Oxidation Potentials of α-Hydroxyalkyl Radicals in Acetonitrile Obtained by Photomodulated Voltammetry

Torben Lund,*,† Danial D. M. Wayner,‡ Mats Jonsson,§ Allan G. Larsen,⊥ and Kim Daasbjerg⊥

Contribution from the Institute of Life Science and Chemistry, Roskilde University Center, DK-4000 Roskilde, Denmark, Steacie Institute of Molecular Sciences, National Research Council Canada, Ottawa, Canada, KIA 0R6, Department of Chemistry, Nuclear Chemistry, Royal Institute of Technology, SE-100 44, Stockholm, Sweden, and Department of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Århus C, Denmark

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Abstract: Oxidation potentials, $E^{\mathrm{ox}}_{1/2}$, of α-hydroxyalkyl radicals of the type $R^1R^2C^\bullet OH$ (denoted $K^1H^\bullet$) have been obtained in acetonitrile by photomodulated voltammetry. The values of $E^{\mathrm{ox}}_{1/2}$ increase as the R^1 and R^2 groups are changed from alkyl to aryl and, in particular, strong electron-withdrawing functionalities such as CN and CF_3. Using rate data available in the literature for the pinacol photoexchange reaction $K + K^1H^\bullet \rightarrow KH^\bullet + K^1$, it is found that as the difference in the standard potential of the ketone K, E°_K, and the oxidation potential of $K^1H^\bullet$, $E^{\mathrm{ox}}_{1/2}$, increases there is a modest increase in the exchange rate constant, k_{ex}. This indicates that even if some charge transfer may occur between the hydroxyalkyl radical and the ketone in the transition state, it is certainly not to the extent of a complete electron transfer. If the exchange reaction is treated as a simple hydrogen atom transfer process within the Marcus model, the intrinsic barrier is found to be 8−13 kcal mol^{-1} due to the changes occurring in bonds, hybridizations, and bond angles. Finally, acid dissociation constants for $K^1H^\bullet$ are provided by means of a thermochemical cycle.

Introduction

Simple α-hydroxyalkyl radicals derived from alcohols, $R^1R^2C^\bullet$-OH, with the oxygen atom attached directly to the radical center may behave as relatively potent reducing agents. These radicals are able to reduce nitro compounds,[1] carbonyls,[2] and organic halides.[3−6] In the classical pinacol photoreaction, the rate constant of the reduction of the ground-state ketone by $R^1R^2C^\bullet$-OH, k_{ex}, is a key parameter for the determination of the product distribution.[7−13] The mechanism of the exchange reaction eq 1 has been described either as a hydrogen abstraction process[14]

$$Ph_2CO + R^1R^2C^\bullet OH \xrightarrow{k_{\mathrm{ex}}} Ph_2C^\bullet OH + R^1R^2C{=}O \qquad (1)$$

or as a concerted transfer of an electron and a proton from the hydroxyalkyl radical to the ketone.[12] Thus, it is expected that there might be a dependence of k_{ex} on the difference between the reduction potential of the ketone, E°_K, and the oxidation potential of the hydroxyalkyl radical, $E^{\mathrm{ox}}_{1/2}$.[13]

Despite the fact that hydroxyalkyl radicals are involved in many redox reactions, few oxidation potentials have been measured previously. Photomodulated voltammetry has provided values of −0.60 V and −1.1 V vs SCE for the oxidation of $(CH_3)_2C^\bullet OH$ in acetonitrile and in a 3:1 mixture of 2-propanol/acetonitrile, respectively.[5] Henglein et al. obtained potentials of −1.30, −1.18 and, −0.98 V vs SCE in water of the $(CH_3)_2C^\bullet$-OH, $CH_3CH^\bullet OH$, and $^\bullet CH_2OH$ radicals, respectivly, using a combination of pulse radiolysis and polarography.[15] These values are more than 1 V lower (i.e., more negative) than those obtained in acetonitrile for the pertinent aliphatic radicals, $(CH_3)_2CH^\bullet$, $CH_3CH_2^\bullet$, and $CH_3^\bullet$.[16] The oxygen atom attached in the α-position relative to the radical center therefore, like nitrogen, shifts the potential of the radical strongly in the negative direction since the singly occupied MO in the radical is antibonding.[16] Oxidation potentials of phenyl-substituted hydroxyalkyl radicals have, to our knowledge, not previously been obtained.

In this paper our aim is to obtain oxidation potentials of a number of hydroxyalkyl radicals by means of photomodulated voltammetry in order to gain insights into the mechanism of

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† Roskilde University Center.

‡ Steacie Institute of Molecular Sciences.

§ Royal Institute of Technology.

⊥ University of Aarhus.

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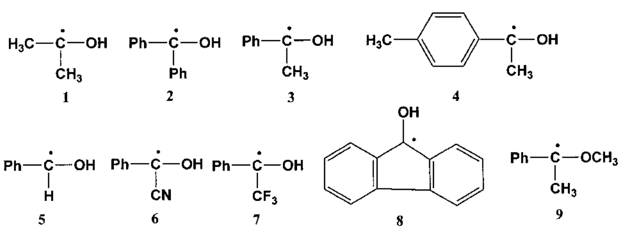
Chart 1



the pinacol exhange reaction. To elucidate the effect of different α-substituents on the reducing power of the radicals, we selected the nine compounds listed in Chart 1, encompassing groups such as alkyl, aryl, CN, and CF_3. These data will allow a test of the relationship between E°_{K}, $E^{ox}_{1/2}$, and some exchange rates known for reactions between aromatic ketones and hydroxyalkyl radicals. Moreover, from the oxidation potentials, the pK_a's in acetonitrile of the radicals may be calculated from a simple thermochemical cycle.

Experimental Section

Materials. All chemicals were commercially available and used as received. Di-*tert*-butyl peroxide (DTBP, Aldrich) was passed through a column of activated alumina before use. The photomodulated voltammetry experiments were performed in acetonitrile with either 0.1 M tetrabutylammonium perchlorate (Bu_4NClO_4) or 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) as supporting electrolyte. In a few cases acetonitrile was distilled over CaH_2 before use, although this was found to have no effect on the voltammetric behavior. Bu_4NClO_4 was recrystallized twice from a mixture of ethyl acetate and hexane (9:1) and dried in a vacuum at 40 °C overnight. Bu_4NBF_4 was prepared and purified by standard procedures. All solutions were carefully deaerated with argon for at least 15 min.

Instrumentation and Procedure. Two slightly different photomodulated voltammetry (PMV) instrumentations were used.[18] The first instrument, described by Wayner et al.,[17] was used to obtain voltammograms of the hydroxyalkyl radicals **1**−**4**. The modulation frequency was in most cases 100 Hz and the sweep rate employed 10 mV s^{-1}. A second PMV instrument was used in the study of all radicals **1**−**9**. This instrument, built recently at the University of Aarhus, has been described by Daasbjerg et al.[19,20] The modulation frequncy was 134 Hz, and the voltammograms were recorded employing sweep rates of 20−100 mV s^{-1}. The main differences between the two instruments are the size of the chamber of the electrochemical flow cell and the working electrode area, both being approximately 5 times smaller for instrument number two. The working electrode was either a gold minigrid (1000 mesh, from Buckby-Mears or Dansk Hollandsk Ædelmetal) or a carbon minigrid (i.e., carbon fibers worn as a net with approximately 40 wires/cm); the latter was used in the second instrument only. The half-wave potentials, $E^{ox}_{1/2}$, were found to be independent of electrode material, instrumentation, and sweep rate, even though slight differences were observed in the shape of the voltammograms (see the Results and Discussion section). A series of 5−10 voltammograms were obtained for each compound on the basis of 50−100 mL of solution and a flow rate of 2−3 mL min^{-1}. Under these conditions, the temperature near the electrode surface was measured to be 24−26 °C. The voltammograms were corrected for the background current recorded in the absence of the substrate. All potentials were measured relative to the ferrocenium/ferrocene (fc^+/fc) redox couple, the potential of which in acetonitrile is equal to 0.41 V against the aqueous saturated calomel electrode (SCE).[21]

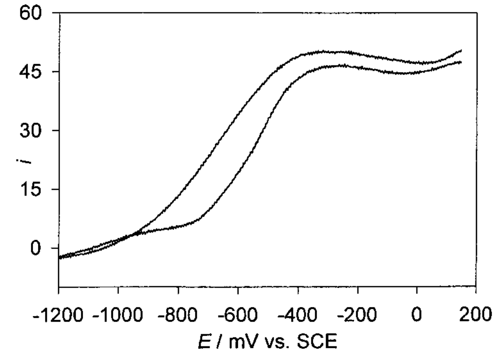


Figure 1. Photomodutated voltammogram of $(CH_3)_2C^{\bullet}OH$ (**1**) generated by photolysis of a mixture of 0.5 M acetone and 1.0 M 2-propanol at a gold electrode in a 0.1 M Bu_4NBF_4/CH_3CN solution (method A). The sweep rate is 0.1 V s^{-1}.

The hydroxyalkyl radicals **1**−**8**, $R^1R^2C^{\bullet}OH$, were generated by three different methods. In method A, the ketone $R^1R^2C{=}O$ (10−100 mM) is mixed with 2-propanol (250−500 mM), which allows the generation of **1**−**8** by the classical fast-exchange pinacol photoreaction as outlined in eqs 2−4.

$$R^1R^2C{=}O + h\nu \rightarrow R^1R^2C{=}O^* \tag{2}$$

$$R^1R^2C{=}O^* + (CH_3)_2CHOH \rightarrow R^1R^2C^{\bullet}OH + (CH_3)_2C^{\bullet}OH \tag{3}$$

$$R^1R^2C{=}O + (CH_3)_2C^{\bullet}OH \rightarrow R^1R^2C^{\bullet}OH + (CH_3)_2C{=}O \tag{4}$$

Method B is a slight modification of this scheme, with 2-propanol being replaced by the alcohol R^1R^2CHOH (20−100 mM). In method C, the radicals are formed in a hydrogen abstraction route involving R^1R^2CHOH (10−1000 mM) and *tert*-butylperoxy radicals generated by photolysis of di-*tert*-butyl peroxide (10% v/v) (eqs 5 and 6). The ether radical **9** was generated by photolysis of methyl (1-phenylethyl) ether (100 mM) and di-*tert*-butyl peroxide (10% v/v).

$$t\text{-BuO}{-}\text{OBu-}t + h\nu \rightarrow 2t\text{-BuO}^{\bullet} \tag{5}$$

$$t\text{-BuO}^{\bullet} + R^1R^2CHOH \rightarrow t\text{-BuOH} + R^1R^2C^{\bullet}OH \tag{6}$$

Results and Discussion

Half-Wave Potentials. Representative photomodulated voltammograms of the radicals **1**, **2**, and **5** are shown in Figures 1−3, respectivly. The steady-state voltammogram of **2** is clearly S-shaped, with the forward and backward sweeps following the same trace. The peak width, $E^{ox}_{3/4} - E^{ox}_{1/4}$, is equal to 196 mV, which is larger than the 56.4 mV expected for a reversible system.[22] For the corresponding voltammogram of the radical **1** shown in Figure 1, a sort of "hysteresis" effect is observed where the half-wave potential, $E^{ox}_{1/2}$, measured for the forward and backward scans is separated by approximately 50 mV. The same curves are obtained even after several cycles, so inhibition and absorption phenomena seem to be of no importance. The peak width is larger in this case, with $E^{ox}_{3/4} - E^{ox}_{1/4} = 225$ mV, which is indicative of relatively sluggish heterogeneous kinetics.

In Tables 1 and 2, we have collected the average results of the photomodulated voltammetry experiments under various experimental conditions. The difference in the half-wave

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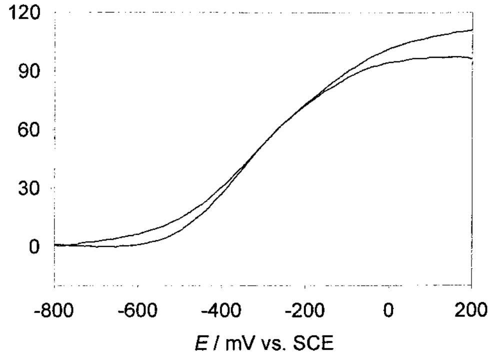

Figure 2. Photomodutated voltammogram of $Ph_2C^{\bullet}OH$ (**2**) generated by photolysis of a mixture of 50 mM benzophenone and 250 mM 2-propanol at a carbon fiber electrode in a 0.1 M Bu_4NBF_4/CH_3CN solution (method A). The sweep rate is 0.1 V s^{-1}.

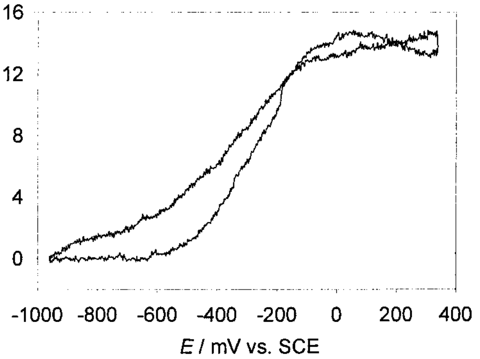

Figure 3. Photomodutated voltammogram of $PhC^{\bullet}HOH$ (**5**) generated by photolysis of a mixture of di-*tert*-butyl peroxide (10 vol %) and 0.10 M benzyl alcohol at a carbon fiber electrode in a 0.1 M Bu_4NBF_4/CH_3CN solution (method C). The sweep rate is 0.1 V s^{-1}.

potentials $E^{ox}_{1/2}$ obtained for the forward and backward scans, $\Delta E^{ox}_{1/2}$, in some cases constituted as much as 100 mV, depending on the method and equipment used. In general, the use of the hydrogen abstraction route (i.e., eqs 5 and 6) as well as small working electrodes gave the most consistent results. We do not believe that these problems are serious for the present study, since $E^{ox}_{1/2}$ determined as the average of the values obtained for the forward and backward scans was found to be constant. The uncertainty on the determination of $E^{ox}_{1/2}$ is ± 20 mV.

The oxidation potential of $(CH_3)_2C^{\bullet}{-}OH$ (**1**) in acetonitrile is −0.61 V vs SCE, which is in agreement with the value previously obtained by Wayner et al.[5] The exact value of this potential is very sensitive to the water content in acetonitrile, as it becomes equal to −1.3 V in a water solution.[5] The main reason for the large solvent effect is probably the much better ion solvation properties of water compared to those of acetonitrile, but the fast deprotonation reaction, eq 8, following the initial oxidation reaction, eq 7, may also play an important role.

$$R^1R^2C^{\bullet}OH \rightleftharpoons R^1R^2C^+{-}OH + e^- \qquad (7)$$

$$R^1R^2C^+\text{-}OH \rightarrow R^1R^2C{=}O + H^+ \qquad (8)$$

In aqueous solution the kinetic shift in the negative potential direction is larger than that in acetonitrile, as the deprotonation reaction in water is much faster than that in acetonitrile, which is a very weak base.

The potentials of **2**−**8** are much less dependent on the water content in acetonitrile, with the variation in $E^{ox}_{1/2}$ constituting less than 100 mV. Presumably, this is due to the delocalizing and stabilizing effect of the phenyl group(s) on the cation formed upon oxidation.

The voltammograms of the hydroxyl alkyl radicals are not reversible due to a combination of slow heterogeneous rate constants recognized by the relatively large $E^{ox}_{3/4} - E^{ox}_{1/4}$ values (85−225 mV) and the potential shift introduced by the deprotonation reaction, eq 8. The question is how far the $E^{ox}_{1/2}$ values are from the true thermodynamic values. In our recent study concerning the redox behavior of thiyl radicals, it was shown that the half-wave potentials obtained by photomodulated voltammetry were within 25 mV of the corresponding standard potentials measured by fast cyclic voltammetry, even when the width was 115 mV.[19] The possible potential shift introduced by the slow heterogeneous electrode kinetics is therefore relatively small.

The $E^{ox}_{1/2}$ values of **1** and **3** are −0.61 V and −0.24 V vs SCE, respectivly, and the corresponding alkyl ether radicals $(CH_3)_2C^{\bullet}{-}OCH_3$ and **9** are −0.45 V[17] and −0.11 V vs SCE, respectivly. The potential differences between the two ether radicals and their related hydroxylalkyl radicals are 160 and 130 mV, respectivly. The ether radicals are oxidized with no follow-up deprotonation reaction. The potential difference 130−160 mV may therefore be taken as a rough estimate of the negative potential shift introduced by the proton abstraction reaction, eq 8. On this basis we conclude that the present $E^{ox}_{1/2}$ values for **1**−**8** all will be close to the thermodynamic redox potential within 150 mV.

As to the substituent effects on $E^{ox}_{1/2}$ revealed by the numbers listed in Table 2, the potentials increase as the groups attached at the radical center are changed from alkyl to aryl and, in particular, strong electron-withdrawing functionalities such as CN and CF_3. In other words, the potential increases with increasing field/inductive constant of the α-substituent. It is peculiar, however, that the potential for $PhC^{\bullet}(OH)CN$ is 200 mV lower than the potential for $PhC^{\bullet}(OH)CF_3$, even though the field/inductive constant for CN is considerably higher than the constant for CF_3. Consequently, the correlation between the potentials and the field/inductive constants is poor, and further interpretation of these potentials is not possible.

Dissociation Constants of α-Hydroxyalkyl Radicals in Acetonitrile. Acid dissociation constants have been obtained by pulse radiolysis for a number of hydroxyalkyl radicals in water.[23] No values have, however, been determined experimentally in aprotic media, and only a few values have been estimated from thermodynamic calculations.[24] The pK_a of hydroxyalkyl radicals, $pK_a(KH^{\bullet})$, can be calculated via a thermochemical cycle involving the pK_a and standard potential of the corresponding protonated ketone, $pK_a(KH^+)$ and $E^{\circ}_{KH^+}$, in combination with the standard potential of the neutral ketone, E°_{K} (Scheme 1 and eq 9). A series of $pK_a(KH^+)$ values of protonated ketones, KH^+,

$$pK_a(KH^{\bullet}) = pK_a(KH^+) + \frac{F}{2.3RT}(E^{\circ}_{KH^+} - E^{\circ}_{K}) \qquad (9)$$

have been determined in water.[25,26] They are surprisingly insensitive to the structure of the ketone, exhibiting a variation of less than 1.1 p*K* units. Unfortunately, the $pK_a(KH^+)$ values

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Table 1. Half-Wave Oxidation Potentials, $E^{ox}_{1/2}$, of the Hydroxyalkyl and Ether Radicals **1**−**9** Obtained by Photomodulated Voltammetry in Acetonitrile by Different Methods and at Different Electrodes[a]

electrode	method[b]	1	2	3	4	5	6	7	8	9
gold	A	−0.58	−0.28	−0.25	−0.44				0.38	
carbon	A		−0.29					0.27		
gold	B	−0.63	−0.22	−0.21		−0.28				
gold	C	−0.63	−0.23	−0.27	−0.47	−0.32	0. 11			−0.11
carbon	C		−0.27					0.35		

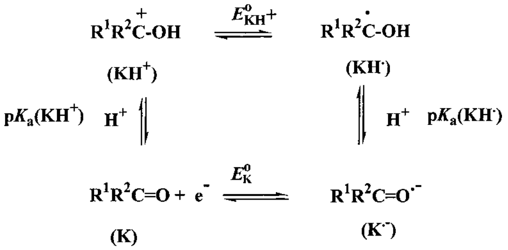
[a] In V vs SCE, average value of the half-wave potentials for the forward and backward sweeps. [b] For a description of the methods, see text. Uncertainties on the $E^{ox}_{1/2}$ values are ± 20 mV.

Table 2. Half-Wave Oxidation Potentials, $E^{ox}_{1/2}$, and Peak Widths, $E^{ox}_{3/4} - E^{ox}_{1/4}$, for the Hydroxyalkyl and Ether Radicals **1**−**9**

radical	$E^{ox}_{1/2}$ [a]	$E^{ox}_{3/4} - E^{ox}_{1/4}$ [b]	radical	$E^{ox}_{1/2}$ [a]	$E^{ox}_{3/4} - E^{ox}_{1/4}$ [b]
1	−0.61	225	**6**	0.11	85
2	−0.25	196	**7**	0.31	170
3	−0.24	200	**8**	0.38	100
4	−0.46	163	**9**	−0.11	127
5	−0.30	200			

[a] V vs SCE; average of the values listed in Table 1. Uncertainties on the $E^{ox}_{1/2}$ values are ±20 mV. [b] In mV.

Scheme 1



of 0.1 and 0.14 for acetone and acetophenone, respectively, are the only values known for ketones in acetonitrile.[25] However, since these two specific compounds represent the extremes in water, it seems to be a reasonable assumption that the pK_a(KH$^+$) values in acetonitrile should be about the same for the six ketones shown in Table 3, i.e., p$K_a \approx 0.1$.[27] As a direct consequence, the variation in the pK_a values of the six hydroxyalkyl radicals is determined exclusively by the potential difference, $E^{\circ}_{KH^+} - E^{\circ}_{K}$. The standard potentials $E^{\circ}_{KH^+}$ were simply approximated by the oxidation potentials of the hydroxy radicals measured herein, $E^{ox}_{1/2}$, as they are close to each other within 150 mV. The standard potentials E°_{K} were either available in the literature[28,29] or measured herein by cyclic voltammetry; these values are listed in column 5 of Table 3. The uncertainty on the calculated pK_a(KH$^\bullet$) values is estimated to be 2 units for all compounds but acetone, in the case of which the uncertainty is larger due to the unknown kinetic shift of $E^{ox}_{1/2}$.

The calculated pK_a(KH$^\bullet$) values of the hydroxyalkyl radicals in acetonitrile are shown in column 7, along with the corresponding values previously determined in water by pulse radiolysis.[23] There is a variation of 12 units going from pK_a(KH$^\bullet$) = 21 for benzaldehyde to pK_a(KH$^\bullet$) = 32 for acetophenone. The average difference of the two sets of values obtained in acetonitrile and water, ΔpK_a(KH$^\bullet$), is 17. In comparison, the corresponding average difference for the protonated ketones in water and acetonitrile, ΔpK_a(KH$^+$), is 6.8. In this context, it is interesting that the average values of ΔpK_a(KH) and ΔpK_a(KH$^+$) for various organic acids, KH, are 16 and 8, respectivly.[25] This is well in line with the results obtained in the present work.

Exchange Reaction. Relatively few rate constants k_{ex} for the exchange reaction shown in eq 1 have been obtained by means of quantum yield measurements,[11] laser flash photolysis,[14] and CIDEP.[30] This fact, combined with the lack of data for the oxidation potentials of the hydroxyalkyl radicals, has so far prevented a better description of the mechanism of the exchange reaction. In Table 4, we have collected all relevant data. For the reactions involving the systems **2/3** and **3/2**, it was not possible to extract absolute k_{ex} values. However, on the basis of product distributions, the latter system is characterized as a fast exchange process since no cross coupling products are observed. In contrast to this behavior, the former system is characterized by a medium fast exchange process since cross coupling products are formed.[13]

Formally, the exchange reaction depicted in eq 1 is a hydrogen atom transfer process. Equivalently, it could be regarded as a one-step concerted transfer of an electron and a proton. In this respect, conditions might even be envisioned in which the electron/proton-transfer steps are separated in that the electron-transfer process depicted in eq 10 involving the hydroxyalkyl radical and the ketone is the rate-controlling step occurring prior to the proton shift (eq 11).

$$Ph_2C{=}O + R^1R^2C^\bullet OH \rightarrow R^1R^2C^+{-}OH + Ph_2C{=}O^{\bullet -} \quad (10)$$

$$R^1R^2C^+{-}OH + Ph_2C{=}O^{\bullet -} \rightarrow R^1R^2C{=}O + Ph_2C^\bullet OH \quad (11)$$

The driving force for this reaction is simply given as $\Delta G^{\circ}_{ET} = F(E^{ox}_{1/2} - E^{\circ}_{K})$. The values of ΔG°_{ET} are included in Table 4 (column 5). It should be noted that the thermodynamic significance of the value listed for the reactions involving $(CH_3)_2C^\bullet OH$ is questionable since its $E^{ox}_{1/2}$ value is affected by a slow heterogeneous rate constant, a fast deprotonation reaction, and large solvent effects, as discussed earlier. In the following discussion, the emphasis will be on the latter four systems.

Overall, there appears to be a weak correlation between log k_{ex} and ΔG°_{ET}. For instance, the rate constant for the exchange reaction of **3** with 4-methylacetophenone ($\Delta G^{\circ}_{ET} = 1.86$ eV) is a factor of 20 lower than the corresponding rate constant for the reaction of **5** with the more easily reduced benzaldehyde

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(27) As pointed out by one reviewer, it is unlikely that the pK_a(KH$^+$) in acetonitrile of trifluoroacetophenone and benzoyl cyanide with the very polar substituents CF_3 and CN should be the same as for acetone and acetophenone. The gas-phase proton affinities of acetone, acetophenone, benzophenone, benzaldehyde, and trifluroacetophenone are 194, 206, 211, 199, and 191 kcal/mol, respectivly (Hunter, E. P.; Lias, S. G. Evaluated Gas-Phase Basicities and Proton Affinities of Molecules: An Update. *J. Phys. Chem. Ref. Data* **1998**, *27* (3), 413). For the first four compounds, the pK_a's in water (see Table 3) are roughly correlated with the proton affinities in the gas phase. Applying this correlation for trifluoroactophenone gives a pK_a value of −7.4 in water, which is only slightly more acidic than acetone. It is therefore possible that the pK_a in acetonitrile should be close to 0.1, even for this ketone.

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Table 3. Calculated Dissociation Constants of α-Hydroxyalkyl Radicals, pK_a(KH$^\bullet$), in Acetonitrile

K	pK_a(KH$^+$), H_2O	pK_a(KH$^\bullet$), H_2O	$E_{1/2}^{ox}$ ^{a}	E_K° ^{a}	pK_a(KH$^+$), CH_3CN	pK_a(KH$^\bullet$), CH_3CN	ΔpK_a(KH$^\bullet$), CH_3CN-H_2O
acetone	−7.2^{b,c}	12.0^d 12.2^e	−0.61	−2.35^d	0.1^b	30	18
acetophenone	−6.1^{b,c}	9.9^e	−0.24	−2.14	0.14^b	32	22
4-methylacetophenone			−0.46	−2.09	0.1^f	28	
benzophenone	−6.2^c	9.2^e	−0.25	−1.71	0.1^f	25	16
benzaldehyde	−7.0^c	7.0^c	−0.30	−1.55^g	0.1^f	21	14
fluorenone	−6.85^c	6.3/9.5^c	+0.38	−1.23	0.1^f	27	21/17

[a] V vs SCE, measured in acetonitrile. [b]From ref 25. [c] From ref 26. [d] From ref 28. [e] From ref 22. [f] Assumed to be the same as for acetone and acetophenone. [g] From ref 29.

Table 4. Thermodynamic and Kinetic Parameters for the Exchange Process between Hydroxyalkyl Radicals and Ketones in Acetonitrile: $K + K^1H^\bullet \rightarrow KH^\bullet + K^1$

K	$K^1H^\bullet$	$KH^\bullet$	k_{ex} ^{a}	ΔG°_{ET} ^{b}	ΔG°_{ex} ^{b}	$\Delta G^\ddagger_{o,ex}$ ^{c}
benzophenone	**1**	**2**	7×10^4 ^{d}	1.10	−0.36	12.9
benzaldehyde	**5**	**5**	8×10^4 ^{e}	1.25	0	12.5
4-methylacetophenone	**3**	**4**	4.2×10^3 ^{f}	1.86	+0.22	8.2
acetophenone	**2**	**3**	medium^g	1.85	−0.01	
benzophenone	**3**	**2**	fast^g	1.45	+0.01	

[a] In M^{-1} s^{-1}. [b] In eV. [c] In kcal mol^{-1}. [d] From ref 14. [e] From ref 31. [f] From ref 11, obtained in benzene. [g] From ref 13.

($\Delta G^\circ_{ET} = 1.25$ eV). Even though this trend is consistent with the changes in ΔG°_{ET}, the strong endergonic nature of the ET reactions certainly precludes them from being the outer-sphere processes. Calculations of the expected outer-sphere ET rate constants on the basis of the Marcus and Eyring equations (using a collision frequency of 3×10^{11} M^{-1} s^{-1} and a reorganization energy of the reactions of 10 kcal mol^{-1}) show that they are prohibitively slow (4×10^{-12} M^{-1} s^{-1} for $\Delta G^\circ_{ET} = 1.10$ eV and 1.5×10^{-40} M^{-1} s^{-1} for $\Delta G^\circ_{ET} = 1.86$ eV, respectively). Reorganization energies larger than 10 kcal mol^{-1} would lower the calculated rate constants further.

An outer-sphere electron-transfer process thus is excluded as a mechanistic pathway for the exchange reaction. This leaves us with the possibilities of (i) an inner-sphere electron-transfer rate-controlling step, (ii) a proton shift that occurs prior to the electron transfer, and (iii) the two steps taking place concertedly as a one-step hydrogen atom transfer route, perhaps via a polar transition state. While the first possibility cannot be excluded rigorously, it does not seem likely, as it would require a stabilization of the transition state (i.e., lowering of the activation barrier) by as much as 20−60 kcal mol^{-1}. The possibility of a proton shift from the hydroxyalkyl radical to the neutral ketone can be excluded on energetic grounds due to the much stronger basicity of the ketone radical anion compared to the neutral ketone. This leaves us with the third and most straightforward possibility, the hydrogen atom transfer route, the energetics of which are favorable. The driving force, $-\Delta G^\circ_{ex}$, for the exchange reaction $K + K^1H^\bullet \rightarrow KH^\bullet + K^1$ may be calculated by a simple thermodynamic cycle according to eq 12. Since all pK_a(KH$^+$) values are similar, as discussed in the previous section, ΔG°_{ex} is simply given by the potential difference of the oxidation potentials of the pertinent hydroxyalkyl radicals involved in the exchange reaction, eq 13.

$$\Delta G^\circ_{ex} = F(E^\circ_{K^1H^+} - E^\circ_{KH^+}) + 2.3RT[pK_a(K^1H^+) - pK_a(KH^+)] \quad (12)$$

$$\Delta G^\circ_{ex} \approx F[E^{ox}_{1/2}(K^1H^\bullet) - E^{ox}_{1/2}(KH^\bullet)] \quad (13)$$

The values of ΔG°_{ex} for the exchange reactions considered in Table 4 are listed in column 6. As can be seen, they are all relatively small, the exception being for the **1/2** system, due to the similarity of the structures of the products and reactants. The great advantage of not considering too exothermic or endothermic processes is that the Marcus equation, as shown in eq 14, is directly applicable to H atom transfer processes.[31]

$$\Delta G^\ddagger_{ex} = \Delta G^\ddagger_{o,ex}(1 + \Delta G^\circ_{ex}/4\Delta G^\ddagger_{o,ex})^2 \quad (14)$$

In this expression $\Delta G^\ddagger_{ex}$ and $\Delta G^\ddagger_{o,ex}$ are the activation and intrinsic barriers, respectively. Combining this equation with the Eyring expression shown in eq 15, where the collision frequency Z is assumed to be equal to 3×10^{11} M^{-1} s^{-1}, allows the calculation of $\Delta G^\ddagger_{o,ex}$ from the values of k_{ex}. The $\Delta G^\ddagger_{o,ex}$

$$k_{ex} = Z \exp(-\Delta G^\ddagger_{ex}/RT) \quad (15)$$

values listed in column 7 vary from 8.2 kcal/mol for the **3/4** system to 13 kcal mol^{-1} for the **1/2** and **5/5** systems, which does not seem unreasonable if it is considered that the hydrogen atom transfer involves the cleavage/formation of an O−H bond and the formation/cleavage of a C═O double bond, as well as major changes occurring in hybridizations and bond angles. Note that k_{ex} was obtained for **3/4** in the more unpolar benzene as solvent rather than acetonitrile. As a consequence, the solvent reorganization would be expected to be smaller for this system than for **1/2** and **5/5**, particularly if the transition states have polar character. This might also provide the explanation why $\Delta G^\ddagger_{o,ex}$ for **3/4** is lower by 5 kcal/mol, as there are no obvious reasons why the inner reorganization should differ for the three systems. However, it is uncertain to what extent ΔG°_{ex} is affected by the solvent effect and how much this would influence the calculated value of $\Delta G^\ddagger_{o,ex}$. As to the polar character of the transition states, the presence of a weak correlation between k_{ex} and the potential difference $F(E^\circ_K - E^{ox}_{1/2})$ indicates that even if some charge transfer is occurring between the hydroxyalkyl radical and the ketone in the transition state of the exchange reaction, it is far from being to the extent of a complete electron transfer. The fact that the driving force is close to zero suggests that there should be a large degree of symmetry of the transition state, and therefore one could imagine that the hydrogen atom functions as a bridge between the oxygen atoms of the two reactants.

Conclusion. Oxidation potentials between −0.61 V and +0.38 V vs SCE of the hydroxyalkyl radicals **1**−**8** have been obtained in acetonitrile by photomodulated voltammetry. The potential of **1** is solvent dependent, which may be explained by differences in ion solvation and the rate of the follow-up deprotonation reaction occurring after the oxidation process. The other oxidation potentials are less solvent dependent and thus

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(31) Blowers, P.; Masel, R. I. *J. Phys. Chem. A* **1999**, *103*, 7047.

expected to be closer to the thermodynamic standard potential of corresponding protonated ketones. The values of $E^{\mathrm{ox}}_{1/2}$ increase as the groups attached to the radical center are changed from alkyl to aryl and, in particular, strong electron-withdrawing functionalities such as CN and CF_3. Rate data available in the literature for the pinacol photoexchange reaction $K + K^1H^\bullet \rightarrow KH^\bullet + K^1$ show that when the difference between the standard potential of the ketone K, E°_K, and the oxidation potential of $K^1H^\bullet$, $E^{\mathrm{ox}}_{1/2}$, is raised, the increase in the rate constant, k_{ex}, is modest. This indicates that even if some charge transfer may occur between the hydroxyalkyl radical and the ketone in the transition state, it is certainly not to the extent of a complete electron transfer. If the exchange reaction is treated as a simple hydrogen atom transfer process within the Marcus model, the intrinsic barrier is found to be 8−13 kcal mol^{-1} due to the changes occurring in bonds, hybridizations, and bond angles. Finally, the pK_a values in acetonitrile of $KH^\bullet$ were calculated by means of a thermochemical cycle. The calculated pK_a values in acetonitrile were approximately 17 units higher than the corresponding pK_a values in water.

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