^{31}P Nuclear Magnetic Resonance Spectra of Phosphorus-containing Esters in the Presence of Transition-metal Ions

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Decoupling of phosphorus–hydrogen spin–spin interactions upon addition of paramagnetic complexing reagents of the first transition series to phosphorus-containing esters has been investigated by ^{31}P n.m.r. spectroscopy. Attempts at complete phosphorus–hydrogen decoupling by use of non-co-ordinating paramagnetic reagents were unsuccessful.

WE have previously reported[1,2] investigations of paramagnetic decoupling of ^{31}P–^{1}H and ^{1}H–^{1}H interactions in phosphorus-containing esters. It is of practical interest to consider the same decoupling process as it would be observed in phosphorus n.m.r. spectra.

Observations of ^{31}P–^{1}H chemical decoupling in systems similar to those we have studied have been reported by several other groups.[3-5] In all of these cases the proton spectra were measured and directly co-ordinating paramagnetic reagents were used. The most intensive of these studies is that by Frankel,[3] who has given a detailed theoretical evaluation of the spectra produced.

We have also noted previously[6,7] chemical decoupling of ^{1}H–^{1}H interactions by a second co-ordination sphere mechanism, not involving direct chemical interaction between paramagnetic reagent and the molecule under consideration. It is predicted[3c] that decoupling of ^{31}P–^{1}H interactions by such a mechanism would not be observed in proton spectra but might be observed in phosphorus spectra. Results obtained by Zumdahl and Drago[8] using non-labile chromium(III) reagents

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[1] R. Engel, *Chem. Comm.*, 1970, 133.

[2] R. Engel and A. Jung, *J. Chem. Soc.* (*C*), 1971, 1761.

[3] L. S. Frankel, (*a*) *J. Chem. Phys.*, 1969, **50**, 943; (*b*) *J. Mol. Spectroscopy*, 1969, **29**, 273; (*c*) *Inorg. Chem.*, 1969, **8**, 1784.

[4] J. P. Fackler, J. A. Fetchin, J. Mayhew, W. C. Seidel, T. J. Swift, and M. Weeks, *J. Amer. Chem. Soc.*, 1969, **61**, 1941.

[5] F. L. Lafferty, R. C. Jensen, and J. C. Sheppard, *Inorg. Chem.*, 1969, **8**, 1875.

[6] R. Engel, *J. Chem. Soc.* (*C*), 1971, 3554.

[7] R. Engel and G. Nathan, *J. Chem. Soc.* (*C*), 1971, 3844.

[8] S. S. Zumdahl and R. S. Drago, *Inorg. Chem.*, 1968, **7**, 2162.

agree with the first part of this prediction, no decoupling having been observed in proton spectra with dimethyl methylphosphonate and dimethyl phosphite.

Investigation of paramagnetic metal ion interaction with phosphorus systems by observation of ^{31}P spectra has not been extensive; the technique has been used with several systems of biological interest to confirm earlier data concerning metal ion binding sites.[9-11] The primary concern has been with simple line broadening and paramagnetic shifts. The interest of the present work is to provide a basis for more detailed investigations of this type.

EXPERIMENTAL

All ^{31}P n.m.r. spectra were measured with a Varian HA-100 spectrometer at 40·5 MHz; proton spectra were measured with a Varian A-60A instrument. All spectra were measured at ambient temperature with operating parameters optimised by use of a standard sample.

TABLE 1

Compound	Paramagnetic reagent	M/L × 10^{3} [a] for phosphorus–hydrogen decoupling	Phosphorus paramagnetic shift at decoupling M/L [b]	Concentration range of compound (mol l^{-1})	Maximum concentration (mol l^{-1}) of paramagnetic reagent
Trimethyl phosphite	$CoCl_2$	0·549	25	0·259—2·51	1·94 × 10^{-3}
	$FeCl_3$	16·7	16	0·259—2·51	4·33 × 10^{-3}
Trimethyl phosphate	$CoCl_2$	1·33	5	0·951—1·61	3·05 × 10^{-3}
	$FeCl_3$	2·71	1	0·951—1·61	4·96 × 10^{-3}
Triethyl phosphite	$CoCl_2$	0·500	0	0·611—2·04	1·94 × 10^{-3}
	$FeCl_3$	5·63	10	0·611—2·04	3·44 × 10^{-3}
Triethyl phosphate	$CoCl_2$	0·229	24	0·246—1·43	1·66 × 10^{-3}
	$FeCl_3$	0·342	7	0·246—1·43	4·51 × 10^{-3}
	$Fe(acac)_3$	10	0	0·246—1·43	2·76 × 10^{-3}
Tri-isopropyl phosphite	$CoCl_2$	0·0913	3	0·170—1·87	1·16 × 10^{-2}
	$FeCl_3$	0·128	7	0·170—1·87	2·41 × 10^{-2}
	$Fe(acac)_3$	10	0	0·170—1·87	3·01 × 10^{-3}
Tributyl phosphite	$CoCl_2$	0·358	0	0·747—1·46	1·95 × 10^{-3}
	$FeCl_3$	3·22	0	0·747—1·46	2·41 × 10^{-3}
Dimethyl methylphosphonate	$CoCl_2$	0·190	42	1·75—1·88	1·66 × 10^{-3}
	$FeCl_3$	0·129	0	1·75—1·88	4·51 × 10^{-4}

[a] Molar concentration ratio of paramagnetic metal ion species to ligand. [b] All shifts are downfield and given in Hz.

Phosphorus chemical shifts were measured relative to external phosphoric acid (85%) by use of a Varian V-4315 frequency counter. Proton chemical shifts were measured relative to the acetonitrile solvent signal.

The anhydrous cobalt(II) chloride, iron(III) chloride, and iron(III) acetylacetonate [$Fe(acac)_3$] were commercial materials and were used without further purification. The phosphites and phosphates were commercial materials and were repurified by distillation. Dimethyl methylphosphonate was prepared by a standard procedure.[12]

The acetonitrile solvent was commercial material of spectrometric quality and was used without further purification.

RESULTS

Concentration data for ^{31}P–^{1}H decoupling as noted by observation of phosphorus signals are summarised in Table 1; those as noted by observation of proton signals, are in Table 2. Paramagnetic shifts of the phosphorus signals at decoupling concentrations are also listed in Table 1.

The ^{31}P n.m.r. spectra of trimethyl phosphite, trimethyl phosphate, triethyl phosphite, tributyl phosphite, and dimethyl methylphosphonate were observed upon association with $CoCl_2$ and $FeCl_3$. In all cases coalescence of the (multiplet) signals to broadened singlets was observed as previously noted for the proton spectra.[2] A higher concentration ratio (of metal to ligand) was required for $FeCl_3$ decoupling than for $CoCl_2$.

At the concentration ratio for decoupling required of the ^{31}P–^{1}H interactions, downfield paramagnetic shifts were noted for the ^{31}P signals in all cases except tributyl phosphite, for which the shift was zero within experimental error, and triethyl phosphite with $CoCl_2$, in which case downfield shifts were noted with increased concentration of the paramagnetic species.

In addition to the foregoing reagents, iron(III) acetylacetonate was used with triethyl phosphate and tri-isopropyl phosphite. With this reagent, in neither case was decoupling noted in the proton spectra and only incomplete decoupling was observed in the phosphorus spectra at the highest concentration ratios used (10^{-2}).

TABLE 2

Compound	Paramagnetic reagent	M/L × 10^{3} for ^{31}P–^{1}H decoupling
Triethyl phosphate	$Fe(acac)_3$	Not observed
Tri-isopropyl phosphite	$CoCl_2$	0·685
	$FeCl_3$	0·770
	$Fe(acac)_3$	Not observed

DISCUSSION

The results are qualitatively similar to those previously reported for proton spectra.[2] There are several noteworthy variations which can be rationalised.

Decoupling of the ^{31}P–^{1}H interaction is observable when paramagnetic species which co-ordinate directly with the ligand molecules are used. In the absence of

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[12] S. R. Landauer and H. N. Rydon, *J. Chem. Soc.*, 1953, 2224.

direct chemical co-ordination of the phosphorus ligand no decoupling is observed in the proton spectra and only partial, incomplete, decoupling in the phosphorus spectra (see later).

Paramagnetic shifts of the phosphorus signals, when present, were in a downfield direction; proton shifts for the same molecules in the same solvent systems were either upfield or downfield. Presumably only positive electron spin density is transferred to the region of the phosphorus upon chemical interaction whereas positive or negative electron spin density may be induced at the proton sites. Conformational dependence of the direction of contact shifts has been noted previously in rigid and semi-rigid systems.[13,14] With (relatively) free conformational interconversion within the ester linkages of the present systems, *a priori* predictions of the directions of contact shifts are hardly possible.

The relative values of the concentration ratios for decoupling are of interest. First, decoupling of the phosphorus–hydrogen interaction is always observed at a lower concentration ratio in the phosphorus spectrum than in the proton spectrum. In fact, what is observed in the phosphorus spectra is probably not the true chemical decoupling, but rather an initial paramagnetic line-broadening effect which partially obscures the signal resolution and occurs prior to true chemical decoupling. This has been discussed by Frankel[3b] for the proton spectrum of nickel(II)–dimethyl methylphosphonate systems. This effect, noted to be of little significance in the proton spectrum, should be of considerably more importance with the phosphorus spectrum owing to the relative closeness of the phosphorus nucleus to the paramagnetic species.

We had noted earlier that in the series $NiCl_2$, $CoCl_2$, $FeCl_3$, the more paramagnetic $FeCl_3$ was most effective in decoupling the proton spectra of phosphites[1] and nitrogen-bound ligands;[6] these observations were made for solutions in benzene and dioxan. In the present work, with acetonitrile as the solvent it is observed that $CoCl_2$ is the most effective in producing decoupling in both the proton and the phosphorus spectra. We presume this to be due to the nature of the solvent system; the competition of ligand with solvent (acetonitrile) for the metal ion is significantly less efficient for $FeCl_3$ than for $CoCl_2$. Detailed studies of the solvent effects on the decoupling process are under way.

We have previously noted[6,7] that $Fe(acac)_3$ can be used in the decoupling of proton–proton interactions, presumably acting by a second co-ordination sphere mechanism rather than by a direct co-ordination process. It is predicted that phosphorus decoupling in the proton spectrum will probably not occur through a second co-ordination sphere mechanism, and thus far the systems investigated have behaved in accord with this prediction.[8] Attempts in the present work, using the non-labile $Fe(acac)_3$, agree with these prior results, no change in the proton spectrum being observed.

However, studies of the phosphorus spectra are inconclusive; only partial, incomplete, decoupling of the phosphorus signals was observed. Concentrations of $Fe(acac)_3$ sufficiently high for complete decoupling could not be used with reliability as severe disturbance of the homogeneity of the magnetic field resulted.

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