orders are obtained employing the appropriate linear combination of Slater determinants for each C.I. eigenstate. The S_1 and S_0 of dimethyl diene allene **18** were also optimized using GAUSSIAN90 with an STO-3G basis set, and CASSCF with an active space of 4 was used for geometry optimization of S_1.

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Solvent Effects on the Competitive β-Scission and Hydrogen Atom Abstraction Reactions of the Cumyloxyl Radical. Resolution of a Long-Standing Problem[1]

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Abstract: Laser flash photolysis (LFP) techniques with detection in the infrared and in UV–visible regions of the spectrum have been used in combination with detailed product studies to assess solvent effects on the hydrogen abstraction and β-scission reactions of cumyloxyl radicals. The variation in the ratio of the products of these two competing processes in solvents with different polarities is due to the solvent's influence on β-scission. The rate constants for β-scission at 30 °C, k_β^{CumO}, were $(2.6_3 \pm 0.2_4) \times 10^5$, $(3.7_5 \pm 0.5_3) \times 10^5$, $(5.5_4 \pm 2.0_0) \times 10^5$, $(5.8_4 \pm 1.0_6) \times 10^5$, $(6.3_3 \pm 0.4_3) \times 10^5$, and $(19._6 \pm 3._4) \times 10^5\ \mathrm{s}^{-1}$ in CCl_4, C_6H_6, C_6H_5Cl, $(CH_3)_3COH$, CH_3CN, and CH_3COOH, respectively. The rate constants for hydrogen abstraction from cyclohexane were essentially identical in these six solvents, viz., $k_a^{\mathrm{CumO}} = (1.2_4 \pm 0.1_2) \times 10^6\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. There is a reasonably good linear correlation between log $(k_\beta^{\mathrm{CumO}}/\mathrm{s}^{-1})$ and certain cybotactic solvent parameters indicating that solvent effects on k_β^{CumO} are due to a localized interaction between the transition state for β-scission and adjacent solvent.

During the 1960's Cheves Walling and co-workers published an extensive series of pioneering papers on the photochemically initiated free-radical chain halogenations of a wide variety of organic compounds by *tert*-butyl hypochlorite and related hypohalites.[4-17] Provided a "contaminating" simultaneous chain reaction which is carried by chlorine atoms has been suppressed by the addition of "chlorine atom traps" (generally alkenes)[17-19] the overall process may be represented by the following:

$$(CH_3)_3COCl \xrightarrow{h\nu} (CH_3)_3CO^\bullet + Cl^\bullet \quad (1)$$

$$(CH_3)_3CO^\bullet \xrightarrow{k_\beta^{t\text{-BuO}}} (CH_3)_2C{=}O + CH_3^\bullet \quad (2)$$

$$(CH_3)_3CO^\bullet + RH \xrightarrow{k_a^{t\text{-BuO}}} (CH_3)_3COH + R^\bullet \quad (3)$$

$$R^\bullet(CH_3^\bullet) + (CH_3)_3COCl \rightarrow RCl(CH_3Cl) + (CH_3)_3CO^\bullet \quad (4)$$

Chlorination of a single substrate RH in an "inert" solvent (i.e., a solvent which does not act as a hydrogen atom donor, or is a poor donor, to *tert*-butoxyl) and measurement of the product ratio $[(CH_3)_3COH]/[(CH_3)_2CO]$ or, alternatively, of the ratio $[RCl]/[(CH_3)_2CO]$ over a range of known substrate concentrations yields the ratio of the rate constants for hydrogen abstraction from RH to β-scission, $k_a^{t\text{-BuO}}/k_\beta^{t\text{-BuO}}$. During the course of such routine measurements the most unexpected and exciting discovery was made: viz., solvents could have a dramatic effect on the magnitude of $k_a^{t\text{-BuO}}/k_\beta^{t\text{-BuO}}$.[12,13] For example,[13] with 0.1 M cyclohexane as RH at 40 °C the $[(CH_3)_3COH]/[(CH_3)_2CO]$ ratios obtained with *tert*-butyl hypochlorite varied from 5.50 in $CFCl_2CF_2Cl$ to 2.62 in benzene and 1.78 in CH_3CN to 0.70 in acetic acid. This solvent effect cannot be attributed to interference from a "contaminating" chlorine atom chain because *tert*-butoxyl radicals generated by thermal decomposition of di-*tert*-butylperoxyloxalate, reaction 5, gave essentially the same results, viz.,

$$(CH_3)_3COC(O)OOC(O)OC(CH_3)_3 \xrightarrow{\Delta} 2(CH_3)_3CO^\bullet + 2CO_2 \quad (5)$$

with 0.1 M cyclohexane at 40 °C the $[(CH_3)_3CO]/[(CH_3)_2CO]$ ratios were 7.5, 3.5, 1.6, and 1.1 in $CFCl_2CF_2Cl$, C_6H_6, CH_3CN, and CH_3COOH, respectively.[13]

The decrease in $k_a^{t\text{-BuO}}/k_\beta^{t\text{-BuO}}$ with increasing solvent polarity could, a priori, be due to the following: (i) a decrease in $k_a^{t\text{-BuO}}$, (ii) an increase in $k_\beta^{t\text{-BuO}}$, or (iii) both a decrease in $k_a^{t\text{-BuO}}$ and an increase in $k_\beta^{t\text{-BuO}}$. As Walling and co-workers were the first to point out,[10,12] "solvent effects on competitive radical reactions must reflect different degrees of solvent interaction with the *transition states* rather than with the *radicals* (assuming (radical-solvent) complexing to be a rapid process)." It was also pointed out that "Solvent interaction with the transition state for β-scission presents no difficulties, but in the transition state involving an alkoxy(l) radical and a substrate such as cyclohexene, solvent molecules should be sterically excluded from close vicinity to the alkoxy(l) radical".[10] Accordingly, Walling and Wagner[13] ascribed "the large solvent effects on $k_a^{t\text{-BuO}}/(k_\beta^{t\text{-BuO}})$ ratios chiefly to solvation of the transition state for the β-scission process". In the preceding quote the word "chiefly" would appear to be present

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[4] Walling, C.; Jacknow, B. B. *J. Am. Chem. Soc.* **1960**, *82*, 6108–6112.

[5] Walling, C.; Jacknow, B. B. *J. Am. Chem. Soc.* **1960**, *82*, 6113–6115.

[6] Walling, C.; Thaler, W. *J. Am. Chem. Soc.* **1961**, *83*, 3877–3884.

[7] Walling, C.; Padwa, A. *J. Am. Chem. Soc.* **1962**, *84*, 2845–2846.

[8] Walling, C.; Fredricks, P. S. *J. Am. Chem. Soc.* **1962**, *84*, 3326–3331.

[9] Walling, C.; Padwa, A. *J. Org. Chem.* **1962**, *27*, 2976–2977.

[10] Walling, C.; Padwa, A. *J. Am. Chem. Soc.* **1963**, *85*, 1593–1597.

[11] Walling, C.; Padwa, A. *J. Am. Chem. Soc.* **1963**, *85*, 1597–1601.

[12] Walling, C.; Wagner, P. *J. Am. Chem. Soc.* **1963**, *85*, 2333–2334.

[13] Walling, C.; Wagner, P. J. *J. Am. Chem. Soc.* **1964**, *86*, 3368–3375.

[14] Walling, C.; Heaton, L.; Tanner, D. D. *J. Am. Chem. Soc.* **1965**, *87*, 1715–1721.

[15] Walling, C.; Wagner, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 5179–5185.

[16] Walling, C. *Pure Applied Chem.* **1967**, *15*, 69–80.

[17] Walling, C.; McGuinness, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 2053–2058.

[18] Zavitsas, A. A.; Pinto, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 7390–7396.

[19] The "contamination" of the simple chain reaction shown in eqs 1–4 was first suggested by Sakurai and Hosomi.[20]

[20] Sakurai, H.; Hosomi, A. *J. Am. Chem. Soc.* **1967**, *89*, 458–460.

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because solvent effects on hydrogen abstraction were not ruled out though they were thought to be "rather small".[13,21]

The proposals of Walling and co-workers regarding solvent effects on alkoxyl radical reactions have received at least some support form other workers. Thus, Zavitsas and Seltzer[23] investigated the temperature dependence of the deuterium isotope effect for the loss of $CH_3^\bullet$ or $CD_3^\bullet$ from $C_6H_6C(CH_3)CD_3O^\bullet$ via β-scission and concluded that the transition state was more akin to products than to reactants, i.e., β-scission involves a late transition state so that solvation of the acetophenone product would be expected to increase k_β. More directly, Neta et al.[24a] generated the cumyloxyl radical by pulse radiolysis in water and determined that its rate constant for β-scission was ca. 1×10^7 s^{-1} at room temperature, a value which is 10 times as great as a value estimated previously in chlorobenzene[46] and ca. 40 times greater than the value we later measured in CCl_4.[27] Also, Mendenhall et al.[24b] showed by laser flash photolysis, with monitoring of the growth of the benzyl radical's absorption in the near-UV, that reaction 6 was much faster in 1-propanol than in benzene and that at −35

$$C_6H_5CH_2CH_2O^\bullet \xrightarrow{k_\beta{}^6} C_6H_5CH_2^\bullet + CH_2O \qquad (6)$$

°C $k_\beta{}^6$ was increased from 1.9×10^6 s^{-1} in neat chlorobenzene to 1.1×10^7 s^{-1} in chlorobenzene containing 0.43 M methanol.

There is, therefore, at least some more-or-less direct evidence to support Walling and co-workers' hypothesis that polar solvents accelerate the β-scission of alkoxyl radicals. However, the effect of such solvents on rates of hydrogen abstraction remains unknown.[25] Thus, solvent effects on very easily measured k_a/k_β ratios are still in need of division into their effect on abstraction and their effect on β-scission. This we have now accomplished in a study of solvent effects on the reactions of cumyloxyl radicals by combining product studies, time-resolved infrared (TRIR), time-resolved ultraviolet (TRUV), and time-resolved visible (TRVis) spectroscopies.

The reactions investigated have been β-scission (reaction 7) and hydrogen atom abstractions from cyclohexane (reaction 8), from the solvent (SH, reaction 9) and from the cumyloxyl radical precursor (PH, dicumyl peroxide, and dicumyl hyponitrite, reactions 10a and b).

$$C_6H_5C(CH_3)_2CO^\bullet \xrightarrow{k_\beta{}^{\mathrm{CumO}}} C_6H_5COCH_3 + CH_3^\bullet \qquad (7)$$

$$C_6H_5C(CH_3)_2CO^\bullet + c\text{-}C_6H_{12} \xrightarrow{k_a{}^{\mathrm{CumO}}} C_6H_5C(CH_3)_2COH + c\text{-}C_6H_{11}^\bullet \qquad (8)$$

$$C_6H_5C(CH_3)_2CO^\bullet + SH \xrightarrow{k_s} C_6H_5C(CH_3)_2COH + S^\bullet \qquad (9)$$

$$C_6H_5C(CH_3)_2CO^\bullet + \underset{(PH)}{[C_6H_5C(CH_3)_2CO]_2} \xrightarrow{k_p{}^{\mathrm{CumO}}} C_6H_5C(CH_3)_2COH + P^\bullet \qquad (10a)$$

$$C_6H_5C(CH_3)_2CO^\bullet + \underset{(PH)}{[C_6H_5C(CH_3)_2CON]_2} \xrightarrow{k_p{}^{\mathrm{CumO}}} C_6H_5C(CH_3)_2COH + P^\bullet \qquad (10b)$$

The cumyloxyl radical was chosen for study because we had previously demonstrated that it undergoes β-scission at ambient temperatures with a rate constant suitable for measurement using our current IR and UV nanosecond technology, i.e., $k_\beta \sim 10^5$–10^6 s^{-1}.[27,28] Our discovery[29] that the cumyloxyl radical has a strong absorption in the visible region of the electromagnetic spectrum (λ_{max} = 485 nm) greatly aided our present investigation, particularly since its UV absorption can be masked by the absorptions due to other transient intermediates and stable products.

Results

Product Studies. Determination of $k_a{}^{\mathrm{CumO}}/k_\beta{}^{\mathrm{CumO}}$. In initial experiments the relative yields of cumyl alcohol and acetophenone were determined by gas chromatography/mass spectrometry after irradiating ca. 0.01 M dicumyl peroxide in the presence of cyclohexane (0.09–0.46 M) in various solvents at ca. 30 °C using a Rayonet reactor with 300-nm lamps. It was discovered, however, that the [cumyl alcohol]/[acetophenone] ratio decreased during the course of the reaction. This problem was traced to the product, acetophenone, which absorbs 300-nm irradiation, is converted to its nπ* triplet, and then undergoes irreversible photoinduced reductive chemistry. In principle, this problem might have been overcome by measuring the alcohol/ketone product ratios as a function of time and then extrapolating back to zero time. In practice, this proved to be an unreliable procedure because plots of the alcohol/ketone ratios vs time were nonlinear.

Since the above-mentioned difficulties would not exist if the cumyloxyl radicals were generated thermally we turned to dicumyl hyponitrite as a cumyloxyl radical source. The hyponitrite (ca. 0.0027 M) was thermolyzed at 30 °C for 6 or more half-lives[30] in the presence of cyclohexane (generally ca. 0.09–0.46 M but ca. 0.44–0.85 M in CH_3COOH) in six different solvents ranging widely in polarity (see Table I). Plots of [cumyl alcohol]/[acetophenone] vs [cyclohexane] showed excellent linearity[37] as would be predicted, eq I:

$$\frac{[\text{cumyl alcohol}]}{[\text{acetophenone}]} = \frac{k_a{}^{\mathrm{CumO}}[\text{cyclohexane}]}{k_\beta{}^{\mathrm{CumO}}} + C \qquad (I)$$

where

$$C = \frac{k_s{}^{\mathrm{CumO}}[\text{SH}] + k_p{}^{\mathrm{CumO}}[\text{hyponitrite}]}{k_\beta{}^{\mathrm{CumO}}} \qquad (II)$$

More than 96% of the cumyloxyl radicals produced could be accounted for as cumyl alcohol, acetophenone, and dicumyl peroxide (the "cage-collapse" product which typically accounted for ca. 3–7% of the cumyloxyl radicals produced). Values of $k_a{}^{\mathrm{CumO}}/k_\beta{}^{\mathrm{CumO}}$ determined via eq I are given in Table I.

Time-Resolved Kinetic Measurements. Determination of $k_\beta{}^{\mathrm{CumO}}$ by TRIR. The cumyloxyl radical was generated by 308-nm LFP of dicumyl peroxide (0.58–0.91 M) in CCl_4 and in acetonitrile

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[21] Though it might be noted that in his Ph.D. thesis[22] Wagner deduced from isokinetic plots that "very polar solvents (had) large effects on abstraction". Today the diagnostic value of isokinetic plots is generally considered to be minimal and such plots have now fallen from favor.

[22] Wagner, P. J., Ph.D. Thesis, Columbia, 1963. University Microfilms, Inc., Ann Arbor, MI, Order No. 64-9213.

[23] Zavitsas, A. A.; Seltzer, S. *J. Am. Chem. Soc.* **1964**, *86*, 3836–3840.

[24] (a) Neta, P.; Dizdaroglu, M.; Simic, M. G. *Isr. J. Chem.* **1984**, *24*, 25–28. (b) Mendenhall, G. D.; Stewart, L. C.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5109–5114.

[25] Indications that there may be quite substantial solvent effects on hydrogen abstraction from hydrocarbons are contained in Wagner's thesis[22] and in work by Russell[26] and for hydrogen abstraction from diphenylmethanol in work by Mendenhall et al.[24]

[26] Russell, G. A. *J. Org. Chem.* **1959**, *24*, 300–302.

[27] Neville, A. G.; Brown, C. E.; Rayner, D. M.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1989**, *111*, 9269–9270.

[28] In contrast, at ambient temperatures the *tert*-butoxyl radical undergoes β-scission at a rate which is too slow for study by our current time-resolved techniques, while many of the other alkoxyl radicals investigated by Walling and co-workers undergo β-scission too rapidly for our techniques.

[29] Avila, D. V.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *114*, 6576–6577.

[30] At 30 °C 1 half-life is ca. 60 min.

[31] Acetonitrile is an extremely unreactive solvent toward "electrophilic" oxygen-centered radicals.[32-35] For example,[32] even at low concentrations the highly reactive[36] (4-methoxybenzoyl)oxyl radical, $4\text{-}CH_3OC_6H_4CO_2^\bullet$, in neat acetonitrile does not attack the solvent ($k \le 1 \times 10^3$ M^{-1} s^{-1} at 24 °C). Instead, this radical decays with second-order kinetics, i.e., by radical/radical coupling.[32] Other highly reactive[36] carbonyloxyl radicals also show little or no reactivity toward acetonitrile.[32-35]

[32] Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 2877–2885.

[33] Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 2886–2893.

[34] Chateauneuf, J.; Lusztyk, J.; Maillard, B.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 6727–6731.

[35] Korth, H. G.; Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Org. Chem.* **1991**, *56*, 2405–2410.

[36] That is, highly reactive toward alkanes, alkenes, and aromatic hydrocarbons.

[37] For five data points per solvent ⟨r⟩ = 0.997, CCl_4; 0.993, C_6H_6; 0.969, C_6H_5Cl; 0.989, $(CH_3)_3COH$; 0.999, CH_3CN; 0.989, CH_3COOH.

Table I. Kinetic Data for Cumyloxyl Radical Reactions in Six Solvents at 30 °C[a,b]

row and eq. no.	kinetic quantity	CCl_4	C_6H_6	C_6H_5Cl	$(CH_3)_3COH$	CH_3CN	CH_3COOH
	product studies						
1, I	$k_a^{CumO}/k_\beta^{CumO}$ (M^{-1}; slope)	**4.5** ± 0.4	**3.2** ± 0.4	**2.0** ± 0.4	**2.3** ± 0.4	**1.9** ± 0.04	**0.69** ± 0.12
2, II	$(k_s^{CumO}[SH]/k_\beta^{CumO})$(intercept)[c]	0.30 ± 0.12	0.32 ± 0.13	0.33 ± 0.18	0.54 ± 0.12	0.16 ± 0.01	−0.24 ± 0.08
	time-resolved studies						
	TRIR						
3, III and IV	$10^{-5}\ k_\beta^{CumO}(+k_s^{CumO}[CH_3CN])$ (s^{-1}; intercept)	2.3 ± 0.2[d]	[e]	[e]	[e]	7.4 ± 1.1[f]	[e]
	TRVis						
4, IV	10^{-5} "k_β^{CumO}" (s^{-1}; k_{exptl}) (308-nm LFP, 0.13 M peroxide)	3.4	4.9	4.1	11.1[g] 5.9[h]	7.5	21.5
5, IV	10^{-5} "k_β^{CumO}" (s^{-1}; k_{exptl}) (266 nm, 2.3×10^{-3} M peroxide)	[i]	[i]	[i]	13.0[g] 7.8[h]	7.6	22.0
6, V	$10^{-6}\ k_a^{CumO}$ ($M^{-1}\ s^{-1}$; slope)	$\mathbf{1.1_8} \pm 0.0_3$[j]	$\mathbf{1.2_2} \pm 0.0_4$[k]	$\mathbf{1.1_2} \pm 0.0_3$	$\mathbf{1.3_4} \pm 0.0_6$	$\mathbf{1.2_1} \pm 0.0_8$	$\mathbf{1.3_5} \pm 0.2_2$
7	$10^{-5}\ k_\beta$ (s^{-1}; row 6/row 1)	$\mathbf{2.6_3} \pm 0.2_4$	$\mathbf{3.7_5} \pm 0.5_3$	$\mathbf{5.5_4} \pm 2.0_0$	$\mathbf{5.8_4} \pm 1.0_6$	$\mathbf{6.3_3} \pm 0.4_3$	$\mathbf{19._6} \pm 3._4$

[a] k_β^{CumO} is the rate constant for β-scission, k_a^{CumO} and k_s^{CumO} are the rate constants for H atom abstraction from cyclohexane and the solvent, respectively, and k_{exptl} is the rate constant measured experimentally. Kinetic data given in bold face are highly reliable. [b] When possible random errors, corresponding to 2σ (95% confidence level), have been calculated from the data. [c] The intercept is expected to be essentially zero for all solvents except $(CH_3)_3COH$ for which we can calculate $k_s^{CumO}[SH]/k_\beta^{CumO} = 5.2 \times 10^5\ s^{-1}/5.8 \times 10^5\ s^{-1} = 0.9$. [d] For comparison we have previously reported[27] that, by TRIR, $k_\beta^{CumO} = (2.2_7 \pm 0.1_3) \times 10^5\ s^{-1}$ at 23 °C in CCl_4. At 0.13 M [peroxide] $k_{exptl} = (2.5 \pm 0.2) \times 10^5\ s^{-1}$ (cf. value in row 4 for CCl_4). [e] Solvent absorbs at 1689 cm^{-1} making kinetic measurements by TRIR impossible. [f] For comparison with the CH_3CN value of $7.5 \times 10^5\ s^{-1}$ given in row 4, the value of k_{exptl} at 0.13 M [peroxide] by TRIR was essentially the same as this extrapolated value of $7.4 \times 10^5\ s^{-1}$. [g] Value of k_{exptl}. [h] Value corrected for H atom abstraction from the solvent (see text). [i] Solvent absorbs at the laser wavelength. [j] For comparison, we have previously reported that by TRIR k_a^{CumO} $(0.95_3 \pm 0.13_5) \times 10^6\ M^{-1}\ s^{-1}$ at 23 °C in CCl_4. [k] For comparison, Scaiano and co-workers[46] using diphenylmethanol as a "probe" to monitor alkoxyl radical decays have reported that, in benzene at 27 °C, $k_a^{CumO} = (2.0_4 \pm 0.7_3) \times 10^6\ M^{-1}\ s^{-1}$ and $k_a^{t\text{-}BuO} = 1.6 \times 10^6\ M^{-1}\ s^{-1}$. This k_a^{CumO} value agrees with ours within the combined experimental errors of both measurements althrough we believe that the present data are probably considerably more reliable.

(0.36–1.65 M peroxide) at 30 °C in a flow system within a calcium fluoride cell.[27] The path lengths in the cell were 2 mm for CCl_4 and 1 mm for CH_3CN, such narrow cells being required in order that the growth of the acetophenone product at 1689 cm^{-1} should not be masked completely by absorptions at this wavelength due to the solvent.[27] Because of these short path lengths the precision of the kinetic data obtained by the TRIR technique is not as high as we would like and the kinetic traces left something to be desired.

Despite the above-mentioned problems, kinetic data for the first-order grow-in of the acetophenone absorption at 1689 cm^{-1} (which are the same under argon or oxygen)[27] were determined at various concentrations of dicumyl peroxide in CCl_4, eq III.

$$k_{exptl} = k_\beta^{CumO} + k_p^{CumO}[\text{peroxide}] \qquad \text{(III)}$$

Extrapolation to zero peroxide concentration yields $k_\beta^{CumO} = (2.3 \pm 0.2) \times 10^5\ s^{-1}$ in this solvent which, of course, contains no hydrogen atoms. However, for cumyloxyl radicals generated in acetonitrile we cannot ignore the possibility that there will be some hydrogen abstraction from the solvent. If this should occur (to any significant extent) then extrapolation of k_{exptl} to zero dicumyl peroxide concentration will yield $k_\beta^{CumO} + k_s^{CumO}[CH_3CN]$ (eq IV) rather than k_β. Fortunately, the $k_s^{CumO}[CH_3CN]$ term in eq

$$(k_{exptl})_{[\text{peroxide}]\to 0} = k_\beta^{CumO} + k_s^{CumO}[CH_3CN] \qquad \text{(IV)}$$

IV is expected to be of negligible importance relative to k_β^{CumO}.[31] In acetonitrile, we can therefore equate the extrapolated value of k_{exptl}, viz. $(7.4 \pm 1.1) \times 10^5\ s^{-1}$, with k_β^{CumO}. Full justification for this action is provided by the good agreement between this directly measured (TRIR) value for k_β^{CumO} and a value of $(6.3_3 \pm 0.4_3) \times 10^5\ s^{-1}$ obtained by combining the results of product experiments in acetonitrile (i.e., the value of $k_a^{CumO}/k_\beta^{CumO}$) with the directly measured (TRVis) value of k_a^{CumO} (vide infra) in acetonitrile.

Determination of k_a^{CumO} by TRIR. Measurements of k_{exptl} for the first-order growth of acetophenone at a fixed peroxide concentration and different cyclohexane concentrations permit the direct measurement of k_a^{CumO} by TRIR. That is

$$k_{exptl} = k_a^{CumO}[c\text{-}C_6H_{12}] + C' \qquad \text{(V)}$$

where $C' = k_\beta^{CumO} + k_s^{CumO}[SH] + k_p^{CumO}[\text{peroxide}]$. Thus, a plot of k_{exptl} vs $[c\text{-}C_6H_{12}]$ yields a straight line with a slope = k_a^{CumO}. We have previously used this procedure to determine k_a^{CumO} in CCl_4 at 23 °C.[27] The value obtained,[27] viz. $(9.53 \pm 1.35) \times 10^5\ M^{-1}\ s^{-1}$, is in excellent agreement with the value of $(11.8 \pm 0.3) \times 10^5\ M^{-1}\ s^{-1}$ found in the present work by TRVis (vide infra). Since the TRVis procedure is experimentally much simpler and more accurate than TRIR we relied in the present work solely on TRVis for obtaining values of k_a^{CumO} in different solvents (vide infra).

Determination of k_β^{CumO} by TRVis. Our discovery[29] that cumyloxyl has an absorption in the visible region has made TRVis monitoring of this species a relatively simple matter. Cumyloxyl radicals were generated by 308-nm LFP of 0.13 M dicumyl peroxide[38] in each of the six solvents used in this study. The experimental (pseudo) first-order rate constant for their decay is given by eq VI. Since we chose solvents which, with the

$$k_{exptl} = \text{“}k_\beta^{CumO}\text{”} = k_\beta^{CumO} + k_s^{CumO}[SH] + k_p^{CumO}[\text{peroxide}] \qquad \text{(VI)}$$

exception of 2-methyl-2-propanol, were expected to be relatively unreactive toward cumyloxyl and since the $k_p^{CumO}[\text{peroxide}]$ term should be negligible with respect to k_β^{CumO} at a peroxide concentration of 0.13 M,[39] we can expect that the value of k_{exptl} should be similar to, or perhaps slightly larger than, the value of k_β^{CumO} obtained by combining $k_a^{CumO}/k_\beta^{CumO}$ values from product studies with k_a^{CumO} values from the TRVis measurements. The agreement between these two methods of measuring k_β^{CumO} is gratifying in all solvents except 2-methyl-2-propanol (see Table I). The k_β^{CumO} values calculated from $k_a^{CumO}/k_\beta^{CumO}$ and k_a^{CumO} will be the most accurate since they do not contain the "hidden" terms due to

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(38) This peroxide concentration is chosen to give an OD of ca. 0.3 in a 7-mm path-length cell at the laser wavelength.

(39) We have previously[27] attempted to measure $k_p^{CumO}[\text{peroxide}]$ by TRIR. The value obtained at 23 °C in CCl_4 for k_p^{CumO} was $(1.94 \pm 0.62) \times 10^5\ M^{-1}\ s^{-1}$ which at 0.13 M peroxide would imply a contribution to k_{exptl} of $2.5 \times 10^4\ s^{-1}$. However, this value of k_p^{CumO} is almost certainly an overestimate. At 37 °C on a perhydrogen basis, the hydrogen atoms on an unactivated methyl group are 5.38 ± 0.33% as reactive toward *tert*-butoxyl radicals as are the hydrogen atoms of cyclohexane.[40] If we now make the reasonable assumptions that this difference in selectivity will be little changed for hydrogen abstraction by cumyloxyl radicals at 37 °C we can calculate (on the basis that $k_a^{CumO} \approx 1.2 \times 10^6\ M^{-1}\ s^{-1}$ for cyclohexane, see Table I) that for dicumyl peroxide (12 primary H atoms) k_p^{CumO} is only ca. $6.5 \times 10^4\ M^{-1}\ s^{-1}$ (i.e., k^{CumO}/primary H = $5.4 \times 10^3\ M^{-1}\ s^{-1}$). That is, for 0.13 M peroxide the likely contribution of the $k_p^{CumO}[\text{peroxide}]$ term to k_β is only ca. $8.4 \times 10^3\ s^{-1}$. (Apparently, the well-documented[41,42] abstraction of the hydroxylic hydrogen atom is of no significance in the cumyloxyl + 2-methyl-2-propanol reaction.)

(40) Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *111*, 5687–5698.

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

(42) Elson, I. H.; Kochi, J. K. *J. Org. Chem.* **1974**, *39*, 2091–2096.

cumyloxyl radical attack on solvent, k_s^{CumO}[SH], and peroxide, k_p^{CumO}[peroxide]. In the case of 2-methyl-2-propanol as solvent the k_s^{CumO}[SH] term cannot be neglected, i.e., product and TRVis measurements gave $k_\beta^{\mathrm{CumO}} = (5.8 \pm 1.1) \times 10^5$ s^{-1}, whereas 308-nm (0,13 M peroxide) TRVis measurements gave k_{exptl} = "k_β^{CumO}" $= k_\beta^{\mathrm{CumO}} + k_s^{\mathrm{CumO}}[\mathrm{SH}] + k_p^{\mathrm{CumO}}[\mathrm{peroxide}] = 11.1 \times 10^5$ s^{-1}. Taking k^{CumO}/primary H = 5.4×10^3 M^{-1} s^{-1},[39] the k_s^{CumO}[SH] term in neat 2-methyl-2-propanol (10.64 M) can be calculated to be 5.2×10^5 s^{-1} (the contribution from attack on the peroxide being essentially negligible, i.e., only ca. 0.1×10^5 s^{-1}).[39] Correction of "k_β^{CumO}" for attack on 2-methyl-2-propanol yields $k_\beta^{\mathrm{CumO}} = (11.1 - 5.2) \times 10^5$ s^{-1} $= 5.9 \times 10^5$ s^{-1}, a value in truly excellent agreement with the $k_a^{\mathrm{CumO}}/k_\beta^{\mathrm{CumO}}$ and k_a^{CumO} derived value for k_β^{CumO} of 5.8×10^5 s^{-1}. For the other solvents, the differences between k_β^{CumO} and "k_β^{CumO}" (308 nm, 0.13 M peroxide) are probably not larger than the experimental errors (though there may be a hint of a very small degree of cumyloxyl radical loss by hydrogen abstraction from CH_3CN and CH_3COOH; see Table I).

Three of the solvents used, $(CH_3)_3COH$, CH_3CN, and CH_3COOH, permitted 266-nm LFP of 2.3×10^{-3} M peroxide[38] because they do not themselves absorb appreciably at this wavelength. A peroxide concentration of 2.3×10^{-3} M truly makes the k_p^{CumO}[peroxide] term in "k_β^{CumO}" negligible. Experimental rate constants for decay of the cumyloxyl radical were monitored directly at 485 nm and at 320 nm (at which wavelength the acetophenone "grow-in" product also absorbs but this fact does not, of course, effect k_{exptl})[43] and indirectly by monitoring the "grow-in" of acetophenone at 275 nm. These three measurements of k_{exptl} were essentially identical—as they should be. The corresponding values for "k_β^{CumO}" are listed in Table I, together with the corrected value in 2-methyl-2-propanol.

Determination of k_a^{CumO} by TRVis. Cumyloxyl radicals were generated in the six solvents by 308-nm LFP of 0.13 M peroxide in the presence of a range of concentrations of cyclohexane sufficient to change k_{exptl} (monitored at 485 nm) by a factor of 5 or more. Excellent plots of k_{exptl} vs [c-C_6H_{12}] ($\langle r \rangle \geq 0.99$ for five solvents, 0.98 for CH_3COOH) were obtained, and k_a^{CumO} values were calculated from their slopes (see eq V). These values should be very reliable.[45] As can be seen in Table I the magnitude of k_a^{CumO} is solvent independent within the accuracy of our experiments.

Discussion

The most highly reliable kinetic data summarized in Table I are given in bold-face type. These results clearly demonstrate that k_a^{CumO} is solvent independent within our experimental accuracy of ca. ±10%, i.e., for cyclohexane at 30 °C, $k_a^{\mathrm{CumO}} = (1.2 \pm 0.1) \times 10^6$ M^{-1} s^{-1}. They also demonstrate that k_β^{CumO} increases with an increase in solvent "polarity". We have therefore completely confirmed Walling's suggestion that the decrease in k_a/k_β (for *tert*-butoxyl and other alkoxyl radicals) with increasing solvent polarity is due to an increase in k_β and that any changes in k_a are of only very minor significance.[47] The increase in k_β with the increase in solvent polarity is, of course, attributable to the increase in stabilization of the transition state for β-scission via increased solvation of the incipient acetophenone product. The solvation energies of ketones are known to increase with increasing polarity of the solvent.[48]

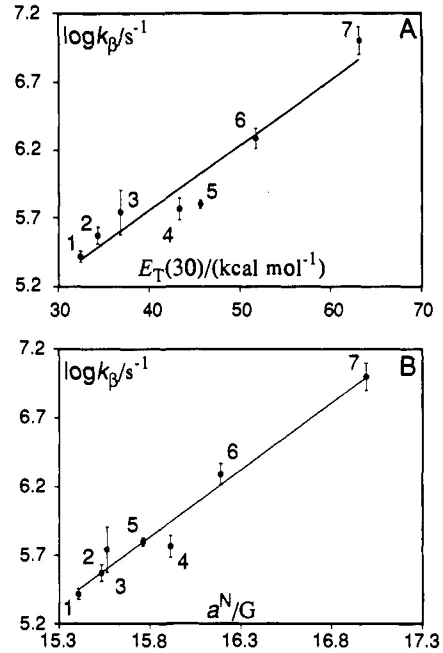
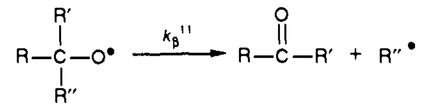


Figure 1. (A) Correlation of log (k_β^{CumO}/s^{-1}) with E_T (30) (kcal/mol) and (B) with a^N (G) for the 4-amino-2,2,6,6-tetramethylpiperidinyl-*N*-oxyl radical in carbon tetrachloride (1), benzene (2), chlorobenzene (3), 2-methyl-2-propanol (4), acetonitrile (5), acetic acid (6), and water (7). Points 1–6 are from present work, point 7 is taken from ref 24a. Error bars for log (k_β/s^{-1}) correspond to two standard deviations.

We presume that our experimental observations will also apply to other alkoxyl radicals. That is, for the generalized reaction 11 not only with k_β^{11} increase with increasing solvent polarity,

 (11)

$$\mathrm{RC(R')(R'')O^\bullet} \xrightarrow{k_\beta^{11}} \mathrm{R{-}C({=}O){-}R'} + \mathrm{R''^\bullet} \tag{11}$$

but also the magnitude of this increase will become greater along the series RCOR′ = $C_6H_5COCH_3 < CH_3COCH_3 < CH_3CHO < H_2CO$ because the strength of the solvation of the carbonyl group by a polar solvent will increase on going from $C_6H_5COCH_3$ to H_2CO.[49] For alkoxyl radical hydrogen atom abstraction from alkanes (and from other substrates which are not, themselves, solvated to a significantly greater extent in polar relative to nonpolar solvents) we expect the abstraction rate constants to be essentially solvent independent. Of course, this rule will not hold if the substrate itself is strongly solvated by certain solvents, e.g., it has been shown that hydrogen abstraction by *tert*-butoxyl from phenols in pyridine and in alcohols is very much slower than in benzene or toluene.[50]

As we have indicated above, the most reliable kinetic data are given in bold-face type in Table I. These data were all obtained from slopes rather than from intercepts. Nevertheless, wherever comparison is possible there is a very gratifying agreement between the k_β^{CumO} values given in row 7 and the (less reliable) intercept-derived values given in rows 3–5 (after correction in the case of 2-methyl-2-propanol for attack of cumyloxyl on the solvent). This "overdetermination" of the kinetic data reinforces our faith in their reliability.

In any analysis of solvent effects on chemical reactions it is customary to seek a linear relation between a solvent parameter and the logarithm of the rate constant for reaction, i.e., a "linear

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[43] The decay of reactant and grow-in of product optical traces will yield the same value for k_{exptl} whenever the reactant is converted to product by a first- or pseudo-first-order process. Monitoring the reaction at a wavelength where the reactant and product both absorb (other than at an isobestic point) obviously will not change the magnitude of k_{exptl}.[44]

[44] See, e.g.: Encinas, M. V.; Wagner, P. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 1357–1360.

[45] Essentially identical values for k_a^{CumO} were obtained in 2-methyl-2-propanol, acetonitrile, and acetic acid using 266 nm LFP of 2.3×10^{-3} M peroxide.

[46] Baignee, A.; Howard, J. A.; Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 6120–6123.

[47] Hats off to Cheves Walling!

[48] See, for example: Haberfield, P. *J. Am. Chem. Soc.* **1974**, *105*, 6526–6527. Ramos, J. J. M.; Reisse, J.; Stien, M.-L. *Chem. Phys. Lett.* **1976**, *42*, 373–375.

[49] There is good evidence that the solvent effects for the $C_6H_5CH_2CH_2O^\bullet \rightarrow CH_2O + C_6H_5CH_2^\bullet$ reaction found by Mendenhall et al.[24] are considerably greater than those found in the present work for $C_6H_5C(CH_3)_2O^\bullet \rightarrow C_6H_5COCH_3 + CH_3^\bullet$.

[50] Das, P. K.; Encinas, M. V.; Steenken, S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4162–4166.

free energy" relationship.[51,52] The extent and strength of solvation of the transition state for the β-scission of an alkoxyl radical clearly requires a solvent parameter which probes the cybotactic region of the solvent, i.e., probes the volume around an alkoxyl radical in which the order of the solvent molecules has been affected by the radical.[51-55] The cybotactic solvent parameter most commonly employed is the Dimroth–Reichardt $E_T(30)$ value,[51,56] and indeed, this does correlate reasonably well ($\langle r \rangle = 0.965$) with log ($k_\beta{}^{\mathrm{CumO}}/\mathrm{s}^{-1}$), see Figure 1a. As we have found previously for a quite different reaction[52,57] there is a slightly better correlation ($\langle r \rangle = 0.983$) between log ($k_\beta{}^{\mathrm{CumO}}/\mathrm{s}^{-1}$) and the nitrogen hyperfine splittings, a^{N}, for the 4-amino-2,2,6,6-tetramethylpiperdinyl-*N*-oxyl radical,[54] see Figure 1b. We suggest that, as a cybotactic probe, the nitroxide moiety is a not unreasonable model for an incipient carbonyl group, i.e.

While the correlation of log ($k_\beta{}^{\mathrm{CumO}}/\mathrm{s}^{-1}$) with a^{N} could possibly be improved by using the hyperfine splittings for a sterically nonprotected nitroxide or by adding an "appropriate" second parameter (such as the solvent's cohesive pressure)[51,52] such "cosmetic" changes appear unnecessary. That is, both correlations shown in Figure 1 imply that solvent effects on $k_\beta{}^{\mathrm{CumO}}$ are due to a localized interaction between the transition state for β-scission and the adjacent solvent molecules. In particular, it would seem very probable that there is nothing "special" about the high value of $k_\beta{}^{\mathrm{CumO}}$ in acetic acid;[58] i.e., there is nothing that is unique to β-scission.

Experimental Section

Materials. All solvents were of high purity and commercially available: acetonitrile (OmniSolve), carbon tetrachloride (OmniSolve), chlorobenzene (BDH), benzene (Aldrich), 2-methyl-2-propanol (Fisher Scientific), and acetic acid (Anachemica). They were used as received since experiments demonstrated that further purification had no measurable effects upon the kinetics. Di-α-cumyl peroxide (Aldrich) was recrystallized three times from methanol. Acetophenone (Aldrich) and 2-phenyl-2-propanol (Aldrich) were used as received.

Di-α-cumyl hyponitrite was prepared by the method of Dulog and Klein,[61] mp 75.5–76.5 °C (lit.[61] mp 75 °C); δ_{H} (200 MHz; $CDCl_3$) 1.58 (12 H, s), 7.06–7.90 (10 H, m).

Yields of acetophenone and 2-phenyl-2-propanol from the decomposition of dicumyl hyponitrite were determined by gas chromatography using a Hewlett-Packard 5890 with a 12-m × 0.02-mm (i.d.) OV-101 column.

The time-resolved infrared spectrometer has been described in detail elsewhere.[62,63]

Acknowledgment. We thank Dr. L. J. Johnston for her friendly advice on the TRVis experiments.

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(51) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, Verlag Chimie: Weinheim, Germany, 1988.

(52) Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4983–4996.

(53) Partington, J. R. *An Advanced Treatise on Physical Chemistry*; Longmans, Green and Co.: London, 1951; Vol. 2, p 2ff; Vol. 5, p 390ff.

(54) Knauer, B. R.; Napier, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 4395–4400.

(55) The dielectric constant, for example, is not a probe of the cybotactic region because it is a macroscopic property of the bulk solvent.

(56) Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, F. *Liebigs Ann. Chem.* **1963**, *661*, 1–37.

(57) The reactions investigated[52] were the trapping of carbon-centered radicals by nitroxides.

(58) For example, the protonation of alkoxyl radicals has been reported to accelerate β-scission.[59,60]

(59) Cookson, P. G.; Davies, A. G.; Roberts, B. P.; Tse, M.-W. *J. Chem. Soc., Chem. Commun.* **1976**, 937–938.

(60) Gilbert, G. C.; Marshall, P. D. R.; Norman, R. O. C.; Pineda, N.; Williams, P. S. *J. Chem. Soc. Perkin Trans. 2* **1981**, 1392–1400.

(61) Dulog, L.; Klein, P. *Chem. Ber.* **1971**, *104*, 895–901.

(62) Rayner, D. M.; Nazran, A. Z.; Drouin, M.; Hackett, P. A. *J. Phys. Chem.* **1986**, *90*, 2822–2888.

(63) Ishikawa, Y.; Hackett, P. A.; Rayner, D. M. *J. Phys. Chem.* **1988**, *92*, 3863–3869.

Experimental Evidence for Ethylidene-d_4

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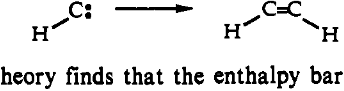
Abstract: Laser flash photolysis (LFP, 351 nm, XeF excimer) of 3-methyldiazirine in the presence and absence of pyridine fails to produce a UV–vis active transient intermediate. However, LFP of 3-methyldiazirine-d_4 in pentane containing pyridine produces a transient absorption attributed to the ethylidene-d_4-pyridine ylide. A double-reciprocal plot of the optical yield of ylide ($A_y{}^{-1}$) versus (pyridine concentration)$^{-1}$ is linear and indicates that the lifetime of ethylidene-d_4 is 500 ps in pentane, assuming that the second-order rate constant of reaction of ethylidene-d_4 with pyridine is 1×10^9 M^{-1} s^{-1}. Laser induced fluorescence spectra of methyldiazirine and methyldiazirine-d_4 are reported and discussed.

I. Introduction

The rearrangement of ethylidene to ethylene is a prototypical carbene process.[1] The simplicity of this reaction has invited numerous theoretical studies, which have recently been tabulated by Houk and Evanseck.[2] Schaefer and Gallo[3] have calculated that ethylidene, like methylene, has a triplet ground state, but that singlet ethylidene is only 5 ± 1 kcal/mol above the ground state.



High-level theory finds that the enthalpy barrier to the exceedingly exothermic rearrangement of ethylidene in its lowest singlet state is either small or 0.[2] The most recent ab initio

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(1) For reviews, see: Baron, W. J.; DeCamp, M. R.; Hendrick, M. E.; Jones, M., Jr.; Levin, R. H.; Sohn, M. B. In *Carbenes*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1973; Vol. I, pp 2–19.

(2) Evanseck, J. D.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 9148. Evanseck, J. D.; Houk, K. N. *J. Phys. Chem.* **1990**, *94*, 5518.

(3) Gallo, M. M.; Schaefer, H. F., III. *J. Phys. Chem.* **1992**, *96*, 1551.