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HALOGENOTRICARBONYLNICKEL ANIONS

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The displacement reaction of the carbonyl group in metal carbonyl by halide ions with formation of halogenometalcarbonyls was previously reported for chromium, tungsten and molybdenum hexacarbonyls1), manganese2), rhenium3) and rhodium4) halogenocarbonyls, pentacarbonyliron5) and dinitrosyldicarbonyliron6).

We now wish to report the formation of halogenotricarbonylnickel anions from tetracarbonylnickel and halide ions, according to the equilibrium [I] :

$$Ni(CO)_4 + MX \rightleftharpoons M[Ni(CO)_3X] + CO \qquad [I]$$

$(X = Cl^-, Br^-, J^-)$

The reaction occurs in aprotic solvents at room temperature.

The monosubstituted product is always obtained even working in a large excess of halide ions. To obtain a complete conversion with evolution of one mole of carbon monoxide per mole of tetracarbonylnickel in the presence of the stoichiometric quantity of halide ions, we adopted the following procedure : 35 ml of anhydrous ether, 30 ml of dimethylformamide, 1.5 ml of tetracarbonylnickel and 3.7g of tetrabutylammonium iodide were mixed in a 100 ml flask under N_2. The solution was heated under stirring until 15 ml of ether were distilled. The distillate was added to the reaction mixture and redistilled. The residual ether was removed under reduced pressure (20 mm Hg) at room temperature. In the solution thus obtained nickel and iodide were present in 1:1 ratio. Tetracarbonylnickel was absent.

The halogenocarbonylnickel complexes are not stable in the pure state. Attempted isolation always resulted in the decomposition of the complex according to the equation [II] :

$$4M[Ni(CO)_3X] \longrightarrow 4\ MX + Ni + 3\ Ni(CO)_4 \qquad [II]$$

The formation of carbonylnickelates of the type $Ni^{++}[Ni_x(CO)_y]^{--}$ from a disproportionation7) reaction was also observed.

The halogenotricarbonylnickel anions are stable in solution in the absence of air even at high temperature (70-80°C). The stability and the rate of formation decrease in the series $J^- > Br^- > Cl^-$. These complexes easily react with triphenylphosphine, giving irreversibly tricarbonyl(triphenylphosphine)nickel [III] :

$$M[Ni(CO)_3X] + P(C_6H_5)_3 \longrightarrow Ni(CO)_3P(C_6H_5)_3 + MX \qquad [III]$$

The frequencies of absorption in the infrared of some of these compounds in the C-O stretching region are reported in Table I.

TABLE I

Infrared Spectra in the C-O Stretching Region of the Halogenotricarbonylnickel Anions

$\nu(C{=}O)cm^{-1}$ and suggested assignments based on a C_{3v} model

	A'	E	Solvent
$Bu_4N[Ni(CO)_3J]$	2049.0 (m)	1958.1 (s)	DMF
$Bu_4N[Ni(CO)_3J]$	2049.0 "	1958.4 "	acetone
$Na[Ni(CO)_3J]$	2048.5 "	1958.0 "	DMF
$Bu_4N[Ni(CO)_3Br]$	2051.0 "	1955.0 "	"
$Bu_4N[Ni(CO)_3Cl]$	2049.0 "	1953.0 "	"
$C_6H_5\text{-}CH_2\cdot Me_3N[Ni(CO)_3Cl]$	2049.0 "	1953.8 "	"
$Ni(CO)_4$	2125.5 (w)	2042.0 "	"

Infrared measurements were recorded on a Perkin Elmer 125 grating spectrophotometer. Frequencies are accurate to ± 0.5 cm^{-1}.

The observed values are in agreement with the postulated C_{3v} 8) structure. According to the literature 9) 10) 11), compounds of the type $Ni(CO)_3L$ show a decreasing stretching frequency on passing from CO to $P(C_6H_5)_3$ and to $P(C_4H_9)_3$. We repeated these determinations in dimethylformamide and found respectively 2125.5, 2068.5 and 2061.0 cm^{-1}. The value of 2049 cm^{-1}, found for X^-, indicates that anions of this kind cause a charge transfer even greater than trialkylphosphines. This seems to be attributed to the fact that in this case the halide ligand derives from a charged species.

The small differences observed in the frequencies of the C-O vibration on varying X^-(Cl^-, Br^-, J^-) indicate an analogous action of the three halides.

As to their properties, the halogenotricarbonylnickel anions appear to be good catalysts for carbonylation of benzyl chloride 12) and much more active than tetracarbonylnickel in promoting the carbonylation with acetylene insertion of acylic halides 13). The activating action of iodide and bromide ions in other reactions catalyzed by tetracarbonylnickel (e.g. acrylic syntheses 14), carbonylation of ethers 15) etc.) is also likely to be due to the formation of the above complexes. Further studies concerning reactivity are in progress.

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