Photolysis of Tetracarbonylnickel, $Ni(CO)_4$, in Rare-gas Matrices at 15°K: Evidence for Tricarbonylnickel, $Ni(CO)_3$

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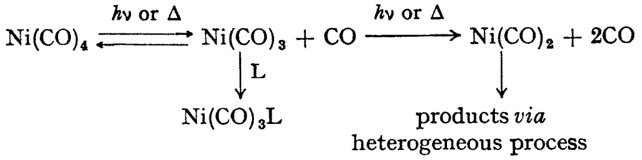
Summary I.r. evidence suggests that photolysis of $Ni(CO)_4$ produces CO and an unstable species which recombine when the temperature is raised from 15°K to 30°K.

THE most recent studies on photochemical behaviour,[1] substitution reactions,[2a] and thermal decomposition[2b] of $Ni(CO)_4$ suggest mechanisms summarised by:



$$\begin{array}{ccc} Ni(CO)_4 \overset{h\nu \text{ or } \Delta}{\rightleftarrows} & Ni(CO)_3 + CO \xrightarrow{h\nu \text{ or } \Delta} & Ni(CO)_2 + 2CO \\ & \downarrow L & \downarrow \\ & Ni(CO)_3L & \text{products via heterogeneous process} \end{array}$$

Photolysis of $Ni(CO)_4$ in inert matrices at 15°K with an iodine-line source (2062 Å) or a medium-pressure mercury arc produced two new i.r. bands in the C–O stretching frequency region. These bands increased and decreased in intensity in the same proportion. The relative intensity of the bands depended on the matrix used (Table). The Figure illustrates an argon matrix experiment.

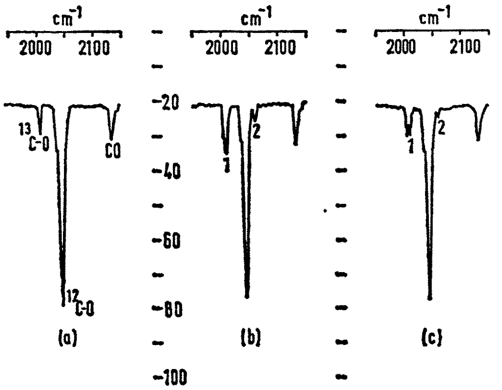


FIGURE. *I.r. spectra from* $Ni(CO)_4$ *in argon* (1:160) *experiment*; (a) *after* 1 *hr. deposition of gas mixture*; (b) *after* 1 *hr. photolysis with medium-pressure mercury arc*; (c) *after* 5 *min. with temperature held at* 30° K *and re-cooled to* 15° K.

We assign the two new bands to the doubly-degenerate (E) and symmetric (A_1) C–O stretching vibrations of a non-planar $Ni(CO)_3$ (C_{3v}) fragment.† The ratio of the E to A_1 vibrational mode intensities increased with increasing size of matrix atom. This suggests that the larger the matrix atom the greater the chance of relaxation to the planar (D_{3h}) configuration, which is probably the stable gas-phase configuration. A further point is that, unlike the case of $HMn(CO)_5$[3] and $M(CO)_6$ (M = Cr, Mo, W),[4] it has not proved possible to reverse the photolytic step by irradiation with light of different frequency. Reversibility depends on the photolytically generated fragment having a different u.v. absorption spectrum from the parent carbonyl; Callear[1] concluded that $Ni(CO)_3$ must have a spectrum identical with that of $Ni(CO)_4$.

On raising the temperature of the matrix to 30° K for 5 min. and re-cooling to 15° K there was approximately 50% reconversion of the fragment plus CO into $Ni(CO)_4$ in all three matrices. This is considerably more recombination than takes place with $HMn(CO)_4$ or $M(CO)_5$ with CO. The thermal reversibility may be due to softening of the matrix and a decrease in its isolating properties. This seems unlikely since the amount of recombination is similar for three matrices whose annealing properties at 30° K are different. We prefer to think that the reverse thermal reaction between $Ni(CO)_3$ and CO is prevented at temperatures well below 30° K by the activation energy for the reaction.

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TABLE

Spectral properties of $Ni(CO)_4$ *and fragment*

	$Ni(CO)_4$, T_2 C—O stretching mode (cm.$^{-1}$)		$Ni(CO)_3$ C—O stretching mode† (cm.$^{-1}$)	
Matrix [$Ni(CO)_4$: matrix]	^{13}C—O	^{12}C—O	$\nu_1(E)$	$\nu_2(A_1)$
Argon (1:160)	2012	2051	2016 (5)	2065 (1)
Krypton (1:190)	2007	2046	2011 (12)	2061 (1)
Xenon + 8% krypton (1:200) . .	2004	2043	2007 (~20)	2058 (1)

† Relative intensities in brackets.

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† A bent $Ni(CO)_2$ fragment would also have two i.r. absorptions in the C–O stretching region, but the amount of CO produced in these experiments suggests that this alternative explanation is unlikely.

[1] A. B. Callear, *Proc. Roy. Soc.*, 1961, *A*, **265**, 71.
[2] J. P. Day, R. G. Pearson, and F. Basolo, *J. Amer. Chem. Soc.*, 1968, **90**, (a) 6927; (b) 6933.
[3] A. J. Rest and J. J. Turner, *Chem. Comm.*, 1969, 375.
[4] A. J. Rest and J. J. Turner, to be published.