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ESR Approach to the Nature of Solvation by Using *s*-Butyl *n*-Heptafluorobutyryl Nitroxide Probe

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Abstract: Stable *s*-butyl *n*-heptafluorobutyryl nitroxide **3** has been generated in an electron–transfer reaction in F113 ($CFCl_2CF_2Cl$) solution at r.t. The a_N values for **3** in 11 aprotic solvents show a linear correlation with cybotactic solvent parameters E_T and Z. The physical significance for slopes, slope × E_T or slope × Z, and the extrapolated intercepts on the a_N axis are well established. The plots of a_N *versus* noncybotactic solvent parameters, such as dipolar moment and dielectric constant, are badly behaved.

Keywords: *s*-Butyl *n*-heptafluorobutyryl nitroxides, a_N, solvent parameters, solvation.

Because the solvent dependency of a_N, g factors and line widths of some bulky and stable di-*t*-alkyl nitroxides[1], ESR has been proved to be a useful tool in searching for the nature of medium effects (solvation) to chemical reactivity. A large number of fluorinated nitroxides with a wide variety of structures have been generated and subjected to extensive studies in our laboratory[2]. Amongst, *t*-butyl perfluoroalkyl nitroxides, much less hindered, with no β-H atoms, have been employed as spin probes in ESR studies of solvation[3]. Now, we expand our studies by using a new type of spin probe, $n\text{-}C_3F_7CON(O^{\cdot})Bu^s$ **3** ($g = 2.0068$, $a_N = 7.26 \times 10^{-4}$ T, $a_H = 0.98 \times 10^{-4}$ T in F113 at 24°C) .

The probe **3** was generated *via* the electron–transfer reaction between O-benzoyl-N-*s*-butyl hydroxylamine **1** and *n*-heptafluorobutyryl peroxide **2**. The typical procedure is as follows, **1** (0.3 g, 1.5 mmol) was dropped into **2** (0.94 g, 1.5 mmol) in F113 (~10 ml) with stirring at r. t. under N_2. Then the reaction mixture then was filtered, washed twice with water, dried with anhydrous Na_2SO_4 and kept under N_2 in a refrigerator before use within 2 days. A tentative mechanism for the reaction is proposed[4]:

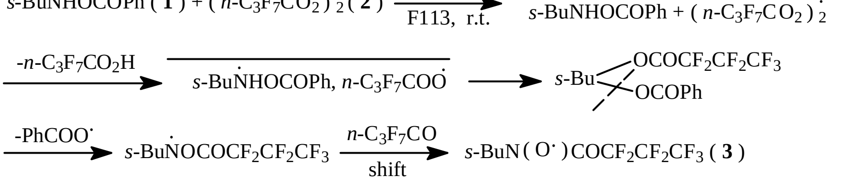

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Table 1 ESR parameters ($\pm 0.02\times10^{-4}$ T) of nitroxide **3**^{a}

solvent	^bE_T	^cZ	^da_N	^da_H	N	solvent	^bE_T	^cZ	^da_N	^da_H	N
1 methanol	55.5	83.6	7.28	1.15	0.220	8 dioxane	36.0		7.28	0.98	0.220
2 *i*-propyl alcohol	48.6	76.3	7.37	0.91	0.223	9 F113	^{e}35		7.26	0.98	0.219
3 acetone	42.2	65.5	7.26	0.93	0.219	10 benzene	34.5	54.0	7.24	0.90	0.219
4 dichloromethane	41.1	64.7	7.35	0.94	0.223	11 di-*t*-butyl ether	33.4	60.1	6.98	0.98	0.208
5 chloroform	39.1	63.2	7.34	1.03	0.222	12 perchloromethane	32.5		7.23	0.78	0.218
6 chlorobenzene	37.5	58.0	7.31	0.89	0.221	13 cyclohexane	31.2		7.19	0.86	0.217
7 tetrahydrofuran	37.4	58.8	7.30	0.95	0.221	14 *n*-hexane	30.9		7.17	0.99	0.212

Note: a data measured under 23~24°C; b E_T (in kcal/mol) quoted from Ref. 5; c Z (in kcal/mol) quoted from Ref. 6; d a_N and a_H in 10^{-4} T; e E_T measured by ESR technique, see Refs. 4 and 5.

Nitroxide **3** appears brownish-red in F113 solution, and may be kept at r. t. without decay for weeks. Its ESR spectra in dilute solutions of different aprotic solvents are all triplet-doublet patterns. The a_N and a_H in 14 solvents, measured on a JEOL ESR spectrometer with modulation frequency 100 KHz, are listed in **Table 1**. For aprotic solvents, the data in the table demonstrate a significant change of a_N with increase in the polarity parameters E_T[5] (Dimroth) and Z constant[6] (Kosowar). **Figure 1** and **Figure 2** show the correlation of those cybotactic parameters with a_N values. The correlation equations thus established are: $a_N = 1.77\times10^{-6}E_T + 6.64\times10^{-4}$ (10 solvents, r = 0.984) and $a_N = 0.97\times10^{-6}Z + 6.73\times10^{-4}$ (5 solvents, r = 0.963). In protic solvents (1~3), with the increase in E_T and Z, a_N keeps almost constant.

As people know so far, the solvation energy corresponds to dispersion forces and dipole interactions between the solute and the solvent. However, electron-pair donor/electron pair acceptor (EPD–EPA) interactions between nitroxides and solvent molecules have been proved to be the main factor[5]. We may use the canonical structure **A** and **B** to show the spin delocalization onto the nitroxyl N and O atoms in **3**[7]. The *n*-C_3F_7CO group attracts the lone pair of electrons from N atom, reduces the resonance interaction between the lone pair and the spin, and so decreases the spin density on N atom ($\rho_N = 0.219$ in F113) , causes a smaller a_N (7.26×10^{-4} T in F113) compared to the a_N for hydrocarbon acyl nitroxides, such as PhCON (O$^\cdot$) Bu^t ($a_N = 8.05 \times10^{-4}$ T in F113[8]) and trifluoromethyl *t*–alkyl nitroxide, such as CF_3N (O$^\cdot$) Bu^t (a_N =

Figure 1 Linear correlation of a_N vis E_T

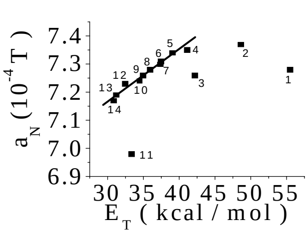
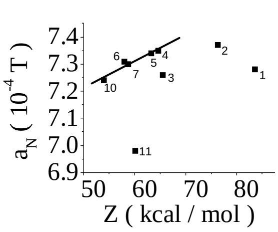
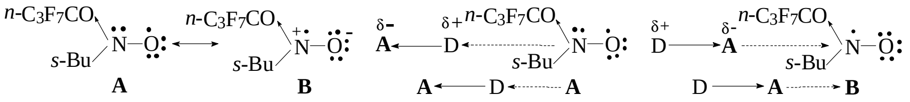


Figure 2 Linear correlation of a_N vis Z



12.10×10^{-4} T in F113). The contribution of **A** becomes much more important than that of **B,** and the spin is largely localized on O atom (ρ_0~0.77). Nitroxide **3** functions mainly as an oxygen radical. If **A**←D depicts a molecule of all solvents studied, the interaction of **A**←D with **3** may be illustrated as follows:



The solvent dipole **A**←D may orient in opposite directions towards **A** and **B**. The electronically dative end D bearing partial positive charge would get close to N atom of the nitroxide bearing a lone pair of electrons (A←D←←A) and thus reduce the spin delocalization onto N atom; Consequently, would cause a decrease in a_N. In contrast, the interaction depicted by D→A→→B would cause an increase in a_N. Highly polar aprotic solvents may favor the contribution of **B** and cause a bigger increase in a_N.

The net increase in a_N is proportional to the E_T value and Z constant of the solvents. The slopes (1.77×10^{-6} and 0.97×10^{-6}) indicate the susceptibility toward the solvation of **3** dissolved in a specific solvent. The term slope$\times E_T$ is a measure of the net increase of a_N due to solvation in a specific solvent. For example, in dichloromethane (E_T = 64.7 kcal/mol), the net increase in a_N of **3** is $\Delta a_N = 1.77\times10^{-6}\times64.7 = 1.15\times10^{-4}$ T.

The extrapolated interceptions (6.64×10^{-4} T and 6.73×10^{-4} T) on the a_N axis ($E_T\rightarrow0$, $Z\rightarrow0$) indicate the coherent a_N value of a specific probe nitroxide under ideal conditions (in gas phase without solvation).

In polar protic solvents, the constancy of a_N value of the probe nitroxide is believed to be caused by H–bonding between the nitroxyl oxygen and the OH group of alcohols and enolic form of acetone. Since the H–bonding interaction is usually much stronger than EPD–EPA, and the later is almost shaded in the studied systems.

In conclusion, **3**, the first *s*-alkyl perfluoroacyl nitroxide with high spin density on the nitroxyl oxygen, is proved to be a valuable new probe in ESR studies of solvation.

References

1. B.R.Knauer, J.J.Napier, *J.Am.Chem.Soc.*, **1976,** *98,* 4396.
2. (a) C.X.Zhao, G.F.Cheng, Y.L.Qu, X.K.Jiang, *J.Am.Chem Soc.*, **1986,** *108,* 3132.
   (b) C.X.Zhao, G.F.Cheng, X.K.Jiang, X.S.Wang, *J.Am.Chem.Soc., Chem. Commun.*, **1986,** 1362.
   (c) C.X.Zhao, G.F.Cheng, *J.Fluorine Chem.*, **1986,** *31,* 417; **1987,** *37,* 597; **1988,** *38,* 391.
   (d) C.X.Zhao, Y.L.Qu, *J.Fluorine Chem.*, **1993,** *61,* 45; **1992,** *59,* 413.
   (e) C.X. Zhao, H.Y. He, Y.L. Qu, X.K. Jiang, *J. Fluorine Chem.*, **1999,** *98,* 67.
   (f) H.Y. He, C.X. Zhao, C.M. Zhao, X.K. Jiang, *Tetrahedron*, **1999,** *55,* 2263.
3. Y.Y. Peng, J. Huang, Y.L. Qu, C.X. Zhao, *Res.Chem.Intermed.*, **2000,** *26,* 587.
4. C.X.Zhao, Y.Y. Peng, Y.L. Qu, *Res.Chem.Intermed.*, **1992,** *18,* 1.
5. (a) V.Gutmann, *Coordination Chemistry in Non-aqueous Solvents*, Springer, New York, **1968.**
   (b) V.Gutmann, *Coord.Chem.Rev.*, **1967,** *2,* 239.

(c) U.Mayer, V.Gutmann, W.Gerger, *Monatsh.Chem.*, **1975,** *106*, 1235.
6. E.M.Kosowar, *J.Am.Chem.Soc.*, **1958,** ***80,*** 3253.
7. J.Gendell, J.H.Freed, G.K.Frenkel, *J.Chem.Phys.*, **1962,** ***37,*** 2832.
8. C.X. Zhao, Y.L. Qu, *J.Fluorine Chem.*, **1992,** *59,* 413.

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