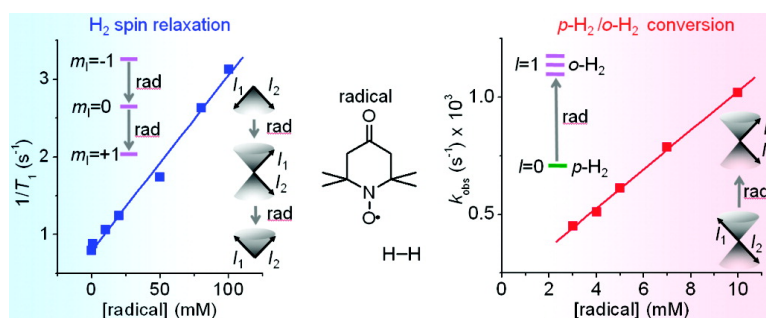


Nitroxide Paramagnet-Induced Para#Ortho Conversion and Nuclear Spin Relaxation of H in Organic Solvents

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Nitroxide Paramagnet-Induced Para–Ortho Conversion and Nuclear Spin Relaxation of H₂ in Organic Solvents

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Abstract: The kinetics of para–ortho conversion and nuclear spin relaxation of H₂ in chloroform-*d*₁ were investigated in the presence of nitroxides as paramagnetic catalysts. The back conversion from para-hydrogen (*p*-H₂) to ortho-hydrogen (*o*-H₂) was followed by NMR by recording the increase in the intensity of the signal of *o*-H₂ at regular intervals of time. The nitroxides proved to be hundreds of times more effective at inducing relaxation among the spin levels of *o*-H₂ than they are in bringing about transitions between *p*-H₂ and the levels of *o*-H₂. The value of the encounter distance *d* between H₂ and the paramagnetic molecule, calculated from the experimental bimolecular conversion rate constant *k*₀, using the Wigner theory of para–ortho conversion, agrees perfectly with that calculated from the experimental relaxivity *R*₁ using the force free diffusion theory of spin–lattice relaxation.

Introduction

The special interplay between nuclear spin statistics and rotational symmetry displayed by the hydrogen molecule was understood in the earliest days of quantum mechanics.¹ Furthermore, the implications of the relative isolation of the ortho (*I* = 1) and para (*I* = 0) forms of H₂ and other small molecules with high symmetry were appreciated about two decades later in the first detailed studies of nuclear spin relaxation.² In the ensuing decades numerous measurements of the rates of conversion (*k*_{po}) between para-hydrogen (*p*-H₂) and ortho-hydrogen (*o*-H₂)^{1c,3} and of nuclear spin relaxation (*T*₁ and *T*₂) in the magnetic, ortho, form have been carried out in the gas, liquid, and solid phases.⁴ More recently, development of techniques for preparing nuclear spin systems in “long-lived” spin states⁵ has stimulated interest in the relationship between processes, such as para–ortho conversion, arising from

changes of the total nuclear spin, *I*, and those, such as spin–lattice relaxation, which primarily induce changes in *m_I*, i.e., the orientation of *I*. In most cases studied to date, however, *k*_{po} and *T*₁ have been studied separately, often using quite different experimental techniques. Even the theoretical descriptions of the two processes have been formulated separately.^{1,2}

One exception to the above situation is the recent report of measurements of both *k*_{po} and *T*₁ for H₂ in a variety of solvents by NMR techniques.⁶ One aspect of this work, and of earlier work where qualitative comparisons of *k*_{po} and *T*₁ carried out in separate laboratories might be made, is the strikingly slower rate of the former process compared to the latter. Since para–ortho conversion is also accompanied by a change in the rotational state, *J*, of the molecule, it might have been expected that strong coupling of *J* to the microenvironment of H₂ would disturb the local symmetry of the molecule sufficiently to provide an efficient means of interconverting the two forms.⁷ In reality, “magnetic catalysis” of *k*_{po}, perhaps the most commonly studied mechanism, acts in the opposite fashion: the magnetic symmetry is removed by a field gradient produced across the two H₂ nuclei during an encounter with a magnetic dipole.⁸ Magnetic catalysis of *T*₁ processes, of course, is well known and has been studied extensively for many decades. We recently reported such relaxivity measurements for H₂ catalyzed by nitroxides in organic solvents.⁹

Given the extent to which magnetic catalysis of both *k*_{po} and *T*₁ has been studied, it is remarkable that there seems to have

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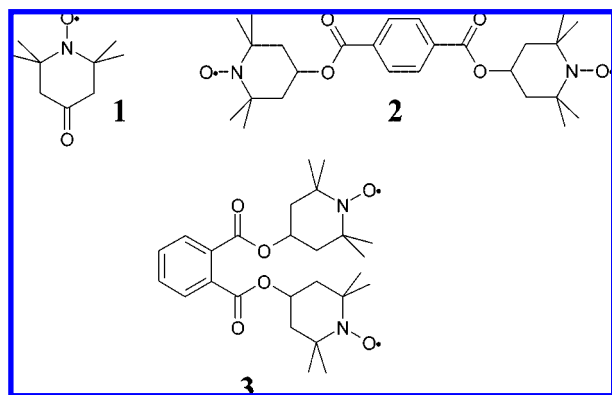
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(7) It is an interesting historical footnote that Robert Oppenheimer (Hall, H.; Oppenheimer, J. R. *Phys. Rev.* **1930**, *35*, 132–133.) at one time considered a mechanism for *p*–*o*-H₂ conversion in which modulation of *J* by collisions produces an indirect effect at the H₂ nuclei via an internal field gradient generated by the rotational magnetic moment of the molecule. The effect was considered undetectable, and the theory seems never to have been pursued further by him.

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Chart 1. Structures of the Nitroxides Used as Relaxants



been no previous report of measurements of both processes employing the same catalyst under identical conditions. While Canet and co-workers⁶ do report measurements of k_{po} and T_1 for H₂ under essentially the same conditions, the mechanisms invoked for the two processes are quite different. As we have also shown,¹⁰ T_1 in this case is dominated by intramolecular dipole-dipole and spin-rotation interactions, whereas k_{po} arises from poorly defined intermolecular magnetic interactions.

We report here an extension of our paramagnet-induced T_1 measurements to include measurements of k_{po} under the same conditions. A mononitroxide (**1**) and two bis-nitroxides (**2** and **3**) (Chart 1) were employed as paramagnetic catalysts of the para-ortho conversion and nuclear spin relaxation of H₂ in chloroform-*d*₁ at 300 K.

Experimental Section

Materials. 4-Oxo-TEMPO (**1**) was purchased from Aldrich. The biradicals **2** and **3** were synthesized as described in the literature.^{11,12} Chloroform-*d*₁ (99.8%) was purchased from Cambridge Isotope Laboratories. H₂ (99.9999%) was obtained from AirGas.

Relaxivity Measurements. Solutions of nitroxides for H₂ relaxation measurements were bubbled with H₂ for 20 min in J-Young NMR tubes and then sealed. ¹H T_1 measurements were performed at 500 MHz (11.7 T) using standard inversion recovery techniques as described previously.^{10a}

Diffusion Coefficients. Measurements of the diffusion coefficient of H₂ were carried out using the DOSY method at 500 MHz with a Bruker probe modified for pulsed field gradient experiments.^{10b} The standard Bruker protocol was used with the *steppgp1s* pulse sequence (STE with bipolar gradient pulse pair, 1 spoil gradient). The gradient strength was incremented in 16 steps from 0.68 to 32 G/cm. A diffusion time, Δ , in the range 12.5–20 ms and a length of the diffusion gradient, δ , in the range 0.75–1.5 ms were used.

***p*-H₂ Preparation and NMR Measurements of *p*-H₂ to *o*-H₂ Conversion.** For the *p*- to *o*-H₂ conversion measurements we used chloroform-*d*₁ solutions of nitroxides **1**, **2**, and **3**. Each sample consisted of 750 μ L of solution in a 7 in. J-Young NMR tube

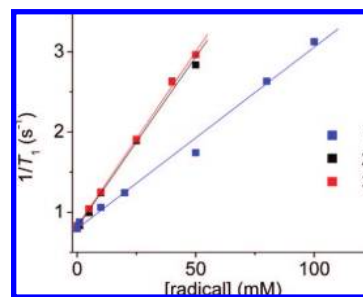


Figure 1. Plot of $1/T_1$ for H₂ vs concentration of relaxants **1–3**, chloroform-*d*₁, 300 K.

(Wilmad) with 5 mm diameter. The space left inside the tube on top of the solution was estimated to be 2.25 mL.

p-H₂ was prepared in an appropriately modified vacuum line by equilibration of gaseous normal H₂ over previously activated charcoal.¹³ The enrichment process took place in a 250 mL flask filled with 1 atm of H₂ at 77 K. After 2 h, *p*-enriched H₂ (about 50% *p*-H₂) in the flask was admitted to the space above a frozen solution in the J-Young NMR tube submerged in liquid nitrogen through an evacuated short glass junction. The nitroxide solution was previously deoxygenated by several cycles of freeze-pump-thaw. Care was taken to avoid air contamination and maintain constant conditions to ensure transfer of the same amount of H₂ to each tube.

The sample then was thawed, and the tube was shaken vigorously for 1 min to allow a fast equilibration of H₂ between the gaseous phase and the solution just prior to measurement (see Results). Five minutes elapsed from the moment the sample was taken out of liquid nitrogen to the moment the NMR experiment started. We estimate from the way the sample was prepared as described above that the pressure of H₂ inside the tube was slightly less than 4 atm at room temperature.

The back conversion from *p*-H₂ to *o*-H₂ was followed by NMR by recording the increase in the intensity of the signal of *o*-H₂ (4.5 ppm) at regular intervals of time. The NMR measurements were performed at 500 MHz (11.7 T), 300 K, without spinning the tube. Spectra were obtained in blocks of 16 scans. The FID was recorded for 2 s with an additional delay of 1 s between two sequential scans. After a further delay of 40 s a new block of 16 scans was recorded. Each point in the kinetics curve therefore represented 90 s of measurement. The whole acquisition lasted typically 10 h, by which time the intensity had nearly returned to a value corresponding to the 3:1 ratio of *o*-H₂ to *p*-H₂ expected at room temperature.^{1c}

All spectra were processed using standard software, and the integral of the *o*-H₂ signal was obtained. In addition, the integral of the chloroform-*d*₁ residual proton signal was calculated as a reference integral. This signal was chosen as a reference because it belongs to a species that was expected not to undergo any kinetic process during the experiment time. It proved to be useful to normalize the integral of H₂ to the integral of CHCl₃.

Results

Spin-Lattice Relaxation of *o*-H₂. Measurements of T_1 for H₂ in chloroform-*d*₁ solutions containing nitroxides **1–3** were carried out in the same manner as reported for earlier measurements using toluene-*d*₈ as the solvent.⁹ Figure 1 shows a plot of $1/T_1$ vs the concentration of relaxant, $[S]$. The relaxivities, R_1 , were obtained by fitting the data to the equation⁹ $1/T_1 = 1/T_{1,0} + R_1[S]$. Values of R_1 for **1–3** are given in Table 1. The values reported previously⁹ using toluene-*d*₈ are also shown for comparison. The observed relaxivities of **2** and **3** are not

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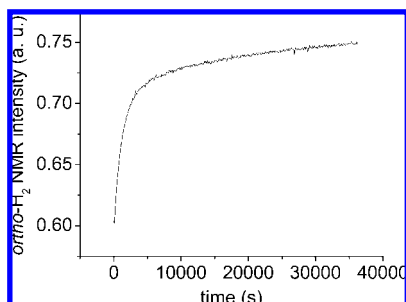
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Table 1. Comparison of Experimental Para–Ortho Conversion Rate Constants, k_0 , and Relaxivities, R_1 , for H_2 in Chloroform- d_1 Induced by Nitroxides 1–3^a

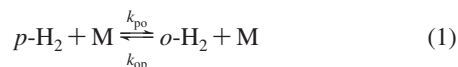
S	k_0 ($M^{-1} s^{-1}$)	R_1 ($M^{-1} s^{-1}$)	R_1/k_0
1	0.083 ± 0.002	22.6 ± 1.0 (14.5 ± 0.4) ^b	$(2.7 \pm 0.2) \times 10^2$
2	0.20 ± 0.01	42.4 ± 1.5 (40 ± 5)	$(2.1 \pm 0.2) \times 10^2$
3	0.16 ± 0.02	43.4 ± 0.6 (40 ± 5)	$(2.7 \pm 0.4) \times 10^2$

^a Unless otherwise indicated, error estimates on k_0 and R_1 of this work are 1 stdev. ^b In parentheses results were determined in toluene- d_8 ; see ref 9.

**Figure 2.** NMR intensity of o - H_2 measured during p - H_2 back conversion in a 7 mM solution of **1** in chloroform- d_1 , 300 K.

significantly different from those reported for toluene- d_8 , whereas the value for **1** is about 50% higher.

p - o - H_2 Conversion. The process of para–ortho conversion of H_2 under the influence of a molecular catalyst, M, may be expressed as a chemical reaction



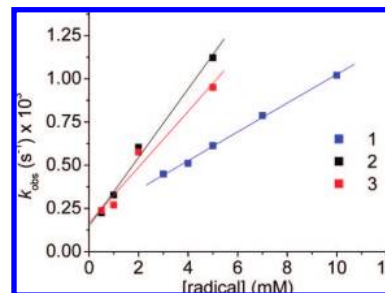
The conversion is described by two kinetic constants: k_{po} for the p - H_2 to o - H_2 conversion and k_{op} for the reverse process. From the solution of the differential equations describing the pseudo-first-order kinetics of the conversion the following expression is obtained for the concentration of o - H_2 as a function of time^{3,6,13}

$$[o\text{-}H_2](t) = [o\text{-}H_2]_{eq} + ([o\text{-}H_2]_0 - [o\text{-}H_2]_{eq})e^{-k_{obs}t}$$

where $[o\text{-}H_2]_{eq}$ represents the equilibrium concentration, $[o\text{-}H_2]_0$ the initial concentration, and $k_{obs} = k_0[S]$ the observed pseudo-first-order rate constant for a particular concentration of paramagnetic catalyst S . In order to satisfy the requirement that $[o\text{-}H_2]_{eq} = 3[p\text{-}H_2]_{eq}$ at room temperature $k_{po} = 3k_{op}$. This implies that $k_{obs} = k_{op} + k_{po} = 4k_{op}$.

Figure 2 shows a typical plot of o - H_2 NMR intensity vs time for a sample initially enriched with p - H_2 , relaxed by a 7 mM solution of nitroxide **1** in chloroform- d_1 . The intensity increases monotonically with a half-life of ca. 1000 s toward a limiting value about 25% larger than the initial value.¹⁴ The ap-

(14) The recovery curve also exhibits a small “slow” component extending over the remainder of the 36 000 s (10 h) recovery time. The presence of the “slow” process was incorporated in the data analysis by fitting to a biexponential function with variable weighting and rate constants for the two exponential functions. In all cases the rate constant for the “slow” process was about $(5.2 \pm 0.5) \times 10^{-5} s^{-1}$, i.e., no more than 5% of the rate of the “fast” component. Given the constancy of the “slow” rate, it seems likely that this effect arises from a physical process indirectly related to the catalyzed para–ortho conversion. One such process might arise from the fact that the NMR signal is detected only from that portion of the H_2 that resides within the sensitive region of the NMR detector coil. In particular, the uncatalyzed, para-enriched H_2 gas in the headspace above the solution would not be detected

**Figure 3.** Plot of p - o - H_2 conversion rate constant, k_{obs} , vs concentration of relaxants 1–3, chloroform- d_1 , 300 K.

proximately 25% increase in intensity corresponds to an initial p - H_2 content of ca. 40%, or a mole fraction, x_p , of 0.40, compared to the equilibrium value $x_e = 0.25$. The increase in intensity is a measure of the effectiveness of the p - H_2 enrichment process. If we define the enrichment of the sample in p - H_2 as $(x_p - x_e)/x_e$, enrichments from sample to sample measured in this way were in the range 50–80%.¹⁵ This is comparable to the enrichments achieved in other studies of para–ortho conversion by NMR.^{3,6} The magnitudes of the rate constants for para–ortho conversion, k_{obs} obtained by fitting to a biexponential function,¹⁴ are roughly what would be expected based on the rates reported for para–ortho catalysis by paramagnetic complex ions.^{3,13}

As shown in Figure 3, the values of k_{obs} depend linearly on $[S]$. The values of k_0 in Table 1 are derived from the data in Figure 3.¹⁶

Comparison of R_1 and k_0 . Column 4 of Table 1 gives the values of the ratio R_1/k_0 for nitroxides 1–3. As expected, the nitroxides are hundreds of times more effective at inducing relaxation among the spin levels of o - H_2 than they are in bringing about transitions between p - H_2 and the levels of o - H_2 . The two larger but geometrically quite different biradicals seem to have about the same effects on R_1 and k_0 .

Discussion

Theories of bimolecular magnetic catalysis of para–ortho conversion in H_2 and spin–lattice relaxation in o - H_2 start with

directly but would nevertheless equilibrate slowly with the solution and be detected there. It therefore seems likely that the “slow” process is a manifestation of a slow rate of exchange between the gas and the solution phases. The need for equilibration of the gas and solution phases was actually noted by Wilmarth in earlier work,¹³ and care was taken to mix the solution with the H_2 in the headspace over the sample. The fact that the “slow” process is not evident in the other NMR studies of para–ortho conversion reported to date probably is due to differences in sample concentration and preparation. Indeed, in contrast to our estimated H_2 pressure of 4 atm, both of the earlier studies seem to have employed H_2 at a pressure of 1 atm or lower, where the solution was prepared by bubbling with H_2 gas.

(15) Inasmuch as the quantity of hydrogen transferred to each sample is constant, variation in the initial o - H_2 signal for different concentrations of paramagnet is likely to be due to loss of the first experimental points in the “dead time” between thawing and the start of the measurement. Indeed, it is observed that the higher nitroxide concentration solutions show a smaller relative increase because the missing initial part is larger due to faster conversion.

(16) Extrapolation of k_{obs} to $[S] = 0$ yields a value corresponding to a lifetime of 1–3 h for p - H_2 in chloroform- d_1 . This value is substantially shorter than reported for other deuterated solvents^{3,6} but approaches the value in pure water.^{1c} It is possible that the enhanced rate arises from magnetic catalysis of para–ortho conversion by the chlorine nuclei. We are not aware of any previous measurement of k_{po} in a chlorinated solvent. The alternative explanation of the presence of a constant low level of paramagnetic impurity in the solvent cannot be ruled out. Since neither effect influences only the uncatalyzed rate it does not affect the conclusions drawn here about the catalyzed processes.

the same primary event: an encounter takes place between H₂ and the paramagnetic center at a distance and of such a geometry that the magnetic field at the protons is changed. In the case of para-ortho conversion it is the difference in field experienced by the two protons that is effective,⁸ whereas spin-lattice relaxation is more sensitive to fluctuations in the value of the field. Both effects are sensitive to the dynamics of the encounter complex,^{2,8} the details depending on the type of effect.

Although various mechanisms for the necessary field changes have been proposed,³ the most common interaction invoked is the intermolecular magnetic dipole interaction between the nuclei and the electron magnetic moment of the catalyst (relaxant). This interaction was treated in Wigner's classic theory⁸ of para-ortho conversion in H₂. Analogously, the earliest explanation for the effects of paramagnetic complexes on the relaxation times of protons in water molecules² also incorporated the dipole interaction.

Although studies of the effects of paramagnetic molecules on para-ortho conversion have been very extensive,^{1c,3} detailed measurements of paramagnetic effects on the relaxation time of H₂ have been almost completely missing from the literature. Such measurements in the gas phase are difficult because the effects on the T₁ of H₂ in the gas phase of small paramagnetic molecules like O₂ and NO are dominated at easily achievable pressures by collisional modulation of J, making it impossible to detect purely magnetic effects.⁴ The substantially longer T₁'s for H₂ in solution should, in principle, make it easier to measure bimolecular paramagnetic effects. Until recently,^{6,10,17} however, T₁ measurements for H₂ in solution have suffered from sensitivity problems resulting from the limited solubility of H₂ in most solvents.

Given the lack of comparative data, there has until now been little incentive to consider formulation of a theory to calculate R₁ and k₀ jointly. In principle, the "independent diffusion" model employed by Hubbard¹⁸ to describe R₁ and Atkins and Clugston¹⁹ to explain k₀ could be applied to analyze our results. Unfortunately both formulations have been criticized for using an unrealistic boundary condition to define a distance of closest approach.²⁰ Furthermore, the description of para-ortho conversion given by Atkins and Clugston applies only to zero magnetic field and would not be expected to be strictly applicable to measurements carried out in a high-field NMR spectrometer. Given these limitations we discuss below our values of R₁ and k₀ in terms only of theoretical formulations that have been developed separately for the two processes.

Spin-Lattice Relaxation of o-H₂. The value of R₁ in Table 1 for relaxation by nitroxide **1** has been used to estimate an encounter distance, d, between **1** and H₂ by the method described previously⁹ using the "force free" diffusion model of Freed.²⁰ As in this previous work, measurement of the diffusion coefficient, D_I, for H₂ in chloroform-d₁ at 300 K was carried out using the DOSY method. The resulting value, D_I = 1.2 × 10⁻⁸ m² s⁻¹, is nearly the same as the value reported for H₂ in toluene-d₈, as expected since the viscosities of the two liquids are nearly the same at 300 K. The value of the diffusion coefficient for **1**, D_S = 1.6 × 10⁻⁹ m² s⁻¹, was consequently assumed to be the same as that estimated for toluene-d₈ solution.

Using eq 1 of ref 9 and the above values of R₁ and D yields a calculated value of d = 2.7 Å. This is substantially shorter than the value 3.6 Å determined from R₁ in toluene-d₈ and is only slightly larger than the estimate⁹ of 2.5 Å for the minimum distance of approach of the spins in **1** and H₂ based on the van der Waals radii of the H atom in H₂ and the spin-bearing O atom of the nitroxide. It should be pointed out, however, that the calculated value of d in this region of values of R₁ is very sensitive to the value of R₁. Further interpretation of the significance of this apparent solvent effect would require an improved understanding of the sources of uncertainty in the measurements of R₁.

Comparison of the relaxivities of **1** with those of biradicals **2** and **3** in the two solvents is also interesting. Because the electron exchange coupling in **2** and **3** is weak, it would be expected that the magnetic effect of the biradicals would mimic that of a monoradical at twice the concentration,^{9,11} i.e., all other parameters being equal, the value of R₁ for the biradicals should be twice as large as for **1**. As can be seen from Table 1, that is exactly true for the measurements in chloroform-d₁, whereas in toluene-d₈ the biradicals are slightly better relaxants than **1**. Given that there is no particular reason to expect identical collision geometry for the monoradical and biradical pairs with H₂, the agreement between the observed and expected R₁s is remarkable.

p-o-H₂ Conversion. A direct comparison of the values of k₀ determined in this work may be made with those determined for paramagnetic complexes by NMR.³ For example, the value of k₀ reported for the spin-one-half complex Cu(OTf)₂ in acetonitrile-d₃ at 298 K is 0.0226 ± 0.0008 M⁻¹ s⁻¹, compared to our value of 0.083 ± 0.002 M⁻¹ s⁻¹ for **1** in chloroform-d₁. Given the different sizes and shapes of the relaxant molecules and the differences in viscosity of the solvents (0.345 and 0.542 cP for acetonitrile and chloroform, respectively)²¹ it is perhaps surprising that the values of k₀ differ by less than a factor of 4. As in the case of R₁, we find that k₀ for the biradicals **2** and **3** is almost exactly twice that for **1**, as expected if the magnetic moment is the only significant variable distinguishing the molecular collisions.

Following on earlier work of Wilmarth and Baes,¹³ Matsu-moto and Espenson^{3a} applied a simple formula derived from Wigner's theory⁸ for para-ortho conversion in the gas phase to estimate, from the value of k₀ at room temperature, the distance of closest approach of the relaxant and H₂, analogous to the parameter d discussed above as determined from R₁

$$d = 1.46(\mu^2/k_0)^{1/6}$$

It should be emphasized that the above value of d, calculated using a theory of para-ortho conversion developed for the gas phase in zero field, agrees perfectly with the estimate derived from the value of R₁ using a theory of spin-lattice relaxation designed to accurately represent the dynamics of liquids. It is not the purpose of the present report to determine whether this agreement is merely fortuitous or portends instead a more fundamental, simplifying, relationship between the processes of para-ortho conversion and spin relaxation that makes the relative effects remarkably insensitive to the medium. It is hoped that comparative measurements such as those reported here, extended to other media, relaxants, and other experimental

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conditions, will stimulate efforts to develop a consistent theory for both processes.

Conclusions

The primary process responsible for paramagnetic catalysis of spin relaxation and para–ortho conversion in H₂ is a collision between the paramagnet, *S*, and the H₂ molecule. In an effort to refine comparison of the two processes we measured the bimolecular rate constant, i.e., relaxivity, *R*₁, for spin–lattice relaxation of *o*-H₂ and the second-order rate constant, *k*₀, for conversion of *p*-H₂ to *o*-H₂ dissolved in chloroform-*d*₁ catalyzed by nitroxides **1**–**3**. As shown in Table 1, the values of *R*₁ exceed those of *k*₀ by a factor of ca. 200, independent of the catalyst. As observed previously for *R*₁,⁹ biradicals **2** and **3** are twice as

effective catalysts as monoradical **1**. The theories of Freed^{9,20} for *R*₁ and Wigner^{3,8,13} for *k*₀ were used to estimate a value for the distance of closest approach, *d*, between **1** and H₂. Remarkably, the theory for *k*₀, developed to describe gas-phase catalysis in the absence of a magnetic field, yields the same value of *d*, 2.7 Å, as the liquid-phase theory for *R*₁. A physically realistic theory describing both processes in solution in a high magnetic field has yet to be developed.

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