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INFLUENCE OF THE LIGAND DONOR ABILITY ON THE IONIZATION POTENTIALS AND FRAGMENTATION PATTERNS OF TRANSITION-METAL NITROSYL COMPLEXES

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In connection to recent measurements on the mass spectra of positive and negative ions[1] for transitional carbonyl complexes, results are now given on the molecular ionization potentials (I.P.'s) and on the fragmentation patterns of some nitrosyl covalent complexes, for which informations were lacking. It is shown that the donor ability of the ligands — as measured by their I.P. — permits to account for the variations both of the molecular I.P.'s and of the carbonyl and nitrosyl vibrational frequencies of the complexes, for substitution of the ligands themselves.

RESULTS AND DISCUSSION

Table 1 gives the I.P.'s of the nitrosyl complexes here studied and of some related ligands. The table shows at once that the I.P.'s of $Co(CO)_3NO$ and of $Fe(CO)_2(NO)_2$ decrease by substitution in the complex of a CO group with a PR_3 phosphine ligand. The lowering is more remarkable for a larger difference in the I.P.'s of CO and of the ligand concerned: the PCl_3 ligand — with an I.P. 3.6 eV lower than that of CO — decreases the I.P. of $Co(CO)_3NO$ by 0.35 eV, while the $P(OC_2H_5)_3$ — with an I.P. 5.7 eV lower than that of CO — decreases the I.P. of $Fe(CO)_2(NO)_2$ by 0.95 eV.

TABLE 1

IONIZATION POTENTIALS IN eV

$Co(CO)_3NO$	8.75	CO	14.1, 14.1 (ref. 2)
$Co(CO)_2NOPCl_3$	8.40	PCl_3	10.50 10.75 (ref. 3), 10.60 (ref. 4)
$Fe(CO)_2(NO)_2$	8.45	$P(OC_2H_5)_3$	8.40
$Fe(CO)(NO)_2P(OC_2H_5)_3$	7.50	NO	9.40 (ref. 2)
C_5H_5NiNO	8.50	$C_5H_5^{\cdot}$	8.72 (ref. 5)

The I.P. of a compound is on the other side a measure, free from steric or solvent effects, of its basicity[6]; this is suggesting that the I.P. of the ligands here concerned be a measure of their σ-donor ability, reflecting in the case of the phosphine ligands the influence of the groups bonded to the phosphorus atom on the energy of the lone-pair electrons at that atom and on the directional character of the corresponding orbital*. The I.P. lowering of the cobalt and iron complexes for introduction of phosphine ligands appears therefore to be parallel to the corresponding decrease of the I.P. of the ligands themselves, that is to the increase of their donor ability. The corresponding lowering[10] of the π-acceptor ability of the ligands in the series CO, PCl_3, $P(OC_2H_5)_3$ does not change anyway the direction of the I.P. shifts of the complexes.

The above shifts of the molecular I.P.'s of the complexes by ligand substitution** appears also to be parallel (presumably involving therefore similar effects) to those of the carbonyl and nitrosyl IR frequencies[10,12],***. As to the ν_{NO}'s, an examination of the data by Beck and Lottes[12] shows that they are influenced by the ligands in a parallel way both for $Co(CO)_3NO$ as for $Fe(CO)_2(NO)_2$. This again justifies the above comparison of the I.P. shifts which was performed on molecules of the same structure but with different central metals. From the present observations it follows the necessity to consider both the π-acceptor ability — as generally done[10,14,15,16]—and the σ-donor ability**** of the ligands on evaluating their influence on properties like I.P.'s and vibrational frequencies of complexes to which they participate. These two features of the ligands act generally in a parallel way.

As to the nature of the less strongly bonded electron in these complexes, the present results seem to suggest it to pertain to an orbital with an essentially metallic character, as previously found for the carbonyls $M(CO)_6$[18]. In fact, the substitution of CO with phosphinic ligands causes an increase of the charge density at the central atom (owing to a parallel variation, as before discussed, of the acceptor and donor abilities of the ligands), and consequently a decrease of the I.P. of the complex. Moreover, the lowering of the carbonyl and nitrosyl stretching frequencies caused by an increased back-donation[10] for a similar ligand substitution, suggests that the electron involved in the ionization be a π one.

The fragmentation patterns of Fig. 1 and of Tables 2 and 3 illustrate some typical features of the behaviour of these organometallic compounds. For the tetracoordinated complexes, in the case of the $(Par-L)^+$ peaks (Par = parent molecule) corresponding to molecular ions which have lost a single ligand, the $(Par-NO)^+$ and $(Par-PR_3)^+$ peaks are much less abundant than the $(Par-CO)^+$ ones. Moreover, for all the four complexes here studied the relative abundancies of these ions decrease by decreasing the I.P. of the ligand detached. This is consistent with the previous observations on the corresponding behaviour of the I.P., ν_{CO} and ν_{NO} of the same complexes. The transition state for the process $Par^+ = (Par-L)^+ + L$, on increasing the donor ability of L will show a lower deficiency of negative charge at the central metal, likely to oppose to the fragmentation process itself. Also, electronic excitations of the parent ion might act similarly.

For the peaks $(Par-2L)^+$, the relative abundancies are instead comparable

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* Other data available for the I.P.'s of alkyl-substituted phosphine ligands, useful for an internal comparison only of the values of a given author, and which again show the above described effect, are in eV the following: $P(C_2H_5)_3$ (8.27), $P(CH_3)_3$ (8.60), $PH_2C_2H_5$ (9.61), PH_2CH_3 (9.72)[7]; PH_3 (10.1)[8]; $P(CH_3)_3$ (9.2), $PH(CH_3)_2$ (9.7), PH_3 (10.3)[9].

** It may be noted that recently[11] a linear correlation has been observed between the I.P.'s of ligands $(CH_3)_nC_6H_{6-n}$ and the ν_{CO}'s of complexes of the type $(CH_3)_nC_6H_{6-n}Cr(CO)_3$.

*** In ref. 13 a similar effect may be observed on $Fe(CO)_5$ for PR_3 substitution.

**** For a case where this factor is considered, see ref. 17.

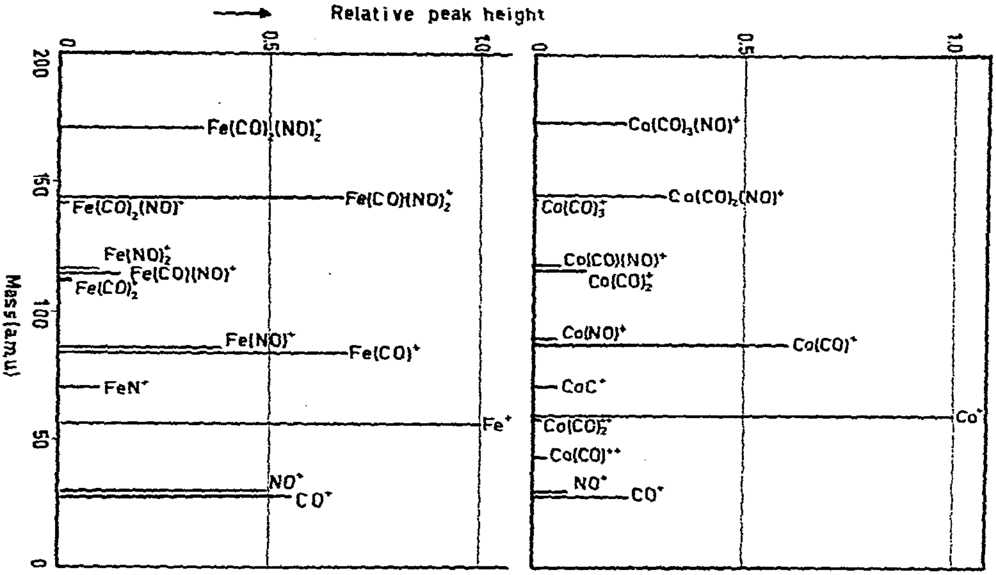

Fig. 1. Cracking patterns for $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$.

TABLE 2

RELATIVE ABUNDANCIES OF THE RELEVANT IONS FROM $Co(CO)_2NOPCl_3$ AND $Fe(CO)(NO)_2P(OC_2H_5)_3$

Ion[a]	*Relative abundancy*[b]		*Ion*[c]	*Relative abundancy*
	Co	*Fe*		*Co*
$Parent^+$	108	4	MPR^+	31
$(Par-CO)^+$	56	43	$M(CO)NO^+$	44.5
$(Par-NO)^+$		<2	$M(CO)_2^+$	10
$(Par-R)^+$	11	3	MR^+	39.5
$(Par-2CO)^+$	40		MNO^+	5.5
$(Par-CONO)^+$	40	100	MCO^+	22
$(Par-2NO)^+$		6	MN^+	6.5
$[Par-(CO)R]^+$	41	4	M^+	86
MPR_3^+	100	20	NO^+	63.5
$M(NO)PR_2^+$	21.5	2	CO^+	500[d]
$M(CO)PR_2^+$	16			
$M(NO)_2PR^+$		25		
MPR_2^+	51	11		
$(Par-PR_3)^+$	6	<1		

[a] R = Cl, OC_2H_5; M = Co, Fe. [b] Corrected, where necessary, to account for the isotopic composition of the fragments. [c] The peaks at *m/e* lower then $P(OC_2H_5)_3$ for $Fe(CO)(NO)_2P(OC_2H_5)_3$ have not been reported owing to possible interferences with the ligand itself and with the reaction solvent; it was observed anyway that $Fe(NO)_2^+$ and $Fe(CO)(NO)^+$ are absent, while the peaks corresponding to $FeNO^+$, $FeCO^+$ and Fe^+ if present should show relative abundancies lower than 10%. [d] This high value of relative abundancy clearly shows that this compound, as well as the others here studied, was in part thermally decomposed in the ion source. Anyway the differences in the relative abundancies of the peaks containing the metal should not generally change more than 10% with respect to the values obtained by using a "cold" ion source (50–60°C)[19].

whatever be the nature of the two neutral ligands detached. The situation is almost completely inverted for the peaks $(Par-3L)^+$ where the relative abundancies are in

TABLE 3

RELATIVE ABUNDANCIES OF THE PRINCIPAL IONS FROM C_5H_5NiNO

Ion	*Relative abundancy*
$C_5H_5NiNO^+$	65
$C_5H_5Ni^+$	100
$C_3H_3Ni^+$	28
$NiNO^+$	1.5
$C_5H_5^+$	2
Ni^+	48
$C_3H_3^+$	5.5
NO^+	2

the order $M(PR_3)^+ > M(CO)^+ > M(NO)^+$. The present observations can be tentatively interpreted in a manner sufficiently reasonable — in the lacking of informations on the behaviour of the corresponding efficiency curves for production of the single ion fragments* — considering some possible paths for the decay of the parent molecular ion from its ground state or from electronically excited states. The simplest situation is found for $Co(CO)_3NO$, with a single non-carbonylic ligand and where, even if other possibilities cannot be ruled out, a relevant fragmentation scheme is as follows:

$$\begin{tikzcd}
Co(CO)_3NO^+ \arrow[r, "B"] \arrow[d, "A"] & Co(CO)_2NO^+ \arrow[r, "B"] \arrow[d, "A"] & Co(CO)NO^+ \arrow[r, "B"] \arrow[d, "A"] & Co(NO)^+ \arrow[d, "A"] \\
Co(CO)_3^+ \arrow[r, "B"] & Co(CO)_2^+ \arrow[r, "B"] & Co(CO)^+ \arrow[r, "B"] & Co^+
\end{tikzcd}$$

In agreement with this scheme, although it appears — as before discussed — more followed starting from the parent ion the primary step involving detachment of CO with respect to the one involving detachment of NO, at the end the fragment $Co(CO)^+$ results to be much more observed than $Co(NO)^+$. In fact, for the first fragment the scheme shows three possible paths of production, but only one for the second; on the other hand, each one of these three paths involves a step (indicated as A in the scheme) of NO detachment from an ion of the type $Co(CO)_xNO^+$, and these steps are presumably equally probable. All other steps (indicated as B in the scheme) involve CO detachment and they should have again similar probabilities. Further support to this interpretation is obtained observing from Table 2 that for $Co(CO)_2NOPCl_3$** (*a*) the fragments $CoPCl_3^+$ and $CoPCl_2^+$ are particularly abundant, (*b*) it is present with high relative abundancy a series of fragments [$Co(CO)_2NOPCl_2^+$, $Co(CO)NOPCl_2^+$, $Co(NO)PCl_2^+$, $Co(CO)PCl_2^+$, $CoPCl_2^+$]*** which apparently retain the PCl_2 grouping from the starting fragment ion $Co(CO)_2NOPCl_2^+$. On the basis of a prevailing tendency for our molecule to retain in the decay processes the

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* As to the importance on this regard of the knowledge of the efficiency curves see ref. 20 for the fragmentation process of $W(CO)_6$.

** The situation is substantially similar for the other phosphinic complex of Table 2, although having presently for it scarcer informations.

*** It is remarkable the absence of the peak for the ion $Co(CO)_2PCl_2^+$, again supporting the fact that by decreasing the I.P. of the ligand the detachment of the ligand itself (here the NO ligand) becomes more difficult.

PCl_3 grouping when starting from the molecular parent ion $Co(CO)_2NOPCl_3^+$ or the PCl_2 grouping when starting from the ion $Co(CO)_2NOPCl_2^+$ (derived primarily from the molecular ion itself), there follow two fragmentation schemes quite similar to the one before reported and which give rise now, for the same reasons, to a high relative abundancy for the ions $CoPCl_3^+$ resp. $CoPCl_2^+$.

The fragmentation pattern of Table 3 for C_5H_5NiNO shows again, as for the tetracoordinated complexes, that in the primary decay step of the parent ion there is retained preferentially the cyclopentadienyl ligand with a lower I.P. (see Table 1)*, as observed in fact for all the complexes of the type $C_5H_5M(CO)_x(NO)_y$ hitherto studied (see ref. 1a of ref. 1).

It is also reasonable, from the schemes above discussed, to find in all the present cases a high relative abundancy for the M^+ ions**; this is a general finding indeed in the mass spectra of transitional complexes[1,18].

EXPERIMENTAL

The I.P.'s (see Table 1; values reproducible within ±0.1 eV) and the fragmentation patterns (see Tables 2 and 3 and Fig. 1) here reported have been obtained with an Atlas Werke CH-4 spectrometer partially modified[22]. The spectra were recorded with an electron capture current of 16 μA, the ions being received on a Faraday collector. The electron energy was kept at 50 eV, this value having been selected in order to have in the largest possible number of cases production of ions at intensities near to their saturation limits, and it is recommended to record spectra of organometallic compounds. For the other experimental conditions see ref. 18.

The compounds here studied have been prepared following literature methods, and in particular: (*a*) $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$ according to ref. 23; (*b*) C_5H_5NiNO according to ref. 24; (*c*) $Co(CO)_2(NO)PCl_3$ according to ref. 10. The compound $Fe(CO)(NO)_2P(OC_2H_5)_3$ has been prepared at room temperature with the method given by Malatesta and Araneo[25] for the triphenylphosphine, triphenylarsine and triphenylstibine derivatives of $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$. The toluene solution containing the compound and small amounts of unreacted starting materials has been introduced without further purification into the mass spectrometer. The spectrum observed (see also Table 2) indicates in the mixture the sure presence of the compound $Fe(CO)(NO)_2P(OC_2H_5)_3$, the probable one of $P(OC_2H_5)_3$ and obviously that of toluene. There have not been observed in the present conditions of preparation and of introduction into the spectrometer $Fe(CO)_2(NO)_2$, $Fe(CO)_5$ [which is generally found in mixture with $Fe(CO)_2(NO)_2$] or the possible $Fe(NO)_2[P(OC_2H_5)_3]_2$.

Also the compound $Co(CO)_2(NO)PCl_3$ has been used without purification, and in Table 2 there are not reported the peaks which might come from unreacted

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* The I.P.'s of ferrocene and nickelocene have been now reevaluated. For comparison with C_5H_5NiNO, obtaining values of 6.99 and 6.75 eV resp. which substantially confirm the previous data[21]. These low values apparently represent, with the present I.P. figure of Table 1 for $Fe(CO)(NO)_2P(OC_2H_5)_3$, the only cases hitherto reported of transitional complexes with an I.P. lower than for the corresponding metal (see ref. 13 of ref. 18), and seem to suggest a particularly strong resonance stabilization of the corresponding ionic molecular states.

** With the apparent exception, not clear, of Fe^+ ion from $Fe(CO)(NO)_2P(OC_2H_5)_3$.

complex or ligand. To the peaks which might have contributions from a parallel fragmentation of unreacted $Co(CO)_3NO$, such contributions have been subtracted. There has not been observed the compound $Co(CO)(NO)(PCl_3)_2$ which according to Horrocks[10] should be formed in the preparation with $Co(CO)_2(NO)PCl_3$. Also the spectrum of $Fe(CO)_2(NO)_2$ of Fig. 1 has been corrected for the parallel occurrence of $Fe(CO)_5$ in the sample used. The ligands employed were commercial products.

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SUMMARY

The molecular ionization potentials (I.P.'s) and the fragmentation patterns of the complexes $Co(CO)_3NO$, $Co(CO)_2(NO)PCl_3$, $Fe(CO)_2(NO)_2$, $Fe(CO)(NO)_2$-$P(OC_2H_5)_3$ and C_5H_5NiNO, and the I.P.'s of the substituent ligands CO, PCl_3 and $P(OC_2H_5)_3$ have been determined. These last I.P.'s are a measure of the σ-donor ability of the ligands themselves; the importance is illustrated to account for this donor ability on evaluating the influence of the ligands on the molecular I.P.'s, on the fragmentation paths and on the carbonyl and nitrosyl vibrational stretching frequencies of the complexes to which they participate. The primary ionization process in these complexes seems to involve an electron pertaining to an orbital of an essentially metallic type and with a partial π character. The fragmentation paths by electron impact of the present nitrosyl complexes are interpreted as involving parallel cascade decay processes. This interpretation considers both the probability of the single fragmentation steps of the cascade and the possible nature of the transitional states involved.

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