Kinetic Solvent Effects on Hydrogen Abstraction from Phenol by the Cumyloxyl Radical. Toward an Understanding of the Role of Protic Solvents

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Ⓢ *Supporting Information*

ABSTRACT: A time-resolved kinetic study of the hydrogen atom abstraction reactions from phenol by the cumyloxyl radical (CumO•) was carried out in different solvents. The hydrogen atom abstraction rate constant (k_H) was observed to decrease by almost 3 orders of magnitude on going from isooctane to MeOH. In TFE, MeCN/H$_2$O 2:1, and MeOH, the measured k_H values were lower than expected on the basis of the Snelgrove−Ingold (SI) equation that correlates log k_H to the solvent hydrogen bond acceptor (HBA) ability parameter β_2^H. As these solvents also act as hydrogen bond donors (HBDs), we explored the notion that a more thorough description of solvent effects could be provided by including a solvent HBD ability term, α_2^H, into the SI equation via $\beta_2^H(1 + \alpha_2^H)$. The inclusion of such a term greatly improves the fitting for TFE, MeCN/H$_2$O 2:1, and MeOH but at the expense of that for tertiary alkanols. This finding suggests that, for the reaction of CumO• with phenol, the HBA and HBD abilities of both the solvent and the substrate could be responsible for the observed KSEs. but this requires that primary and tertiary alkanols exhibit different solvation behaviors. Possible explanations for this different behavior are explored.
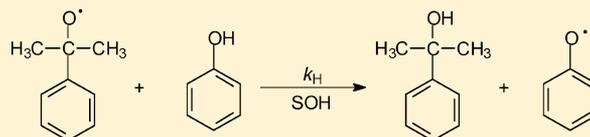
INTRODUCTION

Hydrogen atom abstraction reactions from phenols have attracted considerable interest as these substrates represent the most extensive class of natural and synthetic radical scavenging antioxidants[1−6] and these reactions play a key role in a variety of enzymatic reactions.[7−10]

The study of solvent effects on these reactions has received significant attention. In a series of papers, Ingold and co-workers observed dramatic kinetic solvent effects (KSEs) on hydrogen atom abstractions from phenols by *tert*-alkoxyl radicals (RO•), where a decrease in rate constant (k_H) was observed with increasing solvent hydrogen bond acceptor (HBA) ability.[11−14] Good correlations were generally obtained between log k_H and Abraham's β_2^H values.[15] On the basis of previous studies that had shown that hydrogen atom abstraction from saturated[17] and unsaturated[18] hydrocarbons by the cumyloxyl radical (PhC(CH$_3$)$_2$O•, CumO•) exhibited no KSE, the large KSEs observed for the reactions of phenols with RO• were explained in terms of a hydrogen bond interaction between the phenolic OH group and the solvent as described in Scheme 1.

In this Scheme k_H^0 represents the rate constant measured in a non-HBA solvent (i.e., an alkane for which $\beta_2^H = 0.00$) and K^S is the equilibrium constant for hydrogen bond formation between phenol and solvent S. According to this picture, in relatively strong HBA solvents the substrate must experience desolvation in order to undergo hydrogen atom abstraction and

Scheme 1
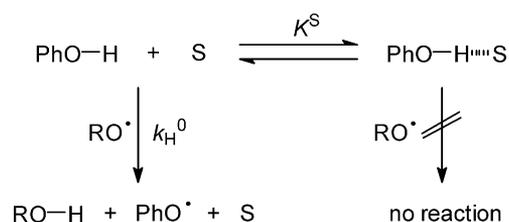
a decrease in reactivity is observed as compared to weaker or non-HBA solvents. In general, the rate constant for hydrogen atom abstraction from phenol in a solvent S, k_H^S, can be expressed in terms of eq 1.

$$k_H^S = k_H^0/(1 + K^S[S]) \tag{1}$$

These studies led to the development of an empirical equation, the Snelgrove−Ingold equation (eq 2),[11,19] that accounts quantitatively for the KSEs observed in these reactions.

$$\log(k_H^S) = \log(k_H^0) - 8.3\alpha_2^H{}_{(subst)}\beta_2^H \tag{2}$$

In this equation $\alpha_2^H{}_{(subst)}$ measures the substrate hydrogen bond donor (HBD) ability (i.e., PhOH),[20] and β_2^H measures

the solvent HBA ability. The Snelgrove–Ingold equation has been applied to the study of KSEs on a variety of hydrogen atom abstraction reactions such as the reactions of phenols and α-tocopherol with *tert*-alkoxyl,[11−14] peroxyl,[21] and the 2,2-diphenyl-1-picrylhydrazyl (dpph•) radicals,[13,19,22] the reaction of *tert*-butyl hydroperoxide with CumO•,[11,14] and the reaction of phenol with a π,π^* ketone triplet.[23] It has also been applied to the self-combination reaction of the hydroperoxyl radical (HOO•)[24] and proton transfer reactions from phenols to the anthracene radical anion.[25] More recently, this kinetic model was employed by Mayer for the development of a procedure that enables the prediction of rate constants for hydrogen atom abstraction reactions by oxygen-centered radicals in various media. This procedure employs the Marcus cross relation and includes adjustments for solvent hydrogen bonding.[26]

In the context of hydrogen abstraction reactions by alkoxyl radicals, it was pointed out that the high reactivity of RO• prohibited kinetic measurements in alcohols other than 2-methyl-2-propanol (*t*-BuOH).[11,19] This appears to be a great limitation because alcoholic solvents have been shown to play a peculiar role in a number of formal hydrogen atom abstraction reactions from phenolic substrates by free radicals. Namely, in the reactions of dpph• with a variety of phenolic substrates, rate constants in alcohols were generally larger than those predicted on the basis of the Snelgrove–Ingold equation.[19,27,28] This behavior was explained in terms of the operation of a sequential proton-loss electron transfer (SPLET) mechanism, where the solvent promotes substrate ionization to give a phenoxide anion that then undergoes electron transfer to the radical.

However, in recent studies of KSEs on hydrogen atom abstraction reactions from carbon by CumO•, we were able to measure rate constants for hydrogen abstraction (k_H) from 1,4-cyclohexadiene,[29,30] aliphatic aldehydes,[30] triethylamine,[29] tetrahydrofuran,[31] cyclohexane[31] and in alcohols such as methanol (MeOH) and, with the exclusion of the amine compound, 2,2,2-trifluoroethanol (TFE). More importantly, our study of the reaction of CumO• with 1,4-cyclohexadiene revealed a small increase in k_H on going from MeCN, benzene, or chlorobenzene (for which $k_H = 6.6-6.9 \times 10^7$ M^{-1} s^{-1}) to MeOH and *t*-BuOH ($k_H = 8.3 \times 10^7$ M^{-1} s^{-1}),[29] with the rate constant increasing by a factor of ca. 3 when the reaction was performed in TFE solution ($k_H = 1.9 \times 10^8$ M^{-1} s^{-1}).[30] A similar behavior was observed for the reaction of CumO• with cyclohexane where a ca. 2-fold increase in k_H was observed on going from MeCN and isooctane to MeOH, and a ca. 4-fold increase in k_H when the reaction was carried out in TFE.[31] This behavior was explained in terms of a hydrogen bond interaction between the radical and the alcohol that leads, as compared to weaker or non-HBD solvents, to a stabilization of the transition state for hydrogen abstraction. These results clearly demonstrate that strong HBD solvents influence the hydrogen abstraction reactivity of alkoxyl radicals.

Following these observations, and in view of the importance of hydrogen atom abstraction reactions from phenols, we decided to extend the available studies on phenol to a larger number of protic solvents to provide a deeper and more general understanding of the role of solvent effects on these reactions. For this purpose we have carried out a detailed time-resolved kinetic study in different solvents (2,2,4-trimethylpentane (isooctane), MeCN, MeCN/H$_2$O 2:1, MeOH, 2-methyl-2-butanol (MBOH), 3-methyl-3-pentanol (MPOH), and TFE) on the reactions of CumO• with phenol.

■ RESULTS

The reactions of CumO• with phenol were studied using the laser flash photolysis (LFP) technique. CumO• was generated by 308 nm LFP of argon-saturated isooctane, MeCN, MeCN/H$_2$O 2:1 (v/v), MeOH, TFE, MBOH and MPOH solutions (*T* = 22 °C) containing dicumyl peroxide (eq 3). CumO• was also

$$\text{(structure)} \xrightarrow{h\nu} 2 \text{(structure)} \quad (3)$$
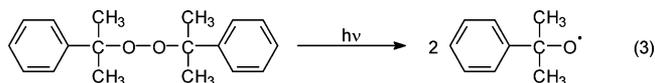
generated by 355 nm LFP of argon-saturated MeCN and MeOH solutions (*T* = 25 °C) containing dicumyl peroxide (eq 3). In isooctane, MeCN and *tert*-alkanol solution, CumO• is characterized by a broad absorption band in the visible region of the spectrum centered at 485 nm,[32,33] the position of which is red-shifted in MeCN/H$_2$O 2:1,[33] MeOH,[34] and TFE.[35] Under these conditions, CumO• decays mainly by C−CH$_3$ β-scission, with the exception of the experiments carried out in MeOH solution where hydrogen atom abstraction from the solvent becomes the predominant reaction.[34]

The time-resolved absorption spectra observed after reaction of CumO• with phenol in MBOH and TFE are displayed in the Supporting Information (Figures S1 and S2, respectively).

The kinetic studies of the reactions of CumO• with phenol in the different solvents were carried out by LFP following the decay of the CumO• visible absorption band as a function of phenol 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• (k_H) from the slopes of these plots. As an example, the plots of k_{obs} vs [PhOH] for the reactions between CumO• and phenol, carried out in TFE (filled circles) and MeOH (empty circles) solutions are shown in Figure 1.
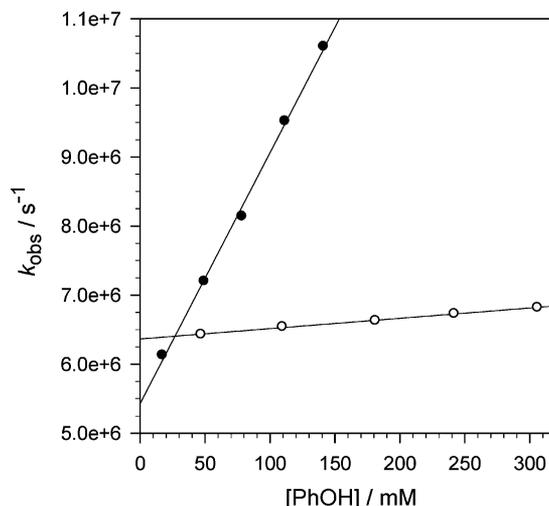
Figure 1. Plots of the observed rate constant (k_{obs}) against [PhOH] for the reactions of the cumyloxyl radical (CumO•) with phenol, measured in nitrogen-saturated TFE (filled circles) and MeOH (empty circles) solutions at *T* = 22 °C, following the decay of CumO• at 520 and 500 nm. From the linear regression analysis: CumO• + PhOH in TFE: intercept = 5.43×10^6 s^{-1}, $k_H = 3.69 \times 10^7$ M^{-1} s^{-1}, r^2 = 0.9978; CumO• + PhOH in MeOH: intercept = 6.36×10^6 s^{-1}, $k_H = 1.50 \times 10^6$ M^{-1} s^{-1}, r^2 = 0.9979.

Table 1. Second-Order Rate Constants (k_H) for Reaction of the Cumyloxyl (CumO•) Radical with Phenol Measured in Different Solvents[a]

solvent	$\alpha_2^{H\,b}$	$\beta_2^{H\,c}$	$\lambda_{ex}^{\,d}$ (nm)	$k_H^{\,e}$ (M^{-1} s^{-1})	
isooctane	0.00	0.00	308	$1.43 \pm 0.02 \times 10^9$	$1.10 \times 10^{9f,g}$
TFE	0.567	0.18	308	$3.8 \pm 0.1 \times 10^7$	
MeCN	0.09	0.44	308	$6.16 \pm 0.07 \times 10^6$	5.8×10^{6f}
			355	$1.10 \pm 0.02 \times 10^{7h}$	
tBuOH	0.319	0.49	308		3.6×10^{6f}
MBOH[i]	0.319	0.49	308	$3.16 \pm 0.04 \times 10^6$	
MPOH[j]	0.319	0.49	308	$3.4 \pm 0.2 \times 10^6$	
MeCN/H$_2$O 2:1[k]	0.246	0.404	308	$2.5 \pm 0.2 \times 10^6$	
MeOH	0.367	0.41	308	$1.55 \pm 0.05 \times 10^6$	
			355	$3.3 \pm 0.1 \times 10^6$	

[a]308 nm LFP: Ar-saturated, [dicumyl peroxide] = 0.092 M, T = 22 °C. 355 nm LFP: Ar-saturated, [dicumyl peroxide] = 0.7−1.0 M, T = 25 °C. [b]Solvent HBD ability, taken from ref 20. [c]Solvent HBA ability, taken from ref 16. [d]Laser excitation wavelength. [e]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• visible absorption band at 490−520 nm. Average of at least two determinations. [f]Reference 11. [g]Determined in octane solution. [h]Reference 36. [i]2-Methyl-2-butanol. [j]3-Methyl-3-pentanol. [k]The α_2^H and β_2^H values for the solvent mixture were obtained by weighting the values for the two pure solvents by their mole fractions: n_{MeCN} = 0.408, n_{H2O} = 0.592. An analogous approach was previously employed for the determination of the β_2^H value of a 1 M solution of benzophenone in benzene (see ref 27c).
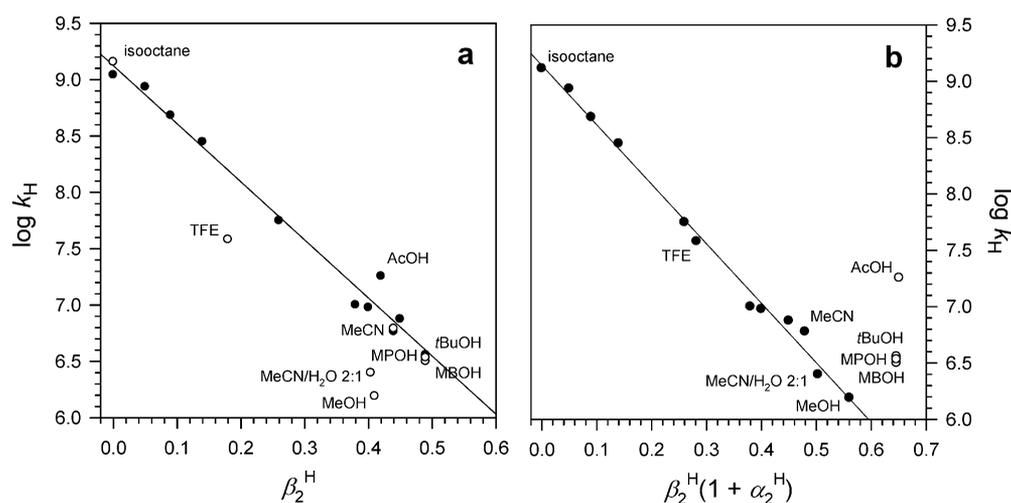
Figure 2. (a) Plot of log k_H vs solvent β_2^H value for the reactions between the cumyloxyl radical and phenol. The filled circles are taken from ref 11. All the k_H values employed for this plot are given in the Supporting Information, Table S1. The empty circles are taken from the fifth column of Table 1 and refer to k_H values measured employing 308 nm LFP. These data points have not been included into the correlation. From the linear regression analysis (filled circles): intercept = 9.12, slope = −5.15, r^2 = 0.9829. (b) Plot of log k_H vs solvent $\beta_2^H(1 + \alpha_2^H)$ values for the same data points displayed in (a). In this plot the data point couples taken from ref 11 and Table 1 shown in (a) for isooctane and MeCN have been averaged to give a single point for each of the two solvents. The data points for AcOH, tBuOH, MBOH, and MPOH (empty circles) have not been included in the correlation. From the linear regression analysis (filled circles): intercept = 9.14, slope = −5.28, r^2 = 0.9929.

Additional plots for hydrogen atom abstraction by CumO• from phenol in the different solvents are displayed in the Supporting Information (Figures S3−S7). All the kinetic data thus obtained are collected in Table 1. Also included in this table (column 6) are the rate constants obtained previously for the reactions of CumO• with phenol[11] and the α_2^H and β_2^H values for the different solvents used.[16,20]

■ DISCUSSION

The reactions of CumO• with phenol were initially studied in MeCN and MeOH employing 355 nm LFP. However, the high concentrations of dicumyl peroxide required for the generation of CumO• under these conditions (0.7−1.0 M) prevented the use of solvents such as TFE and H$_2$O. At 308 nm, the lower concentration of dicumyl peroxide required (0.092 M) allowed us to carry out the kinetic experiments in TFE and in a 2:1 (v/v) MeCN/H$_2$O solvent mixture. Accordingly, for all solvents

the second-order rate constants for hydrogen atom abstraction from phenol by CumO• (k_H) were measured employing this excitation wavelength. Comparison between the k_H values obtained in MeCN and MeOH at the two excitation wavelengths showed a ca. 2-fold increase in rate constant on going from 308 to 355 nm LFP. This effect was discussed previously in terms of a decrease in solvent polarity (and in the solvent HBA ability) induced by the high concentration of dicumyl peroxide employed in the 355 nm LFP experiments.[36]

As shown in Table 1, the k_H values in alkane and MeCN solution are in excellent agreement with those measured previously by Ingold and co-workers under similar experimental conditions.[11] The lowest k_H value was measured when the reaction between CumO• and phenol was studied in MeOH solution (k_H = 1.55 × 10^6 M^{-1} s^{-1}). This value is four times lower than that obtained in MeCN despite the expectation of a higher rate constant on the basis of eq 2 (viz. β_2^H = 0.41 and

0.44 for MeOH and MeCN, respectively). A significantly higher k_H value was measured in TFE solution ($k_H = 3.8 \times 10^7$ M^{-1} s^{-1}). However, this value is lower than the value expected on the basis of eq 2, as evidenced by the higher value measured previously in anisole solution ($k_H = 5.6 \times 10^7$ M^{-1} s^{-1}),[11] despite the relatively large difference in β_2^H between these two solvents ($\beta_2^H = 0.18$ and 0.26 for TFE and anisole,[16] respectively). Similar k_H values ($k_H = 3.2-3.4 \times 10^6$ M^{-1} s^{-1}) were observed when the reaction was studied in *tert*-alkanols (MBOH and MPOH), giving values that are very close to the one measured previously in *t*-BuOH solution ($k_H = 3.6 \times 10^6$ M^{-1} s^{-1}).[11]

Figure 2a shows a plot of log k_H vs the solvent β_2^H of values measured previously by Ingold and co-workers for an extended series of sterically nondemanding[12] solvents (filled circles).[11] Overall, a very good correlation is observed ($r^2 = 0.9829$), with the only outlier solvent being acetic acid (AcOH). The slope obtained from the correlation line (−5.15) gives the magnitude of the observed KSE, quantifying the decrease in reactivity expected on going from an alkane ($\beta_2^H = 0.00$) to the strongest HBA solvent hexamethylphosphoric triamide (HMPT) for which $\beta_2^H = 1.00$.

Also included in Figure 2a are our measured log k_H data taken from the fifth column of Table 1 (empty circles). Interestingly, in Figure 2a the points corresponding to TFE, MeCN/H$_2$O 2:1 and MeOH fall significantly below the log k_H vs β_2^H correlation line, suggesting that the HBA parameters of these solvents do not fully account for the observed KSEs. Following previous indications,[19] a SPLET mechanism would be expected to increase the rate of reactions of CumO$^{\bullet}$ with phenol and so this can be ruled out as a possible explanation for the observation that the rate constants in TFE, MeCN/H$_2$O 2:1 and MeOH are smaller than predicted by eq 2. As mentioned previously, an increase in hydrogen abstraction reactivity was observed for CumO$^{\bullet}$ when its reactions with hydrocarbon substrates such as 1,4-cyclohexadiene and cyclohexane were studied in MeOH and TFE. This behavior was explained in terms of a hydrogen bond interaction between the radical and the solvent.[29−31] Along this line, the lower than expected k_H values measured for the reaction of CumO$^{\bullet}$ with PhOH in MeOH and TFE clearly indicate that, for this reaction, solvent effects on the substrate are significantly more important than those on CumO$^{\bullet}$.

The alkanols and the MeCN/H$_2$O solvent mixture used in our study are all characterized by relatively high β_2^H values (between 0.40 and 0.49), the only exception being TFE for which $\beta_2^H = 0.18$. These solvents also display relatively high HBD abilities as evidenced by the α_2^H values shown in Table 1. Phenol is a fairly good hydrogen bond donor ($\alpha_2^H = 0.596$)[20] but can also act as a hydrogen bond acceptor ($\beta_2^H = 0.22$).[16] This led us to consider that, in protic solvents, KSEs on hydrogen atom abstraction reactions from phenol by CumO$^{\bullet}$ may be more accurately modeled by taking into account the HBA and HBD properties of the solvent. In order to test this hypothesis, the log k_H values displayed in Figure 2a were plotted against the solvent $\beta_2^H(1 + \alpha_2^H)$ values, via eq 4, and the corresponding graph is shown in Figure 2b.

$$\log(k_H^S) = \log(k_H^0) - M_{PhOH}\beta_2^H(1 + \alpha_2^H) \qquad (4)$$

In eq 4, the slope obtained from the log(k_H^S) vs $\beta_2^H(1 + \alpha_2^H)$ correlation, M_{PhOH}, reflects both the substrate (PhOH) HBD and HBA abilities.

Comparison between the graphs displayed in Figure 2a and 2b shows that by inclusion of the solvent α_2^H value via eq 4, the data points corresponding to TFE, MeCN/H$_2$O 2:1 and MeOH now fall on the correlation line (filled circles), leading to an excellent correlation ($r^2 = 0.9929$) with no significant variation in the values of both the slope and the intercept. However, the AcOH point is farther off the correlation line and the *tert*-alkanol points are now poorly correlated (empty circles). Interestingly, analogous deviations from the Snelgrove−Ingold equation were previously observed when the reaction between CumO$^{\bullet}$ and phenol was studied in a number of sterically demanding solvents such as pivalonitrile, *tert*-butyl acetate and methyl pivalate.[12] A deviation was also observed for the hydrogen atom abstraction reactions from 1,4-cyclohexadiene by dpph$^{\bullet}$, where the rate constant increased by a factor 3 on going from a variety of different solvents (CCl$_4$, benzene, MeCN, AcOEt, DMSO, AcOH, MeOH, EtOH) to *t*-BuOH.[37] This behavior was a peculiarity of sterically demanding alcohols and was explained by suggesting that *t*-BuOH provided a "unique solvation shell"[37] around dpph$^{\bullet}$ that enhanced its hydrogen abstraction reactivity because of steric crowding between solvent molecules competing for sites on the radical.

In order to explore the interactions involving CumO$^{\bullet}$ and phenol with MeOH and *t*-BuOH, we carried out calculations using density-funtional theory (B971/6-31+G(d,p)),[38] augmented with dispersion-correcting potentials[40] to better account for noncovalent interaction.[41] The details of the calculations are given in the Supporting Information. The structures displayed in the Supporting Information (Figure S8) show that in both cases phenol can engage in hydrogen bonding with three solvent molecules, one acting as a HBA with the hydroxylic hydrogen atom and two as HBDs toward the oxygen lone pairs. However, structures in which phenol and three solvent molecules are organized into a cyclic arrangement were found to be energetically lower lying (Figure S9, Supporting Information), in line with the results obtained in a recent study on the interaction of these two alcohols with 1-naphthol.[42] The calculations predict that phenol experiences greater stability when solvated by three *t*-BuOH than by three MeOH molecules. Simulations involving solvation of the transition state (TS) structure with four alcohol molecules produced structures in which the incipient oxygen lone-pairs act as HBAs (Figure S10, Supporting Information). In this case, the close contact between reacting species results in steric clashes between solvating *t*-BuOH molecules and consequently less (predicted) TS stabilization over that achieved with MeOH. Therefore, the results of the calculations do not reflect the nature of the kinetic solvent effect involving *t*-BuOH and would likely produce similar results for other sterically demanding solvents.

Although we do not yet have a clear explanation for the observed kinetic behavior, a possibility may be that with MeOH a tighter solvent shell can be formed around the phenol molecule relative to the bulkier *tert*-alkanols. This feature will make the desolvation of the phenolic hydrogen, which is required for hydrogen atom abstraction, more energetically demanding. Based on this hypothesis and on the results of the calculations discussed above, a tighter solvent shell will result in a greater entropy loss for the reaction in MeOH as compared to *tert*-alkanols, in line with the observed reactivities. However, this is at most a working hypothesis that would require support from additional computational and experimental studies.

As pointed out by a reviewer, the Snelgrove−Ingold equation uses for each neat HBA solvent Abraham's β_2^H parameters, which were obtained for the dilute HBA substrate in CCl_4 solution and not for this HBA as a neat solvent. Along this line, the deviation from the correlation line observed in Figure 2a for MeOH and TFE, as compared to t-BuOH, MBOH, and MPOH, may be the result of a different hydrogen bonding pattern of primary alcohols as compared to tertiary ones. Accordingly, the β_2^H values for the primary alcohols MeOH and TFE may not be appropriate for use in the Snelgrove−Ingold equation to describe the interaction of PhOH with these solvents in the *neat* solvent. An alternative possibility may be represented by the use of Abraham's summation scales, $\Sigma \alpha_2^H$ and $\Sigma \beta_2^H$, which provide HBA and HBD indicies that reflect the hydrogen bonding behavior of a solute molecule that is surrounded by solvent molecules.[43] Using $\Sigma \beta_2^H = 0.47$ for MeOH in the Snelgrove−Ingold equation (rather than $\beta_2^H = 0.41$) would reduce the deviation of the MeOH point from the correlation line in Figure 2a; a similar reduction in deviation would result for TFE for which $\beta_2^H = 0.18$ and $\Sigma \beta_2^H = 0.25$. On the other hand, for tertiary alkanols for which $\beta_2^H = 0.49$ and $\Sigma \beta_2^H = 0.60$, the three points for t-BuOH, MBOH and MPOH would reside significantly above the correlation line. Moreover, for MeCN $\beta_2^H = 0.44$ and $\Sigma \beta_2^H = 0.33$ and this would lead to a shift in the MeCN data point well below the correlation line. On the basis of these observations, it is quite clear that the use of the summation scales would lead to a poorer correlation and accordingly this approach can be discarded.

As pointed out previously, strong HBD solvents can influence the hydrogen abstraction reactivity of alkoxyl radicals.[30,31] Accordingly, even though as mentioned above these interactions appear to play a minor role as compared to the interaction of the solvent with phenol, a better understanding of the KSEs observed in these processes could be obtained through the study of hydrogen atom abstraction reactions from phenol by radicals whose reactivity is not expected to be influenced by the interaction with strong HBD solvents, i.e., by alkyl radicals.

In conclusion, we have carried out a time-resolved kinetic study in different solvents on the reaction between CumO• and phenol. Deviations from the Snelgrove−Ingold equation were observed in MeOH, TFE, and $MeCN/H_2O$ 2:1. Inclusion into this equation of the solvent HBD term α_2^H improved the correlation for MeOH, TFE, and $MeCN/H_2O$ 2:1 but resulted in poorer correlations for tertiary alkanols. These findings suggest that the HBA and HBD abilities of both the solvent and the substrate could be responsible for the observed KSEs; however, neither of the proposed approaches can fully account for the observed KSEs, indicating that in the reaction between CumO• and phenol primary and tertiary alkanols exhibit different solvation behaviors. Additional experimental and computational studies are certainly needed in order to achieve a better understanding of the KSEs observed for these important processes.

EXPERIMENTAL SECTION

Materials. 2,2,4-Trimethylpentane (isooctane), acetonitrile, methanol, 2-methyl-2-butanol, 3-methyl-3-pentanol, and 2,2,2-trifluoroethanol used in the laser flash photolysis experiments were spectroscopic grade solvents. Milli-Q-filtered (Millipore) water was used for the $MeCN/H_2O$ 2:1 (v/v) solutions.

Phenol was of the highest commercial quality available (>99%) and was further purified prior to use by crystallization from cyclohexane. Dicumyl peroxide was of the highest commercial quality available and was used as received.

Laser Flash Photolysis Studies. The 355 nm laser flash photolysis (LFP) experiments were carried out with a laser kinetic spectrometer using the third harmonic of a Q-switched Nd:YAG laser, delivering 8 ns pulses. A 3.5 mL Suprasil quartz cell (10 mm × 10 mm) was used for all experiments that were carried out at T = 25 ± 0.5 °C under magnetic stirring. Argon saturated solutions of dicumyl peroxide (0.7−1.0 M) were used, and the conditions were arranged in such a way as to ensure predominant light absorption by the peroxide.

The 308 nm LFP experiments were carried out by employing a Lambda Physik Excimer Laser (CompEX 100; 308 nm, pulse length 15 ns) and a computer-controlled system which has been described elsewhere.[44] A 5 mL Suprasil quartz cell (10 mm × 10 mm) was used for all experiments that were carried out at T = 22 ± 1 °C. Argon saturated solutions of dicumyl peroxide (0.090−0.095 M) were used, in order to have an absorbance of ∼0.3 at the excitation wavelength employed.

Second-order rate constants for the reactions of the cumyloxyl (CumO•) radical with phenol were obtained from the slopes of the k_{obs} (measured following the decay of the CumO• visible absorption band at 490−520 nm) vs [PhOH] 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, for which errors were typically <5%.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Time-resolved spectra observed after reaction of CumO• with phenol in 2-methyl-2-butanol and TFE. Plots of k_{obs} vs [PhOH]. Computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENTS

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