474. *Chemical Applications of Nuclear Quadrupole Resonance. Part IV.*[1] *The Transmission of the Electronic Effect of Various Substituents by a Phosphorus Atom.*

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The ^{35}Cl nuclear quadrupole resonance frequencies of a number of derivatives of phosphoryl chloride and phosphorus trichloride are reported and are shown to be much less sensitive to the nature of the substituents than those of the corresponding carbon compounds. In contradiction to Jaffé and Freedman's ultraviolet spectroscopic observations,[2] substituents appear to be able to conjugate with the chlorine atom. Owing to the flexibility of the molecule, derivatives of phosphorus trichloride appear unlikely to yield easily interpretable quadrupole resonance frequencies.

PARTS I—III of this series [1] have been concerned essentially with the effect of substituents on the ^{35}Cl-nuclear quadrupole resonance frequency of chlorine attached to a carbon atom. The nature of these effects and the mechanisms by which they are transmitted to the chlorine atom are, in this case, relatively well understood, much information being available from the large body of physicochemical experiment directed to the elucidation of the mechanism of organic reactions. When, however, electronic effects are transmitted through a phosphorus atom the situation is not so clear. Data derived from kinetic studies of substitution at a phosphorus atom are difficult to interpret unambiguously since the details of the mechanism of substitution have not yet been established; moreover, the rates of such reactions appear to be affected to a much greater extent by steric factors than are those of corresponding carbon compounds.[3] With these reservations, it appears, however, that the rates of hydrolysis of phosphonochloridates or related compounds are far less sensitive to the nature of the substituents than are those of the corresponding carbonyl compounds; [3] in addition conjugation appears to have far less importance. This is illustrated by the rate-constants shown in Table 1.[3]

TABLE 1. *Relative reactivities of phosphoryl and carbonyl compounds (data from ref.* 5).

Phosphoryl compounds	Relative rate	Carbonyl compounds	Relative rate
$(Et)_2POCl$	15 : 1	Me·COCl	10^4 : 1
MeO·EtPOCl		EtO·COCl	
Me_2POCl	1·3 : 1	Me·COCl	10^2 : 1
PhMePOCl		Ph·COCl	

The apparent absence of conjugative effects has also been demonstrated by the ultraviolet [2] and infrared spectra [4] of phosphonic acids and their derivatives.

In the hope of obtaining further evidence the ^{35}Cl-nuclear quadrupole resonance frequencies of a number of derivatives of phosphorus oxychloride and phosphorus trichloride have been measured.

Experimental.—^{35}Cl-Nuclear quadrupole resonances were detected by using an externally quenched super-regenerative spectrometer based on that of Dean.[5] Frequencies were measured with a war-surplus frequency-meter of type BC 221 and are shown in Table 2. The compounds were supplied either by Dr. R. F. Hudson of this College or by Dr. Childs of Albright & Wilson Ltd. whose assistance is gratefully acknowledged. The main experimental difficulty lay in the purification of these highly reactive compounds and their subsequent crystallisation at 77° K. For almost all the compounds which did crystallise, very slow cooling was essential, and often crystallisation occurred only after numerous fruitless attempts. Often owing to the

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[1] Parts I—III, *J.*, 1958, 2653; *J.*, 1959, 426, 2954.

[2] Jaffé and Freedman, *J. Amer. Chem. Soc.*, 1952, **74**, 1069.

[3] Hudson and Keay, *J.*, 1960, 1859.

[4] Bell, Heisler, Tannenbaum, and Goldenson, *J. Amer. Chem. Soc.*, 1954, **76**, 5185.

[5] Dean, Thesis, Harvard University, 1952.

formation of glasses, experiments with the following substances failed: 2-methylprop-1-enyl- and 2-chloroethyl-phosphonic dichloride; dimethyl- and diphenyl-phosphinyl chloride; diethyl, dibutyl, and diphenyl phosphorochloridate; methyl methylphosphonochloridate; ethyl ethyl- and trichloromethyl-phosphonochloridate; ethylphosphonous dichloride; diphenylphosphinous chloride; ethyl phosphorodichloridite; and diethyl phosphorochloridite.

TABLE 2. ^{35}Cl *nuclear quadrupole resonance frequencies in megacycles per second at* 77° K.

Compound	Frequency
Phosphoryl chloride	28·989 28·935
Methylphosphonic dichloride	26·729 26·426
Ethylphosphonic dichloride	26·332 26·194
Chloromethylphosphonic dichloride	35·050 26·872 26·172
Phenylphosphonic dichloride	25·357
Me phosphorodichloridate	27·468 27·099

Compound	Frequency
Phenylphosphorodichloridate	27·7
NN-Diethylphosphoramidic dichloride	27·034 26·097
NN-Diethyl-*P*-methylphosphonamidic chloride	27·695
Et methylphosphonochloridate	26·744 26·445
Phosphorus trichloride	26·208 26·104
Methylphosphonous dichloride	26·081
Phenylphosphonous dichloride	26·557

Spectra were measured as capillary films on a Grubb–Parsons recording double-beam grating spectrophotometer. The wavelengths of the P–O stretching frequencies were 7·96, 8·01, and 7·91 microns respectively.

Discussion.—Derivatives of phosphoryl chloride. In Table 3 the values of the nuclear quadrupole resonance frequencies of a number of monosubstituted phosphoryl chlorides are compared with the frequencies of the corresponding carboxylic acid chlorides, chloromethanes, and sulphonyl chlorides. Although the effects of the substituents are similar in the four series, the frequency shifts for the phosphorus derivatives are much less than for the others, in qualitative agreement with the kinetic data in Table 1. The reduced ability of phosphorus to transmit electronic effects is in accord with its greater polarisability; the opposite phenomenon is observed when inductive effects are transmitted through an oxygen atom,[6] as is illustrated in Table 4.

TABLE 3. *Comparison of* ^{35}Cl *nuclear quadrupole resonance frequencies of phosphoryl compounds with those of corresponding carbon and sulphur compounds.*

R	$R·POCl_2$	R·COCl	$R·CH_2Cl$	$R·SO_2Cl$
Cl	28·962	35·905 [a]	35·991 [d]	37·717 [d]
$Cl·CH_2$	27·022	30·437 [a]	34·361 [e]	
Me	26·577	29·5 [b]	32·70 [d]	32·519 [h]
Et	26·263	—	32·968 [e]	

R	$R·POCl_2$	R·COCl	$R·CH_2Cl$	$R·SO_2Cl$
Ph	25·357	29·93 [a]	33·627 [d]	32·63 [h]
MeO	27·283	33·858 [c]	30·181 [g]	
PhO	27·70	—		
Et_2N	26·566	—		

[a] Bray, *J. Chem. Phys.*, 1955, **23**, 703. [b] Estimated. [c] $Cl·CO_2Et$: Weatherly and Williams, *J. Chem. Phys.*, 1954, **22**, 958. [d] Livingstone, *J. Phys. Chem.*, 1953, **57**, 496. [e] *Idem*, *J. Chem. Phys.*, 1952, **20**, 1170. [f] Ref. 6. [g] Part III, ref. 1. [h] Bray and Esteva, *J. Chem. Phys.*, 1954, **22**, 570.

TABLE 4. ^{35}Cl *Nuclear quadrupole resonance frequencies at* 77° K.

Compound	Frequency	
$CH_3·CH_2·CH_2Cl$	32·97	$\Delta = 0·07$
$Cl·CH_2·CH_2·CH_2Cl$	33·04 (Av)	
$CH_3·O·CH_2Cl$	30·01(Av)	$\Delta = 2·47$
$Cl·CH_2·O·CH_2Cl$	32·48	

It is generally accepted that the phosphorus–oxygen bond in phosphoryl compounds has at least partial d_π–p_π multiple-bond character, and it is relevant to consider in more detail the structure of phosphorus oxychloride. Assuming that the molecule is held together by a tetrahedral sp^3 σ-bond framework, consider the extreme form where the phosphorus–oxygen bond is co-ordinate, as in amine oxides. The vacant $3d$-orbitals on the phosphorus atom can now (*a*) remove the negative charge on the oxygen atom by

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[6] Hooper and Blay, *J. Chem. Phys.*, 1960, **33**, 334.

multiple-bond formation, and (*b*) overlap with the unshared-electron orbitals on the chlorine atoms. Of these two effects the former is evidently the more important.

The phosphorus oxychloride molecule has C_{3v} symmetry. Let the *z*-axis lie along the P–O bond and thus the two occupied *p*-orbitals on the oxygen atom lie in the *x*–*y* plane. The transformation properties of these two orbitals and of the five *d*-orbitals of phosphorus under the group C_{3v} and of the group $C_{\infty v}$ corresponding to the " local " symmetry of the bond are given in Table 5. This shows that the *p*–*x* and *p*–*y* orbitals can interact to form

TABLE 5. *Orbital transformation properties.*

	C_{3v}	$C_{\infty v}$		C_{3v}	$C_{\infty v}$
dz^2	a_1	a_1	(dxz, dyz)	e	e_1
$(dx^2 - y^2, dxy)$	e	e_2	(x, y)	e	e_1

a multiple bond with the pair *dxz, dyz*. The overlap is illustrated in Fig. 1 and the calculations of Craig *et al.*[7] have shown that the magnitude of the overlap integral is sufficiently great for efficient bond formation.

The phosphorus–oxygen bond is thus seen to have the characteristics of a triple bond since both pairs of orbitals are equally capable of overlap. The charge transfer to the phosphorus atom will, however, be far from complete and the oxygen atom probably retains a net negative charge.

FIG. 1. P–O *d_π–p_π overlap.*

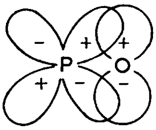
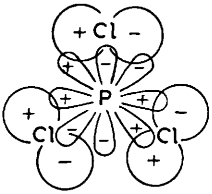


FIG. 2. P–Cl *d_π–μ_π overlap.*



Of the remaining *d*-orbitals the *dz*-orbital does not have the correct symmetry for d_π–p_π double-bonding. The dx^2–y^2 and *dxy* orbitals are, however, correctly oriented to overlap with the lone-pair orbitals on the chlorine atoms, as illustrated in Fig. 2. However, the *x*- and *y*-axes are not defined and the orientation has been arbitrarily chosen to illustrate the overlap. In fact, all three chlorine orbitals overlap equally with the degenerate pair of *d*-orbitals. The overlap will, however, be less than in the case of the phosphorus and oxygen orbitals because the chlorine atoms lie below the *x*–*y* plane containing the phosphorus atom and the phosphorus–chlorine bond is longer than the phosphorus–oxygen bond.

It can be concluded that in phosphoryl derivatives the substituents can conjugate weakly with the phosphorus atom and hence between themselves, but there is no direct conjugation with the phosphorus–oxygen bond. Observations of P–O stretching frequencies[4] are thus not relevant to the problem of the conjugating power of the phosphorus atom with other substituents. It should be noted, however, that the value of the overlap integral of the phosphorus *d*-orbitals with *p*-orbitals is very sensitive to the effective charge on the phosphorus atom and in this way pure inductive substituents could have an indirect conjugative effect.

In Fig. 3 the quadrupole frequencies for the phosphoryl derivatives are plotted against quadrupole frequencies and the carbonyl infrared stretching frequencies of the corresponding carboxylic acid chlorides. In both cases there is a general correlation between the two seta of data. Because the R·COCl group is planar, the substituent R can conjugate with both the carbonyl group and the chlorine atom and any conjugative effect should show up in both nuclear quadrupole and infrared measurements, although probably not to

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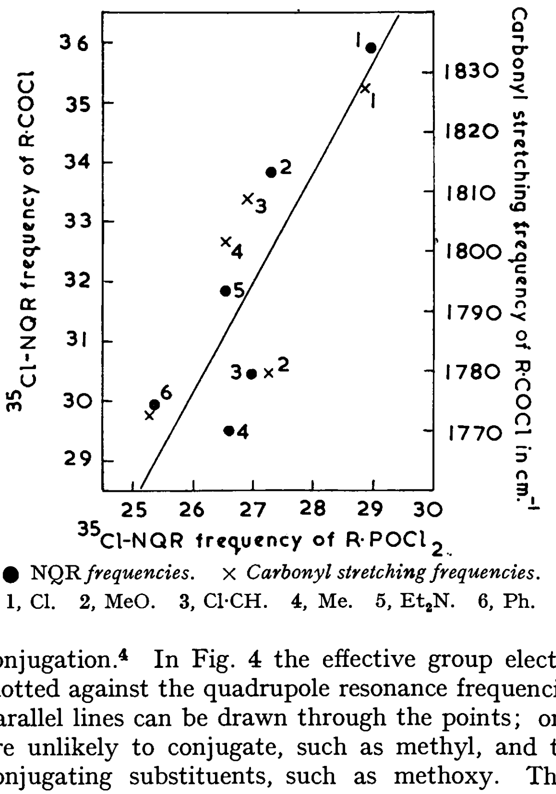
[7] Craig, McColl, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.

the same extent. The correlation illustrated in Fig. 3 thus indicates that the nuclear quadrupole resonance frequencies of phosphoryl chlorides are also affected by conjugation, as predicted by the above theoretical discussion of the structure of these compounds.

The carbonyl stretching frequencies of substituted ketones have been used as a measure of the effective electronegativity of the substituent,[8] but it was recognised that this electronegativity was a mixture of inductive and conjugative effects: In order to isolate the inductive electronegativity the P–O stretching frequencies of substituted phosphoryl compounds have been proposed since, as shown above, they should not be sensitive to conjugation.[4] In Fig. 4 the effective group electronegativities derived in this way are plotted against the quadrupole resonance frequencies. It is seen that two approximately parallel lines can be drawn through the points; one corresponding to substituents which are unlikely to conjugate, such as methyl, and the other corresponding to potentially conjugating substituents, such as methoxy. This again shows that the quadrupole frequencies are sensitive to conjugation.

Fig. 3. *Comparison of* ^{35}Cl *nuclear quadruple stretching frequencies of* R·POCl$_2$ *with the corresponding quadruple frequencies and carbonyl stretching frequencies of* R·COCl. *The scales have been chosen so that the spreads of infrared and quadrupole frequencies correspond.*



● NQR *frequencies.* × *Carbonyl stretching frequencies.*
1, Cl. 2, MeO. 3, Cl·CH. 4, Me. 5, Et$_2$N. 6, Ph.

Fig. 4. *Group electronegativities and* ^{35}Cl *nuclear quadrupole frequencies of* R·POCl$_2$. (*The frequency for* POFCl$_2$ *was taken from ref. e of Table* 3; *the electronegativities of the methyl, ethyl, and chloromethyl groups were derived from infrared measurements taken in this laboratory*).

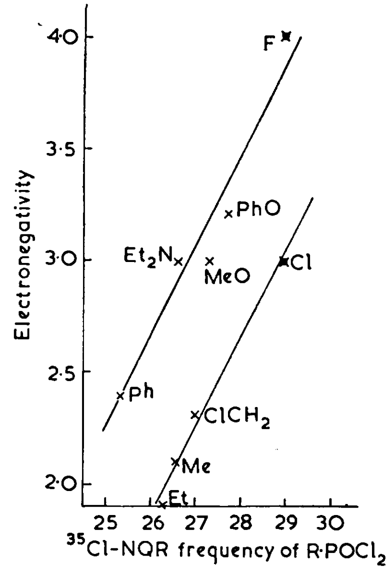


Table 6. *Calculated and observed frequency shifts for disubstituted derivatives of phosphoryl chloride.*

R·POCl$_2$	ΔR $\nu_{(POCl_3)} - \nu_{(R\cdot POCl_2)}$	RR′POCl	$\Delta R + \Delta R'$	ΔR observed
Me·POCl$_2$	2·412	EtO·P(Me)·OCl	3·9	2·39
EtO·POCl$_2$	1·49			
Et$_2$N·POCl$_2$	2·423	Et$_2$N·P(Me)·OCl	4·8	1·29

Although the frequencies of monosubstituted phosphorus oxychlorides are more or less in accord with expectation, the frequencies of the disubstituted derivatives are anomalous. This can be seen by reference to Table 6, the frequencies of the disubstituted

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[8] Kagarise, *J. Amer. Chem. Soc.*, 1955, **77**, 1377.

compounds being much higher than would be expected if the shifts were additive. This phenomenon is also observed in the P=O stretching frequencies[4] and the ^{31}P-nuclear magnetic resonance shifts of phosphoryl derivatives, particularly those having alkoxy- or alkylamino-substituents.[9] It is difficult to give any convincing explanation of this phenomenon and it would be desirable to have further data.

Derivatives of phosphorus trichloride.—Table 1 shows that only two derivatives of phosphorus trichloride gave quadrupole resonances and it is therefore impossible to build a comprehensive theory of the resonance frequencies of these compounds. Consideration of the results available indicates, however, that this is not likely to be profitable. In Table 7 the frequencies of the compounds measured are compared with those of corresponding carbon compounds and not only are the resonance frequencies very insensitive to the nature of the substituent but what effect there is lies in the opposite direction. This is almost certainly due to the fact that the bond angle in the pyramidal phosphorus trichloride molecule will be easily altered by substituents. This will alter the effective electronegativity of the phosphorus atom by changing the hybridisation of the bonds in the sense that the flatter the molecule the greater the *s*-character of the bonds and the greater the electronegativity of the phosphorus atom. It is unlikely, therefore, that further results will show much coherence.

TABLE 7. *Comparison of* ^{35}Cl *nuclear quadrupole resonance frequencies of derivatives of phosphorus trichloride with those of corresponding carbon compounds.*

R	$R{\cdot}PCl_2$	$R{\cdot}CCl_3$	$R{\cdot}CH_2Cl$	RCl
Cl	26·156	40·64	36·235	54·48
CH_3	26·081	37·938	32·704	34·029
Ph	26·557	38·702	33·627	34·622

Conclusion.—The present results appear unfortunately to have confused an already difficult situation. Although the reduced sensitivity of phosphorus compounds to substituent effects is confirmed, the probable existence of a conjugative effect on the quadrupole resonance frequencies appears to contradict the ultraviolet observations of Jaffé and Freedman.[2] In a later paper,[10] however, Jaffé interprets some further ultraviolet measurements as indicating slight conjugation between a phenyl substituent and a phosphorus atom and a small but finite conjugation between two phenyl substituents attached to the same phosphorus atom. The kinetic data in Table 1 are consistent with interpretation of conjugation as less important for phosphorus compounds than for carbon compounds, as predicted in the theoretical discussion above, and the quadrupole results are likewise not inconsistent with this. Further experiment will be necessary to resolve the apparent conflict between the ultraviolet measurements and the present results.

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[9] Muller, Lauterbur, and Goldenson, *J. Amer. Chem. Soc.*, 1956, **78**, 3557.
[10] Jaffé, *J. Chem. Phys.*, 1954, **22**, 1430.