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Solvent Effects on Metal Carbonyls and Related Compounds

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With 6 Figures

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The observed solvent effects on the CO and NO frequencies in metal carbonyls and related compounds are shown to be influenced by the solvent acceptor properties, as expressed by the acceptor number.

The qualitative theory that in metal carbonyls the metal to carbon bonding involves a combination of C → *M* dative σ-bonding with *M* → C dative π-bonding appears universally accepted. The metal—carbon distances may be considered as due to the intermolecular interaction, which induces lengthening of the CO bonds. The CO distances are longer in the complexes than in the gaseous CO molecule[1, 2], where the CO distance is 112.9 pm.

An inverse relationship exists between the C=O and C—Fe distances for different iron(0)-carbonyl compounds: the shorter the Fe—C bond, the longer is the C—O bond[3].

The actual transfer of negative charge involved in the course of complex formation is taking place from the metal atom toward the ligand. In this type of coordination the lower oxidation state is more strongly stabilized than the higher oxidation state, and complexation leads to a shift to more positive potential values[4]. This is interpreted as due to an increase in fractional positive charge at the metal which is greater in the reduced than in the oxidized form.

The back donation theory has been interpreted in a semiquantitative way with regard to the CO stretching force constants and rules have been presented for the effects of substituents[1, 5].

The observed solvent effects on the CO stretching frequencies[6, 7] remained, however, virtually unexplained. For example, the shifts are much larger than previous theories, based on the variation of the dielectric constant of the solvent, would suggest[7]. No relationship

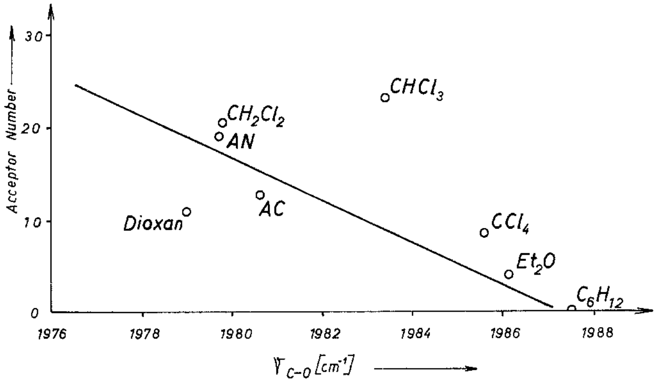


Fig. 1. Relationship between solvent acceptor number and carbonyl vibration of $Mo(CO)_6$

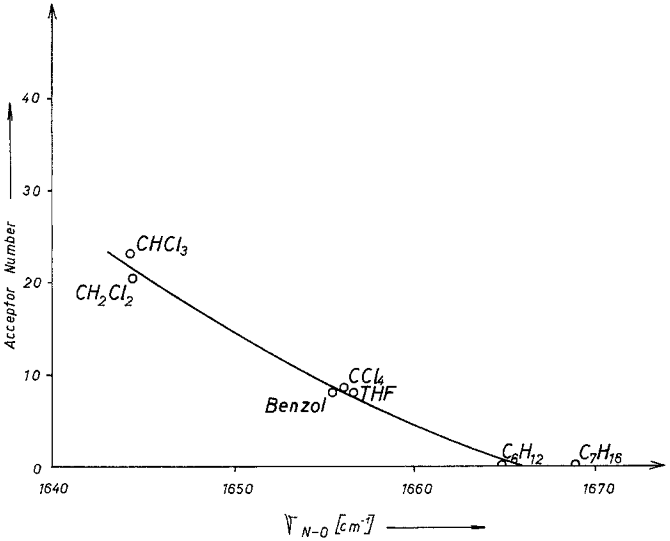


Fig. 2. Relationship between solvent acceptor number and NO valence frequency of $Fe(NO)_2[P(C_6H_{11})_3]_2$

has been found to the solvent polarities, as certain non-polar solvents such as carbon tetrachloride, produce larger shifts than polar solvents such as diethyl ether.

The following consideration follows the simple donor—acceptor approach, which may be refined according to the theories of bonding and of spectra. If the oxygen atom of the carbonyl group acts as donor towards a solvent, a relationship should exist between its properties to the solvent acceptor numbers[8]. Fig. 1 shows the variation of carbonyl vibrations of molybdenum hexacarbonyl[9] as a function of the solvent acceptor number.

In nitrosyl—carbonyl complexes a linear relationship exists between the frequency shifts of ν (N—O) and ν (C—O), the former showing a higher sensitivity toward solvent effects than the latter[6]. The

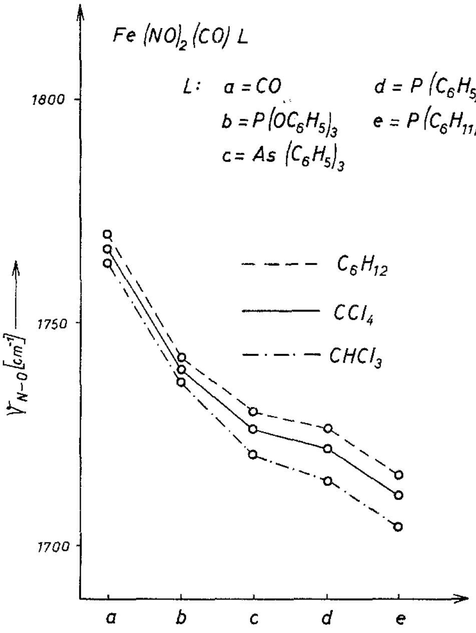


Fig. 3. Variation of NO valence frequency of complexes of the type $Fe(NO)_2(CO)L$ in 3 different solvents

influence of the solvent acceptor number of six different solvents on the N—O valence frequency of $Fe(NO)_2[P(C_6H_{11})_3]_2$ is shown in Fig. 2: increasing acceptor number leads to increasing N—O bond lengthening. A linear relationship is found between the frequencies of the asymmetric and of the symmetric N—O valence oscillations[6]. According to the donor—acceptor approach, the lengthening of the N—O bond is expected to depend on the polarity of the latter, which is altered by the nature and number of the other ligands coordinated to the metal atom. The effect of a given solvent is indeed found to increase as the N—O force constant is lowered[6], which corresponds to increasing π back donation. As can be seen from Fig. 3, the frequency differences of iron nitrosyl carbonyl derivatives of the type $Fe(NO)_2COL$ in three different solvents are increased by increased acceptor number and in the order of increasing strength of the ligands L toward the coordination center:

$$P(OC_6H_5)_3 < As(C_6H_5)_3 < P(C_6H_5)_3 < P(C_6H_{11})_3.$$

A relationship is also found between the N—O valence frequency for $Co(NO)(CO)(t\text{-}buNC)_2$ and solvent acceptor number (Fig. 4).

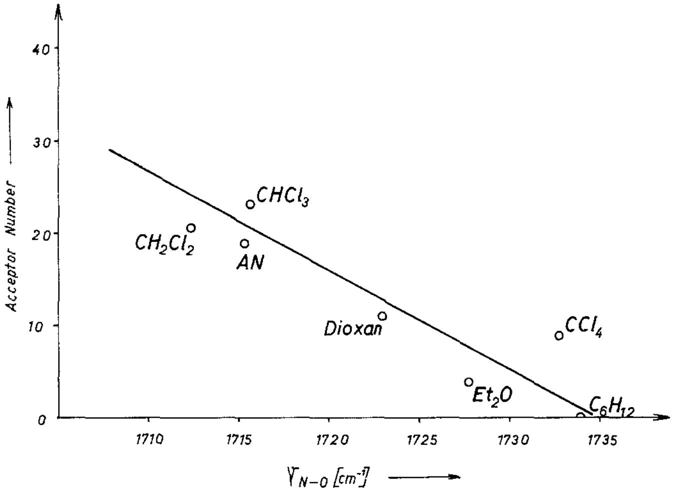
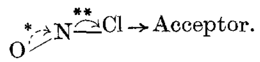


Fig. 4. Relationship between solvent acceptor number and NO valence frequency of $Co(NO)(CO)(t\text{-}buNC)_2$

Carbonyl halides show, however, quite different behaviour. The direction of the shifts is found in the opposite direction to those already considered. Although the shifts are small, "some form of solute—solvent interaction" has been postulated[7]. It is difficult to find an explanation in terms of direct interaction of solvent molecules with the carbonyl groups, since this type of mechanism will always produce a lowering in frequency. A tentative explanation has been based on *Bellamy*'s suggestion for a similar phenomenon with NOCl, who suggested preferential solvation of the chlorine atom by the solvent[10]:



The situation is analogous for carbonyl and nitrosyl halides. For a number of ruthenium nitrosyls of type $Ru(NO)L_2Cl_3$ ($L = PR_3$, AsR_3, SbR_3, $R = et, bu$)[9], the NO frequency increases as the solvent inter-

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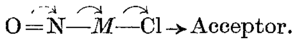
* Induced Bond Shortening.

** Induced Bond Lengthening.

action is enhanced. For aprotic solvents this is related to the solvent acceptor number (Fig. 5). The interaction of the coordinated chlorine atoms with acceptor solvents decreases the electron density at the metal atom to that extent that its ability for back donation is decreased. This leads to lengthening of the nitrogen—metal bond with subsequent decrease of the N—O bond distance.



$$O{=}N{-}M{-}Cl \rightarrow \text{Acceptor.}$$

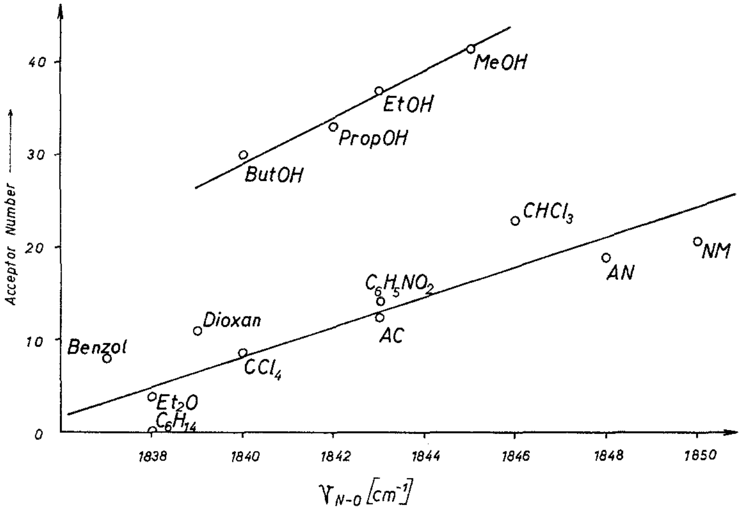


Fig. 5. Relationship between solvent acceptor number and NO valence frequency of $Ru(NO)L_2Cl_3$ in alcoholic and in aprotic solvents

The effect is considerably weaker for alcoholic solvents (Fig. 5). This is explained by additional hydrogen bonding interactions with the oxygen atoms of the N—O groups, which leads to increasing O—N distances. In that way the decrease in N—O bond distance due to the electrophilic attack of the solvent at the halogen atoms is partly compensated.

Edgell and co-workers[11–13] used the vibrational spectrum of the cobalt tetracarbonylate anion $[Co(CO)_4]^-$ as a probe of solution structure at ion sites in different solvents, but they were unable to account satisfactorily for the observations: The C—O stretching vibrations of the $[Co(CO)_4]^-$ anion in six different solvents showed a single absorption band ν_M. Extremely careful computer resolution of the band shape revealed also a very weak band ν_S at the low-frequency side, which was assigned to the ^{13}C species present[13]. This band showed the same trend as a function of the solvent, as does the main band ν_M. It has been concluded that the molecular environment of the anions consists of just one kind of site, with forces coming from the medium which are large enough to influence the rotary-translatory motion and small relative to the forces required to distort the C—O bonds of the anion[13].

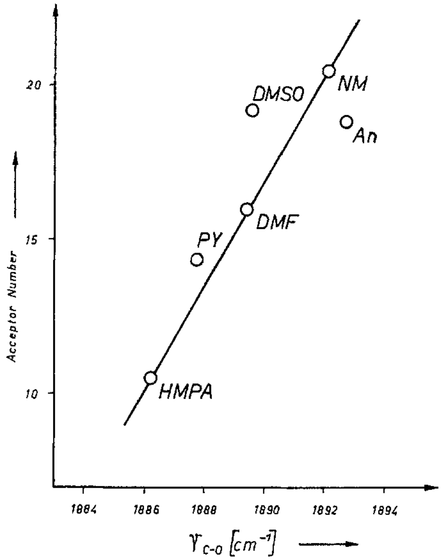


Fig. 6. Relationship between solvent acceptor number and C—O stretching frequency of $[Co(CO)_4]^-$ in 6 different solvents

A correlation exists between the solvent acceptor number[8] and ν_M: Increase in acceptor number causes a slight increase in wave numbers corresponding to shortening of the C—O bonds. The tetracarbonylate ion contains cobalt in the oxidation number —*I* and the Co—C π-bonding is stronger and the C—O bonds are longer than in states of higher oxidation number. The electrophilic solvent attack at the oxygen atoms of the carbonyl groups leads within the $[Co(CO)_4]^-$ ion to a decrease in electron density in particular around the cobalt atom. This leads to weakening of Co—C π-bonding as well as to shortening of the C—O distances. The effects are small, as is the extent of charge transfer between complex unit and solvent.

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