A Quantitative Study of the Nuclear-Electron Overhauser Effect of Phosphorus-31 in Solutions

W. MÜLLER-WARMUTH, H. GRÜTZEDIEK, and R. VAN STEENWINKEL

Magnetic Resonance Laboratory, EURATOM Joint Research Centre, Ispra (Italy),
and Max-Planck-Institut für Chemie (Otto-Hahn-Institut), Mainz (Germany)

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The nuclear-electron Overhauser effect of ^{31}P and its spectral dependence has been studied in free radical solutions of two selected solvents containing phosphorus in the oxidation states three and five. Measurements of the dynamic polarization enhancement factor and of the relaxation times of ^{31}P and ^{1}H have been carried out on trimethylphosphite, $(CH_3O)_3P$, and triethylphosphate $(C_2H_5O)_3PO$ at three widely separated magnetic field values, and at various temperatures. Triple resonance experiments in the same solutions did not show any evidence of a "three spin effect", in contrast to diethylphosphite $(C_2H_5O)_2P(H)O$ which was also investigated. From the polarization coupling parameter and the fluctuations of the dipolar interactions, the importance of scalar contact coupling, the spectral intensity functions and the (scalar) correlation times have been determined. The results have been discussed in terms of the pulse model of molecular collisions, where the average time dependence of the scalar coupling constant is calculated. The phosphorus-unpaired electron coupling is described by different coupling mechanisms of different ranges, depending upon the environment of phosphorus and the hybridization of the bonds. Among the mechanisms capable of affecting the dynamic nuclear polarizations of both triply and quadruply connected phosphorus, the interaction via the lone pair electrons which are present in the first case only, is the most likely to play a dominant rôle.

Dynamic nuclear polarization (DNP) by the nuclear-electron Overhauser effect has provided an extremely sensitive tool for studying weak intermolecular interactions in solutions of free radicals. Most of the work, however, has so far been limited to the proton and fluorine Overhauser effect, respectively. For solvent protons, there are in most cases only dipolar interactions with the unpaired radical electron (see preceding paper[1], hereafter refered to as I), whilst for fluorine nuclei both dipolar and scalar couplings have been observed[2–4]. Moreover, it has been found that the scalar contact interaction depends sensitively upon the chemical environment of ^{19}F and upon the particular type of free radical. Thus dynamic polarization reveals otherwise unobservable details of interaction effects, which are of considerable chemical interest. A study of the behaviour of further nuclei thus seemed to be of importance. Phosphorus is interesting because of its different oxidation states in organic solvent molecules and its significance in biological materials. First qualitative results on the phosphorus-31 Overhauser effect were reported by RICHARDS et al.[5]. Enhancement factors of a greater number of compounds at one frequency have recently been published by POINDEXTER et al.[6–8].

From quantitative experiments, it was hoped to gain information on both the nature of the scalar interaction and on its time scale. Measurements have been made at three widely separated frequencies and at various temperatures in order to determine the spectral intensity function of the solvent-radical hyperfine coupling. Two typical phosphor-organic solvents have been selected, one with trivalent, the other one with pentavalent phosphorus. Solutions of the same free radical have been used. Both solutions are liquid over a large temperature range.

1. Experimental Procedure and Results

The NMR and DNP experiments on ^{31}P nuclei were carried out in magnetic fields of 176, 3420

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[1] W. MÜLLER-WARMUTH, EROL ÖZTEKIN, REYNIR VILHJALMSSON, and AYTAÇ YALÇINER, Z. Naturforsch. **25 a**, 1688 [1970], preceding paper.

[2] W. MÜLLER-WARMUTH, Z. Naturforsch. **21 a**, 153 [1966].

[3] R. A. DWEK, J. G. KENWORTHY, D. F. S. NATUSCH, R. E. RICHARDS, and D. J. SHIELDS, Proc. Roy. Soc. London A **291**, 487 [1966].

[4] E. H. POINDEXTER, J. R. STEWART, and P. J. CAPLAN, J. Chem. Phys. **47**, 2862 [1967].

[5] P. W. ATKINS, R. A. DWEK, J. B. REID, and R. E. RICHARDS, Mol. Phys. **13**, 175 [1967].

[6] E H. POINDEXTER, R. A. DWEK, and J. A. POTENZA, J. Chem. Phys. **51**, 628 [1969].

[7] J. A. POTENZA, E. H. POINDEXTER, P. J. CAPLAN, and R. A. DWEK, J. Amer. Chem. Soc. **91**, 4356 [1969].

[8] R. A. DWEK, N. L. PADDOCK, J. A. POTENZA and E. H. POINDEXTER, J. Amer. Chem. Soc. **91**, 5436 [1969].

and 13 200 gauss. The ^{31}P NMR (and ESR) frequencies were 310 kHz (493 MHz), 5,84 MHz (9.58 GHz) and 22.77 MHz (37 GHz). In the low field region a new type of sensitive double resonance spectrometer was used [9]. The strong field measurements were made on a pulse spectrometer with phase sensitive detection, and on a high resolution spectrometer, respectively. Correction for leakage was always applied in the same way as that described in I. The ^{31}P relaxation times of both, the pure solvent and the solution were therefore measured. The extrapolated enhancement factors and the nuclear-electron coupling parameters [Eq. (2) of I] were determined in the usual manner.

In addition to phosphorus the respective measurements were also made for the protons of the solvent molecule. For this, a few more frequencies and the same techniques as described in I were applied.

The samples chosen were trimethylphosphite, $(CH_3O)_3P$, and triethylphosphate, $(C_2H_5O)_3PO$, both with bisdiphenylene phenyl allyl (BPA) in solution. The samples were degassed and sealed in glass as usual. The results of the ^{31}P and ^1H-DNP measurements are presented in terms of the coupling parameter ϱ in Figs. 1 and 2. The enhancements of

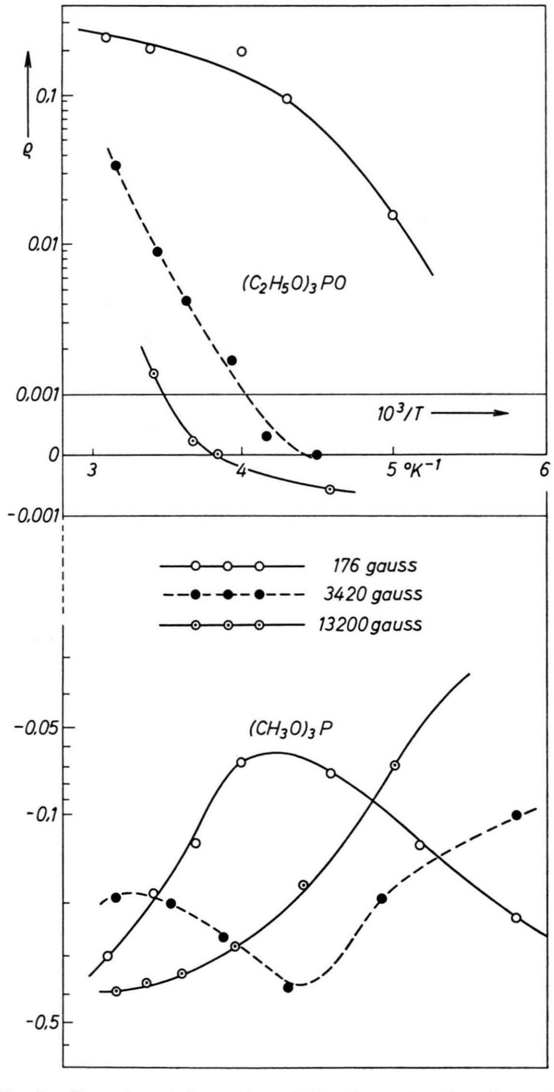

Fig. 1. Experimental results of the dynamic phosphorus-31 polarization (ϱ versus reciprocal temperature) in solutions of trimethylphosphite and triethylphosphate containing BPA. To aid clarity, with the exception of the lowest decade, different logarithmic scales are used.

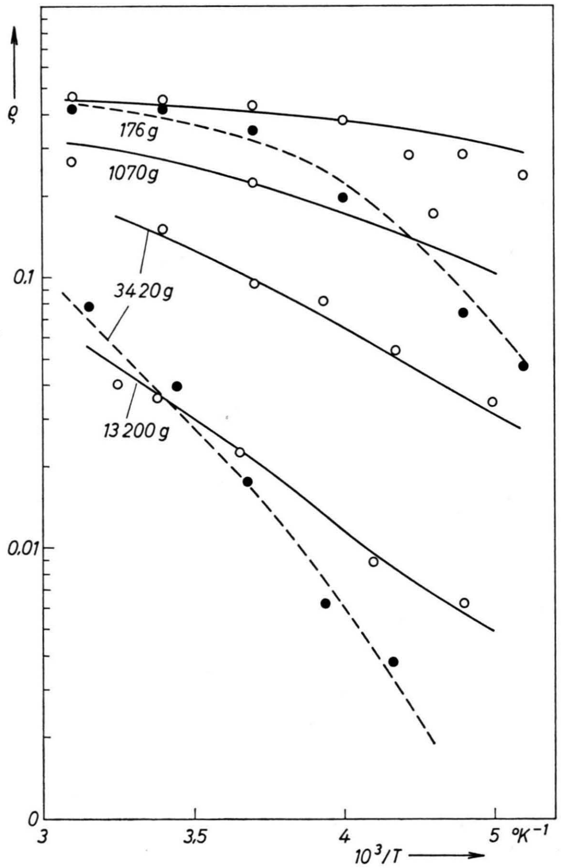

Fig. 2. Proton-electron coupling parameter of solutions of trimethylphosphite (●) and triethylphosphate (○) as measured at different temperatures and magnetic fields. The solid and dotted lines are the result of the interpretation given in the text.

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[9] H. GRÜTZEDIEK, Tagungsband Hochfrequenzspektroskopie, Leipzig, September 1969, S. 361.

^{31}P in solutions of the trivalent compound turn out to be positive (Fig. 1) leading to negative ϱ-values. The pentavalent phosporus signal on the other hand is inversely enhanced, and only at very high frequencies and low temperature is a change of sign observed. Finally the proton signal (Fig. 2) is always inverted whilst saturating the ESR of the radical. At low frequencies and high temperatures the full dipolar value of ϱ is reached, and the differences between the two solutions are only due to the different diffusion behaviour of the molecules.

In both trimethylphosphite and triethylphosphate, the indirect spin-spin couplings between ^{31}P and ^{1}H are very small. No hyperfine structure of the NMR lines has been observed. A triple resonance experiment[10] has ascertained, moreover, that there is no influence of the polarized ^{1}H nuclei upon the phosphorus. All this is quite different in solvent molecules with strong J – J-coupling. Experiments in BPA-solutions of diethylphosphite, $(C_2H_5O)_2P(H)O$, have shown that the ^{31}P enhancement changes very much, if the proton resonance is saturated. There is not only the trivial effect of line collapsing, but in addition a "three-spin-effect", which, however, does not follow the law usually applied[11, 12]. In the triple resonance experiment the NMR line shapes are changed, and the enhancement factors become – even in the case of very strong ^{1}H irradiation – sensitively dependent upon the exact frequency. In the anticipation of acquiring a better understanding of these phenomena in the future no discussion of these results will be given in the present paper.

2. Determination of Scalar Couplings, Intensity Functions and Correlation Times

The variety of experimental data can be utilized for a rather complete evaluation of the problem. From the proton DNP results, which are not affected by scalar interactions, the intensity function of the dipolar coupling and the correlation time of translational diffusion can be derived. With this, it is possible to determine the relative importance of scalar and dipolar coupling between phosphorus and the electron spin. Furthermore, the spectral intensity function of the scalar coupling is obtained if the dipolar functions of ^{1}H and ^{31}P are assumed to be equal. Fourier transformation finally yields the correlation function and its average value, the correlation time.

As a theoretical basis we take the discussion of the preceding paper (I), and we apply Eq. (1) given therein, which we now write in the form

$$\varrho = \frac{[f_t(x) - K\, f_{sk}(\beta\, x)] \cdot 0{,}5}{0{,}7\, f_t(x) + 0{,}3\, f_t\left(\frac{\gamma_I\, x}{\gamma_S}\right) x + 0{,}5\, K\, f_{sk}(\beta\, x)}\,, \qquad (1)$$

where $x = \omega_S\, \tau_t$ and $\beta = \tau_{sk}/\tau_t$. The meaning of the other symbols has already been explained in I. The "rotational contribution" to the dipolar interaction is neglected. Moreover, since diffusion modulates both dipolar and scalar interactions, the same activation law for the temperature dependence of τ_t and τ_{sk} has been assumed. To be more specific, the correlation times will be related to the temperature by an Arrhenius law,

$$\tau = \tau_0 \exp\{E_A/R\,T\}\,, \qquad (2)$$

where E_A is the activation energy of the diffusion process of the molecules.

For the protons of both materials, K in Eq. (1) turns out to be zero. As in most cases of I, the data can be explained by dipolar interaction with the electron spin modulated by translational diffusion of the interacting molecules (solid and dotted lines in Fig. 2). $f_t(x)$, τ_t and E_A are thus obtained (see also Table 2), where – within the limits of accuracy – E_A corresponds to the activation energy of the self diffusion constant of the solvent measured independently[13].

The scalar hyperfine coupling between two partners is supposed to be modulated by the same mechanism of molecular motion. The temperature dependence of the phosphorus results may then be replaced by the dependence upon the correlation time τ_t of translational diffusion, and the ϱ-values can be plotted against x, Fig. 3. Furthermore, since the dipolar part of the phosphorus-electron interaction is described by the same function $f_t(x)$, from $\varrho(x)$ and Eq. (1) both the scalar spectral intensity function f_{sk} and the relative importance of scalar coupling K are determined. In order that the formal procedures may be better understood, the different

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[10] G. J. KRÜGER, Z. Naturforsch. **24 a**, 560 [1969].

[11] K. H. HAUSSER u. F. REINBOLD, Phys. Lett. **2**, 53 [1962].

[12] H. GRÜTZEDIEK and W. MÜLLER-WARMUTH, Z. Naturforsch. **24 a**, 459 [1969].

[13] G. J. KRÜGER and R. WEISS, Z. Naturforsch. **25 a**, 777 [1970].

functions, parameters, transformations and approximations used, are listed together in Table 1. More details may be found in previous papers [1, 10, 14].

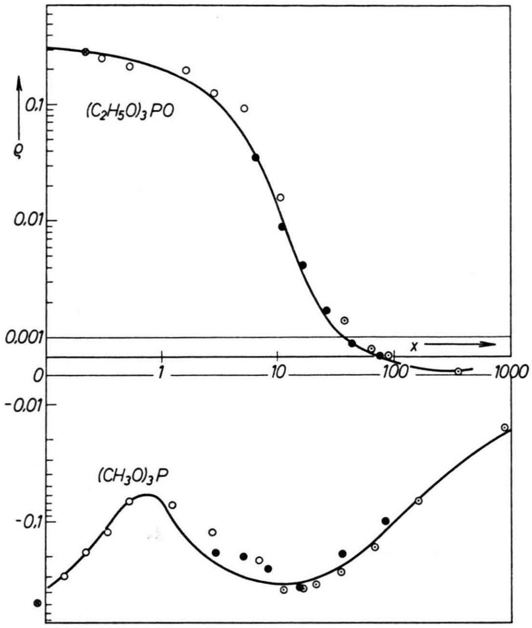

Fig. 3. The ϱ-values for phosphorus of Fig. 1 as a function of $x=\omega_S\,\tau_t$. In order to relate τ_t to the temperature, the proton DNP data were utilized. The results of POINDEXTER [6, 7] obtained at 74 gauss are also indicated (⊗). The solid lines correspond to the theoretical interpretation.

For the purpose of simplicity, we have approximated the scalar intensity function by the square of a sum of exponentials (Table 2). This is of course a more or less arbitrary choice, but simplifies the calculations. With the parameters of the sixth column of Table 2, the functions of Fig. 4 are obtained, which – inserted in Eq. (1) – yield the ϱ-curves drawn in Fig. 3. A more favourable approximation could certainly be found for a better fitting of the $(CH_3)_3P$ data in the medium region of x. It was not done simply because it would involve a more complicated expression without any great improvement in the result. The correlation function and the correlation time τ_{sk} in units of τ_t are directly obtained from f_{sk} (see Table 1). All the numerical parameters are listed in Table 2.

$f_t(x)=\dfrac{J_1^D(\omega_S\,\tau_t)}{J_1^D(0)}$	reduced intensity functions of the fluctuations of dipolar and scalar nuclear-electron coupling occurring at the ESR-frequency ω_S and produced by diffusional motions.
$f_{sk}(\beta\,x)=\dfrac{J^{sk}(\omega_S\,\tau_{sk})}{J^{sk}(0)}$	
$K=\dfrac{2\,J^{sk}(0)}{15\,J_1^D(0)}$	relative importance of scalar and dipolar interaction.
$\tau_t=\dfrac{d^2}{5\,D}$	correlation time of translational diffusion with D_I and D_S being the diffusion constants of solvent and dissolved molecules, resp., and d the distance of closest approach of the interacting spins.
$D=\frac{1}{2}(D_I+D_S)$	
$K(t)=\dfrac{J_{sk}(0)}{\pi\,\tau_t}\displaystyle\int_0^\infty f_{sk}(\beta\,x)\,\cos\left(\frac{t}{\tau_t}x\right)\,dx$	auto-correlation function of the fluctuation of the scalar coupling as obtained by Fourier transformation
$\tau_{sk}=\dfrac{1}{K(0)}\displaystyle\int_0^\infty K(t)\,dt$	scalar correlation time
$f_{sk}(\beta\,x)=(A\,e^{-ax}+B\,e^{-bx}+C\,e^{-cx})^2$	Approximation of the intensity function by a combination of exponentials
$\tau_{sk}=\dfrac{(\pi/2)\,\tau_t}{\dfrac{A^2}{2\,a}+\dfrac{B^2}{2\,b}+\dfrac{C^2}{2\,c}+\dfrac{2\,A\,B}{a+b}+\dfrac{2\,A\,C}{a+c}+\dfrac{2\,B\,C}{b+c}}$	

Table 1. Synopsis of the functions and procedures used in order to determine scalar couplings, intensity functions and correlation times.

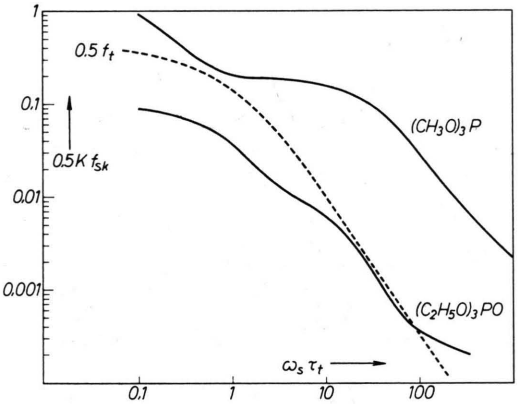

Fig. 4. Scalar coupling strengths and intensity functions that lead to the interpretation of Fig. 3. For comparison, the dipolar spectral intensity function is plotted in the same scale (dotted line).

Solution	K	τ_t (23 °C) in 10^{-11} s	E_A in kcal/Mole	$\beta=\dfrac{\tau_{sk}}{\tau_t}$	Intensity function approximated by
$(CH_3O)_3P$/BPA	3.4	7.0	2.9	0.18	$(0.66\,e^{-5x}+0.25\,e^{-0.017x}+0.09\,e^{-0.001x})^2$
$(C_2H_5O)_3PO$/BPA	0.20	17	3.8	0.35	$(0.635\,e^{-0.9x}+0.30\,e^{-0.05x}+0.065\,e^{-0.001x})^2$

Table 2. Numerical parameters as obtained from the experiments, with the procedures described in this paragraph.

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[14] F. NOACK, G. J. KRÜGER, W. MÜLLER-WARMUTH, and R. VAN STEENWINKEL, Z. Naturforsch. **22 a**, 2102 [1967].

3. Application of the "Pulse Model" of Molecular Collisions

Further discussion of the hyperfine interaction mechanism requires a model in order to explain the intensity and correlation functions derived from the experiments. Due to the results of the last paragraph this model has to be a diffusion model, since a sticking model does not hold for explaining the observed spectral dependences. As a consequence of the general definition, the correlation function can either be represented by a statistical ensemble average or by a time average. A suitable model for the local dependence or the time dependence of the hyperfine coupling constant $A[\mathbf{r}(t)]$ should therefore lead to the correct correlation function $K(t)$. In the literature, only one very special case of a diffusion model is known, were ensemble averaging has been applied[15]. In this, a very short range interaction with an exponential dependence upon the distance was supposed. Since this particular model only agrees in exceptional cases with the experimental behaviour, and since a more general mathematical procedure for obtaining the scalar coupling potential does not seem feasible, we have calculated $K(t)$ by averaging over the time.

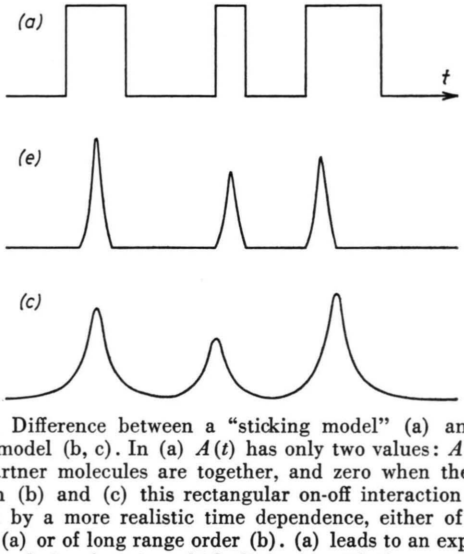

Fig. 5. Difference between a "sticking model" (a) and the pulse model (b, c). In (a) $A(t)$ has only two values: A when the partner molecules are together, and zero when they are not. In (b) and (c) this rectangular on-off interaction is replaced by a more realistic time dependence, either of short range (a) or of long range order (b). (a) leads to an exponential correlation function which disagrees with the present experiments. (b) and (c) lead to correlation functions which depend on the details of the average interaction pulse shape.

In a model proposed earlier[14] the time dependence of $A(t)$ is characterized by a statistical succession of pulses $v(t)$, each occuring at a collision of two interacting partners. The fluctuations of $A(t)$ are supposed to obey a Poisson law, which is equivalent to the validity of the diffusion equation in the ensemble picture. Since the scalar interaction potential has been shown to increase regularly rather than abruptly as the molecules are brought closer together, the time dependence of Fig. 5 (b) or (c) looks more realistic than that of Fig. 5 (a). If the multiplicity of collisions between radical and solvent molecules is taken into account, the "average pulse" in this model is assumed to be a superposition of possibly different pulse shapes for the single collision. The mean difference in time between the occurrence of collisions is given by the Poisson jumping time τ_p. The spectral intensity function is the square of the Fourier transform of the average pulse[14]. As a further parameter, σ^2 the mean square of the pulse amplitudes enter into the model. The surface of one pulse is normalized to $2\,\tau_w$, where the mean interaction time τ_w is of the same order of magnitude as τ_{sk}.

The detailed procedure for computing the pulse shapes in the present study is outlined in Table 3. With the numerical parameters of the last paragraph the average pulse shapes of Fig. 6 are obtained.

$$f_{\mathrm{sk}}(x) = (A\,e^{-ax}+B\,e^{-bx}+C\,e^{-cx})^2 \quad \text{reduced intensity function (see Table 1)}$$

$$V(x) = \sqrt{J(0)\,\frac{\tau_{\mathrm{p}}}{\sigma^2}}\,(A\,e^{-ax}+B\,e^{-bx}+C\,e^{-cx}) \quad \text{pulse spectrum}$$

$$\begin{aligned} v(t) &= \frac{1}{\pi\,\tau_{\mathrm{t}}}\int\limits_0^\infty V(x)\,\cos\left(\frac{t}{\tau_{\mathrm{t}}}\,x\right)\,\mathrm{d}x \quad \text{pulse shape} \\ &= \frac{2\,\tau_{\mathrm{w}}}{\pi\,\tau_{\mathrm{t}}}\left(\frac{A\,a}{a^2+(t/\tau_{\mathrm{t}})^2}+\frac{B\,b}{b^2+(t/\tau_{\mathrm{t}})^2}+\frac{C\,c}{c^2+(t/\tau_{\mathrm{t}})^2}\right) \end{aligned}$$

$$4\,\tau_{\mathrm{w}}^2 \equiv \frac{\tau_{\mathrm{p}}}{\sigma^2}\,J(0)$$

Table 3. Application of the pulse model. The experimental intensity functions is approximated by the square of a sum of exponentials.

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[15] P. S. Hubbard, Proc. Roy. Soc. London A **291**, 537 [1966].

4. Discussion

The extremely strong scalar interaction of the phosphorus-III compound with the radical is the most striking feature of the results. The K value of 3.4 (Table 2) corresponds to 63% scalar relaxation of ^{31}P under extreme narrowing conditions compared with 9% for the $P(V)$ compound. The important difference reflects more the hyperfine coupling constants and the coupling mechanisms rather than the correlation times which are of the same order of magnitude. The principal result agrees with the main conclusions, which other workers drew from single temperature and frequency measurements [5–7]. The quantitative study of the present work has, however, shown that single measurements may imply wrong exrapolations because of the complexity of the frequency and temperature dependence. Moreover, results on dialkyl and diaryl phosphites have to be regarded cautiously since the three-spin-effect (see Chapt. 2) changes the apparent enhancement drastically, and even the sign of the polarization may be different.

The frequency and temperature dependence of the ^{31}P nuclear-electron Overhauser effect in the respective solutions can most easily be studied by an inspection of Fig. 4. In this the scalar contributions to the enhancement factor may be compared with the dipolar part (dotted line). These curves explain why the enhancement is always positive in $(CH_3O)_3P$, and why the negative enhancement of the ^{31}P signal in $(C_2H_5O)_3PO$ becomes rather small and remains more or less constant at high frequencies and low temperatures. Only at a very high x, in the latter case, does the scalar contribution exceed the dipolar function causing an inversion of the NMR signal. In contrast to similar studies on the ^{19}F Overhauser effect in solutions of fluorocarbons [16, 17], in the phosphorus case the scalar intensity functions contain several steps. Beyond this, in $(CH_3O)_3P$ the extreme narrowing conditions are never reached, not even in a rather low magnetic field. Common features, on the other hand, are the slow decays of the scalar interaction at very high frequencies and low temperatures.

This behaviour is reflected in the average time-dependence of the scalar interaction of Fig. 6. The slow decay, demonstrated experimentally by a rather small decrease in the DNP signal with decreasing temperature in the strongest field, corresponds to an extremely short range interaction. The characteristic time of this part of the interaction is of the order of 1/100 of the diffusional correlation time (sharp peak in Fig. 6 a and b). If the relative surface contribution to the total pulse is taken as a measure of a kind of "cross section" of this portion of the contact coupling, it makes up a little less than 10% in both cases. Superimposed one has further interaction mechanisms. The extremely long range part of $(CH_3O)_3P$ with a cross section of 66% has not been observed in other systems so far, whilst an interaction in the intermediate range (here only 25%) is generally found. In solutions of $(C_2H_5O)_3PO$, more comparable with the fluorocarbons, the overwhelming part of the interaction is governed by a coupling mechanism of medium duration (Fig. 6).

The discussion of interaction ranges in terms of characteristic time constants implies certain difficulties, and there is some confusion in the literature concerning the definition of these quantities. In the

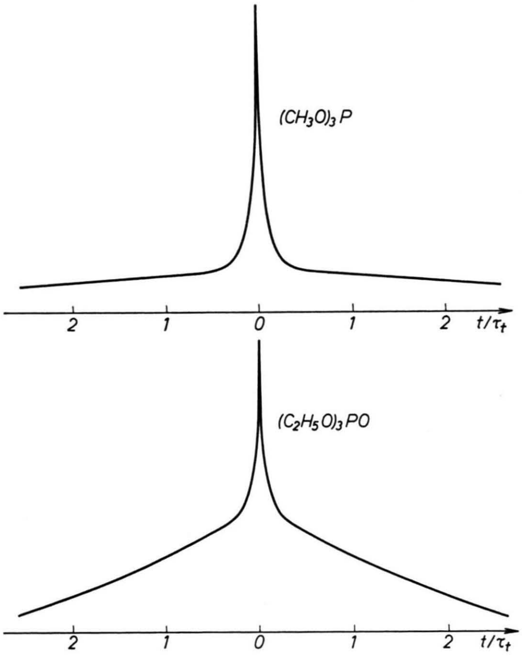

Fig. 6. Mean time dependence of scalar (solvent) phosphorus-(radical) electron coupling in the systems $(CH_3O)_3P$/BPA and $(C_2H_5O)_3PO$/BPA. The pulse shape $\lg[\pi\,\tau_t\,v(t)/2\,\tau_w]$ is plotted against the time in units of the correlation time of translational diffusion.

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[16] W. Müller-Warmuth, R. van Steenwinkel, and F. Noack, Z. Naturforsch. **23 a**, 506 [1968].

[17] W. Müller-Warmuth, R. van Steenwinkel, and Aytaç Yalçiner ,to be published.

quantitative consideration we have therefore confined ourselves to a comparison of the correlation times which are equally and unequivocally defined for the fluctuations of both dipolar and scalar interactions[10]. The scalar correlation times are certain average values and if they have turned out to be only one third or one fifth of the dipolar correlation time (Table 2), this must not necessarily rule out contributions of much shorter and longer interactions. In the present study this is obvious, and the particular interaction times derived from Fig. 6 are not thought to stand for more than one can derive from this picture.

Strong scalar contact coupling of the radical electron to the triply connected phosphorus might be understood from the structure of this solvent molecule. The compound exhibits pyramidal symmetry associated with p^3-hybridization plus some sp^3-character. The phosphorus is therefore poorly shielded and there remains the lone pair of 3s electrons with a certain amount of hybridization. Spin information from the radical may thus be transmitted to the ^{31}P nucleus by a temporary overlap of the unpaired π-electron orbital with the lone pair orbital, and transferred to the nucleus through the s-character. The coupling or a part of it may also be provided by some kind of π-σ exchange polarization, which is known to transmit unpaired π-electron density within a molecule to a nucleus in the nodal plane. These concepts are supported by the small ionization potential of the solvent molecule making it an electron donor, which together with the convenient steric conditions favours complexing with the radical molecule. We may therefore attribute the strong contact coupling and the long range contribution with an interaction time several times the dipolar correlation time, to the mechanism just proposed. There is some similarity with the results obtained from substituted fluorobenzenes[17], in so far as the scalar coupling has proved to be particularly large, if the ionization potential of the solvent was either very small or high.

The interaction via the lone pair electrons is absent in $(C_2H_5O)_3PO$. The quadruply connected phosphorus atom in this compound has tetrahedral environment with sp^3 hybridization of the bonds. In contrast to the triply connected phosphorus these bonds also contain some π-character[18]. Steric hindrance renders the approach of a radical molecule more difficult, and direct coupling seems improbable. Although one has to be careful in the further attribution of coupling mechanisms, one is tempted to correlate the medium range coupling, which has also been found in aromatic fluorocarbone (but not in $(CH_3O)_3P$), with an interaction of the radical electron with the π-system of the solvent. Spin density is then transmitted to the nucleus via σ-π polarization, which is connected with an attenuation of the effect. The very short range interaction, which seems to be important in all dynamic polarization results, is most likely also a consequence of indirect coupling at the minimum approach of the molecules during diffusion. The sharp peak indicating the point of contact may either be a natural part of the interaction, also occurring with longer duration (for instance as a consequence of the anisotropy of collisions), or may belong to an additional mechanism.

Since most studies concerning intermolecular hyperfine contact couplings have so far been carried out on fluorocarbon solutions, the contrast in the time- and frequency dependence of the phosphorus-electron interaction is particularly striking. While in the case of ^{19}F, these dependences are rather smooth functions, here $f_{sk}(\omega\tau)$, $K(t)$ and $V(t)$ decay stepwise. This is probably the consequence of more than one coupling mechanism for ^{31}P as already discussed.

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[18] J. R. Van Wazer, Phosphorus and its Compounds, Interscience Publ. Inc., New York 1958.