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METAL ION INTERACTIONS WITH $Mn(CO)_5^-$ IN ETHER SOLUTIONS

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Summary

Infrared spectra of $LiMn(CO)_5$ and $NaMn(CO)_5$ in the CO stretching region have been examined in ether solvents. These spectra are attributed to an ion-paired species of C_{3v} symmetry in which alkali metal ion is bonded to carbonyl oxygen. Simple force constant calculations yield CO stretching force constants which are reasonable in terms of the structure hypothesized. In THF the $NaMn(CO)_5$ spectra show the presence of an equilibrium between solvent-separated and contact ion-pairs. Treatment of $NaMn(CO)_5$ in THF with Mg^{2+} gives a species whose IR spectrum is also consistent with a Mg—OC interaction. Mixtures of $LiMn(CO)_5$ or $LiCo(CO)_4$ with CH_3Li in ethyl ether were examined at —50° using ^7Li NMR. Only resonances due to the pure components were observed, indicating that no mixed tetrameric species of the form $Li_4Me_nX_{4-n}$ are formed.

Introduction

Edgell and coworkers have concluded [1], on the basis of infrared studies, that in relatively non-polar solvents, such as tetrahydrofuran (THF), certain alkali metal salts, among them $NaCo(CO)_4$, exist primarily as solvated ion-pairs, in which substantial, intimate contact exists between anion and cation. Absorptions in the CO stretching region of the infrared spectrum indicate that bonding to sodium occurs at a single carbonyl group.

Similar behavior seems likely in $Mn(CO)_5^-$ alkali metal salts, but the geometrical possibilities for the interaction are more numerous. We have examined the solution infrared spectra in THF and in the more weakly coordinating, less polar solvent, ethyl ether.

Although the idea of ion pairing in solutions of anionic carbonyl salts has apparently gained acceptance [2—7], little is known regarding multi-associated

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species, e.g., dimers, tetramers, etc., which might occur. Lithium compounds, in particular the alkyls and halides, are known [8] to form oligomeric species in various solvents, including ethers. We have examined the ^{7}Li NMR spectra of mixtures of methyllithium with $LiMn(CO)_5$ and $LiCo(CO)_4$ in ethyl ether in search of mixed oligomeric species of the type observed [9] for alkyllithium—lithium halide mixtures.

Experimental

Materials

Since $NaMn(CO)_5$ and $LiMn(CO)_5$ are extremely air sensitive, great care was taken to exclude oxygen from the samples. All syntheses, preparation of solutions, and loading of sample cells were performed in a dry, oxygen-free atmosphere in a glove box.

$NaMn(CO)_5$ was prepared from $Mn_2(CO)_{10}$ (Pressure Chemical Company) and dilute sodium amalgam in THF [10]. To prepare $LiMn(CO)_5$, a suspension of a six-fold excess of lithium sand (Foote Mineral Company) in Et_2O was stirred vigorously using a glass-covered stirring bar. After about an hour, shiny platelets of lithium metal appeared on the liquid surface; $Mn_2(CO)_{10}$ was then added. The mixture was stirred for about four hours, then filtered. The solvent was stripped off at room temperature to give the product.

$LiCo(CO)_4$ etherate was obtained in a similar manner.

These compounds are too air sensitive to be analyzed by conventional means. However, by utilizing a tared metal sleeve which was filled with sample, sealed, and reweighed, accurate carbon analyses were obtained. These results were in excellent agreement with the calculated percentage of carbon for both $NaMn(CO)_5$ and $LiMn(CO)_5$. The technique also indicated the absence of hydrogen from both samples. A further check on sample purity involved allowing a sample to decompose in air, then analyzing the residues to check for a 1/1 molar ratio of alkali metal to transition metal. For $NaMn(CO)_5$ and $LiCo(CO)_4$ the observed ratio was very close to 1. The $LiMn(CO)_5$ residues gave variable results, but infrared and NMR spectral evidence indicated that the material was of the same purity as the other compounds.

Magnesium bromide monoetherate was prepared by slow addition of freshly distilled 1,2-dibromoethane to a stirred suspension of excess magnesium metal in Et_2O under dry nitrogen. After reaction had ceased, the mixture was filtered, and the solvent removed under vacuum, leaving white, anhydrous $MgBr_2 \cdot Et_2O$. (Found: Mg, 9.58; Br, 62.45; C, 17.43; H, 3.86. $C_4H_{10}Br_2MgO$ calcd.: Mg, 9.42; Br, 61.95; C, 18.60; H, 3.90%.)

Methyllithium was obtained commercially (Foote Mineral Company) as a 1 *M* solution in Et_2O.

Reagent grade Et_2O was purified by distillation from ethyllithium under argon and was stored in an argon atmosphere. THF was distilled under N_2 from $LiAlH_4$ and was stored over sodium wire. Both ethers were stored in amber bottles to minimize peroxide formation. Reagent grade dimethyl formamide (DMF) was dried and deaerated by treatment with 3A molecular sieves and by bubbling dry N_2 through overnight.

We are grateful to E.I. duPont de Nemours and Co., Inc., for a sample of the crown ether, dicyclohexyl-18-crown-6.

Infrared spectra

Solutions of nominal concentrations 0.04 and 0.003 *M* were prepared by adding solvent to the dry salts. Sodium chloride fixed-pathlength cells 0.03 and 0.5 mm were employed.

Spectra were obtained on a Beckman IR-7 spectrophotometer, frequency calibrated to ± 1 cm^{-1} with water vapor. Each sample was run in the double beam mode against a reference cell containing pure solvent.

NMR spectra

The ^{7}Li NMR samples were prepared in standard 5 mm tubes. Since the ^{7}Li chemical shift range is so small, it was necessary to prepare two samples, one containing the external standard (LiBr/methanol) in a capillary tube, and one with no standard. To avoid decomposition in the methyllithium/$LiMn(CO)_5$ and methyllithium/$LiCo(CO)_4$ mixtures, the samples were prepared directly in the NMR tubes, then immediately removed from the dry box and kept at or below dry ice temperature. The ^{7}Li NMR spectra were obtained on a Varian HA-100 spectrometer using the unlocked mode.

Results and discussion

The unperturbed anion, $Mn(CO)_5^-$, should possess D_{3h} symmetry; in diglyme and THF the expected two IR-active CO bands occur at 1863 (E') and 1898 (A_2'') cm^{-1} [11]. In DMF, $NaMn(CO)_5$ gives the simple pattern characteristic of D_{3h} symmetry, with absorptions at 1862 and 1897 cm^{-1}, in approximately 3/2 intensity ratio. Solutions of $NaMn(CO)_5$ and $LiMn(CO)_5$ in Et_2O, however, yield rather complex spectra (Fig. 1 and Table 1). Although some

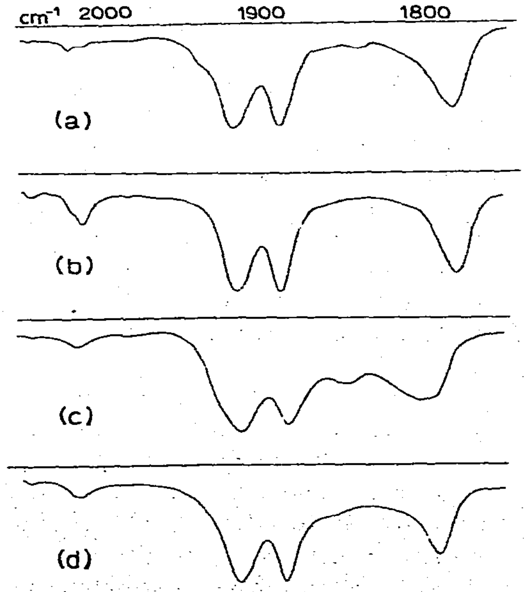

Fig. 1. Infrared spectra in ether. (a) $LiMn(CO)_5$, 0.04 *M*; (b) $LiMn(CO)_5$, 0.003 *M*; (c) $NaMn(CO)_5$, 0.04 *M*; (d) $NaMn(CO)_5$, 0.003 *M*.

TABLE 1

IR BANDS IN CO STRETCHING REGION FOR 0.003 *M* $NaMn(CO)_5$ IN VARIOUS SOLVENT SYSTEMS

Et_2O	5% THF/ 95% Et_2O	50% THF/ 50% Et_2O	THF	$LiMn(CO)_5$/ Et_2O	Assignment
1792 cm^{-1}	1811 ms	1820 m	1828 m	1781 s	Ion-pair (A_1)
N.o. [a] (1803, m(sh)) [b]					Multi-associated ion-pair
N.o. (1851, w)		ca. 1855 w(sh)			Multi-associated ion-pair
		ca. 1865 w(sh)	1862 s		$Mn(CO)_5^-$, D_{3h} (E')
1887 s	1833 s	1878 s	1873 m(sh)	1890 s	Ion-pair (E)
			1899 s(br) }		$Mn(CO)_5^-$, D_{3h} (A_1'')
1916 s	1913 s	1904 s		1918 s	Ion-pair (A_1)
1983 vw					$Mn_2(CO)_{10}$
2013 m (2013 vw(sh))		2013 w [c]	2009 w [c]	2013 m	$Mn_2(CO)_{10}$
ca. 2018 w(sh) (2018 w)	2017 w			N.o. (2020 m)	Ion-pair (A_1)
2046 vw (2046 vvw)				2045 w	$Mn_2(CO)_{10}$

[a] N.o. not observed. [b] Figures in parentheses give data for 0.04 *M* solutions, where these differ from that at 0.003 *M*. [c] We are uncertain whether this peak is due to $Mn_2(CO)_{10}$ formed in situ or to the salt.

details of the spectra vary with concentration or with the alkali metal ion, all four spectra exhibit three strong absorptions in the carbonyl stretching region. Attempts to determine the characteristic absorptions of a relatively unperturbed anion of D_{3h} species in Et_2O were stymied by the insolubility of such salts as $Et_4NMn(CO)_5$. However, a 0.003 *M* Et_2O solution of $NaMn(CO)_5$ containing a slight excess of dicyclohexyl-18-crown-6, which is known [12] to complex strongly with Na^+, exhibits strong absorptions at 1871 and 1902 cm^{-1}. These may be taken as at least upper limits for the frequencies of the D_{3h} species in Et_2O.

We propose that ion-pairing via a carbonyl oxygen—alkali metal interaction is responsible for the three major bands appearing in the Et_2O solution spectra. Variation in band positions with change in cation suggests that a cation—anion interaction of some type is involved. The low frequency peak occurs at too low a frequency to arise from a terminal CO group; it must be due to a bridged carbonyl species of some type. Thus, cation—anion interaction must occur via a carbonyl group, and not at manganese. The alkali metal ion could interact with either the carbon *or* the oxygen of a carbonyl to produce a "bridged" species. However, oxygen is considerably more basic than carbon in this instance, and would thus interact better with the Lewis acid, M^+.

Compounds containing main group—carbonyl oxygen bonds have been known for a few years: magnesium or aluminum have been found to act as the acceptor atom in several cases [2—5]. Recent studies indicate that certain transition metals, e.g., manganese or europium, also bond to carbonyl oxygen [6, 7]. A similar Na^+—OC interaction has been suggested for $NaCo(CO)_4$ in THF [1].

There are three reasonable possibilities for the configuration of the ion-pair in solution. These are shown in Fig. 2 and are labelled with the appropriate point group designations and the numbers of IR-allowed CO stretches. The IR

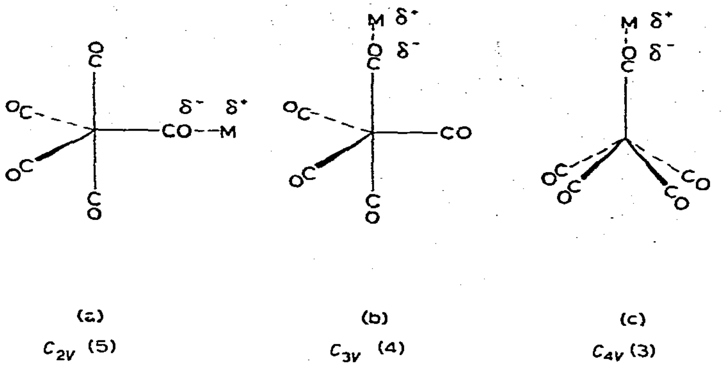

Fig. 2. Possible structures for $MMn(CO)_5$ in ether solution. The number of IR-allowed CO stretching modes is shown in parentheses.

evidence suggests that the solution species has the C_{3v} configuration: We note the existence of a weak, high-frequency band, at 2020 cm^{-1}, in the Li^+ spectra. The asymmetry of the 2013 cm^{-1} $Mn_2(CO)_{10}$ peak in the $NaMn(CO)_5$ spectra indicates that an unresolved peak may lie within the envelope of the curve, at ca. 2018 cm^{-1}. If this weak, high-frequency band arises from the same species as do the three strong absorptions, the band pattern is exactly as would be expected for a C_{3v} species. For $LiMn(CO)_5$, for example, the assignments are: 2020 cm^{-1} w(A_1 planar stretch); 1918 cm^{-1} s (A_1 axial stretch); 1890 cm^{-1} s (E); 1781 cm^{-1} s (A_1 axial stretch of "bridging" carbonyl).

The observed spectrum is not consistent with either of the other two structures in Fig. 2. The number and expected relative intensities of IR-allowed stretches for (a) or (c) do not conform to the observed pattern.

The comparative values obtained for the CO stretching force constants in $Mn(CO)_5^-$ and M^+—$OCMn(CO)_4^-$ provide an interesting insight into the redistribution of electron density which occurs upon contact ion-pair formation. We employ a simplified force field which includes only the CO stretches as diagonal elements in the force constant matrices, and only CO stretch-stretch interactions as off-diagonal elements [13]. Because the vibrational data are very limited, even this simplified force field contains more parameters than can be fixed. The recently-reported Raman and IR data for $Fe(CO)_5$ [14] were employed to calculate the two diagonal and three off-diagonal force constants (See Fig. 3) for that molecule. The off-diagonal elements for $Fe(CO)_5$ were employed along with the two observed IR transitions of $Mn(CO)_5^-$ to calculate k_1 and k_2 for the latter.

The IR vibrational data for $Na^+OCMn(CO)_4^-$ were fit for several different assumptions regarding the off-diagonal terms (Table 2). The values assumed for $Mn(CO)_5^-$ did not permit a reasonable fit in terms of the diagonal elements. It is evident, however, that an acceptable fit can be obtained for satisfactory values of the off-diagonal elements. Further, the diagonal force constants do not change by more than about 0.2 mdyne/Å over a fairly wide range of choices for the off-diagonal terms.

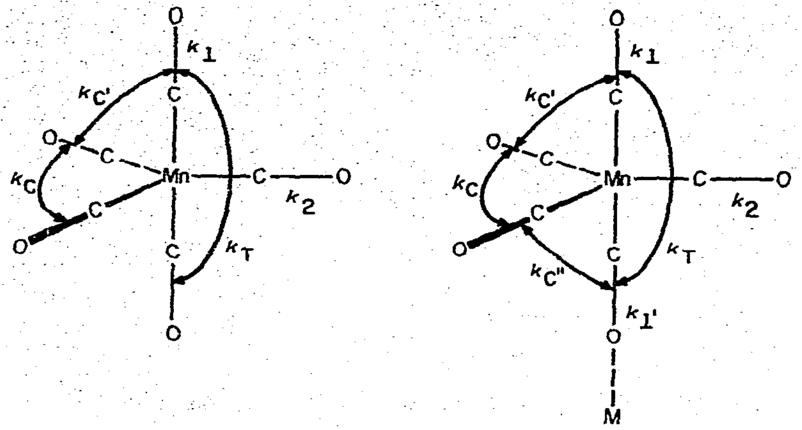

Fig. 3. CO stretching force constants in $Mn(CO)_5^-$ and $M^+\cdots OCMn(CO)_4^-$.

Although these force constant calculations are very crude they serve to support the choice of the C_{3v} model for the alkali metal ion—$Mn(CO)_5^-$ species. The CO force constants for $Mn(CO)_5^-$ are considerably lower than for $Fe(CO)_5$, as expected. The alterations in force constants upon coordination to the alkali metal ion are also in the expected direction. All increase except for the CO which is coordinated. The coordinated CO force constant decreases by about 2 mdyne/Å relative to the value for $Mn(CO)_5^-$. The change is slightly larger for the lithium salt than for the sodium. Polarization of the manganese *d* electrons towards the alkali metal ion could account for these changes. Increased electron flow into the π^* orbital of bridging CO would cause a substantial decrease in the force constant of this group, while the loss of metal d_π electrons from the other carbonyls would cause their valence force constants to increase somewhat above the values in the unperturbed anion.

A calculation was carried out in which a Na—O stretching force constant of 0.9 mdyne/Å and interaction constant with the adjacent CO stretch of 0.3 mdyne/Å were included. The calculated Na—O stretching mode occurs at about

TABLE 2

CARBONYL STRETCHING FORCE CONSTANTS (mdyne/Å)

	$Fe(CO)_5$ (CS_2)	$[Mn(CO)_5]^-$ (DMF)	$NaMn(CO)_5$ [a] (Et_2O)	$LiMn(CO)_5$ (Et_2O)
k_1	16.97	15.05	15.43	15.44
k_2	16.44	14.36	14.80	14.85
k_1'			13.20	13.03
k_c	0.36	0.36	0.42	0.42
k_c'	0.28	0.28	0.40	0.40
k_c''			0.40	0.40
k_t	0.50	0.50	0.50	0.50

[a] Other force constant vectors which reproduced the observed CO frequencies in the calculation are:
(15.36, 14.83, 13.18, 0.44, 0.40, 0.32, 0.60);
(15.67, 14.75, 13.12, 0.36, 0.42, 0.28, 0.50);
(15.33, 14.85, 13.14, 0.47, 0.40, 0.32, 0.50).

400 cm^{-1} ; the value of k'_1 is virtually unaffected. Na$^+$—solvent vibrations are observed at ca. 200 cm^{-1} [1]. Thus our calculated frequency for a Na—O stretch represents an upper limit for the process involved; the actual contribution of this vibration to the adjacent carbonyl stretch must certainly be negligible. Thus it appears that the *relative* CO stretching frequencies are well represented by the simple model.

Several weak, concentration-dependent bands were observed in the IR spectra. The 0.04 M solutions of NaMn(CO)$_5$ and LiMn(CO)$_5$ in Et$_2$O each exhibit a weak band at ca. 1850 cm^{-1}. Also, the asymmetry of both absorptions due to axial CO indicates the presence of additional absorptions in these regions. Since all these weak absorptions disappear upon dilution to 0.003 M, they are probably due to a multi-associated species. Infrared studies of NaCo(CO)$_4$ in THF have indicated presence of triple ions in the 0.03 M concentration range [1].

The alkali metal ion, in addition to being bound to an anion, is bound to a number of solvent molecules. The more strongly the cation is solvated, the weaker must the ion-pair interaction become. The low frequency IR band, which arises from the bridging CO, should reflect most directly the decrease in strength of the M—OC bond as solvent basicity increases.

The spectrum of NaMn(CO)$_5$ (0.003 M) in THF (Fig. 4) is considerably more complicated than that observed in Et$_2$O at the same concentration. Absorptions occur at 1828 m; 1862 s; 1873 m(sh); 1899 s(br); and 2009 cm^{-1} w. The 1899 cm^{-1} absorption is rather broad and may consist of more than one component. The assignments of these bands in relation to those observed for NaMn(CO)$_5$ in ether and DMF are depicted in Fig. 5.

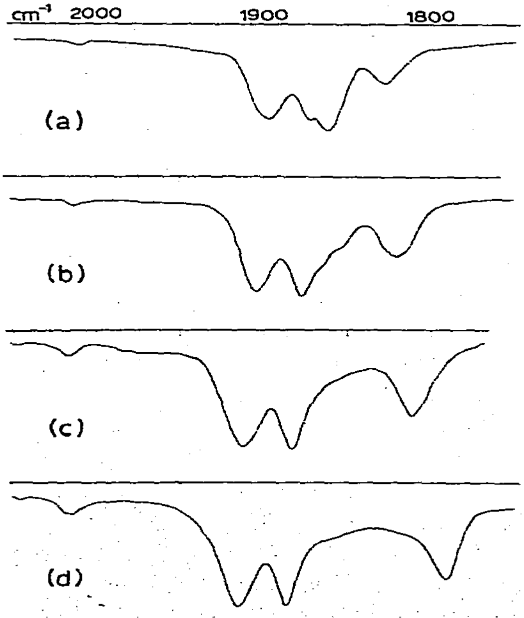

Fig. 4. Infrared spectra in the CO stretching region of 0.003 M NaMn(CO)$_5$ in ether/THF mixtures. (a) Neat THF; (b) 50% THF; (c) 5% THF; (d) 100% ether.

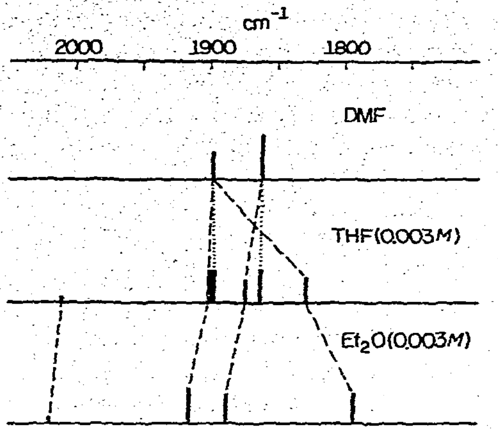

Fig. 5. Schematic diagram of frequency shifts and splittings for $NaMn(CO)_5$ in different solution environments.

The three main bands attributed to the ion pair in Et_2O should be shifted, in THF, towards the frequencies of absorption of the "free" anion; i.e., the 1887 and 1916 cm^{-1} Et_2O bands should be shifted toward the 1862 and 1898 cm^{-1} positions of $Mn(CO)_5^-$. Also, the absorption at 1792 cm^{-1} in Et_2O should be shifted to higher frequencies, due to weakening of the Na—OC bond. Thus, in THF the 1828 cm^{-1} peak is assigned to the bridging CO of the ion pair, and two of the bands in the 1862—1905 cm^{-1} region correspond to the other strong absorptions noted in the Et_2O case. Since the Na—OC bond still retains significant strength in THF (as evidenced by the position of the bridging CO band), these other two absorptions should occur above the frequencies of the unperturbed anion. Hence, 1873 and ≈ 1902 cm^{-1} are assigned to the ion-paired moiety. Bands at ≈ 1898 and 1862 cm^{-1}, the frequencies assignable to free $Mn(CO)_5^-$ in THF, then give evidence that a substantial amount of the solute exists as solvent-separated, or completely dissociated ions. Thus in THF an equilibrium apparently exists between the ionic and ion-paired species:

$$(\text{solvent})Na^+ + Mn(CO)_5^- \rightleftharpoons (\text{solvent})Na^+\text{—}(OC)Mn(CO)_4^-$$

Similar equilibria are probably responsible for "anomalous" IR spectra in THF of sodium salts of other carbonyl anions, e.g., $Na_2[M_2(CO)_{10}]$, (M = Cr, Mo, W) [15].

The 2009 cm^{-1} band found in THF solutions of $NaMn(CO)_5$ may correspond to the high frequency ion-pair absorption observed in Et_2O. However, since $Mn_2(CO)_{10}$ is found to absorb at this frequency in THF, the assignment is not conclusive.

To provide further evidence in support of the THF assignments, we utilized mixtures of THF and Et_2O. The spectra of 0.003 M $NaMn(CO)_5$ in 50/50 THF/Et_2O (by volume) and in 5/95 THF/Et_2O were recorded (Fig. 4 and Table 1). The three most intense absorptions observed in Et_2O shift monotonically as solvent composition approaches that of pure THF. The total frequency shift of the bridging CO band, on going from pure Et_2O to pure THF, is considerably larger than that measured for either of the other two absorptions. This fact simply reflects the greater sensitivity of this carbonyl group to solvent composition, which is reasonable in view of its proximity to the solvated alkali metal ion.

The fact that the ion-paired species absorbs at intermediate frequencies in the mixed solvent media, rather than exhibiting discrete absorptions at roughly the same positions as in each of the pure solvents, is evidence that the $Mn(CO)_5^-$ moieties experience an intermediate environment resulting from the mixed solvation of the cation. For the three most intense ion-pair bands, plots of frequency vs. solvent composition were made (Fig. 6). The large frequency changes which occur with addition of only a small percentage of THF indicate, as would be expected, that THF preferentially solvates the alkali metal ion.

Collman and coworkers have shown [16] that ion-pairing in alkali metal salts of $RFe(CO)_4^-$ (THF solution) dramatically enhances the rate of conversion of aliphatic halides to aldehydes and ketones, while addition of a small amount of a more basic solvent strongly inhibits the process. The first step of the mechanism is a reversible alkyl migration to an adjacent carbonyl. This migration is apparently greatly facilitated if the carbonyl is bound to a polarizing cation; in the presence of added base, the cation is strongly solvated. The equilibrium is thus shifted in favor of relatively unreactive solvent-separated ion pairs. These observations are consistent with our finding that the solution structure of the ion pair in $NaMn(CO)_5$ is highly sensitive to solvent basicity.

Treatment of a THF solution, 0.003 *M* in $NaMn(CO)_5$, with excess $MgBr_2 \cdot Et_2O$ gave a solution whose IR spectrum displays strong absorptions at 1773, 1893, and 1920 cm^{-1} and a well-defined, though weak, band at 2024 cm^{-1}. The spectrum is consistent with that expected for a magnesium—carbonyl

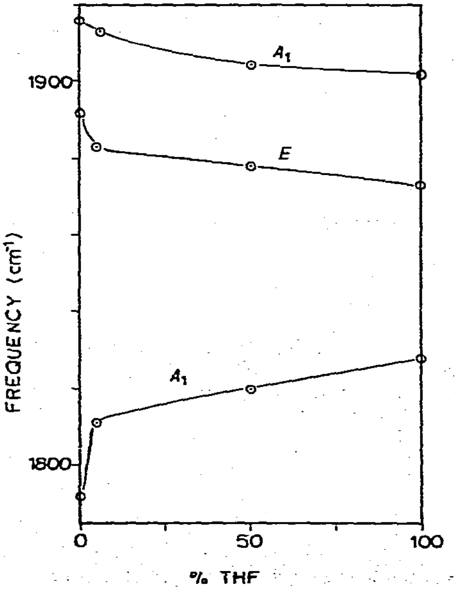

Fig. 6. Carbonyl stretching mode frequencies for $NaMn(CO)_5$ vs. solvent composition.

bonded moiety of local C_{3v} symmetry*. Attempts to study the Mg^{2+}—OC interaction in Et_2O were unsuccessful; apparently the ion pair is unstable with respec to $Mn_2(CO)_{10}$ and an unknown reduction product.

Alkyllithium and lithium halide compounds are known to form oligomeric species in ether [8]. Furthermore, mixtures of alkyllithium compounds and lithium halides in ether have been shown [9], by the use of ^{7}Li NMR, to form mixed tetrameric species, in which all the possible compounds $R_nLi_4X_{4-n}$ exist.

Several attempts were made to determine the degree of association of $LiMn(CO)_5$ in Et_2O using a vapor pressure lowering technique. However, the great sensitivity of the method to any impurity, and the gradual decomposition of $LiMn(CO)_5$ in Et_2O at room temperature made it impossible to obtain any but qualitative measurements, which indicated that the association number of the salt is somewhat larger than one.

^{7}Li NMR experiments were carried out on ether solutions of $LiMn(CO)_5$, $LiCo(CO)_4$, and mixtures of each of these compounds with methyllithium, in an attempt to observe mixed tetrameric species of the sort found for MeLi/LiX mixtures.

The chemical shifts of $LiMn(CO)_5$ and $LiCo(CO)_4$ (relative to external LiBr/MeOH) are 1.08 and 1.05 ppm upfield, respectively. Both of these resonances display rather narrow line widths. The mixtures of the carbonyl species with MeLi were examined at —50°. In neither case was a resonance observed which could be attributed to a mixed oligomeric species; only peaks due to the pure components were seen. In the context of earlier studies of CH_3Li mixtures with LiI or LiBr in ether, these results suggest that neither $LiCo(CO)_4$ nor $LiMn(CO)_5$ has a significant tendency to form highly structured associated species in solution.

Acknowledgements

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* The Mg—O bonded moiety $Mg(py)_4[Mn(CO)_5]_2$/toluene yields carbonyl bands at 1721 s, 1904 s, 1928 s, and 2031 w cm^{-1} [5].

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