Solvent Effects on the Reactivity and Free Spin Distribution of 2,2-Diphenyl-1-picrylhydrazyl Radicals[1]

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There is no kinetic solvent effect (KSE) on hydrogen atom abstraction from a hydrocarbon (cyclohexane) by the cumyloxyl radical.[3] That is, the rate constants for reaction 1 are equal within experimental error ((1.2 ± 0.1) × 10^6 M^{-1} s^{-1} at 30 °C) in CCl_4, C_6H_6, C_6H_5Cl,

$$PhCMe_2O^{\bullet} + c\text{-}C_6H_{12} \rightarrow PhCMe_2OH + c\text{-}C_6H_{11}^{\bullet} \quad (1)$$

$CH_3C(O)OH$, CH_3CN, and $(CH_3)_3COH$. In contrast to C−H bond cleavage, there is a large KSE on abstraction of the hydroxylic hydrogen atom from *tert*-butyl hydroperoxide and from phenol by the cumyloxyl radical.[4] Thus, for the latter reaction, 2:

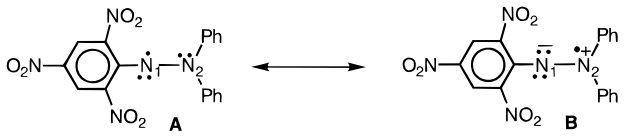
$$PhCMe_2O^{\bullet} + PhOH \rightarrow PhCMe_2OH + PhO^{\bullet} \quad (2)$$

the rate constants at 25 °C in CCl_4, C_6H_5Cl, C_6H_6, $C_6H_5OCH_3$, $CH_3C(O)OH$, CH_3CN, and $(CH_3)_3COH$ are, respectively, 86, 48, 28, 5.6, 1.8, 0.58, and 0.36 × 10^7 M^{-1} s^{-1}.[5] The occurrence of large KSE's on O−H bond cleavage was attributed to hydrogen bond formation between the substrate as the donor and hydrogen bond-accepting (HBA) solvents with abstraction of a hydrogen atom occurring only (or mainly) from substrate molecules which were not hydrogen bonded.[4] Since this is a solvent effect on one of the reactants, i.e., it is a ground state effect, it was predicted that the magnitude of the KSE would be independent of the nature and reactivity of the radical which abstracts the hydroxylic hydrogen atom.[4] That is, for the reaction,

$$XOH + Y^{\bullet} \rightarrow XO^{\bullet} + YH \quad (3)$$

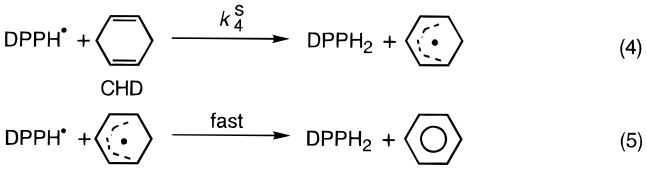
the ratio of the measured rate constants in solvents A and B was predicted to be independent of the structure of Y•, i.e., $(k^A_{XOH/Y})/(k^B_{XOH/Y})$ = constant (for the same XOH). This prediction was largely confirmed[6] for XOH = phenol with Y• = cumyloxyl and 2,2-diphenyl-1-picrylhydrazyl (DPPH•) and for XOH = α-tocopherol (vitamin E) and Y• = *tert*-butoxyl and DPPH•.[8] However, there was one anomalous solvent, *tert*-butyl alcohol. In this solvent the two DPPH• reactions were both ca. 5 times faster than would have been predicted from the rates of the two corresponding alkoxyl radical reactions.

Herein, we report a study of KSE's on C−H bond cleavage induced by the DPPH• radical using 1,4-cyclohexadiene as the substrate. These kinetic results proved that, although the absolute reactivity of DPPH• was very largely solvent independent, it was, indeed, larger in *tert*-butyl alcohol than in any other solvent, including methanol and ethanol in which its reactivity is "normal". In an attempt to understand the DPPH• reactivity-enhancing properties of *tert*-butyl alcohol[9] we also measured the effect of solvents on the distribution of unpaired spin density between the two central nitrogen atoms of DPPH• using EPR spectroscopy. Since these two nitrogen atoms are spectroscopically almost equivalent, we synthesized DPPH• labeled with ^{15}N at the divalent nitrogen (N_1) which is the "formal" radical center (canonical structure **A**).



Results

Kinetic Measurements. The rate constants for reaction of the DPPH• radical with 1,4-cyclohexadiene (CHD) were measured at 30 ± 0.1 °C by spectrophotometry after rapidly mixing concentrated, deoxygenated stock solutions of the two reactants. Initial reagent concentrations were chosen so as to have convenient reaction rates with a large excess of CHD so that pseudo-first-order kinetics obtained. Typically, [DPPH•] at 1.4 × 10^{-4} M was reacted with five different concentrations of CHD in the range (3−15) × 10^{-2} M. The decay of the DPPH• was monitored simultaneously at 6 different wavelengths between 510 and 620 nm, including its band maximum at 520 nm. The overall chemistry can be represented by reactions 4 and 5. Plots of the experimental first-order rate constant,



k^S_{exptl}, versus the CHD concentration in each solvent, S, were linear ($r \geq 0.99$) which proves that the reverse of reaction 4 is unimportant even in the later stages of the reaction. Absolute second-order rate constants, k^S_4, were obtained from these plots by the method of least squares:

$$k^S_{exptl} = k^S_0 + 2k^S_4[CHD]$$

These data are reported in Table 1.

EPR Spectroscopic Measurements. The 2,2-diphenyl-1-picrylhydrazyl radical, DPPH•, was first reported in 1922[10] and was the first free radical for which hyperfine

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(3) Avila, D. V.; Brown, C. E.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1993**, *115*, 466−470.
(4) Avila, D. V.; Ingold, K. U.; Lusztyk, J.; Green, W. H.; Procopio, D. R. *J. Am. Chem. Soc.* **1995**, *117*, 2929−2930.
(5) Additional KSE data on reaction 2 can be found in references 6 and 7.
(6) Valgimigli, L.; Banks, J. T.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1995**, *117*, 9966−9971.
(7) MacFaul, P. A.; Ingold, K. U.; Lusztyk, J. *J. Org. Chem.* **1996**, *61*, 1316−1321.
(8) In the same solvent, $k^A_{PhOH/CumO}/k^A_{PhOH/DPPH}$ = 1.0 × 10^{10} and $k^A_{TOH/BO}/k^A_{TOH/DPPH}$ = 1.6 × 10^6, where TOH is α-tocopherol and BO is *tert*-butoxyl.[6]
(9) Shared to a lesser extent by *n*-butanol and 2-propanol, *vide infra*.
(10) Goldschmidt, S.; Renn, K. *Berichte* **1922**, *55*, 628−643.

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Table 1. Absolute Rate Constants for Hydrogen Atom Abstraction from 1,4-Cyclohexadiene by DPPH• at 30 °C in Twelve Solvents and EPR Parameters for DPPH• in the Same Solvents

no.	solvent	$10^3 \times 2k_4^s$ [a] (M^{-1} s^{-1})	$a(N_1)$[b] (G)	$a(N_2)$ (G)	$a(N_1)/a(N_2)$	$a(N_1) + a(N_2)$	g
1	CCl_4	1.3	9.77 ± 0.02	7.94 ± 0.02	1.23	17.71	2.0036_5
2	benzene	1.4	9.77 ± 0.02	7.94 ± 0.02	1.23	17.71	2.0036_4[c]
3	ethyl acetate	1. 4	9.77 ± 0.02	7.94 ± 0.02	1.23	17.71	2.0036_3
4	γ-valerolactone	1.3	9.78 ± 0.02	7.93 ± 0.02	1.23	17.71	2.0036_3
5	acetonitrile	1.4	9.8 ± 0.1	7.9 ± 0.1	1.2	17.7	2.0036
6	DMSO	1.1	9.3 ± 0.2	8.1 ± 0.2	1.1_5	17.4	
7	acetic acid	1.1	9.60 ± 0.02	8.22 ± 0.02	1.17	17.82	2.0035_6
8	methanol	1.2	9.54 ± 0.02	8.10 ± 0.02	1.18	17.64	2.0035_6
9	ethanol	1.4	9.55 ± 0.02	8.11 ± 0.02	1.18	17.66	2.0035_6
10	*n*-butanol	1.7	9.58 ± 0.02	8.15 ± 0.02	1.18	17.73	2.0035_6
11	2-propanol	2.4	9.60 ± 0.02	8.17 ± 0.02	1.18	17.77	2.0035_8
12	*tert*-butyl alcohol	3.4	9.62 ± 0.02	8.20 ± 0.02	1.17	17.82	2.0035_9

[a] Errors = ±10−15%. [b] Calculated from the measured ^{15}N hfcc by multiplication with the magnetogyric ratio, $\gamma(^{14}N) / \gamma(^{15}N) = 0.7129$. [c] Reference for instrument calibration.

splitting of the EPR signal was observed.[11] Its spectral parameters in single crystals, powders, and glasses[12] and in solution[13] have been carefully evaluated in several investigations by EPR, NMR, ELDOR, ENDOR, and TRIPLE techniques. Solvent effects on the spin distribution and, as a consequence, on the electron-nuclear hyperfine coupling constants (hfcc) of DPPH• were cursorily examined many years ago,[14] and limited evidence was obtained that the ratio of the hfcc for the two central nitrogen atoms was solvent dependent.

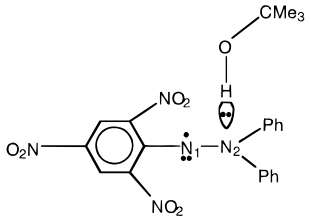
To investigate this solvent effect in greater detail, DPPH-$^{15}N_1$ was synthesized from diphenylamine by diazotization with $Na^{15}NO_2$ to give N-[^{15}N]-nitrosodiphenylamine which was then reduced to [$^{15}N_2$]-1,1-diphenylhydrazine. The hydrazine was isolated as the *p*-toluenesulfonate which was treated with picryl chloride in the presence of sodium carbonate to give 2,2-diphenyl-1-[$^{15}N_1$]-picrylhydrazine. This was subsequently oxidized to give the desired stable free radical.

EPR spectra were recorded at 25 °C using DPPH•-$^{15}N_1$ at concentrations in the range (8−20) × 10^{-5} M in deoxygenated solvents. Spectra were simulated until they were in satisfactory agreement with the experimental spectra in order to obtain the hyperfine coupling constants of the two central nitrogen atoms. The measured *g*-values were corrected with respect to the known value in benzene solution and were confirmed by comparison with the measured value for unlabeled DPPH• powder. These results are given in Table 1.

Discussion

The measured rate constants for hydrogen atom abstraction from 1,4-cyclohexadiene by the DPPH• radical have a probable experimental error of ca. ± 10 to 15%. Thus, the first nine solvents listed in Table 1, including methanol (**8**) and ethanol (**9**), have no significant effect on the intrinsic reactivity of DPPH•.[15] That is, for these nine solvents $2k_4^s = (1.2_5 \pm 0.1_5) \times 10^{-3}$ M^{-1} s^{-1}. However, and as predicted,[6] the reactivity of DPPH• is enhanced in *tert*-butyl alcohol (**12**), there being a threefold increase in $2k_4^{Me_3COH}$ with respect to the nine "normal" solvents. 2-Propanol (**11**) enhances the reactivity of DPPH• by a factor of two ($2k_4^{Me_2CHOH} = 2.4 \times 10^{-3}$ M^{-1} s^{-1}) and there may be a small enhancement of reactivity in *n*-butanol (**10**) ($2k_4^{n-BuOH} = 1.7 \times 10^{-3}$ M^{-1} s^{-1}).

When the enhanced reactivity of DPPH• in *tert*-butyl alcohol was first reported,[6] we hypothesized that it was due to the unpaired electron becoming more localized at its formal site on N_1. The idea was that *tert*-butyl alcohol formed a hydrogen bond to N_2 (structure **C**) and that this reduced conjugative electron delocalization from N_1 to N_2, i.e., structure **A**, would be of greater importance relative to structure **B** in *tert*-butyl alcohol relative to other solvents. This would imply that the N_1 hfcc, $a(N_1)$, would be larger and the N_2 hfcc would be smaller in *tert*-butyl alcohol than in other solvents. An examination of Table 1 reveals that this is not the case.



C

Solvent effects on the hfcc's of the two central nitrogen atoms and on the *g*-value of DPPH are small but significant.[17] The solvent effect on the hfcc of the trivalent nitrogen atom, $a(N_2)$, is similar to, though smaller than, the very well studied solvent effect on the (trivalent) nitrogen atoms' hfcc's of nitroxide radicals[19] (see Figure 1). This is reasonable since hydrazyl radicals and nitroxides are electronically related. In a valence

(11) Hutchinson, C. A., Jr.; Pastor, R. C.; Kowalsky, A. G. *J. Chem. Phys.*, **1952**, *20*, 534−535. In this study only the averaged hfcc of the two central nitrogen atoms was observed. The first report of the inequality of these two nitrogen hfcc's is: Deal, R. M.; Koski, W. S. *J. Chem. Phys.* **1959**, *31*, 1138−1139.

(12) Holmberg, R. W.; Livingston, R.; Smith, W. T., Jr. *J. Chem. Phys.* **1960**, 33, 541−546. Gamo, K.; Masuda, K.; Yamaguchi, J.; Kakitani, T. *J. Phys. Soc. Jpn.* **1965**, *20*, 1730. Gubanov, V. A.; Koriakov, V. I.; Chirkov, A. K. *J. Magn. Reson.* **1973**, *9*, 263−274.

(13) Chen, M. M.; Sane, K. V.; Walter, R. I.; Weil, J. A. *J. Phys. Chem.* **1961**, *65*, 713−717. Hyde, J. S.; Sneed, R. C., Jr.; Rist, G. H. *J. Chem. Phys.* **1969**, *51*, 1404−1416. Gubanov, V. A.; Koryakov, V. I.; Chirkov, A. K. *J. Magn. Reson.* **1973**, *11*, 326−334. Dalal, N. S.; Kennedy, D. E.; McDowell, C. A. *J. Chem. Phys.* **1973**, *59*, 3403−3410. Biehl, R.; Möbius, K.; O'Connor, S. E.; Walter, R. I.; Zimmermann, H. *J. Phys. Chem.* **1979**, *83*, 3449−3456.

(14) Garif'yanov, N. S.; Il'yasov, A. V.; Yablokov, Yu. V. *Dokl. Akad. Nauk SSSR* **1963**, *149*, 876−879. English translation, pp 280−283.

(15) The only related work of which we are aware *and* which appears to have followed "clean" and sensible kinetics involved hydrogen atom abstraction from 9,10-dihydroanthracene by DPPH.[16] However, these rather old results[16] are not congruent with our own in that a solvent effect was observed where we see none (CCl_4 vs PhH) or would expect none (dioxane). Thus, the rate constants reported in CCl_4 are 0.26 and 0.68×10^{-3} M^{-1} s^{-1} at 30 and 50 °C, respectively, in benzene 0.12 and 0.37×10^{-3} M^{-1} s^{-1} at the same two temperatures, and in dioxane 0.22×10^{-3} M^{-1} s^{-1} at 50 °C.

(16) Hogg, J. S.; Lohmann, D. H.; Russell, K. E. *Can. J. Chem.* **1961**, *39*, 1394−1396.

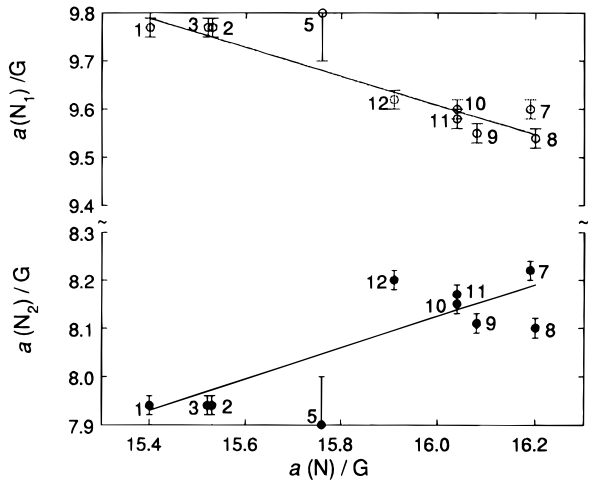
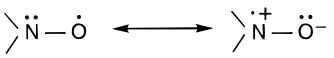


Figure 1. Correlation of values of $a(N_1)$ and $a(N_2)$ for DPPH• in various solvents with reported[19a] values of a(N) for 4-amino-2,2,6,6-tetramethylpiperidin-*N*-oxyl in the same solvents (which are numbered as in Table 1).

bond representation of the nitroxide's three-electron bond, i.e., the two canonical forms, **D** and **E**, make about



D **E**

equal contributions to the overall unpaired electron's distribution, as is also true for DPPH•, structures **A** and **B**. Polar, polarizable, and hydrogen bonding solvents stabilize the dipolar form of nitroxides, **E**, thereby increasing the spin density on nitrogen. The same is true for the N_2 nitrogen of DPPH• as is clearly brought out by a plot of the $a(N_2)$ values from Table 1 against the a(N) values measured by Knauer and Napier[19a] for the 4-amino-2,2,6,6-tetramethylpiperidin-*N*-oxyl radical in the same solvents (see Figure 1).[20] Of course, a solvent-induced increased contribution from the dipolar canonical form, **B**, of DPPH• necessarily implies a decreased spin density on N_1. As can be seen in Figure 1, the plot of $a(N_1)$ vs a(N) for Knauer and Napier's nitroxide has the expected negative slope.

The enhanced reactivity of DPPH• in *tert*-butyl alcohol was originally suggested to be due to increased spin density at the divalent nitrogen atom induced by hydrogen bonding between *tert*-butyl alcohol and DPPH• (e.g., structure **C**).[6] It is now clear that there is no simple correlation between reactivity, $2k_4^s$, and $a(N_2)^s$ (see Table 1). However, if we are willing to ignore the data in DMSO (**6**) (in part because of the large errors in the magnitudes of the two nitrogen hfcc's)[20] *and* in acetic acid (**7**) (for unknown reasons), there may be a weak correlation between the reactivity of DPPH• and the total spin density on its two central nitrogen atoms, $a(N_1) + a(N_2)$. This possible correlation runs from methanol ($2k_4 = 1.2 \times 10^{-3}$ M^{-1} s^{-1}, $a(N_1) + a(N_2) = 17.64$ G) to *tert*-butyl alcohol ($2k_4 = 3.4 \times 10^{-3}$ M^{-1} s^{-1}, $a(N_1) + a(N_2) = 17.82$ G) with all the other solvents (except **6** and **7**) lying in-between. A correlation between reactivity and the total spin density on N_1 and N_2 would appear reasonable.

We initially assumed that enhanced values of $a(N_1) + a(N_2)$ were associated with a solvent-induced reduction of electron delocalization into the aromatic rings of DPPH• due to a solvent-induced twisting of one or more aromatic rings out of conjugation with the SOMO (which is located principally on the two central nitrogen atoms). However, a reviewer pointed out that such a solvent-induced twisting of the aromatic rings could cause a measurable effect on the electronic spectra of DPPH, especially in *tert*-butyl alcohol compared to methanol. Careful measurements revealed no obvious solvent-induced spectral effects.[22] As an alternative to twisting of the aromatic rings this reviewer raised the possibility that *tert*-butyl alcohol provides a unique solvation shell around DPPH because of steric crowding between solvent molecules competing for sites on the DPPH, the idea being that this unique solvation shell would enhance the reactivity of DPPH and increase the total spin density on N_1 and N_2. In the absence of other explanations we gratefully accept this proposal.

In conclusion, we have confirmed our earlier observation[6] that the reactivity of DPPH in hydrogen atom abstractions is significantly enhanced in *tert*-butyl alcohol. With two phenols this enhancement of reactivity amounts to a factor of about 5[6] but with 1,4-cyclohexadiene the enhancement amounts only to a factor of about 3. We have shown that this reactivity enhancement is not a general property of alcohols or other hydroxylic solvents (acetic acid) but seems to be confined to the sterically more demanding alcohols (*tert*-butyl alcohol > 2-propanol > *n*-butanol, with no enhancement in ethanol and methanol).

Experimental Section

Materials. Except for DMSO,[20] solvents were of the purest grade commercially available and were used without further purification. 1,4-Cyclohexadiene (Aldrich 97%) was percolated twice through activated basic alumina immediately prior to use to remove the stabilizer (the absence of which was confirmed by HPLC).

N-[^{15}N]-Nitrosodiphenylamine[23] was prepared by reacting diphenylamine (2.2 g; 13.0 mmol) dissolved in 20 mL of ethanol with 1.6 mL of concd HCl, immediately followed by $Na^{15}NO_2$

(17) Our results are in satisfactory agreement with the early report of Garif'yanov *et al.*[14] that $a(N_1)/a(N_2) = 1.20$ and $a(N_1) + a(N_2) = 17.6 \pm 0.2$ G in benzene (and in toluene and chloroform) and 1.16 and 17.8 ± 0.2 G in methanol. Later, Ryzhmanov and Egorova[18] suggested that solvent effects on $a(N_1)$ and $a(N_2)$ were due to the formation of a charge transfer complex between the DPPH• and a solvent molecule, and these effects were correlated with the ionization potential (IP) of the solvent. Unfortunately, there are no tabulated data in this publication, and the correlation is only shown graphically with the solvents not identified.

(18) Ryzhmanov, Yu. M.; Egorova, A. A. *Dokl. Akad. Nauk SSSR* **1970**, *191*, 148−150. English translation, pp 227−229.

(19) (a) Knauer, B. R.; Napier, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 4395−4400. (b) Reddock, A. H.; Konishi, S. *J. Chem. Phys.* **1979**, *70*, 2121−2130.

(20) The DMSO employed was, unfortunately, an old sample available from previous work[21] which contained some water. Both our EPR data and kinetics in DMSO were probably influenced by this fact. Thus, the point for DMSO (**6**) is not included in Figure 1 because it is much too imprecise. The point for γ-valerolactone (**4**) is not included because we could find no literature value for the nitroxide's hfcc in this solvent. The hfcc of the nitroxide in ethyl acetate (**3**) was not measured by Knauer and Napier[17a] but was estimated from data for di-*tert*-butyl nitroxide, see footnote *f* to Table IV of reference 21.

(21) Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4983−4992.

(22) Band maxima (nm) and absorbance (in parentheses) for 0.25 mM DPPH in various solvents at 20.0 °C. **1**, CCl_4, 518 (2.30), 330 (3.00); **2**, C_6H_6, 520 (2.45), 328 (3.20); **5**, CH_3CN, 516 (2.75), 328 (3.75); **6**, DMSO, 524 (2.90), 324 (3.85); **7**, AcOH, 516 (2.20), 324 (3.85); **8**, MeOH, 516 (3.10), 330 (4.00); **12**, *t*-BuOH, 518 (2.75), 328 (3.75). The only noticeable solvent effect is in acetic acid in which the ratio of the UV/visible absorbances is 1.75 vs a range from 1.29 (MeOH) to 1.36 (CH_3CN and *t*-BuOH) in the other solvents.

(23) Chen, M. M.; D'Adamo, A. F. Jr.; Walter, R. I. *J. Org. Chem.* **1961**, *26*, 2721−2727.

99.8% (1.0 g; 14.3 mmol; 1.1 equiv) in 2 mL of water. The mixture was stirred for 30 min at 0 °C, and the yellow precipitate was collected, washed with water and (briefly) with cooled (−5 °C) ethanol, and dried by suction at room temperature, yield 81%, mp 68 °C.

[$^{15}N_2$]-1,1-Diphenylhydrazine.[23,24] N-[^{15}N]-nitrosodiphenylamine (2.1 g; 10.5 mmol) was reduced with 1.5 equiv of $LiAlH_4$, using the method of inverse addition,[25] in anhydrous ether for 1 h at 0−5 °C. After decomposition of the reduced intermediate (EtOAc 20 mL, wet ether 20 mL, 20% sodium potassium tartrate 70 mL), the organic layer was separated and then combined with ether extracts of the aqueous phase (3 × 50 mL), dried (Na_2SO_4), and concentrated to 100 mL under vacuum. To this solution was added 1.2 equiv of *p*-toluenesulfonic acid dissolved in 30 mL of *tert*-amyl alcohol. The white precipitate was collected, washed well with dry ether, and dried at room temperature, yield 75%, mp 189−190 °C dec. ^{1}H NMR (d_6-DMSO): δ 10.40 (s, NH_3^+, broad), 2.28 (s, CH_3), 7.1 to 7.5 (multiple lines, 14H aromatic). Purity > 97% (by HPLC), isotopic labeling > 99% (by GC/MS of the recovered free base).

2,2-Diphenyl-[$^{15}N_1$]-1-picrylhydrazine.[24] The tosylate salt (7.9 mmol) and picryl chloride (8.3 mmol; 1.05 equiv) were dissolved in 50 mL of methanol to which was added 1.0 g of sodium carbonate in 20 mL of water. The mixture was stirred for 2 h at room temperature under argon, diluted with water (10 mL), and cooled (−5 °C). The brick-red precipitate was collected, washed with methanol/water (5:2), with water, and dried under vacuum (1 mmHg) at room temperature for 10 h. The yield of almost pure product was 99%, mp 172−173 °C dec.

1-Chloro-2,4,6-trinitrobenzene (picryl chloride) was synthesized from 1-hydroxy-2,4,6-trinitrobenzene by standard methods ($POCl_3$/*N*,*N*-diethylamine, 0 °C, 45 min), yield 92%.

DPPH-$^{15}N_1$[23] was prepared by stirring the ^{15}N-labeled hydrazine (7.6 mmol) with PbO_2 (35 g) and Na_2SO_4 (3.0 g) in chloroform for 2 h at room temperature. The solution was filtered, collected with several washings of the residue, and concentrated to 30 mL. The product was completely precipitated by diluting with hexane (100 mL), collected, and dried (1 mmHg, 40 °C) for 5 h, yield 90%, mp 127−130 °C dec. A sample for the EPR work was recrystallized from petroleum ether.

EPR Measurements. Spectra were recorded at 25 °C on a Brucker ESR 300 spectrometer equipped with a Varian NMR gaussmeter and a Systron Donner 6016 frequency counter. Solutions of DPPH-$^{15}N_1$ in the desired solvent were filtered directly into EPR tubes and deoxygenated by bubbling with argon. Measured coupling constants were used to simulate a low resolution experimental spectrum, and these coupling constants were then adjusted until satisfactory agreement with the experimental spectrum was achieved. Measured *g*-values were corrected with respect of the known value for DPPH$^\bullet$ in benzene and were confirmed by comparison with the measured *g*-value for DPPH$^\bullet$ powder.

Kinetic Measurements. A concentrated, deoxygenated stock solution of 1,4-cyclohexadiene (CHD) was rapidly injected into a thermostated, deoxygenated solution of DPPH$^\bullet$ in the same solvent in a 10 × 10 mm^2 quartz cuvette sealed with a rubber septum. The cuvette sat within a Hewlett Packard 8425A diode array spectrophotometer and was thermostated at 30 ± 0.1 °C. The decay of DPPH$^\bullet$ was followed at 6 different wavelengths from 510 to 600 nm, including the band maximum (520 nm). Initial concentrations were typically 1.4×10^{-4} M DPPH$^\bullet$ with $(3-15) \times 10^{-2}$ M CHD. For each solvent, five measurements were made of k^s_{exptl} with different [CHD] and the absolute second-order rate constants $2k^s_4$ were calculated by least squares fitting of plot of k^s_{exptl} vs [CHD] ($r > 0.99$).

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