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NOTE

IRON–PHOSPHORUS BOND DISSOCIATION ENERGIES IN TETRAHEDRAL IRON CARBONYL NITROSYL COMPLEXES

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Although the phosphinic derivatives of metal carbonyls have been extensively studied, no quantitative data have been reported on the metal–phosphorus ($M{-}PX_3$) bond energies, not even comparatively to the M–CO one.

The appearance potentials (*AP*) of the ions at $m/e=282$ obtained from $Fe(CO)(NO)_2P(OC_2H_5)_3$ (Ia) and $Fe(NO)_2[P(OC_2H_5)_3]_2$ [IIa] and of the ions at $m/e=240$ obtained from $Fe(CO)(NO)_2P(OCH_3)_3$ (Ib) and $Fe(NO)_2[P(OCH_3)_3]_2$ have now been determined* (see Table 1). Such ions correspond to the general formula $[Fe(NO)_2PX_3]^+$. The corresponding *AP*'s can therefore be connected to the bond dissociation energies M–CO and $M{-}PX_3$ and to the ionization potentials of the $Fe(NO)_2PX_3$ species, as follows:

$$AP^{\text{I}}[Fe(NO)_2PX_3]^+ = IP[Fe(NO)_2PX_3] + D[CO{-}Fe(NO)_2PX_3] + EE \qquad (1)$$

$$AP^{\text{II}}[Fe(NO)_2PX_3]^+ = IP[Fe(NO)_2PX_3] + D[PX_3{-}Fe(NO)_2PX_3] + EE \qquad (2)$$

By subtracting the first equation from the second and assuming the excess energies *EE* are not greatly different in the two processes, the difference between the

TABLE 1

$Fe{-}PX_3$ AND $Fe{-}CO$ BOND ENERGIES OF IRON CARBONYL NITROSYL COMPLEXES

Complex	*IP* of the complex	*AP* of $Fe(NO)_2PX_3^+$ ion	$D(M{-}PX_3)$[a] (eV)	$D(M{-}CO)$[a] (eV)
$Fe(CO)(NO)_2P(OC_2H_5)_3$	7.50[b]	8.1_5 (Ia)		0.6_5
$Fe(NO)_2[P(OC_2H_5)_3]_2$	7.02	9.4_5 (IIa)	2.4	
$Fe(CO)(NO)_2[P(OCH_3)_3]$	7.66[c]	8.2_0 (Ib)		0.5_5
$Fe(NO)_2[P(OCH_3)_3]_2$	7.25	9.7_5 (IIb)	2.5	
$Fe(CO)(NO)_2P(OC_4H_9)_3$	7.52[c]	7.8_5		0.3
$Fe(CO)(NO)_2P(C_4H_9)_3$	7.30[d]	7.7_0		0.4
			av. 2.4_5	0.4_5

[a] These values have been obtained by using the eqns. (3) and (4) respectively, and approximately neglecting the *EE*. [b] From ref. 9. [c] From ref. 5. [d] Calculated value (see ref. 2): in our experimental conditions the parent ion was much too small to be used for the experimental evaluation of its *IP*.

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* Measurements were performed on an Atlas CH4 mass spectrometer; for the experimental conditions see ref. 1.

Fe–PX$_3$ and Fe–CO bond dissociation energies is found. This difference comes out to be about 33 kcal/mole, averaged over the two cases considered (methyl and ethyl phosphite respectively).

After taking into account the uncertainty in the *AP* measurements we think the value of the above difference can be regarded as correct to within ±10 kcal/mole. Since the value of *D*(Fe–CO) should be about 20–30 kcal/mole[3,4], that of *D*(Fe–PX$_3$) must fall in the range 50–70 kcal/mole.

The above *AP*'s for the [Fe(NO)$_2$PX$_3$]$^+$ ions can also be used to evaluate the M–P and M–CO bond dissociation energies in the Fe(NO)$_2$(PX$_3$)$_2^+$ and Fe(NO)$_2$-PX$_3$CO$^+$ molecular ions* (see columns four and five in Table 1). In particular by using the following equations:

$$AP^{\mathrm{I}}[\mathrm{Fe(NO)_2PX_3}]^+ = IP[\mathrm{Fe(NO)_2PX_3CO}] + D[\mathrm{CO{-}Fe(NO)_2PX_3}]^+ + EE \qquad (3)$$

$$AP^{\mathrm{II}}[\mathrm{Fe(NO)_2PX_3}]^+ = IP[\mathrm{Fe(NO)_2(PX_3)_2}] + D[\mathrm{PX_3{-}Fe(NO)_2PX_3}]^+ + EE \qquad (4)$$

and again making the above assumption for the *EE*, the average difference between the ionic bond dissociation energies of the M–P and M–CO bonds is found to be about 45 kcal/mole (the difference between the average values reported in columns four and five of Table 1, respectively).

The increase in the difference between the M–P and M–CO bond dissociation energies on going from the neutral molecule to the ion is in agreement with previous indications[1] for M(CO)$_5$L complexes; it indicates the poor contribution of back-donation from M to the M–P bond in comparison with that to the M–CO one. Ionization of the complex is known to lower the back-donation capabilities of the central metal[1,5], and this will cause a greater weakening of the M–CO bond than of the M–P bond. This result is particulary valuable in connection with the problem[7,8] of the π contribution to the metal–phosphorus bond in metal complexes.

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* It is to note that the average value here found for the ionic *D*(M–CO) in these molecules is nearly the same to the one previously reported for the penta- and hexa-coordinated metal carbonyls[6].