were performed on bare charged species with no counterions present. Diffusion of the charge by solvation and/or ion pairing with counterions should result in larger red shifts because the uncharged enamine is predicted further to the red. The ketimine and protonated enamine have calculated spectra which are most like Chl *a* in contrast to the protonated ketimine, which has an additional intense transition at 494 nm.

The ground-state energies of both isomers drop with protonation, the enamine somewhat less than the ketimine. As with species **1–5**, protonation should render PChl (and Chl) Schiff base derivatives more difficult to oxidize.

The protonated enamine PChl *a* predicted by the calculations apparently contradicts experimental evidence. Resonance Raman spectroscopy should provide another diagnostic tool for distinguishing between the two isomers. Not only should the C–N stretch differ substantially, but ring V also becomes an integral part of the macrocycle π system in the enamine.

Our resonance Raman results demonstrate the similarity between hydrogen-bonded C═O and protonated C═N vibrational stretching frequencies and the isolation of the peripheral C═O or C═N substituent from the macrocycle ground state. Thus, the resonance Raman spectra which have been interpreted as arising from hydrogen-bonded Chl *a* in in vivo preparations[43] could also be due, in part, to ketimine SB derivatives.[44]

The calculations predict that protonation affects the SB derivatives of PChl somewhat differently than the SB derivatives of **1–5**. Nonetheless, our results suggest that SBH^+ substituents on chlorophyll would enhance the ability of protein environments to modulate spectral and redox properties. Schiff base derivatives of chlorophyll pigments thus warrant further serious consideration as models for electron donors within photosynthetic reaction centers.

Acknowledgment. We thank Michael Zerner for his INDO program, R. M. Pearlstein and G. M. Maggiora for results prior to publication, and G. M. Maggiora and J. Fajer for helpful comments and discussions. This work was supported by the Division of Chemical Sciences, U.S. Department of Energy, under Contract No. DE-AC02-76CH00016 at Brookhaven National Laboratory and by NIH (GM25480 to GTB) and NSF (CKC) at Michigan State University. C.K.C. is an Alfred P. Sloan Fellow (1980–1984) and a Camille and Henry Dreyfus Teacher-Scholar (1981–1985).

Registry No. CHO **1b**, 84195-13-1; SB **1c**, 84195-14-2; SBH^+ **1c**·ClO_2^-, 90432-99-8; diCHO **2b**, 90413-26-6; diSB **2c**, 90413-27-7; SB,SBH^+ **2c**·ClO_4^-, 90433-00-4; diSBH^+ **2c**·$(ClO_4^-)_2$, 90433-01-5; diCHO **3b**, 90413-28-8; diSB **3c**, 90413-29-9; SB,SBH^+ **3c**·ClO_4^-, 90433-02-6; diSBH^+ **3c**·$(ClO_4^-)_2$, 90433-03-7; CHO **4b**, 90413-30-2; SB **4c**, 90413-31-3; SBH^+ **4c**·ClO_4^-, 90413-47-1; diCHO **5b**, 90413-35-7; diSB **5c**, 90413-36-8; diSBH^+ **5c**·$CF_3CO_2^-$, 90433-05-9.

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(43) (a) Lutz, M. *J. Raman Spectrosc.* **1974**, *2*, 497–516. (b) Lutz, M.; Brown, J. S.; Remy, R. In "Chlorophyll Organization and Electron Transfer in Photosynthesis"; Elsevier: Amsterdam, 1979; Ciba Foundation Symposium 61, pp 105–25.

(44) PS I and PS II reaction centers which are free of antenna pigment have not yet been isolated.

Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. 42. Some Reactions of the Bis(trifluoromethyl)aminoxyl Radical[1]

T. Doba[2] and K. U. Ingold*

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.
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Abstract: Absolute rate constants have been determined in Freon solvents over a temperature range from ca. 190 to 300 K for H atom abstraction by $(CF_3)_2NO\cdot$ from 11 substrates and for the addition of this radical to $CH_2{=}CCl_2$. Some values found for log A ($M^{-1}\ s^{-1}$) and E_a (in kcal/mol) are 5.8 ± 0.6 and 10.7 ± 0.7 for cyclopentane, 6.5 ± 0.3 and 5.7 ± 0.5 for 1,4-cyclohexadiene, 5.3 ± 0.3 and 6.9 ± 0.3 for benzaldehyde, 4.8 ± 0.2 and 3.3 ± 0.3 for 2,4,6-tri-*tert*-butylphenol, 5.9 ± 0.7 and 4.3 ± 0.7 for tri-*n*-butylstannane, and 5.3 ± 0.4 and 9.3 ± 0.5 for $CH_2{=}CCl_2$. The preexponential factors are uniformly smaller than the values generally considered "normal" for radical/H atom abstractions and radical/C═C double-bond additions, viz., $10^{8.5\pm0.5}\ M^{-1}\ s^{-1}$. It is concluded that the low A factors are not due to tunneling. It is suggested that they are probably due to geometric constraints on the transition states. For a wide range of substrates exhibiting very different reactivities the absolute rate constant for H atom abstraction by $(CF_3)_2NO\cdot$ and by $Me_3COO\cdot$ at ambient temperatures are virtually equal.

Bis(trifluoromethyl)aminoxyl, $(CF_3)_2NO\cdot$, which was first reported in 1965,[3,4] is a remarkable free radical. It is both more persistent[5] and more reactive than the better known di-*tert*-alkylaminoxyl radicals.[6] There have been some studies of its physical properties[7,8] and numerous studies of the products formed when $(CF_3)_2NO\cdot$ reacts with organic compounds: hydrogen atom abstractions, additions to multiple bonds, and substitution processes having been identified.[9] However, the only kinetic data available

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(1) Issued as NRCC No. 23403. Part 41: Anpo, M.; Sutcliffe, R.; Ingold, K. U. *J. Am. Chem. Soc.* **1983**, *105*, 3580–3583.

(2) NRCC Research Associate 1982–1984.

(3) Blackley, W. D.; Reinhard, R. R. *J. Am. Chem. Soc.* **1965**, *87*, 802–805.

(4) Makarov, S. P.; Yakubovich, A. Ya.; Dobov, S. S.; Medvedev, A. N.; *Dokl. Akad. Nauk SSSR* **1965**, *160*, 1319–1322.

(5) It does not undergo thermal decomposition even at 200 °C; see: Makarov, S. P.; Englin, M. A.; Videiko, A. F.; Tobolin, V. A.; Dobov, S. S. *Dokl. Akad. Nauk SSSR* **1966**, *168*, 344–347.

(6) For review of the chemistry of $(CF_3)_2NO\cdot$, see: (a) Babb, D. P.; Shreeve, J. N. *Intra-Sci. Chem. Rep.* **1971**, *5*, 55–67. (b) Spaziante, P. M. *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One* **1972**, *3*, 141–180. (c) Banks, R. E.; Barlow, M. G. *Fluorocarbon Relat. Chem.* **1971**, *1*, 109–115. (d) Banks, R. E. *Ibid.* **1974**, *2*, 223–235.

(7) Chatgilialoglu, C.; Malatesta, V.; Ingold, K. U. *J. Phys. Chem.* **1980**, *84*, 3597–3599.

(8) Compton, D. A. C.; Chatgilialoglu, C.; Mantsch, H. H.; Ingold, K. U. *J. Phys. Chem.* **1981**, *85*, 3093–3100.

(9) For leading references, see ref 10.

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before we began our own investigations on the reactions of $(CF_3)_2NO\cdot$ with toluene[10] and cyclopropane[11] in solution related to its addition to fluoro olefins in the gas phase.[12-14]

The $(CF_3)_2NO\cdot$ radical does not react with Freon solvents and, except at high concentrations and low temperatures, is monomeric.[3] It is therefore a simple matter to monitor the kinetics of its reactions by EPR spectroscopy. In the present paper, we report detailed kinetic studies, frequently over a temperature range from ca. 190 to 300 K, for its reaction with a variety of organic compounds.

Experimental Section

Materials. Bis(trifluoromethyl)hydroxylamine and aminoxyl were prepared by the method of Makarov et al.,[4] as indicated previously.[10] The remaining compounds, all of which were commerically available, were generally purified either by preparative VPC or by careful distillation on a high-vacuum line. Interestingly, in no case did purification have a significant effect on the measured reaction rates—a result that stands in contrast with the effect of VPC purification on the rates of reaction of toluene and toluene-d_8 reported previously.[10]

Kinetic Studies. The reaction of $(CF_3)_2NO\cdot$ with the organic substrate was monitored on a Varian E-4 EPR spectrometer. The method of choice for reactions in which the decay of the $(CF_3)_2NO\cdot$ EPR signal was not too rapid involved repetitive scanning of one or more peaks in the spectrum. For fast reactions decay was monitored by following the change in peak height of a single line in the spectrum at constant magnetic field.

In our previous study of the $(CF_3)_2NO\cdot$/toluene reaction,[10] samples were prepared and sealed under vacuum, each sample tube containing approximately 7 μL of $(CF_3)_2NOH$, 7μL of CF_3OOCF_3, 300 μL of Freon, and a precisely known concentration of toluene. Brief UV photolysis of these samples in the cavity of the spectrometer yielded $(CF_3)_2NO\cdot$, the decay of which was then monitored. Although this procedure gave individual plots of log $[(CF_3)_2NO\cdot]$ vs. time that generally appeared to be satisfactory, we have now found that under some conditions the substrate derived radical (R·) can abstract hydrogen from $(CF_3)_2NOH$ rather than being trapped by a second $(CF_3)_2NO\cdot$ radical. That is, product studies (vide infra) lead one to expect that the overall process that is being monitored kinetically, whether it is a hydrogen atom abstraction or an addition, should involve a slow and rate-controlling reaction of the substrate with the aminoxyl radical followed by a rapid reaction of R· with a second aminoxyl, e.g.,

$$(CF_3)_2NO\cdot + RH \rightarrow (CF_3)_2NOH + R\cdot \qquad (1)$$

$$R\cdot + (CF_3)_2NO\cdot \rightarrow (CF_3)_2NOR \qquad (2)$$

However, at low $[(CF_3)_2NO\cdot]/[(CF_3)_2NOH]$ ratios, reaction 3 may

$$R\cdot + (CF_3)_2NOH \rightarrow RH + (CF_3)_2NO\cdot \qquad (3)$$

occur rather than reaction 2. This will, of course, lead to a decrease in the measured rate of reaction as the reaction progresses and the decay of the $(CF_3)_2NO\cdot$ radical can be seen not to follow first-order kinetics if the decay is monitored for 3 or more half-lives. We therefore developed a new procedure, which is described below.

About 300 μL of Freon containing a known concentration of substrate was added to an EPR tube, which was left unsealed and was placed in the cavity of the spectrometer. The tube was cooled to the desired reaction temperature, and a fine stream of bubbles of deoxygenated nitrogen or helium was passed through the solution and was generally maintained throughout the experiment. After some minutes, which were allowed for deoxygenation of the solution, about 8 μL of an ca. 5×10^{-3} M solution of $(CF_3)_2NO\cdot$ in Freon 113 was injected directly into the substrate solution. The gas stream produced complete mixing within a few seconds. The decay of the aminoxyl radical was monitored in the usual way. Several injections of the $(CF_3)_2NO\cdot$ solution could be made into a single sample, provided only that allowance was made for its diluting effect on the substrate solution.

The reaction with cyclopentane was rather slow. There was therefore a danger that some of the $(CF_3)_2NO\cdot$ and/or the cyclopentane itself would be lost by evaporation. For this reason, the gas stream was turned off after the $(CF_3)_2NO\cdot$ was thoroughly mixed into the reactant solution and the sample tube was then sealed from atmospheric oxygen by covering its opening with Parafilm. Alternatively, solutions of cyclopentane (or neat cyclopentane) and of $(CF_3)_2NO\cdot$ were separately degassed on a vacuum line and were then cocondensed into an EPR tube. This tube was sealed under vacuum, and the sample was warmed just to its melting point and was rapidly mixed by shaking. It was then immediately placed in the EPR spectrometer, the cavity of which had been preset at the temperature desired for the kinetic measurement. The experimental results obtained by the two techniques were in satisfactory agreement.

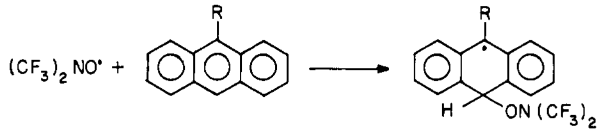
For all three procedures, experiments were generally carried out in Freon 113 ($CF_2ClCFCl_2$) as solvent at temperatures above 250 K and in Freon 11 ($CFCl_3$) at temperatures below 250 K.

Correction for Solvent's Thermal Contraction. For bimolecular reactions, accurate kinetic studies over wide temperature ranges require that substrate concentrations (which were generally measured at ca. 298 K) be corrected for thermal expansion or contraction of the solvent, as described previously for reaction mixtures in Freon 12 and Freon 113.[10] The effect of temperature on the relative volumes of typical reaction mixtures in Freon 11 were measured from 173 to 318 K. The temperature coefficient for volume expansion (referred to the volume at 273 K) was found to be ca. 1.21×10^{-3} K^{-1}. Similar measurements with neat cyclopentane gave a temperature coefficient for volume expansion of 1.08×10^{-3} K^{-1}.

Results

In the absence of reactive substrates bis(trifluoromethyl)aminoxyl does not decay in Freon solvents; even the bubbling with nitrogen or helium produced a negligible decrease in the aminoxyl concentration on the time scale of our kinetic measurements. However, when the aminoxyl solution was injected into the substrate solutions it was destroyed relatively rapidly. Decay followed clean first-order kinetics in all cases, and the reactions were almost always monitored for 3 or 4 half-lives. By an appropriate choice of substrate concentration the kinetic measurements were complete in a few minutes at higher temperatures and in no more than half an hour at lower temperatures.

Product studies suggest that all the substrates examined react initially with two $(CF_3)_2NO\cdot$ radicals. For many substrates including saturated hydrocarbons,[15] alkyl aromatics,[10,16-18] 1,4-cyclohexadiene,[21] aldehydes, and ethers[23,24] the initial, rate-controlling step is expected to be a hydrogen atom abstraction (reaction 1). Our kinetic data are consistent with an initial H atom for all such substrates except 9-methylanthracene. This particular compound was unexpectedly reactive, and for this reason anthracene was also tested. Since it proved to be about half as reactive as the 9-methylanthracene, we assume that addition is the favored initial reaction for both of these hydrocarbons, i.e.,



(4)

R = H, CH$_3$

Aniline, diphenylamine, 2,4,6-tri-*tert*-butylphenol, thiophenol, and tri-*n*-butylsilane, tri-*n*-butylgermane, and tri-*n*-butylstannane, are known to be excellent H atom donors toward a wide variety of organic free radicals, and all of them initially yield the cor-

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[10] Malatesta, V.; Ingold, K. U. *J. Am. Chem. Soc.* **1981**, *103*, 3094–3098.

[11] Anpo, M.; Chatgilialoglu, C.; Ingold, K. U. *J. Org. Chem.* **1983**, *48*, 4104–4106.

[12] Mel'nikova, A. V.; Baranaev, M. K.; Makarov, S. P.; Englin, M. A. *Zh. Obshch. Khim.* **1970**, *40*, 382–385.

[13] Mel'nikova, A. V.; Baranaev, M. K.; Makarov, S. P.; Englin, M. A. *Zh. Obshch. Khim.* **1970**, *40*, 117–118.

[14] Coles, P. F.; Haszeldine, R. N.; Owen, A. J.; Robinson, P. J.; Tyler, B. J. *J. Chem. Soc., Chem. Commun.* **1975**, 340–341.

[15] Banks, R. E.; Haszeldine, R. N.; Justin, B. *J. Chem. Soc. C* **1971**, 2777–2785.

[16] Banks, R. E.; Haszeldine, R. N.; Stevenson, M. J. *J. Chem. Soc. C* **1966**, 901–904.

[17] Banks, R. E.; Choudhury, D. R.; Haszeldine, R. N. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1092–1099.

[18] See introduction in ref 15. For an analogous reaction, see ref 19 and 20.

[19] Mendenhall, G. D.; Ingold, K. U. *J. Am. Chem. Soc.* **1973**, *95*, 2963–2971.

[20] Hussain, S. A.; Jenkins, T. C.; Perkins, M. J.; Siew, N. P. Y. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2803–2808.

[21] Our analysis of the products showed them to be confined to $(CF_3)_2NOH$ and benzene as was expected (see ref 19, 20, and 22).

[22] Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1967**, *45*, 785–792.

[23] Banks, R. E.; Coudhury, D. R.; Haszeldine, R. N. *J. Chem. Soc., Perkin Trans. 1* **1973**, 80–82.

[24] Banks, R. E.; Brown, A. K.; Haszeldine, R. N.; Jefferson, J. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1068–1070.

Table I. Summary of Kinetic Parameters for the Reactions of Some Organic Substrates with $(CF_3)_2NO\cdot$ in Freon Solvents

substrate	temp range, K	log A (M^{-1} s^{-1})[a]	E_a, kcal/mol[a]	$k^{298\ K}$, M^{-1} s^{-1}[b]
cyclopropane (**1**)	295			6×10^{-8}[c,d]
cyclopentane (**2**)	190–308	5.8 ± 0.6[e]	10.7 ± 0.7[e]	9.9×10^{-3}
cyclohexane (**3**)	295			8.9×10^{-3}[d]
toluene (**4**)	295			8.8×10^{-3}[d]
toluene (**5**)	123–327[f]	3.8 ± 0.5[f,g]	7.7 ± 0.6[f,g]	1.4×10^{-2}[f]
toluene-d_8 (**6**)	183–345[f]	3.6 ± 0.6[f]	9.0 ± 0.7[f]	1.1×10^{-3}[f]
ethylbenzene (**7**)	294			3.0×10^{-1}[d]
cumene (**8**)	295			2.9×10^{-1}[d]
sec-butylbenzene (**9**)	293			3.4×10^{-1}[d]
1-methylnaphthalene (**10**)	294			7.6×10^{-1}[d]
naphthalene (**11**)	297			6.4×10^{-2}[d]
9-methylanthracene (**12**)	294			29[d]
anthracene (**13**)	295			15[d]
diphenylmethane (**14**)	295			4.8×10^{-1}[d]
triphenylmethane (**15**)	294			8.8[d]
9,10-dihydroanthracene (**16**)	294			58[d]
1,4-cyclohexadiene (**17**)	192–296	6.5 ± 0.3	5.7 ± 0.5	206
benzaldehyde (**18**)	178–296	5.3 ± 0.3	6.9 ± 0.3	1.8
benzaldehyde-d_6 (**19**)	186–297	5.1 ± 0.5	8.2 ± 0.6	1.2×10^{-1}
diethyl ether (**20**)	178–297	4.2 ± 0.3	7.0 ± 0.4	1.1×10^{-1}
tetrahydrofuran (**21**)	193–297	4.9 ± 0.4	7.3 ± 0.4	3.5×10^{-1}
aniline (**22**)	201			39[d]
diphenylamine (**23**)	210			>230[d]
tri-*tert*-butylphenol (**24**)	193–295	4.8 ± 0.2	3.3 ± 0.3	236
thiophenol (**25**)	190–296	5.5 ± 0.5	4.0 ± 0.5	370
tri-*n*-butylsilane (**26**)	193–296	5.5 ± 0.9	7.7 ± 0.9	6.7×10^{-1}
tri-*n*-butylgermane (**27**)	186–294	6.2 ± 0.3	6.0 ± 0.3	63
tri-*n*-butylstannane (**28**)	184–258	5.9 ± 0.7	4.3 ± 0.7	546
1,1-dichloroethylene (**29**)	205–292	5.3 ± 0.4	9.3 ± 0.5	3.0×10^{-2}

[a] Errors correspond to two standard deviations and include only random errors. [b] Rate constant calculated at 298 K from Arrhenius parameters unless otherwise noted. [c] From ref 11. Reaction is 80% S_H2 at carbon, 20% H atom abstraction. [d] Measured only at the temperature indicated. [e] Calculated from kinetic data obtained in the temperature range 217–308 K. If the data down to 190 K are included then log A (M^{-1} s^{-1}) = 4.5 ± 0.7, E_a = 9.1 ± 0.8 kcal/mol, and $k^{298\ K} = 7.3 \times 10^{-3}$ M^{-1} s^{-1}. [f] From ref 10. Data obtained by photolysis of CF_3OOCF_3 in the presence of $(CF_3)_2NOH$ as the source of $(CF_3)_2NO\cdot$ radicals (see text). [g] Calculated from data obtained in the temperature range 194–327 K.

responding heteroatom-centered free radicals.[25] The initial product of the trimethylsilane–aminoxyl radical reaction has been identified as $(CH_3)_3SiON(CF_3)_2$,[26] which certainly implies that the initial reaction involves hydrogen abstraction. We assume that all of the above-mentioned substrates react with $(CF_3)_2NO\cdot$ by an initial transfer of hydrogen from the heteroatom.[27]

Product studies on the reaction of $(CF_3)_2NO\cdot$ with ethylene,[5,16,29] tetrafluoroethylene,[5,16,29] and a number of other halogenated olefins[16,30] have shown that the major product (ca. 98–99% for C_2F_4) is, in all cases, the corresponding 1,2-substituted bis(hydroxylamine). The overall process with 1,1-dichloroethylene can therefore be represented by

$$(CF_3)_2NO\cdot + H_2C{=}CCl_2 \rightarrow (CF_3)_2NOCH_2\dot{C}Cl_2 \quad (5)$$

$$(CF_3)_2NO\cdot + (CF_3)_2NOCH_2\dot{C}Cl_2 \rightarrow (CF_3)_2NOCH_2CCl_2ON(CF_3)_2 \quad (6)$$

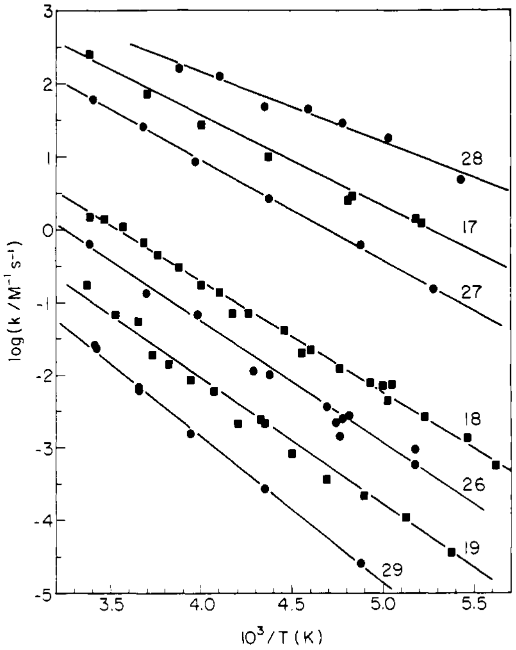

Figure 1. Arrhenius plots for some $(CF_3)_2NO\cdot$ reactions: H atom abstractions, compounds **17**, **18**, **19**, **26**, **27**, and **28**; addition, compound **29**. For the identity of the compounds, see Table I.

It seems highly probable that all of the substrates examined in this work react initially with two $(CF_3)_2NO\cdot$ radicals. The rate-controlling step involves H atom abstraction by, or the addition of, a $(CF_3)_2NO\cdot$ radical, and the new radical that is formed in this step is then rapidly trapped by a second $(CF_3)_2NO\cdot$ radical. Absolute rate constants for the initial step were therefore calculated by dividing the measured first-order rate constant, k_{expt}, by twice the temperature-corrected (see Experimental Section) molar concentration of substrate, i.e.,

$$k = k_{exptl}/2[\text{substrate}]$$

For 12 substrates, kinetic data were obtained over a wide range of temperatures. Most gave excellent Arrhenius plots, which are shown in Figures 1 and 2; the numbers on these figures corre-

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(25) For a general review, see: Ingold, K. U. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 2. See particularly Table VIII.

(26) Ang, H. G. *Chem. Commun.* **1968**, 1320–1321.

(27) This assumption receives support from product studies on the reaction of benzoyl-*tert*-butylaminoxyl with diphenylamine.[28] Product studies on the reaction of this aminoxyl with a number of phenols also imply that the initial step involves the abstraction of the phenolic hydrogen.[28]

(28) Hussain, S. A.; Jenkins, T. C.; Perkins, M. J. *Chem. Soc., Perkin Trans. 1* **1979**, 2809–2814.

(29) Makarov, S. P.; Videiko, A. F.; Tobolin, V. A.; Englin, M. A.; *Zh. Obshch. Khim.* **1967**, *37*, 1528–1531.

(30) Makarov, S. P.; Englin, M. A.; Mel'nikova, A. V. *Zh. Obshch. Khim.* **1969**, *39*, 538–540.

Table II. Absolute Rate Constants ($M^{-1}\ s^{-1}$) for Some Hydrogen Atom Abstractions by Oxygen- and Carbon-Centered Free Radicals at Ambient Temperatures

radical (R)	$(Me_3C)_2C{=}NO\cdot$	$(CF_3)_2CNO\cdot$	$Me_3COO\cdot$	$Me_3CO\cdot$	$CH_2{=}CH(CH_2)_4\cdot$	$C_6H_5\cdot$
D[R–H], kcal/mol	80.9[a]	85.3[b]	88.5[c]	104[d]	100[d,e]	110.5[d]
substrate						
$c\text{-}C_5H_{10}$		1×10^{-2} [b]	9×10^{-3} [f,g]	9×10^{5} [h]		8×10^{6} [i,j]
$C_6H_5CHMe_2$	9×10^{-7} [k]	0.3[b]	0.2[l]	9×10^{5} [m]		1×10^{7} [j]
$1,4\text{-}c\text{-}C_6H_{10}$		200[b]	8.0[g,l,n]	5×10^{7} [m,o]		
C_6H_5CHO		2[b]	0.9[l]	7×10^{7} [p]		
THF[q]		0.4[b]	0.3[g,l]	8×10^{6} [m,r]		5×10^{6} [j]
C_6H_5SH		4×10^{2} [b]	5×10^{3} [s]		2×10^{8} [t]	2×10^{9} [u]
$n\text{-}Bu_3SnH$		5×10^{2} [b]		2×10^{8} [v]	2×10^{6} [w]	

[a] Reference 37. [b] This work. [c] Reference 31–35. [d] Reference 52. [e] References 53 and 54. [f] Reference 43. [g] Values given in original paper were statistically corrected for the number of "active" hydrogens. Values given in this table refer to the whole molecule. [h] Reference 44. [i] Reference 45. [j] Reference 46. [k] Reference 19. Value calculated at 298 K by extrapolation from higher temperatures. [l] Reference 42. [m] Reference 47. [n] Less precise than the other rate constants in this column.[42] The rate constant for H atom abstraction by HOO· is 1480 $M^{-1}\ s^{-1}$. [o] Reference 48. [p] Reference 49. [q] Tetrahydrofuran. [r] Reference 50. [s] Reference 38. [t] Rate constant given in ref 39 has been multiplied by 2.5 to accord with the rate data given in ref 41. [u] Reference 51. [v] Reference 40. [w] Reference 41.

sponding to the compounds as numbered in Table I. The Arrhenius parameters were derived from the best line through all the points on these plots except in the case of cyclopentane for which the Arrhenius plot was curved at low temperatures, an effect we tentatively attribute to small traces of reactive impurities that were not removed by preparative VPC. (The purity was 97.6% before and 99.5% after VPC treatment, but the measured rate constants were the same.) The Arrhenius parameters for cyclopentane were therefore derived from rate data obtained at temperatures ≥217 K, the corresponding Arrhenius line being shown in Figure 2. The Arrhenius parameters for the 12 substrates are given in Table I together with the temperature range covered and absolute rate constants calculated from the Arrhenius parameters at 298 K. Full kinetic data are available as supplementary material. Also included in Table I are data for those substrates that were examined at only one temperature as well as our previous data for the reaction of $(CF_3)_2NO\cdot$ with cyclopropane[11] and toluene.[10]

O–H Bond Strength in $(CF_3)_2NOH$. This bond strength has been measured previously by an EPR technique in which an equilibrium was established between $(CF_3)_2NO\cdot$, $(CF_3)_2NOH$, $(Me_3C)_2C{=}NO\cdot$, and $(Me_3C)_2C{=}NOH$.[10] A value of 82.6 ± 3.0 kcal/mol was obtained. During the course of the present work it became apparent that our kinetic results could be more easily explained if this O–H bond was somewhat stronger than 82.6 kcal/mol. For example, the absolute reactivities of $(CF_3)_2NO\cdot$ and of $Me_3COO\cdot$ were found to be essentialy identical although the O–H bond strength in Me_3COOH is 88.5 ± 1.5 kcal/mol.[31–35] In addition, the magnitude of the activation energy found for the $(CF_3)_2NO\cdot$/cyclopentane reaction (10.7 kcal/mol for data at $T > 217$ K, 9.1 kcal/mol for all data) is acutally *smaller* than the estimated enthalpy for this reaction of ca. 13 kcal/mol (based on $D[(CF_3)_2NO–H] = 82.6$ and $D[c\text{-}C_5H_9–H] = 95–96$ kcal/mol). Certainly a somewhat larger O–H bond strength for $(CF_3)_2NOH$ would seem to be required by this thermochemistry.

For these and other reasons, it was decided to remeasure $D[(CF_3)_2NO–H]$ by a more direct, calorimetric method in which the heat evolved in the reaction of $(CF_3)_2NO\cdot$ with hydrazobenzene was measured.[36,37] This reaction should yield only $(CF_3)_2NOH$ and *trans*-azobenzene, i.e.,

$$2(CF_3)_2NO\cdot + C_6H_5NHNHC_6H_5 \rightarrow 2(CF_3)_2NOH + trans\text{-}C_6H_5N{=}NC_6H_5 \quad (7)$$

The calorimeter consisted of a small, covered Dewar flask containing an iron–constantan thermocouple, a magnetic stirrer, an electrical resistor, which was used for calibration, and a coil of glass tubing through which air could be blown to cool and reequilibrate the system. Hydrazobenzene (8.6×10^{-4} mol) was added as the solid to an excess of $(CF_3)_2NO\cdot$ in 38 mL of CCl_4 at 23 °C. The temperature rise was essentially instantaneous and corresponded to the release of 32.27 cal. The complete conversion of hydrazobenzene to *trans*-azobenzene was confirmed by the absorption spectrum of the product solution (*trans*-azobenzene, $\lambda_{max} = 445$ nm, $\epsilon_{445} = 478\ M^{-1}\ cm^{-1}$).[36] Therefore, the heat of reaction 7 is 37.5 kcal/mol, which, when combined with values[37] for the heats of formation of azobenzene (76.49 kcal/mol) and hydrazobenzene (52.9 kcal/mol) in their standard states as solids at 298 K and the partial molal enthalpy of solution of azobenzene in CCl_4 at infinite dilution (5.28 kcal/mol), yields $D[(CF_3)_2N\text{-}O–H] = 85.3$ kcal/mol with a probable error of ±3 kcal/mol.

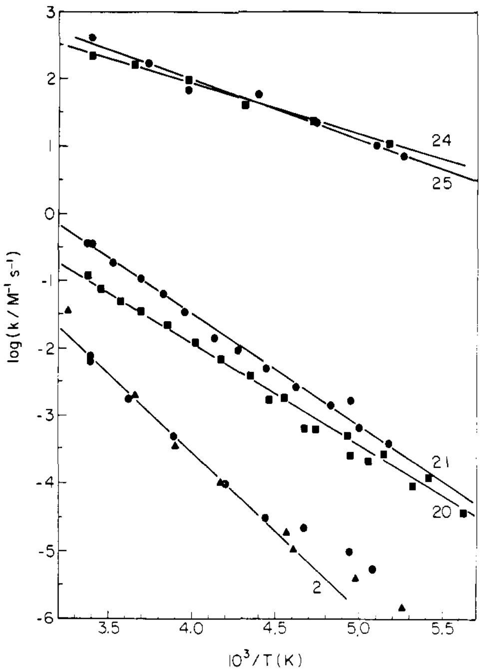

Figure 2. Arrhenius plots for some H atom abstractions by $(CF_3)_2NO\cdot$. For the identity of compounds **2**, **20**, **21**, **24**, and **25**, see Table I. For compound **2**, the circles represent data obtained with samples sealed with Parafilm, and the triangles represent data obtained with samples sealed under vacuum.

Discussion

Although an enormous number of organic free radicals have been identified over the past 80 years, very few of them have had their reactions in solution subjected to detailed kinetic study. The reactivity of the $(CF_3)_2NO\cdot$ radical is compared with the reactivities of five other radicals in Table II. That is, the absolute

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(31) Mahoney, L. R.; DaRooge, M. A. *J. Am. Chem. Soc.* **1970**, *92*, 4063–4067.

(32) Benson, S. W. *J. Am. Chem. Soc.* **1965**, *87*, 972–979.

(33) Nangia, P. S.; Benson, S. W. *J. Phys. Chem.* **1979**, *83*, 1183–1142.

(34) Shum, L. G. S.; Benson, S. W. *Int. J. Chem. Kinet.* **1983**, *15*, 323–339. Heneghan, S. P.; Benson, S. W. *Ibid.* **1983**, *15*, 815–822.

(35) Howard, C. J. *J. Am. Chem. Soc.* **1980**, *102*, 6937–6941.

(36) Mahoney, L. R.; Ferris, F. C.; DaRooge, M. A. *J. Am. Chem. Soc.* **1969**, *91*, 3883–3889.

(37) Mahoney, L. R.; Mendenhall, G. D.; Ingold, K. U. *J. Am. Chem. Soc.* **1973**, *95*, 8610–8614.

Table III. Comparison of Arrhenius Parameters for Some H Atom Abstractions by $(CF_3)_2NO\cdot$ and $Me_3COO\cdot$ Radicals

	$(CF_3)_2NO\cdot$		$Me_3COO\cdot$	
substrate	log *A* (M^{-1} s^{-1})	*E*, kcal/mol	log *A* (M^{-1} s^{-1})	*E*, kcal/mol
cyclopentane	5.8[a]	10.7[a]	9.8[b-d]	16.75[b]
toluene	3.8	7.7	6.9[c,e,f]	11.0[e,f]
1,4-cyclohexadiene	6.5	5.7	9.3[c,e]	11.3[e]
tri-*tert*-butylphenol	4.8	3.3	4.2[g]	0.5[g]
thiophenol	5.5	4.0	4.5[h]	1.1[h]

[a] Even smaller values would have been obtained if the experimental data obtained at temperatures below 217 K had been included in the correlation (see footnote e, Table I). [b] Reference 43. [c] Values of log *A* (M^{-1} s^{-1}) that are given in the original paper were statistically corrected for the number of "active" hydrogens. Values given in this table refer to the whole molecule. [d] Even higher values would be estimated from data given in ref 42 for the reaction of $Me_3COO\cdot$ with hexadecane, tridecane, and cyclohexane. [e] Reference 42. [f] Values are for *p*-xylene. [g] Reference 56. [h] Reference 38.

rate constants for H atom abstraction at ambient temperatures from seven selected substrates by $(CF_3)_2NO\cdot$ have been listed in this table together with most of the available kinetic data for abstraction from these same substrates by other oxygen-centered organic radicals and by two representative and relatively reactive carbon-centered radicals.[19,38-51] The strengths of the bonds formed between the different radicals and hydrogen, i.e., D[radical-H], have also been listed.[10,31-35,52-54]

As mentioned in the Results, the $(CF_3)_2NO\cdot$ and *tert*-butylperoxyl radicals have remarkably similar absolute reactivities at ambient temperatures. This similarity is brought out even more forcefully in Figure 3, which shows a plot for $(CF_3)_2NO\cdot$ vs. $Me_3COO\cdot$ of the logarithms of the rate constants for H atom abstraction from all compounds for which data were available. The line that has been drawn in this figure has a slope of 1.0 and passes through points where the rate constants for these two radicals are equal.[55] However, room temperature is the only temperature at which these two radicals have closely similar reactivities (i.e., it is the isokinetic temperature). The available Arrhenius parameters for H atom abstraction[38,42,43,56] (see Table III) show the reactivities measured at temperatures significantly above or below ambient would not be similar. For example, the preexponential factors and activation energies for the three hydrocarbon substrates are much smaller for $(CF_3)_2NO\cdot$ than for $Me_3COO\cdot$. The former radical will therefore be less reactive toward hydrocarbons than the latter at high temperatures and more reactive at low temperatures. That there should be an isokinetic temperature for H atom abstraction is not too surprising because both the thermochemistries for these two radicals (*D*-[ROO-H] = 88.5 ± 1.5,[31-35] *D*[$(CF_3)_2NO$-H] = 85.3 ± 3.0 kcal/mol) and their spin distributions ($a(^{17}O) = 23.4_5$[57] and 23.6 G[7] for $Me_3CO^{17}O\cdot$ and $(CF_3)_2N^{17}O\cdot$, respectively) are rather similar.

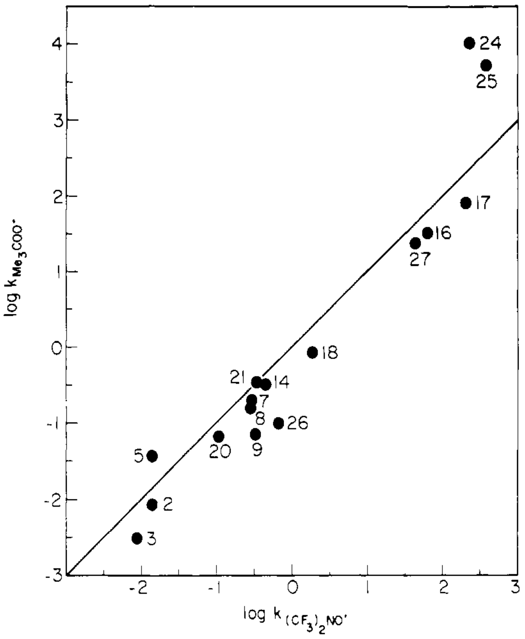

Figure 3. Plot of log *k* for H atom abstractions by $(CF_3)_2NO\cdot$ vs. log *k* for H atom abstractions by $Me_3COO\cdot$. For the identity of the compounds, see Table I. Data for the $Me_3COO\cdot$ reactions are from ref 43 for compounds **2** and **3**, from ref 42 for compounds **5**, **7–9**, **14**, **16–18**, **20**, and **21**, from ref 56 for compound **24**, from ref 38 for compound **25**, and from J. A. Howard (private communication) for compounds **26** and **27**. Note that for **9** the attacking radical was $PhCMe_2OO\cdot$, for **20** the substrate was di-*n*-butyl ether, for **26** the substrate was triethylsilane, and for **27** the substrate was triphenylgermane (triphenylsilane is 40% more reactive toward $Me_3COO\cdot$ than Et_3SiH).

The Arrhenius preexponential factors for all $(CF_3)_2NO\cdot$ reactions are very much lower than those generally considered normal, viz.,[52] $10^{8.5\pm0.5}$ M^{-1} s^{-1}, for H atom abstractions by free radicals and for their additions to C=C double bonds. Nevertheless, our kinetic data should be reliable[58] and the Arrhenius plots are generally linear over a wide range of temperatures (see Figures 1 and 2). The low *A* factors for the H atom abstractions cannot be attributed to quantum-mechanical tunneling for three reasons. In the first place, the deuterium kinetic isotope effect for C_6D_5CDO vs. C_6H_5CHO shows none of the unusual features (i.e., k_H, >> k_D, A_D >> A_H, etc.) commonly attributed to tunneling. Second, tunneling can occur only between states of equal

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(38) Chenier, J. H. B.; Furimsky, E.; Howard, J. A. *Can. J. Chem.* **1974**, *52*, 3682-3688.

(39) Russell, G. A.; Tashtoush, H. *J. Am. Chem. Soc.* **1983**, *105*, 1398-1399.

(40) Scianao, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 5399-5400.

(41) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739-7742.

(42) Korcek, S.; Chenier, J. H. B.; Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1972**, *50*, 2285-2297.

(43) Chenier, J. H. B.; Tong, S. B.; Howard, J. A. *Can. J. Chem.* **1978**, *56*, 3047-3053.

(44) Wong, P. C.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5106-5108.

(45) Bridger, R. F.; Russel, G. A. *J. Am. Chem. Soc.* **1963**, *85*, 3754-3765.

(46) Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 3609-3614.

(47) Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520-4527.

(48) Effio, A.; Griller, D.; Ingold, K. U.; Scaiano, J. C.; Sheng, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 6063-6068.

(49) Chatgilialoglu, C.; Lunazzi, L.; Placucci, G., private communication.

(50) Malatesta, V.; Scaiano, J. C. *J. Org. Chem.* **1982**, *47*, 1455-1459. See also: Malatesta, V.; Ingold, K. U. *J. Am. Chem. Soc.* **1981**, *103*, 609-614.

(51) Kryger, R. G.; Lorand, J. P.; Stevens, N. R.; Herron, N. R. *J. Am. Chem. Soc.* **1977**, *99*, 7589-7600.

(52) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

(53) Castelhano, A. L.; Griller, D. *J. Am. Chem. Soc.* **1982**, *104*, 3655-3659.

(54) Castelhano, A. L.; Marriott, P. R.; Griller, D. *J. Am. Chem. Soc.* **1981**, *103*, 4262-4263.

(55) The linear relationship shown in Figure 3 implies[42] that after statistical correction for the number of "active" hydrogen in each RH, the present data could be correlated with R-H bond strengths (in kcal/mol) via the equation log $k^{RH}{}_{(CF_3)_2NO\cdot}$(per active H) ($M^{-1}$ s^{-1}) = 15.4–0.2 [R-H].

(56) Howard, J. A.; Furimsky, E. *Can. J. Chem.* **1973**, *51*, 3738-3745.

(57) Howard, J. A. *Can. J. Chem.* **1972**, *50*, 1981-1983.

(58) Except for toluene[10] for which the possibility of reversible H atom abstraction, i.e., reaction 3, was not considered.

energy, which, for practical purposes, excludes reactions that are endothermic to any significant extent. Known bond strengths[42,43,59-63] indicate the H atom abstraction by $(CF_3)_2NO\cdot$ would be appreciably endothermic for many of the compounds (e.g., cyclopentane) for which Arrhenius parameters were measured. Third, the preexponential factor for the reaction with $CH_2{=}CCl_2$, which certainly does not involve an H atom transfer, is also appreciably smaller than the values "normal" for radical–molecule addition reactions.

A search of the literature reveals that the Arrhenius parameters for a number of H atom transfers between oxy radicals in solution have been found to be unusually low.[19,31,38,56,64-68] It has been suggested that this is due to the intermediate formation of a hydrogen-bonded free radical–molecule complex[38,56,67] or to the relatively small triplet repulsion energy in the $[RO^{\downarrow}\cdots H^{\uparrow}\cdots{}^{\downarrow}OR]$ transition state[38,68,69] (which leads to a low activation energy and, because of a "tight" transition state, a low *A* factor). Neither suggestion would appear to be applicable to the attack of the $(CF_3)_2NO\cdot$ radical on C-H bonds in hydrocarbons, aldehydes, and ethers.

Reversal within the solvent cage may be important with some substrates because the measured activation energies for H atom abstraction by $(CF_3)_2NO\cdot$ are approximately equal to the estimated thermochemistries of these abstractions. This means that the corresponding back reactions (reaction 3) must be approximately thermoneutral and must occur without any activation energy. Our measured rate constant may therefore be considerably smaller than the "true" rate constant measured in the absence of a solvent cage (i.e., in the gas phase). However, because reaction 3 has no activation energy the importance of cage reversal should increase as the temperature is reduced, thereby reducing the "true" rate constants at low temperatures to a greater extent than it reduces the "true" rate constants at high temperatures. Our measured rate constants would therefore be expected to yield high *A* factors and high activation energies, which is opposite to the experimental observations.

We tentatively propose that our $(CF_3)_2NO\cdot$ reactions have low *A* factors because reaction can occur only via transition states that have a highly restrictive geometry[70] that demands a very specific orientation of the $(CF_3)_2NO\cdot$ relative to the C—H or C=C bond under attack, together perhaps with some local "freezing" of surrounding solvent molecules. We perfer not to speculate further on this problem. However, we do feel compelled to point out that the usual assumption that Arrhenius preexponential factors for radical/molecule reactions in solution will have "normal" (gas phase) values is not valid for at least one radical.

Acknowledgment. We thank Drs. M. Anpo and C. Chatgilialoglu for some preliminary kinetic work, Dr. D. Griller for his help and advice with the calorimetric experiment, Dr. J. A. Howard for allowing us to use some of this unplublished results on the $Me_3COO\cdot$ radical, and an unknown referee for many helpful comments.

Registry No. THF, 109-99-9; $(CF_3)_2NO\cdot$, 2154-71-4; c-C_5H_{10}, 287-92-3; c-C_6H_{12}, 110-82-7; $C_6H_5CH_3$, 108-88-3; $C_6H_5CH_2CH_3$, 100-41-4; $C_6H_5CHMe_2$, 98-82-8; $C_6H_5CH(CH_3)CH_2CH_3$, 135-98-8; $(C_6H_5)_2CH_2$, 101-81-5; $(C_6H_5)_3CH$, 519-73-3; c-1,4-C_6H_8, 628-41-1; C_6H_5CHO, 100-52-7; C_6D_6CDO, 17901-93-8; $(CH_3CH_2)_2O$, 60-29-7; $C_6H_5NH_2$, 62-53-3; $(C_6H_5)_2NH$, 122-39-4; C_6H_5SH, 108-98-5; *n*-Bu_3SiH, 998-41-4; *n*-Bu_3GeH, 998-39-0; *n*-Bu_3SnH, 688-73-3; $H_2C{=}CCl_2$, 75-35-4; 1-methylnaphthalene, 90-12-0; naphthalene, 91-20-3; 9-methylanthracene, 779-02-2; anthracene, 120-12-7; 9,10-dihydroanthracene, 613-31-0; 2,4,6-tri-*tert*-butylphenol, 732-26-3.

Supplementary Material Available: Tables IV–XVI of detailed kinetic data (10 pages). Ordering information is given on any current masthead page.

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(59) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493–532.

(60) Values of 91 kcal/mol for *n*-butyl ether[42] and 93 kcal/mol for dimethyl ether[59] have been estimated.

(61) Jackson, R. A. *J. Organomet. Chem.* **1979**, *166*, 17–19. Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246–252.

(62) Doncaster, A. M.; Walsh, R. *J. Phys. Chem.* **1979**, *83*, 578–581. Almond, M. J.; Doncaster, A. M.; Noble, P. N.; Walsh, R. *J. Am. Chem. Soc.* **1982**, *104*, 4717–4718.

(63) Brokenshire, J. L.; Ingold, K. U. *Int. J. Chem. Kinet.* **1971**, *3*, 343–357.

(64) Kreilick, R. W.; Weissman, S. I. *J. Am. Chem. Soc.* **1962**, *84*, 306–307; **1966**, *88*, 2645–2652.

(65) Howard, J. A.; Schwalm, W. J.; Ingold, K. U. *Adv. Chem. Ser.* **1968**, *No. 75*, 6–23.

(66) Mahoney, L. R.; DaRooge, M. A. *J. Am. Chem. Soc.* **1970**, *92*, 890–899.

(67) Mahoney, L. R.; DaRooge, M. A. *J. Am. Chem. Soc.* **1972**, *94*, 7002–7009.

(68) Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 630–632.

(69) Zavitsas, A. A. *J. Am. Chem. Soc.* **1972**, *94*, 2779–2789.

(70) Geometrically restrictive transition states have been invoked for certain radical–radical reactions that have little or no activation energy; see, e.g.: Morrell, M. L.; Vincow, G. *J. Am. Chem. Soc.* **1969**, *91*, 6389–6390. Griller, D.; Perkins, M. J. *Ibid.* **1980**, *102*, 1354–1357. Schuh, H.-H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2463–2481. Benson, S. W. *Can. J. Chem.* **1983**, *61*, 881–887.