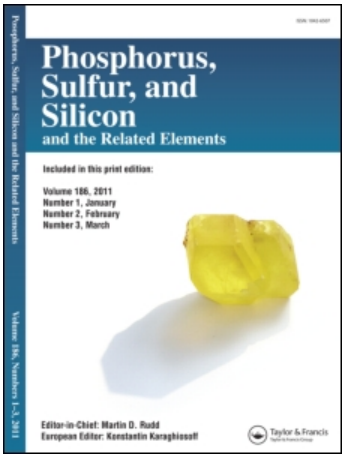

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SPIN-LATTICE RELAXATION PHENOMENA (T_1 VALUES) OF THE ^{31}P NUCLEUS IN CERTAIN CLASSES OF ORGANOPHOSPHORUS COMPOUNDS

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The spin-lattice relaxation process for the ^{31}P nucleus in a few selected phosphines, phosphine oxides, phosphine sulfides and one phosphonium salt as a function of temperature and concentration has been investigated. Relaxation via spin-rotation appears to dominate in triphenylphosphine and 1-phenyl-4-phosphorianone. The relaxation mechanism for the phosphine sulfides has a definite spin-rotation component but the ^{31}P nucleus appears to relax predominately by the chemical shift anisotropy mechanism. The chemical shift anisotropy mechanism appears also to participate in the relaxation of the phosphine oxides. Some contribution from the dipole–dipole *DD* relaxation mechanism appears operative in all systems to some extent. The activation energies for molecular rotational reorientation in those systems in which the *DD* mechanism makes a significant contribution fit reasonably well with the size and shape of the molecules. For most of the systems examined, the T_1 values increased with a decrease in concentration.

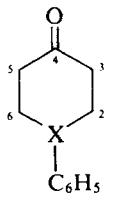
INTRODUCTION

In recent years, a relatively large quantity of work has been published on the relaxation behavior of carbon nuclei,[1] and to a smaller extent, on phosphorus nuclei in inorganic phosphorus systems.[2] Isolated studies involving organophosphorus compounds have appeared in the literature,[3–8] but only recently have there emerged papers reporting T_1 values and NOE data on ^{31}P nuclei.[9–13] These investigations appear to constitute a foundation concerning relaxation mechanisms, the mobility of such molecules in solution and the steric hindrance to internal motion of the groups containing the nuclei of interest.[14] In this paper, we report the influence of temperature and concentration parameters on the T_1 values of ^{31}P nuclei in **1–5**. With the exception of members of **1**, relaxation data for **2–5** are recorded for the first time.

$(C_6H_5)_3X$ **1**

$(C_6H_5)_2X—CH_2—X(C_6H_5)_2$ **2**

$(C_6H_5)_2X—CH_2—CH_2—X(C_6H_5)_2$ **3**



4

$(C_6H_5)_3\overset{+}{P}CH_3, I^-$ **5**

(a) X = P (b) X = P=O (c) X = P=S

METHOD

The approach most commonly used for the measurement of T_1 is the inversion recovery method combined with Fourier transform (IRFT).[15-20] This technique is based on the pulse sequence: $[180\text{-}\tau\text{-}90(\text{FID})\text{-}T]_n$.

The T is a time set to $5(T_1)_{max}$, where $(T_1)_{max}$ is the longest spin-lattice relaxation time to be measured. The T_1 values are computed from Eq. (1), where M_τ and M_0 are the signal intensities corresponding

$$M_\tau = M_0(1 - 2e^{-\tau/T_1}) \tag{1}$$

to τ and "infinite" delay between the 180° and 90° pulses. However, Canet and co-workers[21] have shown that considerable time saving can be achieved by the use of a shorter waiting time, W, between the pulse sequences. In this fast inversion recovery Fourier transform method (FIRFT), the signal intensities are fitted to a two-parameter expression, Eq. (2),

$$M_\tau = M_0[1 - (2 - e^{-W/T_1})e^{-\tau/T_1}] \tag{2}$$

where M_τ and M_0 have the same significance as before. Implicit in Eq. (2) is the assumption that either the number of scans is very large or the first scan is deleted.[21] In obtaining the results reported in this paper, the latter procedure was adopted. Although FIRFT method suffers a loss in dynamic range (or sensitivity) of the signals,[21] by making $W \simeq 2T_1$, this loss can be substantially minimized. All the T_1 values reported in this paper were determined with a waiting time of about $2T_1$.

Kowalewski and co-workers[22] have shown that there is no significant increase in accuracy with larger number of τ values. However, τ values covering a range up to at least 1.5 to $2T_1$ are needed for accurate determinations of T_1 values.[22] In keeping with this finding, approximately 9 to 10 separate τ values covering a range from 1 sec up to about 1.5 T_1 were used to obtain our T_1 measurements. Finally, since the two-parameter expression, Eq. (2), has the disadvantage of being sensitive to systematic errors,[22] the more flexible three-parameter expression (suggested by Sass and Ziessow)[23] of Eq. (3) was used to

$$M_\tau = A + B\,e^{-\tau/T_1} \tag{3}$$

compute T_1 values. In Eq. (3), A, B and T_1 are adjustable parameters.

NOE values (n) were obtained by performing coupling and decoupling experiments alternatively, with a delay time of $\geq 5T$. Decoupler power was set at 5 watts. Samples were weighed and dissolved in $DCCl_3$ (except for the phosphines in which acetone-d_6 was used). The samples were frozen (liq. N_2) and evacuated under a pressure of $<10^{-4}$ torr. After 5–10 min. under vacuum, the sample was disconnected from the vacuum system and allowed to liquify. The cycle was repeated 4–5 times and the sample was sealed at $<10^{-4}$ torr. A typical NOE experiment can be described as follows. A degassed sample was placed in the probe and the instrument was locked onto the deuterium signal in the solvent. To compensate for local fluctuations in the magnetic field, alternate pulses were applied, one with the decoupler frequency set at 45,000 Hz (decoupler on) and one with the decoupler frequency set at 65,000 Hz (decoupler off). At a decoupler power setting of 5 watts and the offset at 65,000 Hz, essentially no ^1H decoupling occurs (deuterium lock on $DCCl_3$ or $D_3CC(O)CD_3$ was used). These alternate pulses were stored in two separate files, and yielded two spectra, one coupled and one fully decoupled. Identical acquisitions of data in each file (A and B) coupled with the technique of alternatively per-

forming the two experiments (using 32 K data points for real and imaginary portions of the spectra) were done so that any variations in experimental conditions (magnetic fluctuation, etc.) affected *both* measurements presumably in an equivalent manner. Peak areas for the ^{31}P NMR signals were evaluated by cutting and weighing the actual area and by use of a planimeter.

Most workers[11,12] have utilized experimental procedures in which a fully decoupled experiment was performed followed by a gated decoupling experiment on the same sample. The areas of the peaks from the two spectra were then compared in order to obtain the NOE factor.[5,9] However, such a technique almost surely results in greater differences in instrument variations between the two experiments and could lead to possible errors in the NOE value. Calculation of the NOE factor η and the percent of (*DD*) contribution were obtained via Eq. (4) and Eq. (5) below.[14]

$$\eta = \frac{\text{area of decoupled peak}}{\text{area of coupled peak}} - 1 \tag{4}$$

$$\%\ DD\ \text{Contribution} = \eta/1.235[(100)] \tag{5}$$

IRFT vs FIRFT

In order to determine whether a shorter waiting time ($\simeq 2T_1$) between the pulse sequences would lead to T_1 values significantly different from the ones obtained with a longer time delay, the relaxation times of ^{31}P nuclei in a few selected compounds were determined by both the FIRFT and IRFT methods. The results are reported in Table I. It is to be noted that the differences in T_1 values are small.

As the results in Table II indicate, small changes in pulse characteristics do not significantly affect the T_1 values. Similar observations have been made by Canet and co-workers[21] with ^{13}C relaxation measurements.

TABLE I

Comparison of IRFT with FIRFT

Cpd.	Conc. (moles/liter)[a]	Temp. (C°)[b]	T_1 values (sec)[c,d] IRFT	FIRFT
1b	0.2	35	19.1 ± .6(100)	18.4 ± .8(40)
1c	0.2	35	31.6 ± .7(150)	32.4 ± .1(60)
			31.8 ± .8(150)	32.6 ± .2(40)
		15	27.7 ± .3(150)	27.7 ± .5(60)
			28.1 ± .2(150)	27.4 ± .2(40)
2c	0.2	35	11.8 ± .1(50)	11.9 ± .1(25)
		15	8.35 ± .14(75)	8.5 ± .14(20)
3c	0.2	35	8.93 ± .08(100)	9.23 ± .11(18)
			8.77 ± .28(100)	9.05 ± .14(20)
			9.01 ± .11(50)	9.14 ± .09(20)
		15	6.60 ± .06(40)	6.63 ± .08(15)
			6.65 ± .05(40)	6.60 ± .08(15)

[a] In $DCCl_3$. All solutions were degassed.
[b] Temperature accurate to ±2°C.
[c] Waiting time, in sec, between the pulse sequences are given in the parentheses.
[d] ± variations are averages of a minimum of three values.

TABLE II

Effect of pulse angle on T_1

Cpd.	T_1(sec)[a] 180°-τ-90°	T_1(sec)[a] 172°-τ-86°
2c	11.9 ± .1(35)	11.9 ± .1(35)
	8.69 ± .08(15)	8.50 ± .14(15)
3c	9.05 ± .14(35)	9.14 ± .09(35)
	6.65 ± .05(15)	6.60 ± .08(15)

[a] Temperature values in °C are given in the parentheses. Pulse angles are adjusted by controlling the duration of the pulse width.

RESULTS AND DISCUSSION

Tables III–V have relaxation and activation energy (for the *DD* process) data for **1–5**. At least two and, in some cases, up to four measurements, were made on *separate* samples at each concentration, and the T_1 and NOE values reported were the average of these separate measurements. Relaxation data for the phosphines were collected in acetone-d_6. For all other compounds, $DCCl_3$ was the solvent employed. Although T_1 values of ^{31}P in phosphines have been reported in $DCCl_3$ solvent,[4,9,12] we observed that the use of $DCCl_3$ for phosphines resulted in T_1 values that were irreproducible and continuously decreased with time. Although reactions of phosphines with deuteriochloroform[24] and the reaction of triphenylphosphine with CCl_4,[25,26] as well as with $HCBr_3$ at 150°C, have been reported, no systematic analysis of the reaction mixture has been recorded to our knowledge.[27] Whether or not $HCCl_3$ reacts with phosphines to a small extent on extended exposure is still apparently an unanswered question and could be the cause of the lack of consistency in the T_1 values found in our studies.

Three mechanisms, namely, dipole–dipole (*DD*) interaction, spin-rotation (*SR*) interaction and chemical shift anisotropy (*CSA*) could contribute to the relaxation of the ^{31}P nucleus in the systems examined.[14] In general (for most of the compounds

TABLE III

Relaxation data for systems **1–5**

Cpd.	Conc. (mole/liter)	T_1(sec) 15°C	25°C	35°C
1a	0.05	23.2 ± .4	20.2 ± .3	17.3 ± .2
2a	0.05	20.6 ± .7	21.3 ± .3	22.7 ± .2
3a	0.05	16.5 ± .4	19.1 ± .1	21.1 ± .2
4a	0.05	16.0 ± .2	16.0 ± .2	14.9 ± .1
1b	0.2	14.4 ± .2	15.6 ± .6	18.7 ± 1.2
2b	0.2	6.4 ± .07	7.07 ± .23	8.37 ± .14
3b	0.2	3,78 ± .02		6.28 ± .47
4b	0.2	8.79 ± .04	9.85 ± .07	11.3 ± .3
1c	0.2	27.5 ± .3	29.7 ± .2	32.5 ± .1
2c	0.2	8.60 ± .1	9.90 ± .2	11.9 ± .1
3c	0.2	6.61 ± .07	7.98 ± .16	9.14 ± .1
4c	0.2	13.2 ± .0	14.7 ± .3	16.0 ± .1
5	0.2	9.78 ± .05	10.8 ± .2	12.6 ± .2

TABLE IV

Relaxation data for systems **1–4**

Cpd.	Conc. (mole/liter)	T_1(sec) 15°C	25°C	35°C
1a	0.03	27.8 ± .7	23.1 ± .3	21.1 ± .5
2a	0.03	20.2 ± .7	23.3 ± .2	25.2 ± .7
3a	0.03	17.5 ± .5	18.8 ± .3	20.1 ± .4
4a	0.03	15.4 ± .2	14.4 ± .1	14.0 ± .2
1b	0.1	18.9 ± .2	19.9 ± .6	24.3 ± 1.2
2b	0.1	6.45 ± .1	7.45 ± .14	9.94 ± .45
3b	0.1	5.42 ± .05	6.25 ± .11	7.03 ± .25
4b	0.1	10.4 ± .3	11.1 ± .3	12.1 ± .3
1c	0.1	27.4 ± .2	29.7 ± .3	32.9 ± .2
2c	0.1	9.48 ± .06	10.7 ± .1	12.2 ± .2
3c	0.1	7.15 ± .04	8.30 ± .08	9.75 ± .12
4c	0.1	13.3 ± .1	15.7 ± .5	16.6 ± .3

under the conditions investigated), the relaxation time *increased* with a rise in temperature. However, for both triphenylphosphine (**1a**) and 1-phenyl-4-phosphorinanone (**4a**), the relaxation times were found to *decrease* with increasing temperature, a trend that should be expected if spin-rotation interaction was the predominate relaxation mechanism.[14] A similar trend was observed by Kooli and co-workers in triethylphosphine and triphenylphosphine (in $DCCl_3$).[4] Usually the *SR* mechanism plays an important role in small, symmetrical molecules and in small segments of larger molecules. Hence, it was surprising that this process initially appeared to be the predominant relaxation mechanism for a molecule of the size of triphenylphosphine. In the absence of geminal or vicinal protons, the *DD* interaction *cannot* be the dominant relaxation mechanism. Data in Tables VI and VII show the percent of dipole–dipole contribution to the overall relaxation mechanism and are in agreement with those values found by Wilke[9] for triphenylphosphine, triphenylphosphine oxide and triphenylphosphine sulfide. As can be seen in the Tables, dipole–dipole interactions contribute only a small part to the total relaxation process for the ^{31}P nucleus. This consideration and the fact that the molecule pos-

TABLE V

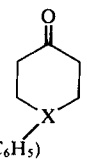
Activation energies for molecular rotational reorientation

Cpd.	Conc. (moles/liter)[a]	Coefficient of Determination[b]	ΔE (kcal/mole)
3a	0.05	0.988	2.2
3b	0.1	0.997	2.3
4b	0.1	0.994	1.4
1c	0.2	0.998	1.5
2c	0.2	0.994	2.9
3c	0.2	0.991	2.9
4c	0.2	0.995	1.7
1c	0.1	0.995	1.6
2c	0.1	0.999	2.3
3c	0.1	1.000	2.8

[a] Compound **3a** is in acetone-d_6 solvent and all other compounds are in $DCCl_3$.
[b] The coefficient of determination corresponds to the plot of log T_1 vs $1/T$.

TABLE VI

NOE values expressed as η and % *DD* as a function of *T* and concentration for systems **1–4**.

		X = phosphine						X = P-oxide						X = P-sulfide					
	conc.[a]	15°		25°		35°		15°		25°		35°		15°		25°		35°	
		η	% *DD*	η	% *DD*	η	% *DD*	η	% *DD*	η	% *DD*	η	% *DD*	η	% *DD*	η	% *DD*	η	% *DD*
1 $(C_6H_5)_3X$	*a*	0.09	7.3	0.10	8.1	0.14	11.3	0.09	7.3	0.07	5.7	0.11	8.9	0.23	18.6	0.20	16.2	0.18	14.6
	b	0.11	8.9	0.10	8.1	0.12	9.7	0.09	7.3	0.13	10.5	0.09	7.3	0.25	20.2	0.27	21.9	0.22	17.8
2 $[(C_6H_5)_2X]_2CH_2$	*a*	0.08	6.5	0.13	10.5	0.09	7.3	0.09	7.3	0.07	5.7	0.04	3.2	0.19	15.4	0.25	20.2	0.27	21.9
	b	0.08	6.5	0.06	4.9	0.06	4.9	0.10	8.1	0.06	4.9	0.05	4.2	0.26	21.0	0.28	22.7	0.22	17.8
3 $[(C_6H_5)_2XCH_2]_2$	*a*	0.10	8.1	0.10	8.1	0.09	7.3	0.07	5.7	0.04	3.2	0.07	5.7	0.09	7.3	0.09	7.3	0.07	5.7
	b	0.10	8.1	0.12	9.7	0.19	15.4	0.08	6.5	0.05	4.0	0.09	7.3	0.06	4.9	0.05	4.0	0.04	3.6
 **4**	*a*	0.15	12.1	0.19	15.4	0.26	21.1	0.06	4.9	0.05	4.0	0.04	3.2	0.23	18.6	0.18	14.6	0.15	12.2
	b	0.17	13.8	0.20	16.2	0.24	19.4	0.04	3.2	0.09	7.3	0.07	5.7	0.27	21.9	0.25	20.2	0.24	19.2

[a] $a = 0.05$ M, $b = 0.03$ M for phosphines; $a = 0.2$ M, $b = 0.1$ M for oxide and sulfides.

TABLE VII

NOE values expressed as η and % *DD* as a function of *T* and concentration for **5**.

5		15°		25°		35°	
$(C_6H_5)_3\overset{+}{P}CH_3$	conc.	η	% *DD*	η	% *DD*	η	% *DD*
I^-	0.2	0.14	11.3	0.14	11.3	0.17	13.8

sesses an axis of symmetry (passing through the lone pair and phosphorus) may perhaps account for the dominance of *SR* mechanism. This result is also in keeping with a similar observation made by Dale and Hobbs[5] on trimethyl phosphite, a compound with similar symmetry properties as that of triphenylphosphine. Although the change in T_1 with temperature for 1-phenyl-4-phosphorinanone (**4a**) was in the same direction as in triphenylphosphine (**1a**), it was not as significant as in the latter. The presence of neighboring protons H(2) and H(6) may permit the *DD* mechanism to compete more favorably with the *SR* mechanism in the former compound. This trend can be seen in examination of the NOE value (η) found for triphenylphosphine which was smaller than that found for 1-phenyl-4-phosphorinanone (**4a**). This suggests that the presence of H(2) and H(6) protons does permit more *DD* mechanism to contribute to the relaxation of the phosphorus nucleus.

Changes in molecular symmetry may also reduce somewhat the contribution of the *SR* mechanism. It is quite possible that the combined motion of ring reversal and molecular rotation in **4a** lowers the tumbling rate of the molecule with a subsequent increase in effective correlation time τ_c. This lengthening of the τ_c value in the region of motional narrowing may also account for the improved efficiency of the *DD* mechanism.[14] The temperature dependences of these two mechanisms are in the opposite directions.[14] Hence, it is conceivable that the decrease in T_1 with increase in temperature (due to *SR*) is moderated by the opposing trend (due to *DD*) with a predominance of the *SR* mechanism effecting the net result.

Since the contribution of dipolar relaxation depends on the effective correlation time $\tau_c[T_{1(DD)} = f(\tau_c)]$[8] and since the temperature dependence of the latter can be written in the form of an Arrhenius Eq. (6),

$$\tau_c = \tau_{c_1} e^{\Delta E/RT} \tag{6}$$

then if *DD interaction is a contributing relaxation mechanism,* a similar Arrhenius type equation could be written involving the relaxation time $T_{1(DD)}$:

$$T_{1(DD)} = K\, c^{-\Delta E/RT} \tag{7}$$

Since $\tau_c[T_{1(CSA)} = f(\tau_c)]$ holds, the *CSA* interaction possesses a temperature dependency similar to that for T_1 values which depend upon dipole–dipole interactions.[28] Shown in Figures 1–2 are the plots of the logarithm of the $T_{1(DD)}$ versus the reciprocal temperature. The activation energies, ΔE values for molecules of the size investigated were in the range of 0.07–2.3 kcal/mole. The relatively small and symmetrical molecule, triphenylphosphine sulfide (**1c**), had a low activation energy, implying that the molecule tumbled easily in solution. Indeed the less symmetrical and relatively large molecule, such as **2c**, $(C_2H_5)_2P(S)CH_2P(S)(C_2H_5)_2$, had a lower activation energy for this process. Intuitively, the data for the latter two compounds seems to be in reverse order. However, the rotational reorientation of these molecules in solution is undoubtedly different due to their different sizes and shapes. Each molecule has dissimilar motional characteristics. Since all angular displace-

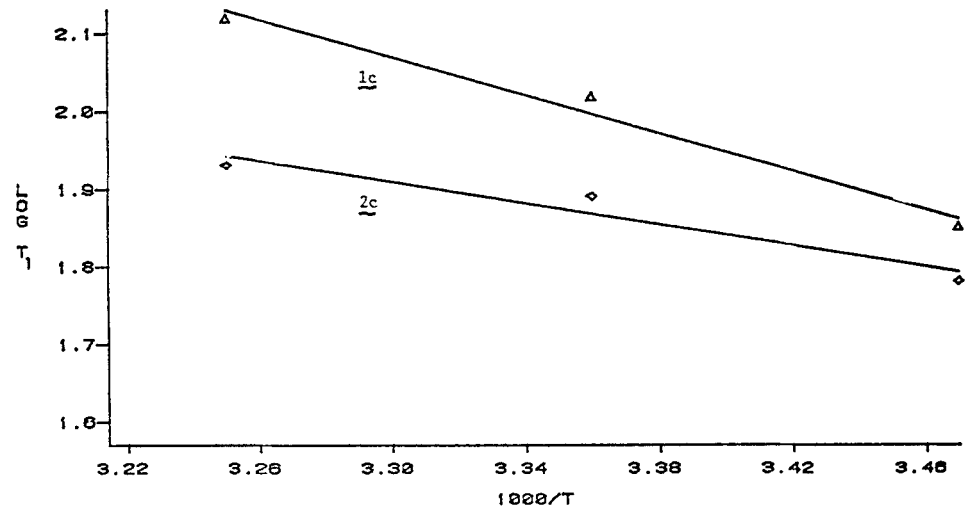


FIGURE 1 Temperature dependence of spin-lattice relaxation times in **1c** and **2c**. Δ represents 0.1 M **1c**; ◇ represents 0.1 M **2c**.

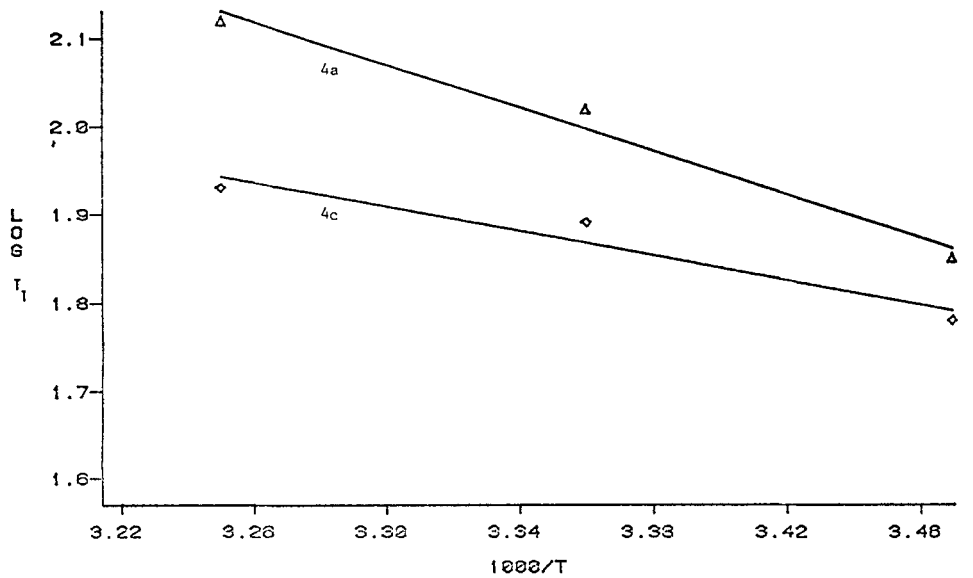


FIGURE 2 Temperature dependence of spin-lattice relaxation times in **4a** and **4c**. Δ represents 0.5 M **4a**; ◇ represents 0.5 M **4c**.

ments are not equally effective in causing relaxation via one particular mechanism,[28] the activation energies reflect the reorientation of the molecule with respect to the motions that cause relaxation by a particular process.[28] This is demonstrated for **4a** (cyclic phosphine) and **4c** (cyclic P-sulfide). The activation energy for **4a** is 2.3 kcal/mole while the value is 1.4 kcal/mole for **4c**. These data would seem to be in reverse order again since **4a** is a small molecule and less rigid than **4c**. Examination of the T_1 values for **4a** with respect to temperature revealed that the *SR* mechanism was probably operative (T_1 decreases as temp increases) while for **4c** the *CSA* mechanism likely *dominated* (T_1 increases as temp increases). In view of the observed NOE values for **4a** and **4c**, we assume that the *DD* mechanism also participated to relax ^{31}P in these molecules. Consequently, different motions occur in each system and therefore the ΔE values [which are a measure of the rotational reorientation of a molecule with respect to those motions causing relaxation by a *DD* process] cannot be legitimately compared.[28] Activation energies reported herein are for the dipole–dipole rotational process only.

Data in Tables III and IV show the influence of structure and temperature on the T_1 values of phosphines **1a–3a**, phosphine oxides **1b–3b** and phosphine sulfides **1c–3c**, each at two different concentrations and three different temperatures. For both the sulfides and oxides, the change in structure from $(C_6H_5)_3X$ to $(C_6H_5)_2X—CH_2—X(C_6H_5)_2$ resulted in a large decrease in the T_1 values for the ^{31}P atom at all the temperatures and concentrations investigated. The increased size of the biphosphine sulfides (with likely longer correlation time) as well as the added C—H bonds in the methylene group (more *DD* contribution) probably are responsible for this phenomena. A similar decrease in the T_1 values for the oxides cannot be indicative of increased contribution from *DD* in view of the NOE values observed (Table VI) for **1b–3b**. Introduction of another —CH_2-group, such as in going from $(C_6H_5)_2X—CH_2—X(C_6H_5)_2$ to $(C_6H_5)_2X—CH_2CH_2—X(C_6H_5)_2$, resulted in a slight *decrease* in T_1 values under all the conditions examined and also suggested a small increase in contribution of (*DD*) to the relaxation process for sulfides and oxides.

Interestingly, the ^{31}P nucleus in $(C_6H_5)_3P$ (**1a**) and 1-phenyl-4-phosphorinanone (**4a**) apparently relaxed by the *SR* mechanism as demonstrated by a *decrease* in T_1 values as the temperature increased (Table IV).[29] Of course, the effect was greater in **1a** than in **4a** the former being smaller. In **4a**, *DD* must also contribute in a significant manner, as stated previously, as evidenced from examination of the NOE values in Table IV. We tentatively suggest that the more symmetrical and rigid **4a** molecule has an increased *DD* relaxation process for ^{31}P compared to that for the open biphosphine systems **2a** and **3a** which also have a smaller number of CH_2 groups.

In comparing $(C_6H_5)_2PCH_2P(C_6H_5)_2$ with $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, a decrease in T_1 was observed for all the three temperatures and the two concentrations examined of the latter compound. This suggested a greater *DD* contribution. At 15°C, however, there was a monotonous decrease in T_1 in going from **1a** to **3a** for both the concentrations. At this lower temperature, the molecules apparently tumbled slowly in solution, and this lower tumbling rate was favorable to *DD*.

At every temperature and concentration studied, the phosphine oxides were found to have *lower* T_1 values compared to the sulfides. If the oxides and the sulfides relaxed by the same mechanism, the relatively heavier sulfides, tumbling rather slowly in solution, should be more efficiently relaxed. The smaller T_1 values for the oxides suggested that a different mechanism was operating. Kooli and co-workers[4] concluded that in the case of triphenylphosphine oxide, the results of their observa-

tion were consistent with the operation of the *CSA* mechanism. The presence of a *CSA* mechanism has also been noted in some phosphoryl compounds[5] (such as $OP(OCH_3)_3$ containing the P=O bond. It is probable this mechanism was dominant in all oxides investigated in our work. Presumably, the P=O bond disturbed the isotropic electron distribution around the ^{31}P nucleus resulting in substantial values for the anisotropy tensor.[4] It is quite probable that different proportions of the *DD* and *CSA* relaxation mechanisms are operative in the phosphine oxides compared to the phosphine sulfides. The NOE data indicate that the *DD* mechanism participates to a larger extent in the sulfides than in the phosphine oxides (Table VI).

Lowering the concentration resulted in an increase in T_1 values for both the sulfides and oxides at all the three temperatures studied. It is probable that lowering the concentration reduced constraints on molecular tumbling and consequently reduced the efficiency of the *DD* (or *CSA*) contribution to the overall relaxation. The effect of concentration on the relaxation time of phosphines was found to be irregular.

Compared to the triphenylphosphine sulfide and triphenylphosphine oxide, the salt methyltriphenylphonphonium iodide (**5**) had a lower T_1 value at each of the three temperatures examined. This may be due to the presence of nearby protons in the $-CH_3$ group. However, a more important cause may be the formation of ion-pairs in solution.[4] As a result, the tumbling rate of the phosphonium ion would be restricted and consequently the effective correlation time τ_c in the region of motional narrowing could account for the improved efficiency of the *DD* mechanism (or *CSA* mechanism).

EXPERIMENTAL

All ^{31}P spin-lattice relaxation times were measured at 40.5 MHz in an XL-100(15) Varian spectrometer coupled to a Nicolet TT-100 computer system using 5 mm tubes. The 180° and 90° pulses were obtained with pulse widths of 24 μs and 12 μs respectively. The deuterium in the solvent provided the necessary lock signal. All sample solutions were purged with dry, oxygen-free nitrogen (5 min) and then degassed by repeated (at least 5 times) freezing, evacuation and thawing. The tubes were finally sealed under vacuum with a hand torch. A Varian temperature regulator was used for temperature control during the T_1 measurements. A sealed capillary filled with methanol and a trace of HCl placed in 5 mm NMR tube containing 0.5 ml acetone-d_6 was used as a check to measure the temperature according to the method of van Geet.[30]

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