Hydrogen Atom Transfer from 1,2- and 1,3-Diols to the Cumyloxyl Radical. The Role of Structural Effects on Metal-Ion Induced C–H Bond Deactivation

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2) Experimental section

Materials. Spectroscopic grade acetonitrile was used in the kinetic experiments. Dicumyl peroxide, 2-propanol, 1,2-ethanediol, 1,2-propanediol (racemic), 1,3-propanediol, meso-1,2-diphenyl-1,2-ethanediol, (1R,2R)-1,2-diphenyl-1,2-ethanediol, cyclopentanol, cyclohexanol, cis-1,2-cyclopentanediol, trans-1,2-cyclopentanediol (racemic), cis-1,2-cyclohexanediol, trans-1,2-cyclohexanediol (racemic), were of the highest commercial quality available and were used as received. Lithium perchlorate (LiClO$_4$), magnesium perchlorate (Mg(ClO$_4$)$_2$), and calcium perchlorate (Ca(ClO$_4$)$_2$) were of the highest commercial quality available and were used without any drying procedure.

Laser flash photolysis studies. The time-resolved kinetic studies have been carried out by LFP employing a laser kinetic spectrometer using the third harmonic (355 nm) of a Q-switched Nd:YAG laser, delivering pulses of the duration of 8 ns. The laser energy has been adjusted by the use of the appropriate filter to $\leq$ 10 mJ/pulse. A 3.5 mL quartz cell (Suprasil, 10 mm $\times$ 10 mm) has been used and all the experiments have been carried out at $T = 25 \pm 0.5$ °C under magnetic stirring. Experiments have been typically carried out employing argon or nitrogen saturated acetonitrile solutions containing 1.0 M dicumyl peroxide. The observed rate constants ($k_{obs}$) have been obtained following the decay of the cumyloxyl radical (CumO$^*$) absorption band at 490 nm as a function of the concentration of added substrate. Second order rate constant ($k_{H}$) for the reactions of CumO$^*$ with the alcohol and diol substrates, in acetonitrile and in acetonitrile containing the metal ion salts, have been obtained from the slopes of the $k_{obs}$ vs [substrate] plots at constant salt concentration.
The concentration variation was performed by direct addition of the substrate to solutions containing dicumyl peroxide and the metal ion salt. The \( k_H \) values are the average at least two values obtained through independent experiments, with typical errors being \( \leq 10 \% \). In all the graphs displayed in the following section (Figures S1-S11), the different intercepts of the plots reflect the effect of the metal ion on the CumO\(^•\) \( \beta \)-scission.\(^{S1}\)

The upper limit to \( k_H \), estimated for the reactions of CumO\(^•\) with 1,2- and 1,3-diol substrates carried out in the presence of Ca(ClO\(_4\))\(_2\) (Table 1), is derived from the comparison of the kinetic effects observed in these reactions, with those observed previously in the corresponding reactions of CumO\(^•\) with \( N,N \)-dimethylformamide and \( N,N \)-dimethylacetamide where, for both substrates, strong deactivation toward HAT was observed in the presence of Ca(ClO\(_4\))\(_2\), up to [substrate]/[Ca(ClO\(_4\))\(_2\)] = 4.\(^{S1}\) Along this line, the comparable decrease in \( k_{obs} \) observed following substrate addition for 1,2-diols, 1,3-diols and tertiary alkanamides, points toward a negligible contribution of HAT to \( k_{obs} \), leading, by comparison with the results obtained in the presence of LiClO\(_4\), to an upper limit to the rate constant for HAT from these substrates \( k_H < 2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1} \).  

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\(^{S1}\)
3) **Laser flash photolysis studies: \( k_{\text{obs}} \) vs [substrate] plots**

**Figure S1.** Plots of the observed rate constant (\( k_{\text{obs}} \)) against [2-propanol] for the reaction of CumO\(^\bullet\) generated by 355 nm LFP of an Ar-saturated MeCN solution containing 1.0 M dicumyl peroxide in the presence of a) 0.5 M LiClO\(_4\) (white circles); b) 0.5 M Mg(ClO\(_4\))\(_2\) (black squares); c) 0.4 M Ca(ClO\(_4\))\(_2\) (black triangles) measured at \( T = 25 \, ^\circ \text{C} \) following the decay of CumO\(^\bullet\) at 490 nm. From the linear regression analysis: a) intercept = 1.39 \( \times \) 10\(^6\) s\(^{-1}\), \( k_H = 1.01 \times 10^6 \, \text{M}^{-1} \, \text{s}^{-1}, r^2 = 0.9990; \) b) intercept = 1.01 \( \times \) 10\(^6\) s\(^{-1}\), \( k_H = 7.90 \times 10^5 \, \text{M}^{-1} \, \text{s}^{-1}, r^2 = 0.9918; \) c) intercept = 1.71 \( \times \) 10\(^6\) s\(^{-1}\), \( k_H = 1.18 \times 10^6 \, \text{M}^{-1} \, \text{s}^{-1}, r^2 = 0.9978.\)

**Figure S2.** Plot of the observed rate constant (\( k_{\text{obs}} \)) against [1,2-propanediol] for the reaction of CumO\(^\bullet\) generated by 355 nm LFP of an Ar-saturated MeCN solution containing 1.0 M dicumyl peroxide in the presence of a) 0.5 M LiClO\(_4\) (white circles); b) 0.5 M Mg(ClO\(_4\))\(_2\) (black squares); c) 0.4 M Ca(ClO\(_4\))\(_2\) (black triangles) measured at \( T = 25 \, ^\circ \text{C} \) following the decay of CumO\(^\bullet\) at 490 nm. From the linear regression analysis: a) intercept = 1.45 \( \times \) 10\(^6\) s\(^{-1}\), \( k_H = 7.42 \times 10^5 \, \text{M}^{-1} \, \text{s}^{-1}, r^2 = 0.9971; \) b) intercept = 1.04 \( \times \) 10\(^6\) s\(^{-1}\), \( k_H = 7.42 \times 10^5 \, \text{M}^{-1} \, \text{s}^{-1}, r^2 = 0.9971; \) c) intercept = 1.59 \( \times \) 10\(^6\) s\(^{-1}\).
**Figure S3.** Plots of the observed rate constant ($k_{obs}$) against [1,3-propanediol] for the reaction of CumO* generated by 355 nm LFP of an Ar-saturated MeCN solution containing 1.0 M dicumyl peroxide in the presence of a) LiClO$_4$ 0.5 M (white circles); b) Mg(ClO$_4$)$_2$ 0.5 M (black squares); c) Ca(ClO$_4$)$_2$ 0.39 M (black triangles), measured at $T = 25$ °C following the decay of CumO* at 490 nm. From the linear regression analysis: a) intercept = $1.43 \times 10^6$ s$^{-1}$, $k_H = 5.35 \times 10^5$ M$^{-1}$ s$^{-1}$, $r^2 = 0.9967$; b) intercept = $1.02 \times 10^6$ s$^{-1}$, $k_H = 7.02 \times 10^5$ M$^{-1}$ s$^{-1}$, $r^2 = 0.9906$; c) intercept = $1.64 \times 10^6$ s$^{-1}$, $r^2 = 0.9720$.

**Figure S4.** Plots of the observed rate constant ($k_{obs}$) against [meso-hydrobenzoin] for the reaction of CumO* generated by 355 nm LFP of an Ar-saturated MeCN solution containing a) 1.0 M dicumyl peroxide (black circles); 1.0 M dicumyl peroxide in the presence of b) LiClO$_4$ 0.3 M (white circles); c) Mg(ClO$_4$)$_2$ 0.3 M (black squares); d) Ca(ClO$_4$)$_2$ 0.35 M (black triangles) measured at $T = 25$ °C following the decay of CumO* at 490 nm. From the linear regression analysis: a) intercept = $7.71 \times 10^6$ s$^{-1}$, $k_H = 2.15 \times 10^6$ M$^{-1}$ s$^{-1}$, $r^2 = 0.9935$; b) intercept = $1.04 \times 10^6$ s$^{-1}$, $k_H = 1.22 \times 10^6$ M$^{-1}$ s$^{-1}$, $r^2 = 0.9995$; c) intercept = $8.19 \times 10^5$ s$^{-1}$, $k_H = 9.66 \times 10^5$ M$^{-1}$ s$^{-1}$, $r^2 = 0.9999$; intercept = $1.48 \times 10^6$ s$^{-1}$, $r^2 = 0.9999$. 
**Figure S5.** Plots of the observed rate constant ($k_{\text{obs}}$) against [(R,R)-hydrobenzoin] for the reaction of CumO• generated by 355 nm LFP of an Ar-saturated MeCN solution containing a) 1.0 M dicumyl peroxide (black circles) and 1.0 M dicumyl peroxide in the presence of b) LiClO$_4$ 0.3 M (white circles); c) Mg(ClO$_4$)$_2$ 0.3 M (black squares); d) Ca(ClO$_4$)$_2$ 0.35 M (black triangles), measured at $T = 25$ °C following the decay of CumO• at 490 nm. From the linear regression analysis: a) intercept = $7.02 \times 10^5$ s$^{-1}$, $k_H = 8.86 \times 10^5$ M$^{-1}$ s$^{-1}$, $r^2 = 0.9999$; b) intercept = $1.02 \times 10^6$ s$^{-1}$, $k_H < 3 \times 10^4$ M$^{-1}$ s$^{-1}$; c) intercept = $8.55 \times 10^5$ s$^{-1}$, $k_H = 6.63 \times 10^5$ M$^{-1}$ s$^{-1}$, $r^2 = 0.9999$; d) intercept = $1.51 \times 10^6$ s$^{-1}$, $k_H < 3 \times 10^4$ M$^{-1}$ s$^{-1}$.

**Figure S6.** Plots of the observed rate constant ($k_{\text{obs}}$) against [cyclopentanol] for the reactions of CumO• generated by 355 nm LFP of an Ar-saturated MeCN solution containing 1.0 M dicumyl peroxide in the presence of a) LiClO$_4$ 0.5 M (white circles); b) Mg(ClO$_4$)$_2$ 0.5 M (black squares); c) Ca(ClO$_4$)$_2$ 0.39 M (black triangles), measured at $T = 25$ °C following the decay of CumO• at 490 nm. From the linear regression analysis: a) intercept = $1.47 \times 10^6$ s$^{-1}$, $k_H = 1.26 \times 10^6$ M$^{-1}$ s$^{-1}$, $r^2 = 0.9997$; b) intercept = $9.28 \times 10^5$ s$^{-1}$, $k_H = 1.20 \times 10^6$ M$^{-1}$ s$^{-1}$, $r^2 = 0.9991$; c) intercept = $1.68 \times 10^6$ s$^{-1}$, $k_H = 1.45 \times 10^6$ M$^{-1}$ s$^{-1}$, $r^2 = 0.9999$. 
Figure S7. Plots of the observed rate constant ($k_{obs}$) against $[\text{cis-1,2-cyclopentanediol}]$ for the reactions of CumO$^\bullet$ generated by 266 nm LFP Ar-saturated MeCN solution containing 1.0 M dicumyl peroxide in the presence of a) LiClO$_4$ 0.6M (white circles); (b) Mg(ClO$_4$)$_2$ 0.5 M (black squares) measured at $T = 25$ °C following the decay of CumO$^\bullet$ at 490 nm. From the linear regression analysis: a) intercept = $1.70 \times 10^6$ s$^{-1}$, $k_H < 2 \times 10^4$ M$^{-1}$ s$^{-1}$; b) intercept = $9.35 \times 10^5$ s$^{-1}$, $k_H = 5.98 \times 10^5$ M$^{-1}$ s$^{-1}$, $r^2 = 0.9978$.

Figure S8. Plots of the observed rate constant ($k_{obs}$) against $[\text{trans-1,2-cyclopentanediol}]$ for the reactions of CumO$^\bullet$ generated by 355 nm LFP of an Ar-saturated MeCN solution containing 1.0 M dicumyl peroxide in the presence of a) LiClO$_4$ 0.5 M (white circles); b) Mg(ClO$_4$)$_2$ 0.5 M (black squares) measured at $T = 25$ °C following the decay of CumO$^\bullet$ at 490 nm. From the linear regression analysis: a) intercept = $1.35 \times 10^6$ s$^{-1}$, $k_H = 4.53 \times 10^5$ M$^{-1}$ s$^{-1}$, $r^2 = 0.9965$; b) intercept = $9.36 \times 10^5$ s$^{-1}$, $k_H = 3.53 \times 10^5$ M$^{-1}$ s$^{-1}$, $r^2 = 0.9958$. 
Figure S9. Plot of the observed rate constant \( k_{\text{obs}} \) against [cyclohexanol] for the reactions of CumO\(^*\) generated by 355 nm LFP of an Ar-saturated MeCN solution containing 1.0 M dicumyl peroxide in the presence of a) LiClO\(_4\) 0.5 M (white circles); b) Mg(ClO\(_4\))\(_2\) 0.5 M (black squares); Ca(ClO\(_4\))\(_2\) 0.39 M (black triangles) measured at \( T = 25 \, ^\circ\text{C} \) following the decay of CumO\(^*\) at 490 nm. From the linear regression analysis: a) intercept = 1.74 \times 10^6 \text{ s}^{-1}, k_H = 1.35 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}, r^2 = 0.9980; b) intercept = 8.77 \times 10^5 \text{ s}^{-1}, k_H = 1.55 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}, r^2 = 0.9997; c) intercept = 1.74 \times 10^6 \text{ s}^{-1}, k_H = 1.51 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}, r^2 = 0.9892.

Figure S10. Plot of the observed rate constant \( k_{\text{obs}} \) against [cis-1,2-cyclohexanol] for the reactions of CumO\(^*\) generated by 355 nm LFP of an Ar-saturated MeCN solution containing 1.0 M dicumyl peroxide in the presence of a) LiClO\(_4\) 0.5 M (white circles); b) Mg(ClO\(_4\))\(_2\) 0.5 M (black squares) measured at \( T = 25 \, ^\circ\text{C} \) following the decay of CumO\(^*\) at 490 nm. From the linear regression analysis: a) intercept = 1.58 \times 10^6 \text{ s}^{-1}, k_H = 1.13 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}, r^2 = 0.9995; b) intercept = 9.44 \times 10^5 \text{ s}^{-1}, k_H = 1.11 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}, r^2 = 0.9978.
Figure S11. Plot of the observed rate constant ($k_{\text{obs}}$) against $[\text{trans-1,2-cyclohexanol}]$ for the reactions of $\text{CumO}^\cdot$ generated by 355 nm LFP of an Ar-saturated MeCN solution containing 1.0 M dicumyl peroxide in the presence of a) LiClO$_4$ 0.5 M (white circles); b) Mg(ClO$_4$)$_2$ 0.5 M (black squares) measured at $T = 25$ °C following the decay of $\text{CumO}^\cdot$ at 490 nm. From the linear regression analysis: a) intercept = $1.70 \times 10^6$ s$^{-1}$; b) intercept = $9.97 \times 10^5$ s$^{-1}$, $k_H = 3.87 \times 10^5$ M$^{-1}$ s$^{-1}$, $r^2 = 0.9959$. 
4) References