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Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. 37. The Reaction of Bis(trifluoromethyl) Nitroxide with Toluene. Evidence for Quantum Mechanical Tunneling in an Intermolecular Hydrogen Atom Abstraction[1]

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Abstract: Rate constants for hydrogen atom abstraction from toluene and for deuterium abstraction from toluene-d_8 by bis(trifluoromethyl) nitroxide in chlorofluorocarbon solvents have been measured by kinetic EPR spectroscopy over a wide range of temperatures. Quantum mechanical tunneling may play a role in this reaction since the Arrhenius preexponential factors are unusually low, $A_H \approx A_D = 10^4$ M^{-1} s^{-1}, and the activation energy difference, $E_D - E_H$, is 1.6 kcal/mol, which is unusually large. The O–H bond strength in $(CF_3)_2NOH$ has been found to be 82.6 kcal/mol by using an EPR equilibrium technique.

In previous work from this laboratory[3-5] kinetic EPR spectroscopy has been used to show that 2,4,6-tri-*tert*-butylphenyl and certain other sterically hindered aryl radicals decay by intramolecular hydrogen atom migrations and that quantum mechanical tunneling is rather important in these isomerizations. Other workers[6-17] have used kinetic EPR spectroscopy to show that quantum mechanical tunneling is also important in intermolecular hydrogen atom abstractions in solid matrices at very low temperatures. In both intramolecular[3-5,18] and intermolecular[6-17] processes a certain limited number of hydrogen atoms surround each radical center and the radical (eventually) reacts with one of these hydrogens, there being no other pathway by which it could decay.

Convincing evidence for quantum mechanical tunneling has not yet been presented for any intermolecular hydrogen atom abstraction in solution.[19] If tunneling is to be identified unequivocally in any such process, then considerable difficulties must be overcome. Consider the generalized reaction

$$X\cdot + RH \rightarrow XH + R\cdot \qquad (1)$$

occurring in solution. The technique that will be most likely to uncover tunneling in this reaction is demonstrably kinetic EPR spectroscopy.[3-18] For this technique to be applied the following criteria must be met. (i) X· must be observable by EPR spectroscopy. (ii) Reaction 1 must be (relatively) rapid; i.e., X· must be highly reactive and/or RH must be a "good" H atom donor. (iii) Reaction 1 must be irreversible. (iv) X· must be destroyed only by reaction 1; i.e., there must be no bimolecular self-reaction of X· ($2X\cdot \nrightarrow$ products), no unimolecular rearrangement or scission of X· ($X\cdot \nrightarrow$ products), and no reaction of X· with the solvent ($X\cdot$ + solvent $\nrightarrow$ products). (v) The solvent must have an extremely low freezing point and should be liquid over a wide range of temperatures. This condition obtains because tunneling is most readily identified by measuring the rate of reaction 1 down to temperatures near those of liquid air.

Several reaction systems we explored failed to meet one or more of the above criteria.[21] However, we have now found that the reaction of bis(trifluoromethyl) nitroxide with toluene in Freon solvents comes close to meeting all these criteria.

$$(CF_3)_2NO\cdot + C_6H_5CH_3 \xrightarrow[\text{Freon}]{k_H} (CF_3)_2NOH + C_6H_5CH_2\cdot \qquad (2)$$

$$(CF_3)_2NO\cdot + C_6H_5CH_2\cdot \xrightarrow{\text{fast}} (CF_3)_2NOCH_2C_6H_5 \qquad (3)$$

Bis(trifluoromethyl) nitroxide was first reported in 1965.[24,25] In the absence of compounds with which it can react it is quite

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[19] "Tunneling" has been invoked to explain experimental H and D atom-transfer data on many occasions, but the supporting evidence has occuasionally been equivocal. The same observation applies to proton "tunneling" in solution; see, e.g., reference 20.

[20] Rogne, O. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 559. Blanch, J. H.; Rogne, O.; Rossemyr, L. I. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1905 and references cited. See also: Bulska, H.; Chodowska, A. *J. Am. Chem. Soc.* **1980**, *102*, 3259.

[21] Most of the initial work was on the reaction of 2,2,6,6-tetramethylpiperidyl radical with toluene since an earlier kinetic study[22] had yielded data which could be interpreted in terms of tunneling. The tetramethylpiperidyl radical was generated by photolysis of the parent tetrazene,[22] but, unfortunately, in inert solvents and at low toluene concentrations, it decayed by attack upon the tetrazene.[23]

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remarkably persistent.[26] However, it is much more reactive in abstractions, additions, and substitutions than are dialkyl nitroxides.[28-30] There have been numerous studies of the products of many $(CF_3)_2NO\cdot$ reactions, must notably by Banks, Haszeldine, and co-workers[29] and by Englin, Makarov, and co-workers,[30] but the only kinetic and thermodynamic data relate to the addition to fluorinated olefins.[30e,30f,31] Hydrogen atom abstraction is known to occur from many substrates,[29a,d,h,i,k-m,30b] including toluene,[29a,i] and it is surprising that the rate constants, Arrhenius parameters, and thermochemistry of such processes have not been investigated previously but such appears to be the case.

Experimental Section

Materials. Bis(trifluoromethyl)hydroxylamine was prepared from CF_3NO and NH_3 by Makarov et al.'s procedure.[24] It was distilled before use, and its purity was checked by ^{19}F NMR in Freon 12, $\phi = 69$ (s). Freon 12 (CF_2Cl_2, Matheson) and bis(trifluoromethyl)peroxide (PCR, Inc.) were used as received. Freon 113 ($CF_2ClCFCl_2$, Matheson) was purified by washing with N/10 NaOH and then water, drying over $CaCl_2$, and distilling from concentrated H_2SO_4, bp 48 °C (760 torr).

Toluene (Fisher spectrograde) and toluene-d_8 (98 atom % D; Merck, Sharp and Dohme; found by mass spectrometry: toluene-d_8 94.5%, toluene-d_7 3.9%, and toluene-d_6 1.6%; the small amount of hydrogen in this material was shown by NMR to be randomly distributed between the aromatic ring and the methyl group) were carefully purified by preparative VPC on a 10-ft Carbowax 20M on H.P. Chromosorb W column at 55 °C. In our initial experiments this precaution was not taken, and although the rates of reaction at the higher temperatures were quite unaffected, those measured at low temperatures were very significantly larger than the values subsequently obtained by using the purified toluenes. For example, for unpurified toluene at 123 K $\log (k_H/s^{-1})$ was ca. −6.5, after purification the value dropped to ca. −8.0; similarly for unpurified toluene-d_8 at 183 K $\log (k_D/s^{-1})$ was ca. −6.0 but was −7.0 after purification. The impurity induced enhancement of rate at low temperatures led to strongly curved Arrhenius plots—which we naturally took to be strong evidence for tunneling in this reaction![32]

Kinetic Studies. Reaction samples were prepared by the most careful high vacuum techniques in EPR suprasil tubes (3-mm i.d.). At 297 K they contained approximately 10 μL of $(CF_3)_2NOH$, 10 μL of CF_3OOCF_3, 460 μL of Freon, and 11 μL (0.2 M), 22 μL (0.4 M) or 55 μL (1.0 M) of toluene or toluene-d_8. Very brief UV photolysis of these mixtures in the cavity of a Varian E-4 EPR spectrometer gave the well-known spectrum of $(CF_3)_2NO\cdot$.[25,33] The decay of this radical was monitored by standard methods.[34] The spectrometer conditions were adjusted to avoid signal distortion, and corrections werre made for any day-to-day fluctuations in spectrometer sensitivity. At low temperatures the kinetic runs took, days, or weeks, or even months. In such cases, the samples were not kept in the EPR spectrometer—for obvious reasons. For runs of medium length (≤ca. 14 days) the samples were kept at the appro-

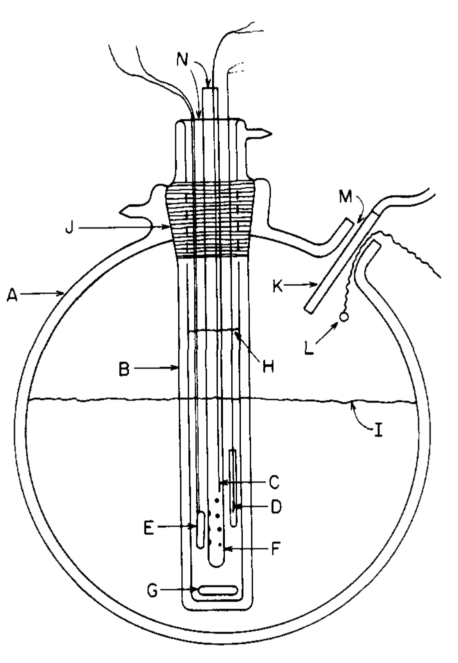

Figure 1. Low-temperature thermostated bath. Key: A, main Dewar flask containing liquid N_2 (evacuated and silvered except for a 1-cm window running vertically around the entire circumference; the diameter of A is 21.5 cm and it rests on a magnetic stirrer); B, inner evacuated but unsilvered Dewar flask containing isopentane (dimensions: height, 29 cm; o.d., 4.75 cm; i.d., 3.4 cm; from bottom of joint to bottom of B, 18.5 cm); C, thermocouple for continuous monitoring of sample temperature (the cold junction is an external bath held at 0 °C; the output is fed to a digital volt meter and a strip chart recorder which operates continuously); D, thermocouple used to control temperature (the output is fed to a black box which controls the power sent to E); E, 4-ω heater (power input controlled via D); F, sample holding glass tube 35 cm long, 1.8 cm o.d., with holes in side near bottom to allow isopentane to move freely in and out (up to four standard quartz EPR tubes could be dropped into F with colored threads attached for identification and simple and rapid removal). G, magnetic stirring bar; H, isopentane level; I, liquid-N_2 level (this varies from a depth of 17 cm at the start to 10 cm at the end of each 8-h cycle); J, 55/50 standard taper joint wrapped with Teflon tape; K, liquid-N_2 inlet tube; L, thermistor used to sense the liquid-N_2 level during the fill cycle (output goes to a black box which is switched on by a timer for 30 min every 8 h; the black box also operates a solenoid valve with a pressure bleed-off which admits gaseous N_2 to a 50-L container of liquid N_2, thus forcing the liquid N_2 through K into A; the 50-L container of liquid N_2 was replaced every 7–9 days); M, escape for gaseous N_2, heavily insulated; N, layer of parafilm to prevent moisture getting into isopentane (this is covered with a thick layer of insulation).

Table I. Effect of Temperature on Relative Volumes of Freons

Freon 12		Freon 113	
T, K	V_T/V_{273}	T, K	V_T/V_{273}
318	1.063	333	1.066
301	1.048	317	1.043
295	1.019	295	1.026
282	1.010	273	1.000
273	1.000	262	0.989
251	0.967	253	0.979
225	0.923	245	0.970
203	0.906		
177	0.863		
157	0.840		
130	0.804		
120	0.783		

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(26) It does not undergo thermal decomposition even at 200 °C.[27]

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Table II. Rate Constants for H Atom Abstraction from Toluene and Toluene-d_8 by $(CF_3)_2NO\cdot$

Freon	$[C_7H_8]$,[a] M	T, K	$\log (k_H/M^{-1}\ s^{-1})$	Freon	$[C_7H_8]$,[a] M	T, K	$\log (k_H/M^{-1}\ s^{-1})$
113	1.0	327	−1.04	12	1.0	226	−3.79
113	1.0	305	−1.69	12	1.0	220	−3.84
113	1.0	296	−1.79	12	1.0	213	−4.07
12	1.0	289	−1.88	12	1.0	201	−4.49
12	0.2	287	−2.27	12	1.0	194	−4.90
12	1.0	284	−2.33	12	0.4	183	−4.61
113	1.0	283	−2.18	12	1.0	180	−4.92
113	1.0	280	−2.36	12	0.2	180	−4.85
12	1.0	280	−2.58	12	1.0	179	−5.09
12	0.2	265	−2.73	12	1.0	164	−5.79
113	1.0	263	−2.56	12	1.0	160	−6.02
12	0.2	253	−2.81	12	1.0	123	−7.89
113	1.0	252	−2.74	12	1.0	123	−7.96
12	1.0	246	−2.93	12	1.0	123	−7.96
113	1.0	244	−2.91	12	0.4	123	−7.67
12	1.0	243	−3.38	12	0.4	123	−8.15
Freon	$[C_7D_8]$,[a] M	T, K	$\log (k_D/M^{-1}\ s^{-1})$	Freon	$[C_7D_8]$,[a] M	T, K	$\log (k_D/M^{-1}\ s^{-1})$
113	1.0	345	−2.11	113	1.0	280	−3.25
113	1.0	333	−2.06	12	1.0	267	−3.79
113	1.0	323	−2.48	113	1.0	263	−3.67
113	1.0	313	−2.64	113	1.0	257	−3.84
113	1.0	308	−2.79	12	1.0	248	−4.59
12	1.0	295	−3.47	12	1.0	219	−5.29
				12	1.0	195	−6.69
				12	1.0	183	−6.97

[a] Concentration at 25 °C.

priate temperature in a cooled stream of dry N_2 gas in a previously described cryostat[35] equipped with an automatic liquid-N_2 refill system. This cryostat was not suited for longer runs for a variety of reasons, including its profligate consumption of a liquid N_2. The low-temperature thermostated bath shown diagrammatically in Figure 1 proved to be far more economical and reliable. This bath held a temperature of 123 K for 4 months and consumed only 6–7 L of liquid N_2 per day. In both low-temperature systems the constancy of the temperature, which was monitored continuously, was better than ±1 K. Radical decays were followed, at appropriate time intervals, by transferring the sample quickly first into an isopentane slush bath and from there into the precooled EPR cavity. The major problem during long runs was the fact that the variable-temperature insert in the EPR spectrometer could not be moved while a decay experiment was in progress. Some slow decays were not followed for as long as they should have been because the insert had to be changed in order to carry out other EPR experiments.

Correction for Solvent's Thermal Contraction or Expansion. The toluene concentration measured at 24 °C will increase if the sample is cooled and decrease if it is warmed because of the thermal contraction and expansion of the solvent. Because of the large temperature range covered in the present work, this phenomenon cannot be ignored. The effect of temperature on the relative volumes of typical reaction mixtures in both Freon 12 and Freon 113 as solvent were determined by measuring liquid heights in sealed quartz tubes placed in the homemade N_2 gas-cooled cryostat.[35] The results are given in Table I. The temperature coefficients for volume expansion (referred to the volume at 0 °C) of Freon 12 and Freon 113 were calculated to be 1.41 and $1.09 \times 10^{-3}\ {}^\circ C^{-1}$, respectively.

Thermochemical Measurements. In order to calculate the enthalpy of reactions 2, we estimated the O–H bond strength in $(CF_3)_2NOH$ by measuring the equilibrium constant for the reversible H atom-transfer reaction between $(CF_3)_2NO\cdot$ and di-*tert*-butylketoxime. The general procedure has been described previously.[36] The $(CF_3)_2NO\cdot$ was condensed into an EPR tube containing 250 μL of sodium-dried and carefully deoxygenated benzene, and its concentration was measured by EPR spectroscopy in the usual way[34,37] (1.3×10^{-2} M at 22 °C). To this solution was then added 250 μL of a 1.5×10^{-1} M solution of the ketoxime in benzene, and after being further degassed, the EPR tube was sealed. Both the nitroxide and the di-*tert*-butylketiminoxy radical can be observed although there is some overlap of their EPR spectra. (The $M_I = +1$ line of the iminoxy overlaps partially with the second low-field line of the nitroxide, and the $M_I = -1$ line completely overlaps the highest field line of the nitroxide.) The concentrations of the two radicals could, however, be determined by scale expansion and double integration of the $M_I = +1$ iminoxy line and a nonoverlapping line of the nitroxide. The equilibrium was established very rapidly, and the radical concentrations showed no change during the course of a series of experiments.

Results and Discussion

Kinetics. Bis(trifluoromethyl)nitroxide was generated photochemically at concentrations of ca. 10^{-6} M. In Freon 12 and Freon 113 containing toluene or toluene-d_8 the radical decayed with "clean" pseudo-first-order kinetics under all conditions. The radical decay was monitored for 5 or more half-lives for all runs for which the half-life of the radical was less than ca. 1 day. For slower runs the decay was followed for as long as practicable (up to 4 months at 123 K, though even this length of time was considerably less than even 1 half-life). The true bimolecular rate constants, k_H (and k_D), for hydrogen (deuterium) abstraction from toluene (toluene-d_8) were obtained by dividing by *twice* the *corrected* (see Experimental Section) molar concentration of the hydrocarbon. That is, $k_H = k_{exp}/2[RH]$ the factor of 2 arising because, after the abstraction, a second nitroxide radical is destroyed by reaction 3. The bimolecular rate constants are listed in Table II.

The Arrhenius plot for deuterium abstraction from toluene-d_8 (Figure 2) gives a good straight line over the experimental temperature range, which can be represented by

$$\log (k_D/M^{-1}\ s^{-1}) = 4.0 - 9.5/\theta$$

where $\theta = 2.3RT$ kcal/mol. An Arrhenius preexponential factor of $10^4\ M^{-1}\ s^{-1}$ appears unreasonably small for a hydrogen or deuterium atom abstraction from toluene.[38] The A factors for such reactions have been generally found to be ca. $10^8\ M^{-1}\ s^{-1}$.[38] For example, Perkins and co-workers[39] have studied the comparable reaction.

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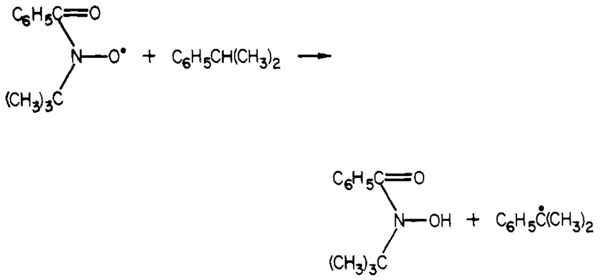

(4)

For this reaction the Arrhenius equation, based on kinetic EPR measurements from 333 to 363 K, is [39]

$$\log (k_4/\mathrm{M}^{-1}\ \mathrm{s}^{-1}) = (7.93 \pm 0.56) - (17.9 \pm 0.9)/\theta$$

An unexpectedly low *A* factor in a hydrogen atom abstraction is *one* of the indicators that quantum mechanical tunneling may play an important role in the reaction in question. However, *A* factors for deuterium atom abstractions are not normally reduced by tunneling to nearly the same extent as *A* factors for the corresponding hydrogen atom transfer; i.e., when tunneling is important, it is expected that $A_H \ll A_D$, and when it is unimportant, that $A_H \approx A_D$. It can be seen from Figure 2 that an *acceptable* Arrhenius relation, viz.

$$\log (k_H/\mathrm{M}^{-1}\ \mathrm{s}^{-1}) = 4.0 - 7.9/\theta$$

exists for hydrogen atom abstraction which has the *same A* factor as for deuterium abstraction, *provided* the rate data obtained at 123 K are ignored. These particular data are the least reliable because the reactions were not followed for a full half-life (see Experimental Section). A decision as to whether or not quantum mechanical tunneling is, or is not, important will thereore largely depend on whether the Arrhenius preexponential factor is, or is not, too small for a "normal" hydrogen atom abstraction from toluene. We *tentatively* suggest that tunneling is responsible for the low *A* factor.

If tunneling is accepted, the hydrogen abstraction data at 123 K can also be *tentatively* accepted. This would lead to curvature in the Arrhenius plot in the direction consistent with tunneling. Of course, Arrhenius plots curved in the same direction will arise if there are two competing reactions having different activation energies. With toluene attack on the aromatic ring might, in principle, compete with H abstraction since $(CF_3)_2NO\cdot$ is known to react with benzene at room temperature.[27,30b,48] However, product studies on toluene have shown that attack occurs exclusively at the benzylic hydrogens.[29a,29l] We have confirmed this indirectly by showing that the reaction of $(CF_3)_2NO\cdot$ with benzene in Freon is incredibly slow at low temperatures. Thus, even at 213 K with both 0.2 and 1.0 M benzene in Freon 12 there was no detectable change in the $(CF_3)_2NO\cdot$ concentration over the course of 1 week. A second possibility would be a competing reaction with an impurity. We are particularly sensitive to this possibility since our initial measurements with toluene and toluene-d_8 which had not been purified by preparative VPC did give enhanced decay rates at low temperatures (see Experimental Section).

It should perhaps be pointed out that if the Arrhenius plot is indeed curved, the curvature cannot be due to the dimerization of $(CF_3)_2NO\cdot$ to a diamagnetic product, which is known to occur at low temperatures.[24,25,33c]

$$2(CF_3)_2NO\cdot \overset{K_5}{\rightleftharpoons} [(CF_3)_2NO]_2 \qquad (5)$$

In the presence of dimer the overall kinetic rate expression can be represented as

$$2k_H[RH]_t = 4K_5([(CF_3)_2NO\cdot]_0 - [(CF_3)_2NO\cdot]_t) + 2.3 \log ([(CF_3)_2NO\cdot]_0/[(CF_3)_2NO\cdot]_t)$$

where the subscripts 0 and *t* refer to radical concentrations at time = 0 and *t*, respectively. It is readily apparent that if dimerization were to become significant at low temperature, the Arrhenius plot would curve in the *opposite* sense to that observed experimentally. That is, if a significant fraction of the $(CF_3)_2NO\cdot$ were tied up in a dimer the apparent rate of reaction would be *slower* than the true rate since the dimer would dissociate and continuously replenish the radical as the latter reacted with the toluene.[40] Independent experiments carried out in Freon 12, but in the absence the toluene, showed that $(CF_3)_2NO\cdot$ at the concentrations used in the kinetic experiments did not dimerize significantly even at 123 K. Therefore, our rate data do not require a correction for radical dimerization.

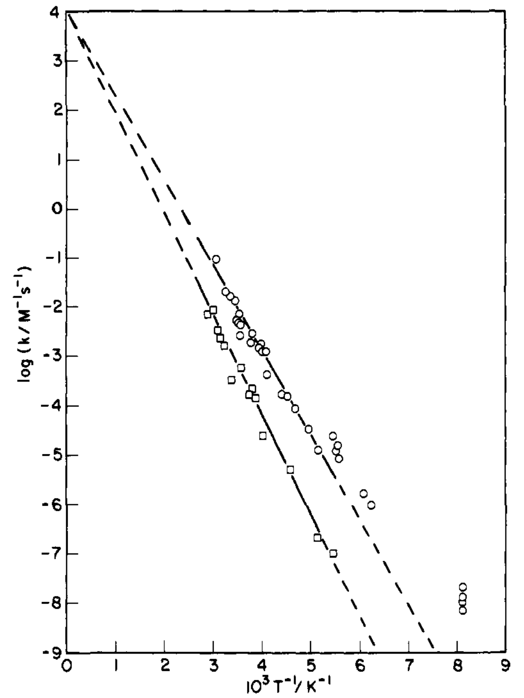

Figure 2. Arrhenius plot of the rate constants for the reaction of $(CF_3)_2NO\cdot$ with toluene (circles) and toluene-d_8 (squares) in Freon 12 and 113. The experimental points are taken from Table II.

Tunneling in a hydrogen atom transfer is normally accompanied by a large deuterium kinetic isotope effect. In the present reaction, the isotope effects are not at all exceptional, ranging from ca. 10 at the highest common temperature (≈330 K) to ca. 100 at the lowest (~180 K). However, *relatively* small kinetic isotope effects should perhaps be expected in the present system and in other intermolecular hydrogen atom transfers in solution. That is, the toluene-d_8 was not 100% deuterated and therefore the measured value of k_D will have a contribution from H atom abstraction which will become relatively more important at low temperatures. This problem is not encountered in H/D atom transfers that are intramolecular[3-5,18] or that occur intermolecularly but are studied in rigid matrices[6-17] because the available hydrogen (typically 1–2% in a well-deuterated substrate) will be rapidly consumed. In such systems most radicals are therefore *forced* to react with deuterium. In contrast, for an intermolecular H/D atom transfer in solution the radical is free to move through the solvent ignoring fully deuterated molecules and reacting only when it encounters a hydrogen-containing substrate molecule. Even if the "true" isotope effect was enormous, the measured isotope effect would be relatively small and would be determined by the extent of deuteration of the substrate.

Although the magnitude of the kinetic isotope effect at any temperature does not provide evidence for tunneling, such evidence is provided by a comparison of the measured activation energies for H and D transfer. The activation energy difference, $E_D - E_H$, is 1.6 kcal/mol. This is probably less than the difference that would have been found if 100% deuterated toluene has been

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(40) In preliminary experiments[23] the $(CF_3)_2NO\cdot$ + toluene reaction was studied at relatively high (ca. 10^{-3}–10^{-4} M) radical concentrations. Extensive dimerization occurred at low temperatures, and reliable kinetic data could not be obtained.

available because the contribution from H atom abstraction to the measured values of k_D (vide supra) will tend to reduce E_D. At all events, the measured value of $E_D - E_H$ is certainly larger than the clasically allowed maximum of 1.4 kcal/mol.[41,42] Not only does this lend supporting evidence for a significant tunneling contribution to the reaction but also, since all or most of the zero-oint energy would appear to be lost in the transition state, it seems probable that the transition state is linear and approximately symmetric.[18,41,43] This is not unexpected for a nearly thermoneutral reaction (vide infra).

Thermochemistry. The reaction between $(CF_3)_2NO\cdot$ and di-*tert*-butylketoxime yields an equilibrium mixture of nitroxide and iminoxy radicals.

$$(CF_3)_2NO\cdot + (Me_3C)_2C{=}NOH \overset{K_6}{\rightleftharpoons} (CF_3)_2NOH + (Me_3C)_2C{=}NO\cdot \quad (6)$$

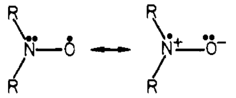
The equilibrium constant, K_6, was measured in benzene at 22 °C.

$$K_6 = \frac{[(CF_3)_2NOH][(Me_3C)_2C{=}NO\cdot]}{[(CF_3)_2NO\cdot][(Me_3C)_2C{=}NOH]} = 18.7 \pm 4$$

With the usual assumption that ΔS for such a hydrogen atom-transfer equilibrium is negligible,[36] we can write

$$\Delta H = \Delta G = RT \ln K_6 = 1.72 \pm 0.13 \text{ kcal/mol}$$

This quantity will be approximately[36] equal to the difference in O—H bond strengths for $(CF_3)_2NOH$ and $(Me_3C)_2C{=}NOH$. The O—H bond strength for the latter compound, D-$[(Me_3C)_2C{=}NO{-}H]$, has been measured by calorimetry and found to be 80.9 kcal/mol[36] which means that $D[(CF_3)_2NO{-}H]$ is ca. 82.6 kcal/mol. This value should be reliable to within ±3 kcal/mol, It is considerably larger than the O—H bond strengths of dialkyl nitroxides. The latter are generally ca. 71 ± 2 kcal/mol.[36,44] The increase in bond strength brought about by the two CF_3 groups can be attributed to their electronegativity.[45] This will decrease the extent of conjugative electron delocalization onto the nitrogen atom when compared with the delocalization which occurs in a dialkyl nitroxide; i.e., canonical structure **1** is relatively more important than **2** when R = CF_3 than when R = alkyl.[45]



1 2

As a consequence, a^N for $(CF_3)_2NO\cdot$ is smaller (9.5 G) and a^O is larger (23.6 G) than the values found for $(Me_3C)_2NO\cdot$ (viz., 15 and 19.4 G, respectively).[45] Furthermore, with less delocalization of the unpaired electron the radical is less stabilized and so the O—H bond strength is greater.

An independent estimate of $D[(CF_3)_2NO{-}H]$ can be derived from Haszeldine et al.'s[31] study of the addition of $(CF_3)_2NO\cdot$ to tetrafluoroethylene.[46] The heat of addition $[2(CF_3)_2NO\cdot + C_2F_4]$ was found to be −246 kJ/mol and that for the addition of ethoxy $[2EtO\cdot + C_2F_4]$ was estimated to be −420 kJ/mol. The difference (174 kJ/mol ≈ 42 kcal/mol) implies that $(CF_3)_2NO\cdot$ is stabilized by ca. 21 kcal/mol with respect to EtO·. Since D[EtO-H] ≈ 104 kcal/mol,[38] $D[(CF_3)_2NO\text{-}H] \approx 104 - 21 \approx 83$ kcal/mol in good agreement with the value measured in the present work.

Since the benzylic C—H bond strength in toluene is ca. 85 kcal/mol,[38] reaction 2 is probably endothermic by ca. 2 kcal/mol. However, the experimental errors involved in bond strength measurements are such that this reaction might be thermoneutral or even slightly exothermic.

Summary

The abstraction of hydrogen from toluene by $(CF_3)_2NO\cdot$ is approximately thermoneutral. The small value of the preexponential factor for this reaction (10^4 M^{-1} s^{-1}), the large difference in the activation energies for deuterium abstraction and hydrogen abstraction (1.6 kcal/mol), and the possible curvature of the Arrhenius plot for hydrogen abstraction, all suggest that quantum mechanical tunneling may play a role in this reaction. The experimental data are not, however, of sufficient accuracy to warrant detailed tunneling calculations of the type developed by Le Roy and co-workers.[16,47]

Our experience shows that it will be extremely difficult to obtain unequivocal evidence for quantum mechanical tunneling in intermolecular H atom transfers in solution.

Acknowledgment. We should like to thank Dr. P. Knittel for some exploratory work on this subject. We are also grateful to Mr. J. Vandenhoff for the construction and Mr. D. A. Lindsay for the design and operation of the low-temperature bath shown in Figure 1. K.U.I. also acknowledges stimulating discussions on tunneling with Professor L. Lunazzi which were made possible by a NATO Research Grant.

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(41) Bell, R. P. *Chem. Soc. Rev.* **1974**, *3*, 513.

(42) The maximum is obtained if the zero-point energies for both stretching and bending vibrations are lost in the transition state.[41] If only stretching vibrations are considered, the maximum value for $E_D - E_H$ is 1.1 kcal/mol.[41]

(43) See, e.g.: Melander, L. "Isotope Effects on Reaction Rates"; Ronald Press: New York, 1960. Bunton, C. A.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1961**, *83*, 3214. Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265. Pryor, W. A.; Kneipp, K. G. *J. Am. Chem. Soc.* **1971**, *93*, 5584 and references cited therein.

(44) Caceres, A.; Lissi, E. A.; Sanhueza, E. *Int. J. Chem. Kinet.* **1978**, *10*, 1167.

(45) Chatgilialoglu, C.; Malatesta, V.; Ingold, K. U. *J. Phys. Chem.* **1980**, *84*, 3597.

(46) The Arrhenius preexponential factor is $10^{7.6}$ M^{-1} s^{-1} which is "normal", as would be expected, since tunneling will not be involved in such a reaction.

(47) Le Roy, R. J.; Sprague, E. D.; Williams, F. *J. Phys. Chem.* **1972**, *76*, 546. Le Roy, R. J.; Quickert, K. A.; Le Roy, D. J.; *Trans. Faraday Soc.* **1970**, *66*, 2997. University of Wisconsin Theoretical Chemistry Institute Report, WIS-TCI-384, 1970.

(48) **Note Added in Proof**: Recent studies cast some doubt on the accuracy of this earlier work: Banks, R. E.; Brown, A. K.; Haszeldine, R. N.; Kenny, A.; Tipping, A. E., private communication.