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Kinetic Solvent Effects on Hydrogen Abstraction Reactions from Carbon by the Cumyloxyl Radical. The Importance of Solvent Hydrogen-Bond Interactions with the Substrate and the Abstracting Radical

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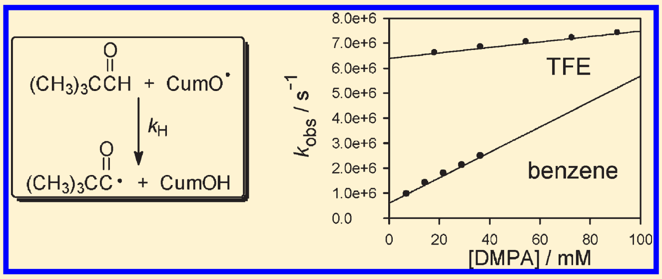
S *Supporting Information*

ABSTRACT: A kinetic study of the hydrogen atom abstraction reactions from propanal (PA) and 2,2-dimethylpropanal (DMPA) by the cumyloxyl radical (CumO$^•$) has been carried out in different solvents (benzene, PhCl, MeCN, *t*-BuOH, MeOH, and TFE). The corresponding reactions of the benzyloxyl radical (BnO$^•$) have been studied in MeCN. The reaction of CumO$^•$ with 1,4-cyclohexadiene (CHD) also has been investigated in TFE solution. With CHD a 3-fold increase in rate constant (k_H) has been observed on going from benzene, PhCl, and MeCN to TFE. This represents the first observation of a sizable kinetic solvent effect for hydrogen atom abstraction reactions from hydrocarbons by alkoxyl radicals and indicates that strong HBD solvents influence the hydrogen abstraction reactivity of CumO$^•$. With PA and DMPA a significant decrease in k_H has been observed on going from benzene and PhCl to MeOH and TFE, indicative of hydrogen-bond interactions between the carbonyl lone pair and the solvent in the transition state. The similar k_H values observed for the reactions of the aldehydes in MeOH and TFE point toward differential hydrogen bond interactions of the latter solvent with the substrate and the radical in the transition state. The small reactivity ratios observed for the reactions of CumO$^•$ and BnO$^•$ with PA and DMPA ($k_H(BnO^•)/k_H(CumO^•)$ = 1.2 and 1.6, respectively) indicate that with these substrates alkoxyl radical sterics play a minor role.



INTRODUCTION

Hydrogen atom abstraction by alkoxyl radicals has attracted considerable interest as these reactions play a key role in a variety of important chemical and biological processes such as the oxidative damage to biomolecules and polymers,[1−8] the radical scavenging activity of natural and synthetic antioxidants,[9−11] and the degradation of volatile organic compounds in the atmosphere.[12]

One aspect that has received particular attention is the study of solvent effects on these reactions.[9,13−20] For example, Ingold and co-workers observed dramatic kinetic solvent effects (KSEs) for hydrogen atom abstractions from phenols by alkoxyl radicals,[9,13] where a decrease in rate constant (k_H) was observed with increasing the solvent hydrogen bond acceptor (HBA) ability, and good correlations were obtained between log k_H and the solvent HBA parameter β_2^H.[21] This effect was explained on the basis of a hydrogen bond interaction between the phenolic OH group and the solvent. Accordingly, in relatively strong HBA solvents the substrate must experience desolvation in order to undergo hydrogen atom abstraction, and consequently, a decrease in reactivity is observed as compared to weaker or non-HBA solvents.

On the other hand, when dealing with C−H bonds it is generally assumed that abstractions by alkoxyl radicals display negligible KSEs. With substrates that are not solvated to a significantly greater extent in polar relative to nonpolar solvents (e.g., cyclohexane and 1,4-cyclohexadiene), this behavior has been explained on the basis of the lack of solvent effects on the reactivity of the abstracting alkoxyl radical.[19,20] In this context, we have recently observed very similar rate constants for hydrogen abstraction (k_H) from 1,4-cyclohexadiene (CHD) by the cumyloxyl radical (CumO$^•$) when the reaction was studied in MeCN, benzene, or chlorobenzene.[16] However, a small (∼20%) and reproducible increase in k_H was observed when the same reaction was studied in MeOH and *t*-BuOH, suggesting that in these solvents hydrogen-bond interactions with the alkoxyl radical may play a role.

With substrates that bear polar groups in proximity of the abstractable hydrogen atom such as triethylamine (TEA), we have recently observed a 7-fold decrease in rate constant for α-C−H abstraction by CumO$^•$ on going from apolar solvents (benzene, chlorobenzene) to MeOH.[16] This behavior has been explained in terms of a hydrogen-bond interaction between the nitrogen lone pair and the solvent. This interaction results in

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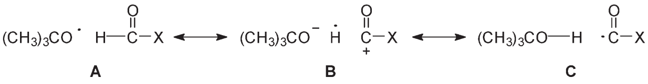
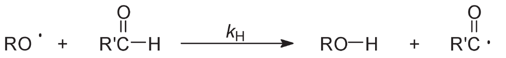
Scheme 1



a decrease in the degree of overlap between the α-C−H bond and the nitrogen lone pair in the transition state for hydrogen atom abstraction, thus lowering the reactivity. To our knowledge, this represents the largest KSE observed for hydrogen atom abstraction from carbon by an alkoxyl radical.

Aldehydes are known to react efficiently with alkoxyl radicals via hydrogen atom abstraction from the carbonyl C−H bond to give acyl radicals (eq 1).[23−28]

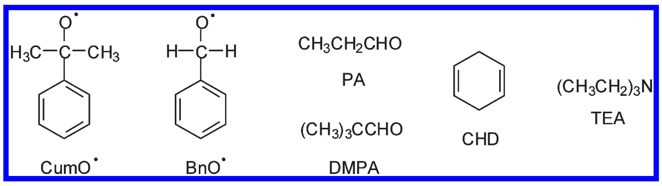
 (1)

$$RO^{\bullet} + R'C(=O)-H \xrightarrow{k_H} RO-H + R'C^{\bullet}(=O) \qquad (1)$$

Second-order rate constants (k_H) between 10^7 and 10^8 M^{-1} s^{-1} have been measured for the reaction of aromatic and aliphatic aldehydes with the *tert*-butoxyl radical (*t*-BuO$^\bullet$).[26] In this study, comparable rate constants have been measured for propanal and benzaldehyde (k_H = 8.9 × 10^7 and 6.8 × 10^7 M^{-1} s^{-1}, respectively), whereas a significant decrease in rate constant has been observed when the alkyl or aryl group has been replaced by an electron-withdrawing substituent such as dimethylamino in *N*,*N*-dimethylformamide and ethoxy in ethyl formate. The observed reduction in rate constant has been explained in terms of the greater contribution of the polar structure (Scheme 1, structure **B**) to the transition state for hydrogen atom abstraction from XCHO by *t*-BuO$^\bullet$ for benzaldehyde and propanal (X = Ph and Et, respectively) as compared to *N*,*N*-dimethylformamide and ethyl formate (X = NMe_2 and OEt, respectively).[26]

Quite interestingly, this explanation points toward a relatively polar transition state for hydrogen atom abstraction from aldehydes and suggests in particular that these reactions may experience sizable KSEs.

Along this line, in order to probe this issue and to provide a deeper and more general understanding of the role of solvent effects on hydrogen atom abstraction reactions from carbon by alkoxyl radicals, we have carried out a detailed time-resolved kinetic study in different solvents (benzene, chlorobenzene (PhCl), acetonitrile (MeCN), 2-methyl-2-propanol (*t*-BuOH), methanol (MeOH), and 2,2,2-trifluoroethanol (TFE)) for the reactions of CumO$^\bullet$ with propanal (PA) and 2,2-dimethylpropanal (DMPA), whose structures are displayed below.



The results obtained are discussed and compared with those previously obtained for the corresponding reactions of CumO$^\bullet$ with 1,4-cyclohexadiene (CHD) and triethylamine (TEA),[16] where however, with the former substrate, in order to probe the possible role of hydrogen bond interactions between the solvent and the alkoxyl radical, the rate constant for reaction in TFE has also been measured. In order to gain information on the role of alkoxyl radical structure on these processes, the rate constants for hydrogen abstraction from PA and DMPA by the benzyloxyl radical (BnO$^\bullet$) have also been determined, limited, however, to MeCN solvent.[29]

RESULTS

The reactions of CumO$^\bullet$ and BnO$^\bullet$ with the substrates shown above have been studied using the laser flash photolysis (LFP) technique. CumO$^\bullet$ and BnO$^\bullet$ have been generated by 266 nm LFP of nitrogen-saturated MeCN and, for the former radical, TFE solutions (T = 25 °C) containing dicumyl and dibenzyl peroxide, respectively (eq 2). CumO$^\bullet$ has been also generated by 355 nm LFP of nitrogen-saturated MeCN, benzene, PhCl, *t*-BuOH, and MeOH solutions (T = 25 °C) containing dicumyl peroxide (eq 2).

$$RO-OR \xrightarrow{h\nu} 2\ RO^{\bullet} \qquad (2)$$

R = $PhC(CH_3)_2$
$PhCH_2$

In MeCN solution, CumO$^\bullet$ is characterized by a broad absorption band in the visible region of the spectrum centered at 485 nm,[31,32] whose position is red-shifted in MeOH and TFE (λ_{max} = 500[33] and 515 nm,[34] respectively). For BnO$^\bullet$ λ_{max} = 460 nm in acetonitrile.[31,35] Under these conditions, CumO$^\bullet$ decays mainly by C−CH_3 β-scission,[20,32] with the exception of the experiments carried out in MeOH solution where hydrogen atom abstraction from the solvent is instead the predominant reaction.[33] The decay of BnO$^\bullet$ can be mainly attributed to hydrogen atom abstraction from the solvent.[30]

The time-resolved spectra observed after reaction of CumO$^\bullet$ with DMPA in MeCN solution are reported in the Supporting Information (Figure S2).

The reactions of CumO$^\bullet$ and BnO$^\bullet$ with PA and DMPA have been studied by LFP. As mentioned above, it is well-established that these reactions proceed by hydrogen atom abstraction from the carbonyl C−H bond by the alkoxyl radical, as described in eq 1.[23−28]

The kinetic studies have been carried out by LFP following the decay of the CumO$^\bullet$ and BnO$^\bullet$ visible absorption bands at 490−515 and 460 nm, respectively, as a function of the aldehyde concentration. The observed rate constants (k_{obs}) gave excellent linear relationships when plotted against substrate concentration and provided the second-order rate constants for hydrogen atom abstraction from the substrates by CumO$^\bullet$ and BnO$^\bullet$ (k_H) from the slopes of these plots. As an example, the plots of k_{obs} vs [DMPA] and of k_{obs} vs [CHD] for the reactions between CumO$^\bullet$ and both DMPA (filled circles) and CHD (empty circles) carried out in benzene (a) and TFE (b) solution are shown in Figure 1. In these plots, the 1 order of magnitude increase in the intercept value observed on going from benzene to TFE reflects the significantly faster β-scission reaction of CumO$^\bullet$ in the latter solvent as compared to the former one.[20,32,34] Additional plots for hydrogen atom abstraction by CumO$^\bullet$ and BnO$^\bullet$ from the two aldehydes in the different solvents are displayed in the Supporting Information (Figures S3−S16). All the kinetic data thus obtained for the reactions of CumO$^\bullet$ are collected in Table 1. The hydrogen atom abstraction reactivity of CumO$^\bullet$ and BnO$^\bullet$ in MeCN solution is compared in Table 2, where the $k_H(BnO^\bullet)/k_H(CumO^\bullet)$ ratios are also displayed. Also included in the two Tables are the rate constants obtained previously under analogous experimental

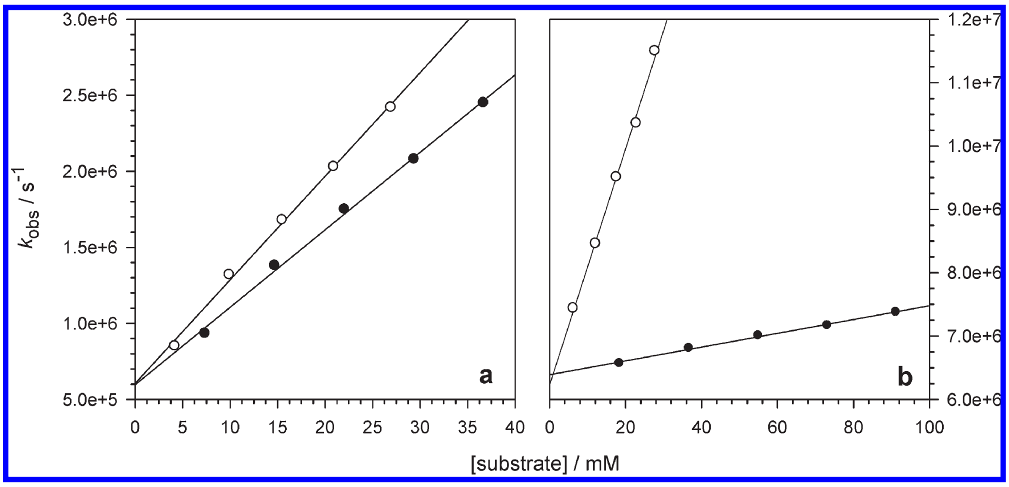


Figure 1. Plots of the observed rate constant (k_{obs}) against [substrate] for the reactions of the cumyloxyl radical (CumO$^\bullet$) with 2,2-dimethylpropanal (filled circles) and 1,4-cyclohexadiene (empty circles), measured in nitrogen-saturated benzene (a) and TFE (b) solutions at T = 25 °C, following the decay of CumO$^\bullet$ at 490 and 515 nm. From the linear regression analysis: (a) CumO$^\bullet$ + DMPA in benzene: intercept = 5.97 × 10^5 s^{-1}, k_H = 5.09 × 10^7 M^{-1} s^{-1}, r^2 = 0.9972; CumO$^\bullet$ + CHD in benzene: intercept = 6.05 × 10^5 s^{-1}, k_H = 6.81 × 10^7 M^{-1} s^{-1}, r^2 = 0.9974. (b) CumO$^\bullet$ + DMPA in TFE: intercept = 6.39 × 10^6 s^{-1}, k_H = 1.09 × 10^7 M^{-1} s^{-1}, r^2 = 0.9960; CumO$^\bullet$ + CHD in TFE: intercept =6.23 × 10^6 s^{-1}, k_H = 1.86 × 10^8 M^{-1} s^{-1}, r^2 = 0.9972.

Table 1. Second-Order Rate Constants (k_H) for Reaction of the Cumyloxyl (CumO$^\bullet$) Radical with Hydrogen Atom Donors Measured in Different Solvents at T = 25 °C.[a]

		k_H/M^{-1} s^{-1} [c]			
solvent	λ_{ex} [b] (nm)	PA	DMPA	CHD	TEA
benzene	355	(4.27 ± 0.07) × 10^7	(5.0 ± 0.3) × 10^7	(6.79 ± 0.02) × 10^7 [d]	(2.8 ± 0.1) × 10^8 [d]
PhCl	355	(4.89 ± 0.02) × 10^7	(4.47 ± 0.02) × 10^7	(6.90 ± 0.05) × 10^7 [d]	(2.7 ± 0.1) × 10^8 [d]
MeCN	266	(1.76 ± 0.02) × 10^7	(2.33 ± 0.07) × 10^7	(6.65 ± 0.02) × 10^7 [d]	(2.0 ± 0.1) × 10^8 [d]
	355	(2.23 ± 0.05) × 10^7	(2.69 ± 0.05) × 10^7	(6.56 ± 0.01) × 10^7 [d]	(2.19 ± 0.05) × 10^8 [d]
t-BuOH	355	(3.58 ± 0.02) × 10^7	(3.7 ± 0.2) × 10^7	(8.3 ± 0.1) × 10^7 [d]	(1.61 ± 0.03) × 10^8 [d]
MeOH	355	(9.55 ± 0.03) × 10^6	(1.7 ± 0.1) × 10^7	(8.25 ± 0.03) × 10^7 [d]	(3.8 ± 0.1) × 10^7 [d]
TFE	266	(9.3 ± 0.3) × 10^6	(1.04 ± 0.05) × 10^7	(1.89 ± 0.03) × 10^8	

[a] 266 nm LFP, N_2-saturated, [dicumyl peroxide] = 10 mM. 355 nm LFP, N_2-saturated, [dicumyl peroxide] = 0.7−1.0 M. [b] Laser excitation wavelength. [c] Determined from the slope of the k_{obs} vs [substrate] plots, where in turn k_{obs} values have been measured following the decay of the CumO$^\bullet$ visible absorption band at 490−515 nm. Average of at least two determinations. [d] Reference 16.

Table 2. Second-Order Rate Constants (k_H) for Reaction of the Cumyloxyl (CumO$^\bullet$) and Benzyloxyl (BnO$^\bullet$) Radicals with Hydrogen Atom Donors Measured in MeCN at T = 25 °C[a]

	k_H/M^{-1} s^{-1} [b]		
substrate	CumO$^\bullet$	BnO$^\bullet$	k_H(BnO$^\bullet$)/ k_H(CumO$^\bullet$)
PA	(1.76 ± 0.05) × 10^7	(2.19 ± 0.02) × 10^7	1.2
DMPA	(2.33 ± 0.07) × 10^7	(3.76 ± 0.06) × 10^7	1.6
CHD	(6.65 ± 0.02) × 10^7 [c]	(1.29 ± 0.02) × 10^8 [d]	1.9
TEA	(2.0 ± 0.1) × 10^8 [c]	(4.3 ± 0.1) × 10^9 [d]	21.5

[a] 266 nm LFP, N_2-saturated, [dicumyl peroxide] = 10 mM, [dibenzyl peroxide] = 8 mM. [b] Determined from the slope of the k_{obs} vs [substrate] plots, where in turn k_{obs} values have been measured following the decay of the CumO$^\bullet$ or BnO$^\bullet$ visible absorption band at 490 and 460 nm, respectively. Average of at least two determinations. [c] Reference 16. [d] Reference 35.

conditions for the reactions of CumO$^\bullet$ and BnO$^\bullet$ with CHD and TEA.[16,35]

■ DISCUSSION

A first and very important observation is represented by the 3-fold increase in reactivity measured for the reaction between CumO$^\bullet$ and CHD on going from benzene, PhCl, and MeCN to TFE (Table 1). This represents the first observation of a sizable KSE for hydrogen atom abstraction reactions from hydrocarbons by alkoxyl radicals and clearly indicates that strong hydrogen bond donor (HBD) solvents can influence the reactivity of alkoxyl radicals in these processes, in contrast with the results of previous studies, that were, however, limited to weaker HBD or non-HBD solvents.[13,19,20,36] In the transition state of the CumO$^\bullet$ + CHD reaction, electron density is moved toward the oxygen of the alkoxyl radical, leading to a certain degree of charge separation with the development of a partial negative charge on the oxygen atom and a partial positive charge on the incipient carbon centered radical (Scheme 2, X = PhC(CH$_3$)$_2$, where, for the sake of simplicity, CHD is represented as R−H).

TFE can engage in hydrogen bonding with a CumO$^\bullet$ oxygen lone pair, and, on approaching the transition state, as a partial negative charge develops on the oxygen atom the strength of the hydrogen bond interaction increases.[38] This interaction results in a greater extent of stabilization for the transition state as compared to the reactants and in a corresponding increase in hydrogen atom abstraction reactivity as compared to weaker or non-HBD solvents. The slight increase in reactivity observed on going from benzene, PhCl, and MeCN to MeOH and *t*-BuOH[16] can be explained analogously in terms of a hydrogen-bond interaction between the radical and the protic solvent, where the significantly larger increase in k_H observed on going from the former solvents to TFE is in line with the greater HBD ability of TFE as compared to MeOH and *t*-BuOH.[37,40,41]

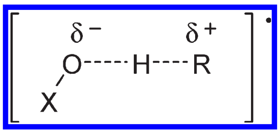
A similar explanation in terms of the importance of polar contributions to the transition state for hydrogen atom abstraction has been recently put forward by Tanko and co-workers to account for the increase in reactivity observed for hydrogen atom abstraction reactions from hydrocarbons (R−H) by the hydroxyl radical ($^\bullet$OH) on going from MeCN to MeCN/H_2O 9:1 (Scheme 2, X = H).[42] As compared to MeCN, the presence of H_2O, that can engage in hydrogen bonding with the oxygen atom of $^\bullet$OH, leads to a stabilization of the transition state and to a corresponding increase in reactivity. Taken together, this mechanistic picture provides a rationale for the KSEs observed on going from apolar solvents to strong HBD solvents for hydrogen atom abstraction reactions from hydrocarbons by both alkoxyl and hydroxyl radicals.

An implication of these findings is that when studying KSEs on hydrogen atom abstraction reactions by oxygen-centered radicals, in addition to solvent/substrate interactions, solvent/radical interactions should also be considered whenever strong HBD solvents are employed (see below).

The k_H value measured for hydrogen atom abstraction from PA by CumO$^\bullet$ in benzene solution is in reasonable agreement with the one measured previously in benzene/di-*tert*-butyl peroxide 1:2, for the corresponding reaction of *t*-BuO$^\bullet$.[26] With both PA and DMPA, a slight decrease in k_H has been observed in MeCN on going from 355 to 266 nm LFP for CumO$^\bullet$ generation. As mentioned previously,[43] these differences can be attributed to variations in solution composition (and polarity) determined by the significantly higher concentration of dicumyl peroxide employed in the 355 nm LFP experiments as compared to the 266 nm LFP ones ([dicumyl peroxide] = 1.0 and 0.01 M, respectively).

The data displayed in Table 1 show that in C−H abstraction reactions from the formyl group by CumO$^\bullet$ a slight increase in reactivity is generally observed on going from PA to DMPA. As pointed out previously,[26] the rate constant for hydrogen atom abstraction reactions from aldehydes and formyl derivatives XCHO by alkoxyl radicals is influenced by the nature of the X group, decreasing by increasing the electron-withdrawing character of X. Along this line, the observed differences in reactivity between PA and DMPA can be explained in terms of the slightly higher electron-releasing effect of a *tert*-butyl group as compared to an ethyl group.[44]

Scheme 2



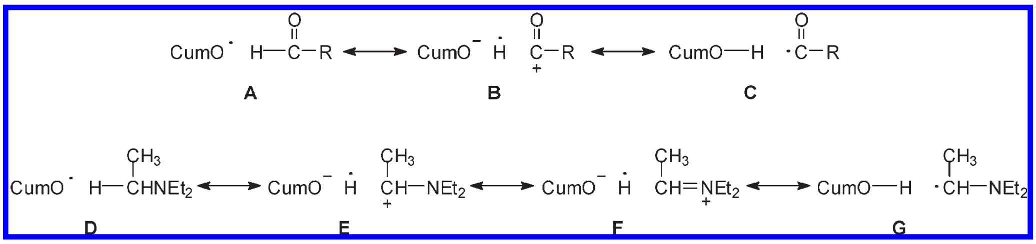
Very interestingly, the rate constants measured for reaction of CumO$^\bullet$ with PA and DMPA in benzene and chlorobenzene are about 5 times higher than those measured in MeOH and TFE. This observation points toward a hydrogen-bond interaction between a carbonyl lone pair and the latter solvents, similar to the one described previously for MeOH on the CumO$^\bullet$ + TEA reaction.[16] The KSEs observed in the reaction between CumO$^\bullet$ and TEA were explained on the basis of a hydrogen-bond interaction between the nitrogen lone pair and the solvent, an interaction that decreases the degree of overlap between the α-C−H bond and the nitrogen lone pair in the transition state for hydrogen atom abstraction. The acyl radicals formed following hydrogen atom abstraction from both PA and DMPA are σ radicals and their structure prevents efficient overlap between the aldehydic C−H bond and an oxygen lone pair in the transition state for hydrogen atom abstraction.

A more general description of the KSEs observed for these reactions can be obtained by representing the transition states for hydrogen atom abstraction from the aldehydes and from TEA by CumO$^\bullet$ in valence-bond terms,[26,45] as the hybrids of structures **A**−**C** and **D**−**G**, respectively (Scheme 3).

On the basis of Scheme 3, the decrease in k_H observed for PA and DMPA on going from aprotic solvents to MeOH and TFE is in line with the importance of polar contributions to the transition state for hydrogen atom abstraction mentioned above.[26] Accordingly, when the solvent engages in hydrogen bonding with the carbonyl oxygen atom, this interaction results in a decrease in electron density at the incipient acyl radical center and thus reduces the importance of the polar contribution (structure **B**) to the transition state for hydrogen atom abstraction. A similar explanation can be also extended to the CumO$^\bullet$ + TEA reaction where interaction of the solvent with the nitrogen lone pair reduces the importance of structures **E** and **F**. Structure **G** would instead account for the previously mentioned importance of orbital overlap between the α-C−H bond and the nitrogen lone pair in the transition state.[16,46−48]

Quite interestingly, a relatively small decrease in reactivity has been observed for both PA and DMPA on going from MeOH to TFE, despite the significantly greater HBD ability of TFE as compared to MeOH.[41] We propose that this behavior is the result of differential hydrogen-bond interactions of the solvent TFE with both the substrate and the alkoxyl radical. As discussed above, the interaction of TFE with CumO$^\bullet$ results in an increase

Scheme 3



in hydrogen atom abstraction reactivity for this radical, as evidenced by the 3-fold increase in k_H measured for the CumO$^•$ + CHD reaction on going from benzene, PhCl, and MeCN to TFE. This difference can be reasonably taken as a quantitative measure of the effect of the solvent (TFE) on the reactivity of CumO$^•$. The 3- to 5-fold decrease in reactivity observed for the reactions between CumO$^•$ and both PA and DMPA on going from benzene and PhCl to MeOH mostly reflects the effect of the latter solvent on the reactivity of the aldehydes. This assumption is based on the observation of a relatively small increase in k_H (~20%) for the CumO$^•$ + CHD reaction on going from benzene, PhCl, and MeCN to MeOH (Table 1).[16] In other words, in TFE solution the decrease in reactivity determined by hydrogen bonding between the solvent and the carbonyl group is compensated by the increase in reactivity due to the interaction of the solvent with the alkoxyl radical, resulting in k_H values that are very similar to those measured in MeOH, a solvent where only the former interaction (solvent/substrate) appears to play an important role. On the basis of the transition-state representation of Scheme 3, while as described above, MeOH destabilizes structure **B** via preferential hydrogen bonding with the aldehyde oxygen lone pair, the stronger HBD solvent TFE can interact efficiently with the oxygen atom of both the aldehyde and the radical. These differential interactions result in an overall effect that is comparable to that observed for MeOH.

In contrast with the results obtained for TEA, where a decrease in reactivity was observed on going from MeCN to *t*-BuOH, an opposite effect has been instead observed with PA and DMPA, with k_H that increases on going from MeCN to *t*-BuOH. At present we do not have any clear-cut explanation for these subtle solvent effects.[49,50] Another point of interest is represented by the decrease in reactivity observed for all four substrates on going from benzene and PhCl to MeCN, with the effect that is significantly more pronounced for TEA, PA, and DMPA as compared to CHD and exceeds in particular a factor of 2 for the aldehydes. This effect can be reasonably associated to the weak HBD character of MeCN.[52]

The hydrogen atom abstraction reactivity of CumO$^•$ and BnO$^•$ toward PA and DMPA in MeCN solution has been also compared by means of the $k_H(\text{BnO}^•)/k_H(\text{CumO}^•)$ ratios. The data displayed in Table 2 clearly show that the reactions of the two radicals with PA and DMPA are characterized by relatively small and comparable reactivity ratios ($k_H(\text{BnO}^•)/k_H(\text{CumO}^•)$ = 1.2 and 1.6, respectively), indicating that with these substrates the sterics of the alkoxyl radical play a minor role. The increase in reactivity ratio observed on going from PA to DMPA reasonably reflects the increased steric hindrance in proximity of the carbonyl group in DMPA determined by the presence of the two α-methyl groups. A similar ratio ($k_H(\text{BnO}^•)/k_H(\text{CumO}^•)$ = 1.9) has been previously determined by us for the reactions of CHD with the two radicals.[35] We have recently shown that in MeCN the reaction of BnO$^•$ with TEA proceeds through the formation of a hydrogen bonded complex between the BnO$^•$ α-C−H and the amine lone pair, wherein hydrogen atom transfer occurs.[35] Accordingly, with TEA a large decrease in k_H was observed on going from BnO$^•$ to CumO$^•$ ($k_H(\text{BnO}^•)/k_H(\text{CumO}^•)$ = 21.5). The large difference in $k_H(\text{BnO}^•)/k_H(\text{CumO}^•)$ observed between the aldehydes and TEA clearly indicates that with the former substrates no such interaction is operating. This observation is in full agreement with the lower HBA ability of aldehydes as compared to trialkylamines.[53]

In conclusion, by means of detailed time-resolved kinetic studies, new information on the role of solvent effects on hydrogen atom abstraction reactions from carbon by the cumyloxyl radical have been provided. The KSEs observed for the reactions of the cumyloxyl radical with aldehydes and amines have been explained on the basis of a general mechanistic scheme where the importance of hydrogen-bond interactions of the solvent with the heteroatom lone pair and, in strong HBD solvents, the radical oxygen atom is highlighted. A 3-fold increase in reactivity has been observed for the reaction between the cumyloxyl radical and CHD on going from aprotic solvents to TFE. This represents the first example of a significant KSE for hydrogen atom abstraction from hydrocarbons by alkoxyl radicals and is indicative of a hydrogen bond interaction between the solvent and the alkoxyl radical. A consequence of this finding is that in strong HBD solvents solvent/radical interactions can play an important role in the kinetics of hydrogen atom abstraction reactions by oxygen-centered radicals.

EXPERIMENTAL SECTION

Materials. Acetonitrile, benzene, chlorobenzene, methanol, 2-methyl-2-propanol, and 2,2,2-trifluoroethanol used in the laser flash photolysis experiments were spectroscopic grade solvents.

1,4-Cyclohexadiene was of the highest commercial quality available and was further purified prior to use by filtration over neutral aluminum oxide. Commercial samples of propanal and 2,2-dimethylpropanal of the highest commercial quality available were further purified prior to use by distillation. The purity of the substrates employed in the kinetic studies was checked by GC prior to the kinetic experiments and was in all cases >99.5%.

Dicumyl peroxide was of the highest commercial quality available and was used as received. Dibenzyl peroxide was prepared in small portions by reaction of KO_2 with benzyl bromide in dry benzene, in the presence of 18-crown-6 ether, according to a previously described procedure.[30,54] The product was purified by column chromatography (silica gel, eluent hexane/dichloromethane 1:1) and identified by ^{1}H NMR (see the Supporting Information, Figure S1). ^{1}H NMR ($CDCl_3$): δ 7.34 (s, 10H, ArH), 4.95 (s, 4H, CH_2).

Laser Flash Photolysis Studies. Laser flash photolysis (LFP) experiments were carried out with a laser kinetic spectrometer using the third harmonic (355 nm) or the fourth harmonic (266 nm) of a Q-switched Nd:YAG laser, delivering 8 ns pulses. The laser energy was adjusted to ≤10 mJ/pulse by the use of the appropriate filter. A 3.5 mL Suprasil quartz cell (10 mm × 10 mm) was used for all experiments. Nitrogen-saturated solutions of dicumyl peroxide (0.01−1.0 M) or dibenzyl peroxide (0.008 M) were used. In the 266 nm LFP experiments a 10 mM concentration of dicumyl peroxide or a 8 mM concentration of dibenzyl peroxide was employed. In the 355 nm LFP experiments, concentrations of dicumyl peroxide between 0.7 and 1.0 M were instead employed. In all experiments the conditions were arranged in such a way as to ensure predominant light absorption by the peroxide.

All the experiments were carried out at T = 25 ± 0.5 °C under magnetic stirring. The observed rate constants were obtained by averaging 3−6 individual values that were reproducible to within 5%.

Second-order rate constants for the reactions of the cumyloxyl (CumO$^•$) and benzyloxyl (BnO$^•$) radicals with the hydrogen atom donors were obtained from the slopes of the k_{obs} (measured following the decay of the CumO$^•$ and BnO$^•$ visible absorption bands at 490−515 and 460 nm, respectively) vs [substrate] plots. Fresh solutions were used for every substrate concentration. Correlation coefficients were in all cases >0.99. The given rate constants are the average of at least two independent experiments, typical errors being <5%.

In order to assess the possible formation of hemiacetals following the reaction of the aldehyde with the alcoholic solvent, the stability of propanal and 2,2-dimethylpropanal in alcoholic solution was checked by UV—vis spectroscopy monitoring the intensity of the aldehyde $n \rightarrow \pi^*$ absorption band (in MeOH λ_{max} = 285 and 290 nm, respectively) as a function of time. In TFE no significant decrease in intensity was observed after 1 h. In methanol and 2-methyl-2-propanol a ≤30% decrease in intensity was instead observed after 1 h, a behavior that can be reasonably associated to the formation of an hemiacetal. The decrease in intensity was ≤3% after 5 min. Accordingly, in order to minimize hemiacetal formation, in the kinetic experiments propanal and 2,2-dimethylpropanal were added in pure form to thermostated cuvettes containing dicumyl peroxide in methanol or 2-methyl-2-propanol, and the solutions were photolyzed immediately after mixing. No significant decrease in k_{obs} was observed on kinetic traces obtained from successive laser shots on the same solution, indicating negligible substrate consumption (hemiacetal formation) during the experiment time. As a matter of comparison, a significantly lower value of the rate constant for hydrogen atom abstraction ($k_H = 4.2 \times 10^6$ M^{-1} s^{-1} as compared to 9.55×10^6 M^{-1} s^{-1}, see Table 1) was instead obtained when the experiment was performed by successive additions of portions of a solution of propanal in methanol to thermostatted cuvettes containing dicumyl peroxide in methanol. This observation suggests that under these conditions significant hemiacetal formation has occurred in the parent methanolic propanal solution prior to addition.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Time-resolved spectra observed after reaction of CumO$^\bullet$ with DMPA. Plots of k_{obs} vs [substrate]. This material is available free of charge via the Internet at http://pubs.acs.org.

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(50) A ~3-fold increase in rate constant has been observed for the hydrogen abstraction reaction from CHD by the 2,2-diphenyl-1-picrylhydrazyl radical ($DPPH^\bullet$) on going from a variety of different solvents (CCl_4, benzene, MeCN, AcOEt, DMSO, AcOH, MeOH, EtOH) to *t*-BuOH.[51] It has been shown that this behavior is not a general property of alcohols or other hydroxylic solvents but appears to be a peculiarity of sterically demanding alcohols. We thank a reviewer for drawing our attention to this study.

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