Rotational Motions in *n*-Hexane Phosphonic Acid Diethyl Ester Studied Combining ²H, ¹³C, and ³¹P NMR. Analysis of the Phosphorus-31 Spin-Lattice Relaxation

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Spin-lattice relaxation of ¹³C and ¹³P in neat H₃C(CH₂)₅P(O)(OC₂H₅)₂ and of ²H and ³¹P in H₃C(CH₂)₄C²H₂P(O)(OC₂H₅)₂ and H₃C(CH₂)₅P(O)(OC₂²H₅)₂ have been measured in the temperature range from -70 to 160° C and at different fields. By using the NOE and the selectivity deuterated compounds the contributions of different segments to the total proton-phosphorus dipole-dipole relaxation were determined. Quantitative analysis of the ³¹P relaxation yields the result that, at the phosphorus resonance frequencies of 36.44 and 145.76 MHz and at all temperatures studied, at least two interaction mechanisms contribute. Further, the α -CH₂ segment, the ester groups, and the hexyl residue without the α -CH₂ segment, each gives approximately one-third of the total proton-phosphorus dipole-dipole contribution. The spin-lattice relaxation of ²H, ¹³C, and ³¹P is described on the basis of the Woessner model in the whole temperature range studied with one set of motional parameters. The relaxations of the spins in the H₂CP(O)O₂ and ²H₂CP(O)O₂ segments are mainly determined by the overall reorientation whereas this motion has at most a small effect on the ¹³C relaxation of the other segments and on the ²H relaxation of the ester groups.

INTRODUCTION

Phosphonic acid esters are used as herbicides and defoliants (1, 2). The efficiency of the compounds is determined by their solubility as well as by their structural and dynamical properties (3). The rotational motion in a special ester, namely in *n*-hexane phosphonic acid diethyl ester (PAE6) is the main subject of this paper. The results obtained from the pure compound can be used as reference data for the elucidation of motional processes under the condition of interaction with other (biological) components. They can also serve as a guide for the study of other phosphonic acid esters. Häkkinen (4) has undertaken the first attempt to investigate the rotational motions in some esters by NMR, but these results can be regarded only as more or less qualitative.

Nuclear magnetic spin-lattice relaxation has in the past been applied to study motional processes in a large number of liquids and solutions (5). Although general theoretical relations for systems with multiple degrees of freedom are available (6, 7), usually simplified models are applied in special systems, e.g., in the case of relatively small molecules; the model of Woessner (8) is an example.

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If one uses experimental data of only one nucleus, obtained at one frequency and in a relatively small temperature region (e.g., in the region of extreme narrowing), then a good fit of the experimental data is always possible using the model of Woessner. The linear dependence of $\ln T_1$ over 1/T found in many cases is often cited as the evidence of the validity of the model or for the good quality of the quantitative results obtained (T_1 is the spin-lattice relaxation time and T the absolute temperature). But these conclusions are often not justified. If one considers the ³¹P T_1 relaxation in PAE6 in a relatively large temperature region, for instance, one which comprises the extreme narrowing region and the region of the T_1 minimum, then it can be described with different sets of parameters on the basis of the model of Woessner for isotropic overall molecular reorientation and one intramolecular motion (8). An unambiguous decision about the correct parameter set is not possible because the sums of the square errors of the different sets differ only slightly. One possibility is the utilization of different nuclei, e.g., ²H, ¹³C, and ³¹P, which have various orientations of the nuclear interaction vectors. In this paper it is shown that it is possible to determine one set of parameters which describes the relaxations of the three nuclei on the basis of one model with the same accuracy.

Phosphorus relaxation is of great interest because many phosphorus-containing compounds, e.g., phospholipids, play an important role in biological systems. PAE6 is a smaller molecule than the very important lipid dipalmitoylphosphatidylcholine, but it contains in part the same segments neighboring phosphorus. The detailed ³¹P relaxation analysis of PAE6 should contribute to a better understanding of phosphorus relaxation in lipids (9–14) which still is poor, even in isotropic systems.

Finally, the ³¹P relaxation analysis gives some information about the screening tensors in phosphonate groups. Although the ³¹P screening tensors in phosphate groups have been extensively studied, only three papers (15-17) to our knowledge have been published concerning the tensor in phosphonate groups.

THEORY

We consider only intramolecular interactions. Intermolecular interactions can be completely neglected in the case of ²H and ¹³C relaxation but they can give small contributions to ³¹P relaxation.

The ³¹P spin-lattice relaxation time, T_1 , can be separated into dipolar, T_{1DD} , chemical-shift anisotropy, T_{1CSA} , and spin-rotational, T_{1SR} , contributions:

$$\frac{1}{T_1} = \frac{1}{T_{1\text{DD}}} + \frac{1}{T_{1\text{CSA}}} + \frac{1}{T_{1\text{SR}}}.$$
[1]

The dipole-dipole contribution to the ${}^{31}P$ relaxation is the result of the dipole-dipole interactions of ${}^{31}P$ with the different hydrogen-containing segments present in PAE6. Generally, the hydrogen contribution decreases with increasing distance of the segment from the phosphonate group because of increasing average distance (cf. (3)).

If we use the following notation for the contributions of the ester groups, T_{1DD}^{est} , of the hexane substituent, T_{1DD}^{hex} , of the α -CH₂ segment, T_{1DD}^{α -CH₂}, of the hexane substituent without the α -CH₂ segment, T_{1DD}^{rest} , then

$$\frac{1}{T_{1DD}} = \frac{1}{T_{1DD}^{hex}} + \frac{1}{T_{1DD}^{est}} = \frac{1}{T_{1DD}^{\alpha-CH_2}} + \frac{1}{T_{1DD}^{rest}} + \frac{1}{T_{1DD}^{est}}.$$
 [2]

The total proton phosphorus dipole-dipole contribution, T_{1DD} , was determined at high temperatures (extreme narrowing) by measuring the ³¹P{¹H} NOE and applying the relation

$$T_{1\text{DD}} = \frac{1.235}{\eta} T_1$$
 [3]

where η is the enhancement of the ³¹P signal intensity.

The anisotropy contribution is given by (17, 21)

$$\frac{1}{T_{1\text{CSA}}} = \frac{1}{15}\omega^2 [(\sigma_{33} - \sigma_{11})^2 + (\sigma_{33} - \sigma_{22})^2 + (\sigma_{22} - \sigma_{11})^2] \frac{\tau_{\text{CSA}}}{1 + (\omega\tau_{\text{CSA}})^2}$$
[4]

assuming isotropic reorientation of the molecular frame in the coordinate system with the origin at the ³¹P atom, in which the ³¹P tensor is diagonal. The quantities σ_{11} , σ_{22} , and σ_{33} are the principal values of the screening tensor in ppm.

The spin-rotational contribution is given for spherical molecules by (22, 23)

$$\frac{1}{T_{1SR}} = \frac{2kT}{h^2} I_s C^2 \frac{\tau_{SR}}{1 + (\omega \tau_{SR})^2}$$
[5]

where I_s is the moment of inertia, C is the spin-rotational coupling constant in radians s^{-1} , and τ_{SR} is the spin-rotational correlation time. From these assumptions Hubbard (24) derived the relation

$$\tau_{\rm SR}\tau_{\rm c} = \frac{\rm I_s}{6kT}.$$
[6]

The ¹³C relaxation in PAE6 is determined by dipole-dipole interactions with the attached protons. This is evidenced by the nuclear Overhauser effect. The ²H relaxation is determined only by the quadrupolar interaction between the electric quadrupole moment of deuterium and the electric field gradient at deuterium nucleus.

PAE6 is a relatively small molecule in which different large-amplitude conformational changes take place. For isotropic overall reorientation of the molecule with the correlation time $\tau_{\rm M}$ and one internal motion with the correlation time $\tau_{\rm G}$, the dipolar (18) and quadrupole (8) contributions are given by

$$\frac{1}{T_{1DD}} = \frac{1}{10} \frac{\mu_0^2}{(4\pi)^2} \frac{\gamma_1^2 \gamma_S^2 \hbar^2}{r^6} \left[A \chi_A + B \chi_B + C \chi_C \right]$$
[7]

$$\frac{1}{T_{1Q}} = \frac{3}{40} \frac{(e^2 q Q)^2}{\hbar^2} \left\{ A[J_A(\omega) + 4J_A(2\omega)] + B[J_B(\omega) + 4J_B(2\omega)] + C[J_C(\omega) + 4J_C(2\omega)] \right\}.$$
[8]

Here

$$A = \frac{1}{4}(3\cos^2\theta - 1)^2, \qquad B = 3\sin^2\theta\cos^2\theta, \qquad C = \frac{3}{4}\sin^4\theta$$
$$\chi_i = J_i(\omega_{\rm I} - \omega_{\rm S}) + 3J_i(\omega_{\rm I}) + 6J_i(\omega_{\rm I} + \omega_{\rm S})$$

with

$$J_i(h)=\frac{\tau_i}{1+h^2\tau_i^2}.$$

If the internal motion can be described by diffusion

$$\tau_A^{-1} = \tau_M^{-1}, \qquad \tau_B^{-1} = \tau_M^{-1} + (6\tau_G)^{-1}, \qquad \tau_C^{-1} = \tau_M^{-1} + 2(3\tau_G)^{-1}$$

and if by a jump process between three sites of equal population

$$\tau_B^{-1} = \tau_C^{-1} = \tau_M^{-1} + \tau_G^{-1}.$$

The value $e^2 q Q/h$ of 170 kHz (19) was used as the quadrupole coupling constant in aliphatic bonds. The gyromagnetic ratios of the nucleus observed and of the nucleus with which it interacts are γ_1 and γ_s and r is the internuclear distance. Further, θ is for ²H relaxation the angle between the C-²H vector, and for the dipole-dipole contribution that between the I-S vector, and the axis of internal motion. I denotes the nucleus observed. For thermally activated reorientation processes

$$\tau_{\rm M} = \tau_{\rm M}^0 \exp(E_{\rm M}/RT)$$
 and $\tau_{\rm G} = \tau_{\rm G}^0 \exp(E_{\rm G}/RT)$.

 $E_{\rm M}$ and $E_{\rm G}$ are the activation energies for the overall reorientation of the molecule and for the intramolecular motion, respectively. If the interaction vector coincides with the axis of rotation, $\theta = 0$, the internal motion has no influence upon the relaxation and the expressions [7] and [8] turn to the well known formulas for the simple model of isotropic reorientation (20).

EXPERIMENTAI

 $H_3C(CH_2)_5P(O)(OC_2H_5)_2$ is denoted by PAE6 and $H_3C(CH_2)_4C^2H_2P(O)(OC_2H_5)_2$ by PAE6- d_2 . They were synthesized from sodium diethylphosphite and 1-bromohexane and 1-bromo-1,1- d_2 -hexane, respectively, by the Michaelis-Becker reaction (25). $H_3C(CH_2)_5P(O)(OC_2^2H_5)_2$ is denoted by PAE6- d_{10} . It was synthesized according to Ref. (26) from hexane phophonic acid dichloride and perdeuterated ethanol, obtained from Isocommerz, Berlin. The compound was purified by repeated washing with water and finally by vacuum distillation. All compounds were distilled under vacuum (10 Pa) in special tubes. The pressure in the tubes after their filling was adjusted to 50 kPa with oxygen-free N₂ and then the tubes were sealed. Special tubes were used to avoid errors due to diffusion as described by Levy and Peat (27). Care was also taken to ensure that the compound was completely inside the receiver coil.

The relaxation time T_1 was measured by the fast inversion recovery method (28, 29) under the condition of proton noise decoupling. In the case of ¹³C relaxation the phosphorus was additionally irradiated in order to avoid cross-relaxation effects. The parameters of the measurements were chosen appropriately to lie in the favourable regions proposed by Hanssum (30). For the calculation of the relaxation times the peak areas were used according to a procedure recommended by Sass and Ziessow (31). The ³¹P{¹H} NOE was determined by the gated decoupling technique. The temperature of the samples was controlled with an accuracy of ±0.5 K. The measurements were performed at frequencies of 13.81 MHz (home-built spectrometer) and 30.72 MHz (WP-200) for ²H, 22.64 MHz (WH-90) for ¹³C, and 36.44 MHz (WH-90) and 145.76 MHz (NM-360) for ³¹P.

RESULTS AND DISCUSSION

The motion of the $H_2C-P(O)O_2$ segment. Figure 1 shows values of T_1 for ³¹P of PAE6 measured at 36.44 and 145.76 MHz and of PAE6- d_2 at 36.44 MHz as a function of inverse temperature and the dipole-dipole contribution T_{1DD} to the ³¹P relaxation obtained above room temperature by ³¹P{¹H} NOE according to [3]. From Fig. 1 it is evident that the spin-rotational contribution is significant at temperatures higher than 60°C. There is no other explanation for the decrease of T_1 with increasing temperature. Further, the comparison of the curves obtained at 36.44 and 145.76 MHz shows that the chemical-shift-anisotropy contribution is considerable at high frequency. If we consider the T_1 minima at the two frequencies and assume only an overall reorientation we obtain as a first approximation a chemical-shift-anisotropy contribution of 80% at high and 20% at low frequency.

The dipole-dipole contribution, resulting from α -CH₂ segment and represented in Fig. 2 was determined from the equations

$$\frac{1}{T_{1\text{DD}}^{\alpha\text{-CH}_2}} = \frac{1}{T_1^{\text{PAE}}} - \frac{1}{T_1^{\text{PAE}-d_2}} \quad \text{at} \quad t < 20^{\circ}\text{C}$$



FIG. 1. Plot of ³¹P T_1 versus 1/T: T_1 (\blacktriangle) and T_{1DD} (\bigtriangleup) in PAE6 at 36.44 MHz; T_1 (\blacksquare) and T_{1DD} (\Box) in PAE6- d_2 at 36.44 MHz; T_1 (\blacklozenge) in PAE6 at 145.76 MHz.



FIG. 2. Plot of T_1 of the segments H₂C-P(O)O₂ or ²H₂C-P(O)O₂ versus 1/T: ³¹P $T_{1DD}^{\alpha CH_2}$ (\Box) in PAE6 at 36.44 MHz; ¹³C T_1 (\bigcirc) in PAE6 at 22.64 MHz; ²H T_1 in PAE6- d_2 at 13.81 ($- \bullet -$) and 30.72 MHz (\bullet). Solid lines calculated.

and

$$\frac{1}{T_{1DD}^{\alpha}CH_2} = \frac{1}{T_{1DD}^{PAE}} - \frac{1}{T_{1DD}^{PAE-d_2}} \quad \text{at} \quad t > 20^{\circ}C$$

If one also applies the former relation at high temperatures, the errors are large because of the small difference between the spin-lattice relaxation rates of PAE6 and PAE6- d_2 . T_{1DD}^{α} -CH2 reaches a minimum which lies at the same temperature as the minimum of $T_1^{\text{PAE6-}d_2}$ (cf. Figs. 1 and 2).

In contrast to the dipole-dipole contribution of the α -CH₂ segment to the ³¹P relaxation, ¹³C T_1^{α -CH₂} and ²H T_1^{α -CH₂} represented in Fig. 2 exhibit no minima in the temperature region studied. The deuterium relaxation measured at 13.81 and 30.72 MHz agrees within the error limits of the measurements. Obviously it is mainly the intramolecular motion of the α -CH₂ segment which determines the ¹³C and ²H relaxations.

To deduce parameters characterizing the motions we use the simple model of Woessner: isotropic overall reorientation of PAE6 phosphonate group and a jump process for the intramolecular motion of the α -CH₂ segment (cf. (8)). The assumption of isotropic reorientation seems to be very crude. However, Monte Carlo calculations of an isolated PAE6 molecule (no intermolecular interactions) yield approximately a spherical effective molecular shape (32) with a gyration radius of 360 pm. This radius increases only up to 370 pm (33) if one takes into account intermolecular interactions in a molecular field approximation.

The geometry of the segment is not known. The P-C bond length in various phosphonate compounds (33, 34) differs only slightly; we use a value of 178 pm. For the C-H bond length in the α -CH₂ group of phosphonate compounds very different values were published (cf., e.g., (34-37)). We deduced a value of 112.6 pm from $T_{1Q}^{PAE-d_2}$ and ${}^{13}C T_{1Q}^{\alpha-CH_2}$ by using

$$\frac{T_{\rm 1DD}}{T_{\rm 1O}} = \frac{15}{80} \frac{(e^2 q Q/\hbar)^2 r^6 16\pi^2}{\mu_0^2 \gamma_1^2 \gamma_5^2 \hbar^2}$$
[9]

resulting from [7] and [8] under the condition of extreme narrowing. This value is too large compared to the standard bond length of 110 pm (38). But we have to take into account that we obtained the mean bond length which is an average over the atomic oscillation and not the equilibrium bond length determined, for example, by electron diffraction (39). Using 112.6 pm for the C-H bond length and 109.5° for the PCH angle we obtain a P-H distance of 241.2 pm and an angle between the P-H vector and the rotational axis (P-C bond) of $\theta = 26.1^{\circ}$.

The sum of the least-squares deviation of the phosphorus and deuterium relaxation was minimized. The ¹³C relaxation was not included because it has the same spectral density as ²H relaxation and since the C-H bond length was obtained as mentioned above. The fitting procedure gives the motional parameters of the first two rows in Table 1. The relaxation times as a function of temperature calculated with these parameters are shown in Fig. 2 (solid lines). Considering the relaxation of only one nucleus, a better fit can be reached. The application of a motional model with anisotropic reorientations of a symmetric top molecule and one intramolecular motion (8)

Motional Parameters of the $H_2C-P(O)O_2$ Segment				
Motion	$ au^{0}(s)$	$E (kJ mol^{-1})$		
Overall ^a	1.2×10^{-15}	27.5		
Internal ^a	$1.9 imes 10^{-12}$	8.6		
Overall ^b	1.1×10^{-15}	27.3		

TABLE 1

^{*a*} Deduced from ³¹P $T_{1DD}^{\alpha-CH_2}$ and ²H $T_1^{\alpha-CH_2}$.

^b Deduced from ³¹P T_{1CSA} .

will not give a better fit over the whole temperature region studied. Also with this model the calculated ³¹P $T_{1DD}^{\alpha-CH_2}$ contribution and ²H $T_{1Q}^{\alpha-C^{2H_2}}$ relaxation always become too high at high temperatures. These deviations are of systematic origin and larger than the errors of the measurements. As a conclusion we consider the motional parameters of Table 1, first two rows, as the most representative values in the frame of the model of Woessner.

The activation energy $E_{\rm M} = 27.5$ kJ mol⁻¹ for the overall reorientation of PAE6 seems rather high if one compares it with values obtained in similar large molecules by using only the extreme narrowing region (40, 4). A fitting procedure of our data in the extreme narrowing region gives also a distinct smaller value of about 20 kJ mol⁻¹. $E_{\rm G} = 8.6$ kJ mol⁻¹ for the intramolecular motion is in the order of magnitude expected (41, 42). The dipole-dipole contribution at low temperatures is determined mainly by the isotropic overall reorientation. Only measurements in a large enough temperature range and their analysis yield justified values for the motional parameters. Considering only small temperature ranges, one can deduce different activation energies.

The motions of the other segments. The C-H bond length in the CH₂ and CH₃ segments was determined in the same way as that of the α -CH₂ segment. The results are 112 and 113 pm. We used in the calculation 112.6 pm as in the case of the α -CH₂ segment. If we apply to the ²H relaxation the model of an isotropic overall reorientation and one intramolecular diffusional motion (8) and if we use the motional parameters of the overall reorientation in row 1 of Table 1, we obtain the parameters

$$\tau_{\rm G}^0({\rm C}^2{\rm H}_2) = 7.0 \times 10^{-13} \,\text{s}$$
 $E_{\rm G}({\rm C}^2{\rm H}_2) = 7.6 \,\text{kJ mol}^{-1}$ $\theta({\rm C}^2{\rm H}_2) = 67^\circ$
 $\tau_{\rm G}^0({\rm C}^2{\rm H}_3) = 5.5 \times 10^{-13} \,\text{s}$ $E_{\rm G}({\rm C}^2{\rm H}_3) = 7.0 \,\text{kJ mol}^{-1}$ $\theta({\rm C}^2{\rm H}_3) = 61^\circ.$

In fact, an internal motion is possible about two axis for the CH₂ segment and three axis for the CH₃ segment. Therefore, the angle θ also was considered as an adjustable parameter. The ¹³C and ²H relaxation times calculated with these parameters are represented in Figs. 3 and 4 (solid lines). At low temperatures the deviations are larger than the errors of the measurements.

We also tried to describe the relaxations of the ester segments only by an isotropic motion because the degrees of freedom increase. Further, the factors of the spectral density functions of the overall reorientation obtained are only 0.07 for CH₂ and 0.02 for CH₃. Therefore, the application of the simpler model of an effective isotropic reorientation seems justified. The fitting of the ²H T_1 data gives

and

 $\tau^0 = 8.6 \times 10^{-15} \text{ s}$ $E = 18.1 \text{ kJ mol}^{-1}$ for CH₂

 $\tau^0 = 1.7 \times 10^{-14} \text{ s}$ $E = 15.3 \text{ kJ mol}^{-1}$ for CH₃.

The ²H and ¹³C relaxation times calculated with these parameters are also represented in Figs. 3 and 4 by broken lines. The agreement with the experimental points is better than that reached by considering one intramolecular motion.

The ¹³C relaxation times of the hexane substituent without the α -CH₂ segment are also analyzed. The effective correlation times at room temperature obtained on the basis of a model with isotropic reorientation are



FIG. 3. Plot of T_1 of the methylene ester groups versus $1/T_1^{-13}$ C T_1 (O) in PAE6 at 22.64 MHz; ²H T_1 (\bullet) in PAE6- d_{10} at 30.72 MHz. Solid lines are calculated on the basis of an isotropic overall reorientation and one intramolecular diffusional motion; broken lines are calculated without internal motion.

$$\tau_{\beta} = 2.21 \times 10^{-11} \text{ s} \qquad \tau_{\gamma} = 2.13 \times 10^{-11} \text{ s} \qquad \tau_{\delta} = 1.53 \times 10^{-11} \text{ s}$$
$$\tau_{\epsilon} = 1.23 \times 10^{-11} \text{ s} \qquad \tau_{\varphi} = 4.97 \times 10^{-12} \text{ s}.$$

The correlation times decreases toward the end of the alkyl chain as expected in an agreement with other long chain compounds (see, e.g., (43, 44)).

³¹P T_{1CSA} and ³¹P T_{1SR} . The chemical-shift-anisotropy contribution cannot simply be deduced from the relaxation rates at the different frequencies because the condition of extreme narrowing is not fulfilled for ³¹P relaxation. We used the following procedure. At first we assume that at 36.44 MHz the ³¹P relaxation is determined by the dipoledipole interactions and the isotropic overall reorientation. In this case, applying [7] and considering the relation τ (minimum) = $0.72\omega^{-1}$, we obtained a good fit to the experimental data. Then we calculated the dipole-dipole contribution at 145.76 MHz. The chemical-shift-anisotropy contribution in a first approximation is given by the difference of the measured relaxation rates of T_1^{PAE} and of T_{1DD} estimated at 145.76 MHz. With this result the chemical-shift-anisotropy contribution at 36.44 MHz was estimated by formula [4]. Now the dipole-dipole contribution was estimated using the rates of the experimental T_1^{PAE} and of the chemical-shift-anisotropy contribution estimated. After



FIG. 4. Plot of T_1 of the methyl ester groups versus 1/T: ¹³C T_1 (O) in PAE6 at 22.64 MHz; ²H T_1 (\bullet) in PAE6- d_{10} at 30.72 MHz. Solid and broken lines are calculated as described in Fig. 3.

performing the iteration procedure described three times, the changes of the adjustable parameters were only 3%. This means that the changes of the calculated relaxation times are smaller than the errors of the measurements. The results are collected in row 3 of Table 1. The agreement of the motional parameters obtained from ³¹P T_{1CSA} with the corresponding obtained from ³¹P $T_{1DD}^{\alpha-CH_2}$ and ²H $T_1^{\alpha-CH_2}$ are excellent (cf. Table 1). From

TABLE 2

at Selected Temperatures						
Temperature (°C)	Frequency (MHz)	$\frac{1/T_{1\text{DD}}}{1/T_1}$	$\frac{1/T_{1CSA}}{1/T_1}$	$\frac{1/T_{1SR}}{1/T_1}$		
-50	36.44 145.76	0.82	0.18	0.001		
-35	36.44	0.84	0.15	0.004		

0.22

0.78

0.32

0.16

145.76

36.44

145.76

36.44

20

160

0.78

0.09

0.68

0.005

0.002

0.08

0.03

0.83

Different Contributions to the Total ³¹P Relaxation Rate

Relaxation Rate at Selected Temperatures				
Temperature (°C)	$\frac{1/T_{\rm 1DD}^{\alpha-\rm CH_2}}{1/T_{\rm 1DD}}$	$\frac{1/T_{\rm 1DD}^{\rm est}}{1/T_{\rm 1DD}}$	$\frac{1/T_{\rm 1DD}^{\rm rest}}{1/T_{\rm 1DD}}$	
-50	0.53	0.29	0.2	
20	0.37	0.22	0.4	
160	0.36	0.23	0.4	

TABLE	3
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The Different Contributions to the Total ³¹P Dipole–Dipole Relaxation Rate at Selected Temperatures

 T_{1CSA} the quantity $\sqrt{(\sigma_{33} - \sigma_{11})^2 + (\sigma_{33} - \sigma_{22})^2 + (\sigma_{22} - \sigma_{11})^2} = 218$ ppm was estimated. It agrees satisfactorily with that (e.g., 235 ppm for hexadecane phosphonic acid diethyl ester) obtained from powder spectra of similar but solid phosphonic acid esters.

The different contributions to the total ³¹P relaxation rate at some temperatures and two frequencies are collected in Table 2. The table shows that at all temperatures we studied, more than one interaction mechanism must be taken into account. In Table 3 the different dipole-dipole contributions to the total ³¹P dipole-dipole contribution are collected. The table shows that the α -CH₂ segment, the ester groups, and the rest of the alkyl chain each contribute approximately one-third of the total dipoledipole relaxation.

The activation energy of the spin-rotational correlation time τ_{SR} obtained by a fitting procedure of T_{1SR} is $E_{SR} = 11.9 \text{ kJ mol}^{-1}$. Obviously the Hubbard equation [6] is not valid since E_{SR} is not equal to E_M . One reason for this is that the assumptions in the derivation of the Hubbard equation are not fulfilled (45, 46).

The ³¹P, ¹³C, and ²H spin-lattice relaxations of the $H_2C-P(O)O_2$ and ² $H_2C-P(O)O_2$ segments are mainly determined by the overall reorientation whereas this motion has at most a small effect on the relaxation of the other segments.

We are well aware of the crude approximations in our treatment. The deviations of the predicted relaxation from the experimental data indicate the limitations of the model used. We think that it is not useful to apply a more elaborate model to the present experimental data.

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