MAGNETIC RESONANCE IN CHEMISTRY, VOL. 35, 357–362 (1997)

Muonium Adducts of the Nitro Group: Muoxynitroxides

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Implantation of positive muons in liquid samples of nitroalkanes leads to radicals, detectable by the transverse field muon spin rotation (TF-μSR) technique, with small hyperfine couplings (*ca.* 26 MHz). The results indicate that muonium has added to one of the oxygen atoms of the nitro group and that the bound muon remains close to the 'nodal' region of the nitrogen $2p_z$ orbital, which contributes to the SOMO. This is a consequence of π-bonding in the O—N—O(Mu) unit, which is maximally preserved. An abrupt change is found for the nitrobenzene adduct, in which the coupling is raised to 37.14 MHz. Semi-empirical (PM3) calculations provide an explanation for this in terms of the different geometries of $RNO_2H^{\cdot}$ and $PhNO_2H^{\cdot}$ radicals, the former being bent at the nitrogen centre while $PhNO_2H^{\cdot}$ is planar. When $PhNO_2H^{\cdot}$ is located in NaX zeolite, its coupling is increased; this is thought to be due to the electrostatic field from Na^+ cations. © 1997 by John Wiley & Sons, Ltd.

Magn. Reson. Chem. **35**, 357–362 (1997) No. of Figures: 1 No. of Tables: 5 No. of References: 19

Keywords: nitro group; muonium adducts; muoxynitroxides

Received 3 June 1996; revised 12 December 1996; accepted 13 December 1996

INTRODUCTION

Owing to the strongly electron-affinic nature of the nitro group, there has been a great effort made over many years to decide whether nitro compounds could usefully be employed as radiosensitizers in radiotherapy.[1,2] In various media, electron addition to nitro compounds leads to the formation of their radical anions, in which the unpaired electron is largely confined to the nitro group itself: depending on precise details of the structure, these electron adducts will protonate, giving radicals $RNO_2H^{\cdot}$, with a characteristic pK_a. In the case of metronidazole (2-methyl-5-nitro-1-imidazoleethanol) which *has* proved effective as a radiosensitizer, the pK_a is *ca.* 6, so that at physiological pH (7) one anion in ten will be protonated, and so may be significant to its activity. In the present work, we have formed the muon analogues, $RNO_2H^{\cdot}$, from very simple nitro compounds, nitroalkanes, so to focus as far as possible on the $NO_2Mu^{\cdot}$ function, weakly perturbed by the remainder of the molecule; this may be considered as an extension of our previous investigations[3] of carbonyl–muonium adducts, $R_2COMu^{\cdot}$.

EXPERIMENTAL

The samples of nitroalkanes and nitrobenzene were deoxygenated by four freeze–pump–thaw cycles and were sealed into 35 mm o.d. thin-walled Pyrex ampoules; one further sample was prepared by adsorption of nitrobenzene from the gas phase into NaX zeolite cooled to 77 K in a Pyrex ampoule; this was degassed as above and sealed off. The TF-μSR measurements were made using the μE4 beamline of the Paul Scherrer institute, with a momentum of 85 MeV/*c*; details of the method have been given previously. Specific aspects are that (i) an external magnetic field of 2 kG (0.2 T) was applied to the sample ampoule while it was irradiated with the muon beam, (ii) typically, 4×10^7 good decay events were accumulated, in four data histograms and (iii) the muon precession frequencies were obtained by fitting the usual theoretical function in Fourier space.

MO calculations were made on the John Moores University Vax cluster using the semi-empirical PM3 method (the normal hydrogen basis set was used, there not being one available for muonium).

RESULTS

The muon coupling constants measured for $RNO_2H^{\cdot}$ radicals in nitroalkane and in nitrobenzene solutions are shown in Table 1. The near constancy of the coupling (*ca.* 26 MHz) in the nitroalkanes is striking, and entirely in contrast with results for ketone adducts where the coupling in $Bu_2{}^tCOMu^{\cdot}$ is nearly three times that in $Me_2COMu^{\cdot}$.[3] The increase to *ca.* 37 MHz in

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Contract grant sponsor: UK Engineering and Physical Sciences Research Council.
Contract grant sponsor: Leverhulme Trust.
Contract grant sponsor: Swiss Natural Science Foundation.
Contract grant sponsor: Paul Scherrer Institute.

CCC 0749–1581/97/060357–06 $17.50

Table 1. Parameters for muonium adducts of nitro compounds measured by TF-μSR

Radical	A_μ (MHz)[a]	$A_{\mu'}$ (10^{-4} T)[b]	λ (μs^{-1})[c]	T (K)
$MeNO_2Mu^{\cdot}$	27.20	3.05	4.75	293
$EtNO_2Mu^{\cdot}$	26.82	3.01	3.70	293
$Pr^nNO_2Mu^{\cdot}$	26.76	3.00	3.17	293
	28.01	3.14	3.53	313
	29.01	3.26	4.34	329
$Pr^iNO_2Mu^{\cdot}$	25.66	2.88	4.09	293
$Bu^tNO_2Mu^{\cdot}$	26.10	2.93	6.29	293
$PhNO_2Mu^{\cdot}$	37.14	4.17	4.11	293
/NaX	38.68	4.34	0.70	293
	38.84	4.36	2.56	301
	40.37	4.53	3.12	332

[a] Muon–electron hyperfine coupling.
[b] Coupling corrected for muon/proton magnetic moment ratio (3.1833) and converted into units of 10^{-4} T (≡G).
[c] Relaxation rate (proportional to the linewidth).

$PhNO_2H^{\cdot}$ is therefore highly significant, and cannot be due to a steric effect since the effective steric volumes of isopropyl and phenyl groups are similar, and must be electronic in origin. We have explored the structures of these adducts with semi-empirical (PM3) calculations (see later) and found that the essential difference is that in $PhNO_2H^{\cdot}$ the $NO_2H^{\cdot}$ unit is planar, whereas the nitroalkane adducts are predicted to have markedly pyramidal nitrogen centres; defining the geometry in terms of the dihedral angle, (H)O—N—C—O, this amounts to *ca.* 147° in all cases (for reference, 180° is obtained for planar and 120° for tetrahedral structures).

We attempted to form these radicals in NaX zeolite, but discovered that a vigorous chemical reaction took place on adding the nitroalkanes to the zeolite which evolved brown fumes. This did not occur with nitrobenzene, and we found that the muon coupling in $PhNO_2H^{\cdot}$ is increased by *ca.* 2 MHz in NaX from that in liquid nitrobenzene.

DISCUSSION

The formation of a radical $RNO_2H^{\cdot}$ may be depicted as the formal addition of muonium to an oxygen atom of the nitro group:

$$RNO_2 + Mu^{\cdot} \rightarrow RN(O^{\cdot})OMu$$

in analogy with carbonyl adducts:[3]

$$R_2CO + Mu^{\cdot} \rightarrow R_2COMu^{\cdot}$$

However, in this analogy we should also consider alternative *ionic* routes. As stated above, nitro compounds are strongly electron-affinic and will readily capture radiolytic electrons:

$$RNO_2 + e^- \rightarrow RNO_2^{-\cdot}$$

and subsequent muon addition would yield $RNO_2Mu^{\cdot}$. Another possibility is that a muon adds first:

$$RNO_2 + Mu^+ \rightarrow RNO_2Mu^+$$

and this (extremely electron-affinic) species then scavenges an electron:

$$RNO_2Mu^+ + e^- \rightarrow RNO_2Mu^{\cdot}$$

In the case of acetone, certainly two thirds of the Me_2COMu radical yield is from true muonium addition,[4] while the remainder should probably be ascribed to separate muon/electron addition events. Species RNO_2Mu^+ are equivalent to $H_2NO_3{}^+$, formed during nitration reactions as a precursor to $NO_2{}^+$, which is expected to be significant only in strongly acidic media;[5] however, implantation of 'bare' muons (chemically equivalent to protons) in materials amounts to a strongly acidic *local* environment, as the thermalized muons are available to bond to those molecules present.

Structural details

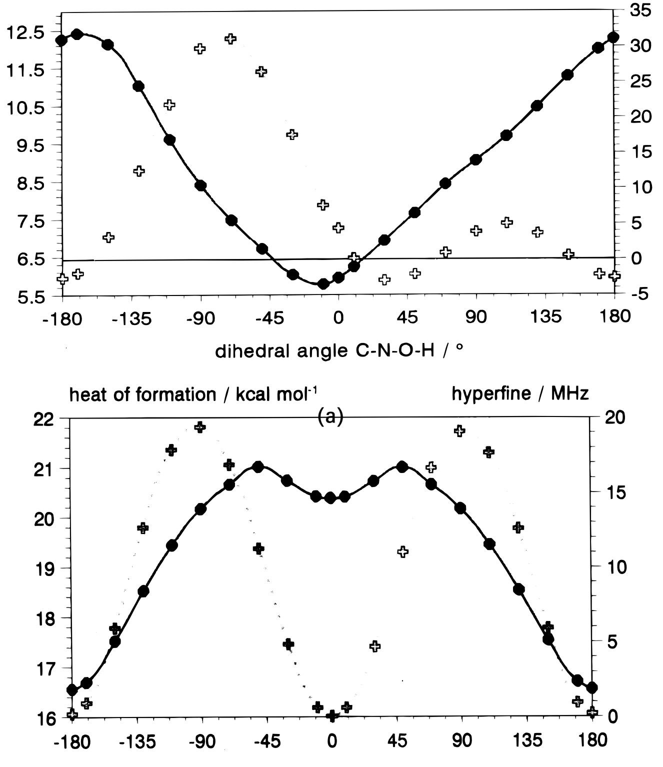
In principle, muonium addition to nitrogen or to oxygen atoms is possible, but the small size of the coupling shows that the muon is located near the radical plane, as expected for an oxygen adduct in which π-bonding is mainly retained in the $NO_2(Mu)$ unit; this is similar to carbonyl adducts where the preservation of π-bonding 'locks' the muon in the nodal region of the radical,[3,6,7] the unpaired electron occupying the C—O π^* level. Since the unpaired electron will be delocalized over the $NO_2(Mu)$ unit, there are two contributions to the muon coupling, one being spin polarization of the O—Mu bond which induces negative spin density in the muonium 1s orbital, and a hyperconjugative interaction between the O—Mu bond and spin density at the nitrogen atom, when the muon oscillates away from the nodal region. This means that the coupling, in principle, could be negative or positive. We can, however, make recourse to the temperature-dependent behaviour of the coupling to decide upon its sign: at higher temperatures, the vibrational amplitude will increase and the coupling become more positive, so in absolute magnitude a negative coupling will decrease and a positive one increase on raising the temperature. We find the latter case for 1-nitropropane, and given the similarity of all the nitroalkane adduct couplings, we believe that they are all of positive sign. A substantial rotation of the N—(OMu) unit from the nodal region would deconjugate the oxygen atom from the π-system and so is disfavoured.

To our knowledge, there are no theoretical results published for $RNO_2H^{\cdot}$ radicals, and so there is no existing insight into the variation in the total energy of these radicals and the change in the OH coupling constant as the R—N—O—H dihedral angle varies, as would be incurred by torsional oscillation of the OH group. In order to elucidate further structural details and to account for the substantially larger coupling in the $PhNO_2Mu^{\cdot}$ radical, we resorted to semi-empirical calculations on the H analogues, $RNO_2H^{\cdot}$, at the PM3 level. The results are largely similar for all the nitroalkane H adducts, for which strongly bent nitrogen centres (**I**) are predicted (relevant calculated geometrical details are given in Table 2); representative plots of ΔH_f

Table 2. Relevant geometries calculated for hydrogen atom adducts of nitro compounds using the PM3 method

(I) R	φ (O—N—C—O) (°)	φ (H—O—N—C) (°)
Me	146	168
Et	147	168
Pr^i	148	166
Bu^t	146	167
Ph	180	180

and of A(H) *vs.* H—O—N—C torsional angle are shown for $\mathrm{MeNO_2H^{\cdot}}$ in Fig. 1(a). On average, the (H)O—N—C—O dihedral angle (ϕ) is *ca.* 147°, not quite at the tetrahedral angle ($\phi = 120°$), but having made a considerable departure from planarity ($\phi = 180°$); furthermore, there is just a single clear energy minimum at which the O—H group lies in opposition to the alkyl group R (**I**), and taken with the very similar curves plotted as a function of torsional angle, would explain why the coupling is little affected by the nature of R. In the case of the ketone adducts $\mathrm{Bu_2{}^tCOMu^{\cdot}}$ and $\mathrm{Me_2COMu^{\cdot}}$,[3,6] it is impossible for the muonium atom to avoid steric clashes with the alkyl groups, hence the greatly increased coupling in $\mathrm{Bu_2{}^tCOMu^{\cdot}}$, as the bulky substituent forces the muonium atom partly away from the nodal region and into that of stronger coupling. We do note, however, a slight but clear inflection on the curve which we believe to be an attempt to locate a second minimum in which the O(H) lies to the other side of the molecule (**II**), rotated from (**I**) through *ca.* 100°, but corresponds to a largely deconjugated structure through it must be close to the steric minimum. However, it does not actually find a minimum and the energy rapidly decreases to the overall minimum where the H atom and R are opposed (**I**).



(b)

Figure 1. (a) Rotational energy barrier and calculated hyperfine coupling constants (UHF) in the $\mathrm{CH_3N(O)OH}$ radical. (b) Rotational energy barrier of —C—N—O—H— and calculated spin densities (UHF) in the radical PhNOOH.

The hyperfine coupling calculated as a function of C—N—O—H torsional angle [Fig. 1(a)] shows two inequivalent maxima, as is typical of the variation in β-proton couplings in non-planar radicals, for instance in imine radical cations $\mathrm{R_2C{=}N{-}C(H)R_2^{+\cdot}}$,[8–11] the greater maximum occurring when the H atom eclipses the rear lobe of the N-centred orbital and the smaller one corresponding to the alternative eclipse with the frontal lobe.[9] This curve is almost identical for all nitroalkane H adducts and indicates that the differing electronic effect of the alkyl groups has little influence on the spin density distribution in these radicals.

The situation is different for the nitrobenzene H adduct, which is predicted to have a planar $\mathrm{C{-}NO_2H}$ unit (**III**).[†] This has dramatic consequences both on the energetics and hyperfine coupling in relation to the C—N—O—H angle [Fig. 1(b)]. There are now two clear energy minima, the lowest corresponding to the furthest separation of the phenyl group and O(H) atom, ϕ(C—N—O—H) = 180°, and the other when they are eclipsed; both structures maximise π-bonding in the system, and the difference in enthalpies of formation between them (*ca.* 4 kcal mol^{-1}) corresponds to the difference in steric energy between a hydrogen atom which is eclipsed by either an oxygen atom or a phenyl group in the $\mathrm{NO_2H}$ system. The hyperfine coupling shows two equivalent maxima corresponding to structures **IV** and **V**, and it is noteworthy that even though these are fully deconjugated, they are not energy maxima, which are only reached by a further rotation through 45°; we propose that due to steric forces, as the O(H) atom approaches the phenyl ring, further rotation leads to a maximum at $\phi = 0°$ as conjugation is maximized and overcomes the steric energy, although only by *ca.* 0.6 kcal mol^{-1}. Whereas the coupling is predicted to be negative at the energy minimum in all the nitroalkane adducts, it is marginally positive at the overall minimum in $\mathrm{PhNO_2H^{\cdot}}$; assuming that the N—OH (N-OMu) group oscillates in the torsional potential that

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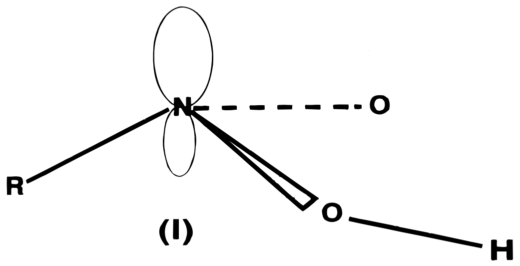
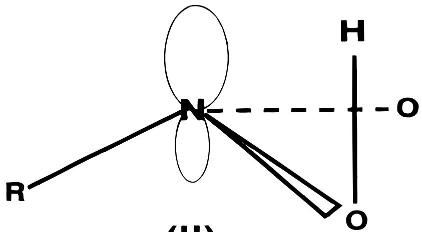
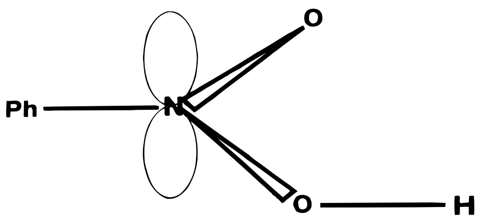
[†] While no calculations have been reported on $\mathrm{RNO_2H^{\cdot}}$ radicals, the related radical anions have been investigated using the INDO method.[19] Since the $\mathrm{PhNO_2^{-\cdot}}$ radical anion is predicted to be planar, it is reasonable that the $\mathrm{PhNO_2H^{\cdot}}$ analogue will also be so. The alkyl derivatives, $\mathrm{RNO_2^{-\cdot}}$, are predicted to possess angular nitrogen centres, but consideration of simple bonding theory suggests that protonation of one of the oxygen atoms will reduce the N 2p$_z$ population and hence the degree of bending; however, our calculations at the higher PM3 level predict that the N centres in $\mathrm{RNO_2H^{\cdot}}$ radicals remain pyramidal, and that the N centre in $\mathrm{PhNO_2H^{\cdot}}$ is indeed planar. Further consideration of the resulting torsional potentials associated with these structurally distinct species then provide a rationalization of the higher coupling measured in the $\mathrm{PhNO_2Mu^{\cdot}}$ radical than in the alkyl derivatives.



(I)

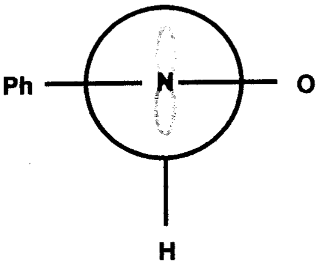


(II)

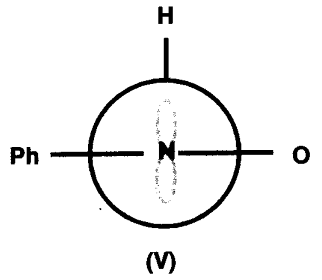


(III)

exists for each radical, and remains mainly confined towards the region of weak overlap with the N $2p_z$ orbital, it is qualitatively in accord with experiment that averaging the coupling over a potential with regions of positive and negative coupling could lead to a smaller overall value than averaging over all positive values. Preliminary results obtained by averaging the coupling over the calculated barrier do indeed indicate that the coupling should be higher for $PhNO_2Mu^{\cdot}$ than for $RNO_2Mu^{\cdot}$ (Table 3); however, their lower than experimental values would imply that there is a positive OMu/OH hyperfine isotope effect operating in all cases. The existence of an effect is borne out by the limited experimental data for $RNO_2H^{\cdot}$ radicals (Table 4), albeit measured mainly in aqueous rather than RNO_2 solutions, but which is apparently negative for $Pr^iNO_2H^{\cdot}$ (see later discussion); $PhNO_2H^{\cdot}$ (see later) appears to be an unknown species as far as hyperfine data are concerned, so we are unable to appeal to experimental evidence regarding the possible $PhNO_2Mu^{\cdot}/PhNO_2H^{\cdot}$ isotope effect.



(IV)



(V)

$PhNO_2Mu^{\cdot}$ in NaX zeolite

As part of our current programme[12] to study the properties of organic radicals in zeolites, we decided to

Table 3. Calculated muon hyperfine couplings for muonium adducts of nitro compounds[a]

R	Coupling (MHz)
Me	23.40
Et	23.97
Pr^n	22.63
Pr^i	25.47
Bu^t	22.65
Ph	27.25

[a] Coupling calculated by averaging over the torsional potentials [Fig. 1(a)] and multiplying by 3.18; it is assumed that the potential is the same for $RNO_2Mu^{\cdot}$ and $RNO_2H^{\cdot}$; the disparity with the slightly higher experimental numbers implies that a hyperfine isotope effect may operate, owing to the greater vibrational amplitude of the muon.

Table 4. Comparison of coupling constants for radicals $RNO_2H^{\cdot}$ and $RNO_2Mu^{\cdot}$

R	A(OH)[a]	A(OMu)[b]	A_μ/A_H
Me	2.0[c] (2.62)[d]	3.05	1.52
Et	2.55[c] (2.69)[d]	3.01	1.18
	3.2[e]		0.94
Pr^i	3.55[c] (2.86)[d]	2.88	0.81
	3.6[e]		0.8

[a] In Gauss from Refs 17 and 18.
[b] Muon coupling corrected for the muon/proton magnetic moment ratio (3.1833) and converted into 10^{-4} T (≡G).
[c] Ref. 18.
[d] Numbers in parentheses obtained as in footnote a to Table 3, and converted into units of 10^{-4} T (≡G).
[e] Ref. 17.

Table 5. Comparison of muon *vs.* proton coupling constants in related carbonyl adducts of Mu–H[a]

Radical	Muon–proton coupling (10^{-4} T)	A_{μ}/A_{H}
$But_2{}^tCOMu/H$	7.0/3.00	2.33
$HC(OMu/H)OMe$	6.8/3.06	2.22
Me_2COMu/H	2.8/0.7	4.0

[a] All values taken from Ref. 6.

discover whether the muon coupling in $RNO_2Mu^{\cdot}$ radicals is sensitive to the electrostatic fields present in NaX zeolite, since we have previously shown that the muon coupling in the carbonyl adduct, $Me_2COMu^{\cdot}$, was raised in NaX[13] compared with that in *n*-hexane solution or indeed with that in pure acetone.[3,6,7] As it transpired, we could only study the $PhNO_2Mu^{\cdot}$ radical in this medium since only $PhNO_2$ did not react with NaX, all the nitroalkanes being immediately decomposed on contact with the zeolite. We found that the coupling is raised from that in liquid $PhNO_2$ by *ca.* 4%, and we suggest that this is a consequence of the electrostatic field from Na^+ cations: the increase is significantly less than that in $Me_2COMu^{\cdot}$ measured in NaX and in pure liquid acetone (+20%) and may reflect that any solvent or Na^+ interactions are with the $PhN(O^{\cdot})OMu$ oxygen atom rather than the $PhN(O^{\cdot})OMu$ group directly, hence diminishing their influence on the coupling compared with in $Me_2COMu^{\cdot}$.

The relaxation rate (λ) listed in Table 1 may be considered to be related to the linewidth for the following discussion. It is striking that the linewidth for $PhNO_2Mu^{\cdot}$ radicals is much less in NaX than in $PhNO_2$. We propose that this is due to the suppression of a chemical reaction in the zeolite which occurs in the pure $PhNO_2$ medium: in fact, all these adducts (Table 1) show broad lines and we suggest further that there is a reaction common to all the compounds investigated here. In Pr^nNO_2, the lines broaden on raising the temperature, which supports the idea of a chemical process; we believe that this is a muon transfer:

$$RNO_2Mu^{\cdot} + RNO_2 \rightarrow RNO_2^{-\cdot} + RNO_2Mu^{+}$$

for which support is found in studies of nitroimidazole H atom adducts by ESR spectroscopy.[14] It is interesting that the lines do broaden for $PhNO_2Mu^{\cdot}$ in NaX, but even at 332 K are still sharper than those in $PhNO_{2(l)}$ at 293 K. One explanation for the possible suppression of a chemical process in NaX is that the zeolite matrix impedes encounters between $PhNO_2(Mu)^{\cdot}PhNO_2$ molecules compared with a simple liquid system, but which become more rapid at elevated temperatures, hence the lines are broadened by the increasing reaction rate.

Finally, we note that there are clear differences in linewidth (relaxation rate) between the nitroalkane adducts, and is particularly high for the *tert*-butyl derivative. The *tert*-butyl group is that with the greatest electron releasing power, and probably encourages the muon transfer from its counterpart $Bu^tNO_2Mu^{\cdot}$ radical at a greater rate than for the other derivatives: while the relaxation rate does accord with the donor power of the alkyl group along the series Et, Pr^i, Bu^t, the outlying point for Me suggests the operation of some as yet undetermined additional factor.

Comparison of $RNO_2H^{\cdot}$ with $RNO_2H^{\cdot}$ radicals

The identification of the $PhNO_2H^{\cdot}$ radical is contentious. It was first proposed by Ward[15] that photolysis of $PhNO_2$ in tetrahydrofuran led to H atom abstraction by excited $PhNO_2$ molecules, and this was assumed to be correct by several subsequent workers.[16] If this were correct, the small ESR doublet coupling ascribed to the N—OH proton of 0.39 G (0.039 mT) would accord with a substantial Mu/H hyperfine isotope effect, as our calculations imply; however, strong evidence has been presented that the radical is actually the adduct of $PhNO_2$ with the tetrahydrofuran-2-yl radical,[16] and we are not aware of any fully convincing evidence for the formation of $PhNO_2H^{\cdot}$ which is believed to be highly reactive, on kinetic grounds.[16]

The literature on (aliphatic) $RNO_2H^{\cdot}$ radicals is scant, there being only two reports[17,18] of measurements of nitroalkane–H atom adducts in the liquid phase. These were formed by the addition of $CH_3{}^{\cdot}$ radicals to the (protonated) *aci* form of the lower nitroalkane homologue, using flow systems, i.e.

$$CH_3{}^{\cdot} + CH_2{=}NO_2H \rightarrow CH_3CH_2NO_2H^{\cdot}$$

$$CH_3{}^{\cdot} + CH_3CH{=}NO_2H \rightarrow (CH_3)_2CHNO_2H^{\cdot}$$

or by direct protonation of the radical anion in the case of $MeNO_2$. The ascription of these radicals as being of the $RNO_2H^{\cdot}$ type relies upon the resolution of a small (2–4 G, Table 4) doublet splitting, in contrast with the corresponding nitroalkane radical anions which have been well characterized by ESR[19] and studied theoretically using semi-empirical theory (INDO).[19]

Compared with results for $R_2COMu^{\cdot}/R_2COH^{\cdot}$ radicals (Table 5), where substantial positive (>1) Mu/H hyperfine isotope effects are found in all cases where comparison can be made, the ratios (Table 4) for $RNO_2Mu^{\cdot}/RNO_2H^{\cdot}$ radicals are small or even negative (<1); all couplings are taken as being of positive sign given their relatively large magnitudes.[3,6] It is also apparent that the muon couplings vary very little in $MeNO_2$, $EtNO_2$ and Pr^iNO_2, but actually decrease slightly in this order, while there is pronounced variation in the corresponding H couplings, which increase along the series. In view of our recent work on the $PhCHOMu^{\cdot}$ radical in different solvents,[7] we consider that there may be differential solvation effects between RNO_2 and aqueous media (in which the $RNO_2H^{\cdot}$ radicals were measured); indeed, the radial $EtNO_2H^{\cdot}$ shows a significant difference in the OH coupling (Table 4) depending on the medium in which it is formed. However, we defer further judgement on this matter until more comprehensive results are available.

Acknowledgements

We thank the Engineering and Physical Sciences Research Council of the United Kingdom, the Leverhulme Trust, the Swiss National Science Foundation and the Paul Scherrer Institute for grants in support of this work.

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