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Does Metal Ion Complexation Make Radical Clocks Run Fast? An Experimental Perspective

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ABSTRACT

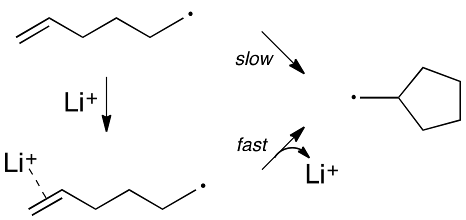
The rate constant for the β-scission of the cumyloxyl radical (k_β) was measured in the presence of various added electrolytes in acetonitrile and DMSO solvent. The results show that in CH_3CN, k_β increases in the presence of added electrolyte, roughly paralleling the size of the cation: $Li^+ > Mg^{2+} \approx Na^+ > {}^nBu_4N^+ >$ no added electrolyte. This effect is attributable to stabilizing ion-dipole interactions in the transition state of the developing carbonyl group, a conclusion supported by MO calculations (gas phase). Compared to the gas phase predictions however, this effect is seriously attenuated in solution because complexation of the cation to the electrophilic alkoxyl radical (relative to the solvent, CH_3CN) is very weak. Because the interaction of Li^+ and Na^+ is much stronger with DMSO than with CH_3CN, addition of these ions has no effect on the rate of β-scission.

INTRODUCTION

Radical clocks,[1] usually based upon unimolecular fragmentations or rearrangements with known absolute rate constants, are used to measure the rate constants of competing bimolecular products through competition kinetics. The underlying assumption in these experiments is that the unimolecular rate constant for the clock reaction is constant and not affected by reaction conditions.

In 2003, Horn and Clark posed the intriguing question "*Does Metal Ion Complexation Make Radical Clocks Run Fast?*"[2] To answer this question, these workers studied, computationally, the Δ^5-hexenyl radical rearrangement (Scheme 1), postulating that complexation of a metal ion to the double bond would decrease the activation energy (E_a). These authors found that cations (in general) were predicted to decrease the activation barrier to ring closure. For alkali metals, the predicted decrease in E_a paralleled the size of the ion. For Li^+, which exhibited the most dramatic effect, the barrier decreased from 8.3 to 3.2 kcal/mol (CBS-RAD-(QCISD,B3-LYP), which equates to a three order of magnitude rate acceleration in the presence of Li^+. The magnitude of this effect, of course, would likely be diminished in a polar solvent (vs. the gas phase) but the calculations nonetheless predicted a ca. 1.7 kcal/mol reduction of the barrier in THF (obtained via explicit solvation of the reactants and transition state).[2]

Scheme 1. Complexation of Lithium Ion to the Double Bond of Δ^5-Hexenyl Radical is Predicted to Enhance the Rate of Cyclization



The rationale for Horn and Clark's hypothesis, *i.e.*, that Li^+ will complex to a double bond and lower the activation barrier for intermolecular radical additions, has received some experimental and computational support in the polymer literature as Li^+ complexation has been demonstrated to "catalyze" the free radical polymerization of olefins, increase the propagation rate constant, etc.[3-6] However, the original question posed about radical clocks (unimolecular reactions) in their 2003 paper remains unanswered. Moreover, questions about how metal ions might affect rates of other classes of clock reactions have yet to be addressed.

Our interest in this question comes from a slightly different perspective. Neutral free radicals can be generated by the electrochemical oxidation and reduction of anions and cations, respectively. Because electrochemical techniques such as cyclic voltammetry can be used to measure rate constants for reactions following electron transfer (illustrated for oxidation of an anion in Scheme 2), and electrochemical oxidations/reductions require a supporting electrolyte, the possibility that an ion can change the rate of a neutral radical reaction becomes an important issue.

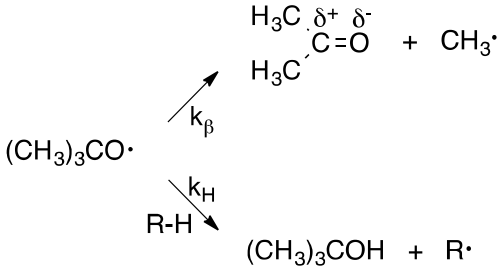
Scheme 2. Neutral Radicals Generated by the Electrochemical Oxidation of the Corresponding Anions

$$A^- \longrightarrow A\cdot + e^-$$

$$A\cdot \longrightarrow \text{Product}$$

To test whether the unimolecular rate constant for a neutral radical clock reaction would vary in the presence of a cation, we examined the rate constant for β-scission of alkoxyl radicals. In work dating back to the early 1960s, Walling and co-workers used the β-scission of t-butoxyl radical as a free radical clock to measure the rate constants for competing hydrogen abstraction reactions (Scheme 3).[7] Walling and Wagner also suggested that k_β increased with solvent polarity (attributable to an increase in dipole moment of the transition state associated with the formation of a polar carbonyl group),[8] a hypothesis that was subsequently confirmed three decades later.[9-11]

Scheme 3. β-Scission of t-Butoxyl Radical is Faster in Polar Solvents



Based upon this precedent, it was quite reasonable to suspect that if the transition state for β-scission is stabilized by a polar solvent (dipole-dipole interaction), the transition state might also be stabilized by an ion-dipole interaction as well. As a test, the rate constant for β-scission of cumyloxyl radical was measured in the presence of various electrolytes typically used for electrochemical studies, as well as added water. Cumyloxyl, rather than t-butoxyl, radical was used because of its characteristic absorbance at 485 nm that could be used to monitor the kinetics of the reaction.[9,10,12]

EXPERIMENTAL AND THEORETICAL METHODS

Dicumyl peroxide (98%), lithium perchlorate ($LiClO_4$, 99.9%), magnesium perchlorate ($Mg(ClO_4)_2$, ACS grade), and sodium perchlorate ($NaClO_4$, ACS grade) were purchased from Aldrich and used as received.

n-Tetrabutylammonium perchlorate (Bu_4NClO_4) was prepared by ion exchange reaction,[13] recrystallized 3-5 times from ethyl acetate/hexane, dried at 80 °C in a vacuum oven for 24 hours, dried over P_2O_5 in a vacuum desiccator and transferred under *vacuo* into the glovebox. D_2O (Aldrich, 99.9 atom % D) in 0.6 mL vials were purchased and used as received.

Steady-state UV-vis spectra were recorded on a Hewlett-Packard diode array UV-vis spectrophotometer (HP 8452A). Laser flash photolyses were performed with an Applied Photophysics LKS.80 spectrometer using the third harmonic of a Continuum Surelite I-10 Nd:YAG laser (4 – 6 ns pulse, 355 nm). Transient signals were monitored by a Hewlett-Packard Infinium digital oscilloscope and analyzed with the Applied Photophysics Spectra Kinetic Workstation software (version 4.59.) Variable temperature experiments were performed with a jacketed cell holder connected to a VWR Scientific Products (PolyScience) variable temperature-circulating bath (model 1150-A). The cell holder was equipped with a thermocouple to measure the temperature directly adjacent to the cuvette.

Steady-state UV-Vis spectra were recorded on all solutions to verify that dicumyl peroxide was the only species absorbing at the excitation wavelength prior to photolysis. Solutions containing the cumyloxyl radical precursor (dicumyl peroxide) and desired electrolyte were prepared in acetonitrile (or DMSO) solvent and purged for 10 minutes prior to photolysis. To test for possible laser power dependence on the apparent rate constant, solutions were flashed at various laser intensities. Within experimental error, k_β was constant, verifying that no other second order competing side reactions were occurring (*e.g.*, dimerization.)

For the variable temperature work, to minimize thermal decomposition of the peroxide, multiple samples were prepared and only exposed to high temperatures during the actual laser flash experiment. Samples were thermally equilibrated prior to photolysis by placing the cuvettes in a tray in the circulating bath for 10 min. Afterward, the samples were placed in the spectrometer and equilibrated for an additional 5 min. Temperature dependent studies were performed over the range -11 to 75 ^{o}C.

Calculations were performed using the Gaussian 09 computational software package.[14] Conformational analysis was performed at the B3LYP/6-31G* level of theory and basis set. All optimized reactant, transition state, and product structures, as well as potential energy surface profiles, were obtained at the B3LYP/6-311+(3df,2pd) level of theory and basis set (where the unrestricted method was used for open-shell systems). All optimized structures were verified, and thermochemical corrections to the electronic energies were obtained from frequency jobs at the same theory and basis set. Single point energies for all optimized structures were obtained with the CCSD(T)/Aug-CC-pVTZ theory and basis set. Thermochemical corrections from the lower level frequency jobs were applied to the single point energies from the CCSD jobs to obtain the thermochemical data presented in Tables 3 and 4. For $M^+ = {}^{n}Bu_4N^+$, the optimization and frequency jobs were only performed at the B3LYP/6-31G* level of theory and basis set and the single point energies were obtained with the CCSD/ 6-31G* theory and basis as the large size of the cation made more expensive methods unfeasible. Additionally, the convergence criteria for the single point job of the parent cumyloxyl radical/$^{n}Bu_4N^+$ structure had to be reduced by one significant figure in order to achieve convergence. The visualization software MOLDEN was used to visualize the Gaussian output files.[15]

RESULTS AND DISCUSSION

Rate Constants and Activation Parameters

Cumyloxyl radical (**1**) was generated by flash photolysis of dicumyl peroxide at 355 nm in acetonitrile, and its characteristic absorption at *ca.* 485 nm was used to follow the kinetics.[9,10,12] Rate constants measured in the presence of various electrolytes (that were sufficiently soluble in CH_3CN) are summarized in Table 1. We also determined the rate constant in the presence of H_2O, D_2O, and in the presence of electrolyte plus water. These results are summarized in the Supporting Information.

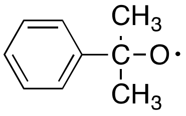


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Table 1. Rate Constants for the β-Cleavage of Cumyloxyl Radical in the Presence of Various Electrolytes in CH_3CN at 25 °C

	$k_\beta/10^5$ s^{-1}			
[Electrolyte] /mol·L^{-1}	$LiClO_4$	$NaClO_4$	$^nBu_4NClO_4$	$Mg(ClO_4)_2$
0	8.1 (0.2)			
0.08	9.2 (0.2)	8.4 (0.2)	8.2 (0.2)	8.3 (0.3)
0.15	10.1 (0.2)	8.6 (0.2)	8.6 (0.2)	9.5 (0.3)
0.23	10.0 (0.2)	9.0 (0.2)	8.7 (0.2)	9.7 (0.3)
0.31	11.5 (0.3)	9.4 (0.2)	9.1 (0.3)	9.2 (0.3)
0.39	12.6 (0.2)	10.2 (0.2)	9.5 (0.3)	
0.62	16.4 (0.3)	11.2 (0.2)	10.5 (0.3)	
0.77	19.2 (0.8)	11.9 (0.2)	10.7 (0.3)	
1.15			11.8 (0.4)	
1.54			12.8 (0.5)	

Arrhenius parameters for β-cleavage in CH_3CN with added electrolyte, H_2O, and D_2O were determined via non-linear regression analysis in accordance with the Arrhenius equation (Eq 1); reported errors are based upon 95% confidence limits. The results are summarized in Table 2.

$$k = Ae^{-E_a/RT} \qquad (1)$$

Table 2. Arrhenius Parameters for the β-Cleavage of Cumyloxyl Radical in the Presence of Various Additives (M) in CH_3CN

M	[M]/mol·L^{-1}	log(A/s^{-1})	E_a/kcal·mol^{-1}	k_β /10^5 s^{-1} at 30 °C
None	0.00	11.5 (0.2)	7.7 (0.7)	11.2 (0.6)
$LiClO_4$	0.23	11.5 (0.2)	7.5 (0.3)	14.4 (0.5)
	0.39	11.6 (0.4)	7.5 (0.5)	17.6 (0.7)
	0.77	11.6 (0.9)	7.4 (0.7)	21.8 (0.7)
$NaClO_4$	0.39	11.1 (0.2)	7.0 (0.6)	13.7 (0.8)
$^nBu_4NClO_4$	0.39	11.2 (0.6)	7.2 (0.6)	12.8 (0.9)
$MgClO_4$	0.39	11.5 (0.2)	7.5 (0.7)	12.7 (0.9)
H_2O	2.1	11.3 (0.2)	7.1 (0.3)	14.0 (0.6)
D_2O	2.1	11.5 (0.2)	7.4 (0.2)	13.2 (0.4)

To obtain further insight, the free energy of activation for the β-cleavage of the t-butoxyl radical (complexed to Li^+, Na^+, K^+, and $^nBu_4N^+$) were obtained through molecular orbital calculations (gas phase, Table 3). To assess the relative binding affinity of the cations (M^+) to t-butoxyl radical relative to the solvent (CH_3CN), ΔG for the following exchange reaction was determined: $CH_3CN/M^+ + {}^tBuO\bullet \rightarrow CH_3CN + {}^tBuO\bullet/M^+$; the results are summarized in Table 4.

Table 3. Calculated (CCSD(T)/uB3LYP) Activation Free Energies for β-Scission of t-Butoxyl Radical Complexed to a Cation in the Gas Phase

M^+	$\Delta G^\ddagger$/kcal·mol^{-1}
None	13.8
K^+	7.6
Na^+	5.8
Li^+	2.8
${}^nBu_4N^+$	14.0[a]

[a] Obtained from CCSD/uB3LYP theory and 6-31G* basis set. See note in experimental methods. The values above are calculated based on

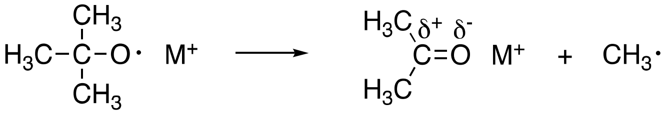

Table 4. Calculated (CCSD/B3LYP) ΔG for Binding of t-Butoxyl Radical to Cations (Relative to CH_3CN) in the Gas Phase

M^+	ΔG/kcal·mol^{-1}
K^+	4.0
Na^+	5.5
Li^+	5.3
${}^nBu_4N^+$	2.91[a]

[a] ΔE obtained from B3LYP/6-31G* theory and basis set. See note in experimental methods. The values above are calculated based on

$$CH_3CN/M^+ + {}^tBuO\cdot \longrightarrow CH_3CN + {}^tBuO\cdot/M^+$$

In all cases, the addition of electrolyte increased the rate constant for β-scission of the cumyloxyl radical (Table 1; Figure 1) in the order $Li^+ > Mg^{2+} \approx Na^+ > {}^nBu_4N^+$; for clarity, the results for $Mg(ClO_4)_2$ were omitted from the figure. The magnitude of the effect increased with increasing electrolyte concentration. This study was somewhat limited by the solubility of the electrolyte in CH_3CN solvent; *e.g.*, $KClO_4$ was not sufficiently soluble.

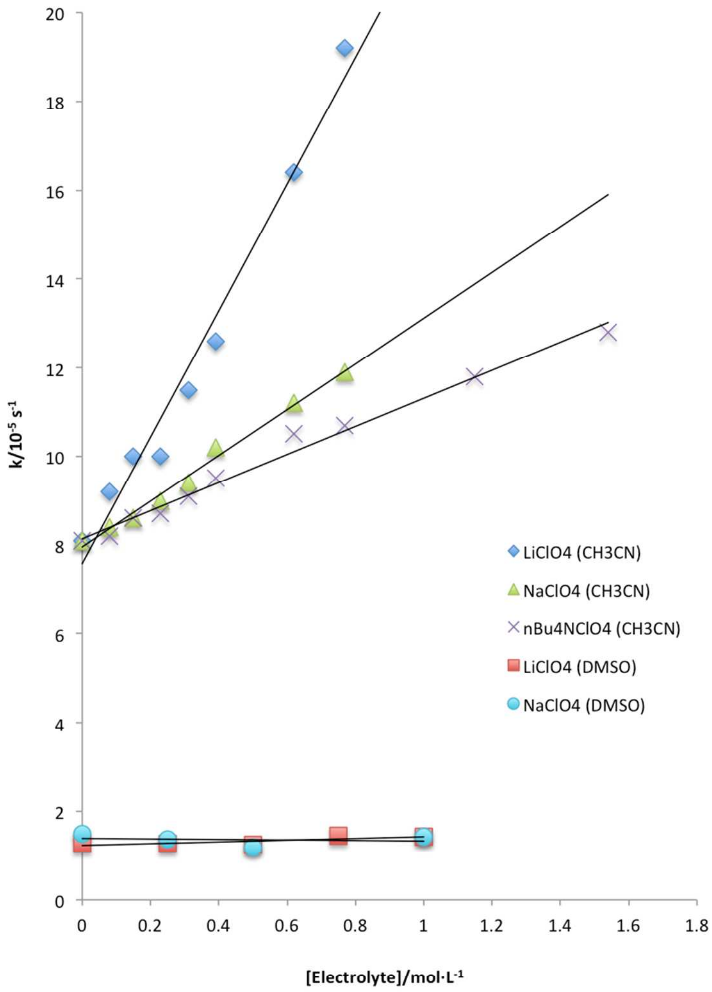

Figure 1. Rate Constants for the β-Scission of Cumyloxyl Radical in the Presence of Added Electrolytes (CH_3CN and or DMSO Solvent, Ambient Temperature)

The activation energy for β-scission was also examined in the presence and absence of electrolyte (Table 2). Although the results seem to suggest a lowering of the barrier when M^+ is present, the effect is too small to be detected (*i.e.*, for all the cations, differences in the measured activation energies are within experimental uncertainty). Consequently, to further probe whether the observed trend was consistent with the hypothesis that cation complexation with the developing C=O in the transition state was responsible for the observed rate enhancement, MO calculations (gas phase) were performed to model the effect of cations on the analogous β-scission of t-butoxyl radical. The results are summarized in Table 3.

Although *qualitatively* consistent with the notion that complexation of M^+ to an alkoxyl radical will lower the barrier to β-cleavage, the most striking result from the gas phase calculations is that the effect is predicted to be much greater than what was experimentally observed. Almost certainly, the explanation is that in solution, complexation of M^+ to an electron deficient species such as an alkoxyl radical is strongly disfavored (relative to complexation to the solvent, CH_3CN). The calculations summarized in Table 4 clearly support this interpretation.

A reviewer of this manuscript suggested that these conclusions might be further amplified by performing these experiments in an additional solvent, and in response, some of these experiments were repeated in DMSO with $LiClO_4$ and $NaClO_4$ (two of the electrolytes that exhibited the largest effect in acetonitrile). Cumyloxyl radical is known to abstract hydrogen from DMSO ($k_H = 1.8\ (\pm 0.1) \times 10^4\ M^{-1}s^{-1}$),[16] but this competing pathway constitutes less than 10% of the observed rate constant, and is easily corrected for ($k_\beta = k_{obs} - k_H[DMSO]$.)

As shown in Figure 1, over the same range of concentrations, added Li^+ or Na^+ has no effect on the rate constant for β-scission when DMSO is the solvent. This result makes perfect sense because Li^+ and Na^+ are much more strongly solvated by DMSO compared to CH_3CN; the free energies of transfer from $CH_3CN \rightarrow$ DMSO are –14.9 and –5.9 kcal/mol, respectively.[17]

We also examined whether k_β would be lowered with the addition of water, perhaps as a result of hydrogen bonding to the developing C=O in the transition state. As shown in Figure 2, in the presence and absence of electrolyte ($^nBu_4NClO_4$), k_β increased modestly with increased water concentration (CH_3CN solvent.)

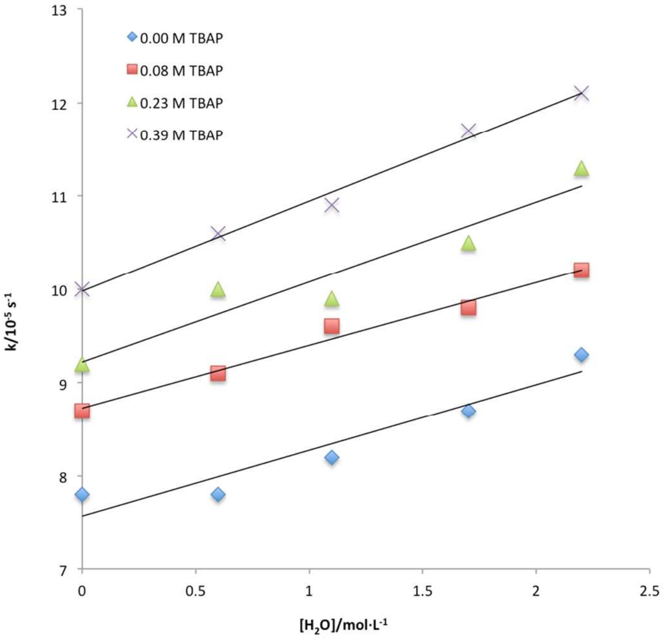

Figure 2. The Combined Effect of Electrolyte ($^nBu_4NClO_4$) and Water on the Rate Constant for β-Scission of t-Butoxyl Radical (CH_3CN Solvent, Ambient Temperature)

It was also thought that if H-bonding to the transition state were important, the system might exhibit a modest secondary kinetic isotope effect. Within experimental error however, there was no significant difference between H_2O and D_2O in either the observed rate constants or activation parameters (Table 2). To the extent there was an isotope effect, these measurements were not sensitive enough to detect it. Hence, these results do not reveal whether the rate increases because the transition state is stabilized by H-bonding to water, or simply because the solvent polarity increases with water addition.

CONCLUSIONS

The results demonstrate that through complexation, the absolute rate constants for radical clock reactions such as the β-scission of alkoxyl radicals are influenced by cations ($Li^+ > Mg^{2+} \approx Na^+ > {}^nBu_4N^+$). This effect is attributable to stabilizing ion-dipole interactions in the transition state of the developing carbonyl group, a conclusion supported by MO calculations. In solution however, this effect is seriously attenuated because complexation of the cation to the electrophilic alkoxyl radical (relative to the solvent, CH_3CN) is very weak. Presumably the effect would be greater in a non-polar solvent, but this would be difficult to test experimentally because of solubility issues. In DMSO, which binds Li^+ and Na^+ more tightly, this effect is not observed. Addressing the original question posed by Horn and Clark, yes, metal ion complexation can cause radical clocks to run fast—and for reasons that make sense based on fundamental principles. However, these results also go one step further by showing that that even if the complexation between the radical and ion is unfavorable, a significant effect can be observed if, in cases such as studied herein, there is an increase in dipole moment going from reactant → transition state.

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SUPPORTING INFORMATION. Tables of rate constants summarizing results shown in Figures 1 and 2, rate constants measured in the presence of D2O/H2O, pertinent Arrhenius plots, cartesian coordinates and Gaussian log archival data for all optimized structures, and the full Gaussian reference.pd

ACKNOWLEDEMENT

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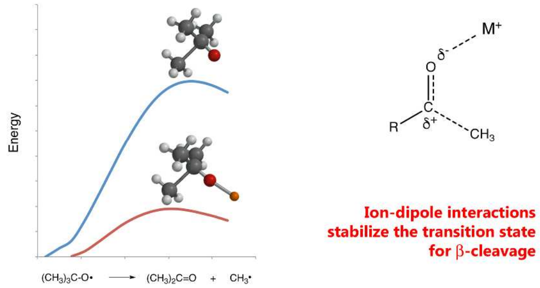

Ion-dipole interactions stabilize the transition state for β-cleavage