}CO$ was prepared by thermal exchange. Using the methods of Darling and Ogden[6] the carbonyl i.r. intensities of the matrix isolated parent and substituted carbonyls gave a ratio of $^{13}CO/^{12}CO$ ($=x$) of 0·4. After 5 min of vacuum u.v. photolysis four new bands appeared in the low frequency region at 1857·9, 1838·3, 1825·6, and 1814·7 cm$^{-1}$. This is a band pattern typical of an isotopically substituted tricarbonyl containing a $C_3$ axis, and the relative intensities calculated for this geometry[6] for $x = 0{\cdot}4$ agree well with those observed. In the high frequency region an absorption appeared at 2129·2 cm$^{-1}$ a shift of 48·7 cm$^{-1}$ (theoretical shift = 48·6 cm$^{-1}$).

Vacuum u.v. photolysis of $Cr(CO)_6$ matrix isolated in Ar led to spectral features similar to those previously observed (i) after the co-condensation at 12K of alkali-metal atoms and subsequent u.v. photolysis[3] of $Cr(CO)_6$–Ar mixtures, and (ii) on electron bombardment[7] of $Cr(CO)_6$ matrix isolated in Ar.

In both cases the anion $Cr(CO)_5^-$ was identified. By direct analogy the new nickel carbonyl species observed in this work is probably $Ni(CO)_3^-$. [This species is isoelectronic with $Cu(CO)_3$ but although i.r. evidence exists[8] for a binary copper carbonyl the species has not been definitely identified.] Thus, whilst u.v. photolysis of matrix isolated $Ni(CO)_4$ gives[4] $Ni(CO)_3 + CO$, vacuum u.v. photolysis of this carbonyl appears to lead to the charged species $Ni(CO)_3^-$ and $CO^+$. The frequency shift from neutral carbonyl to anion (*ca.* 160 cm$^{-1}$) is significantly larger than for[9] $Co(CO)_4$ to $Co(CO)_4^-$ (80—100 cm$^{-1}$) and may not be unconnected with the $d^{10}s^1$ configuration of the $Ni(CO)_3^-$ system. No absorption was found in the region 1950—1900 cm$^{-1}$ which could be assigned to the $a_1$ carbonyl stretching frequency of the $Ni(^{12}CO)_3^-$ anion. This suggests a planar or near planar geometry. Using the four absorptions found for the $^{12}CO/^{13}CO$ $Ni(CO)_3^-$ species, and the Cotton–Kraihanzel force field $f_{CO} = 14{\cdot}4 \pm 0{\cdot}1$ mdyn/Å and $f_{CO,CO} = 0{\cdot}5 \pm 0{\cdot}1$ mdyn/Å.

Similar experiments involving the vacuum u.v. photolysis of $Fe(CO)_5$ lead to two new i.r. bands around 1850 cm$^{-1}$, probably due to a Jahn-Teller distorted $d^9$ $Fe(CO)_4^-$ system. The frequencies lie approximately midway between $Fe(CO)_4$[10] and $Fe(CO)_4^{2-}$.

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