**Table I.** Isotope Effect Results

| reaction | $^{14}k/^{15}k$ |
|---|---|
| acyl transfer to hydroxide[a] | 1.0002 ± 0.0001[c] |
| acyl transfer to phenolate[b] | 1.0010 ± 0.0002 |

[a] 2 mM p-nitrophenyl acetate, 100 mM CHES buffer (pH 9.0), 23 °C; $t_{1/2} \approx 2.5$ h. The rate of reaction was independent of buffer concentration, and this pH is well within the range where solvolysis is known to be solely catalyzed by hydroxide.[11] [b] 1.5 mM p-nitrophenyl acetate, 15 mM phenol, 50 mM CHES buffer (pH 9.5), 5 °C; $t_{1/2} \approx 8$ min. This reaction was approximately 25-fold faster than that with hydroxide at the same pH and temperature, and the rate varied in a linear fashion with added phenol. [c] Errors reported are the standard errors.

Prior experimental evidence in favor of the concerted process comes from reactions of aryl esters with phenoxide nucleophiles.[4] Recent theoretical arguments concur and also conclude that the reaction of hydroxide with aryl acetates should have no intermediate of significant lifetime.[7] The ^{15}N isotope effects have been measured for the acyl-transfer reactions of p-nitrophenyl acetate with hydroxide and with phenolate under the conditions given in Table I. The $pK_a$ values of both these nucleophiles satisfy the requirement that nucleophilic attack, coupled or not with leaving group displacement, occurs at the rate-limiting step.

The small and possibly insignificant isotope effect on the hydroxide reaction is consistent with a tetrahedral mechanism, but it cannot rule out a concerted process where bond cleavage to the leaving group is only slightly advanced in the transition state. Due to the small magnitude of the ^{15}N isotope effects, this method is not sensitive enough to measure changes in bond order smaller than about 15%.

The isotope effect for the phenolate reaction indicates that the bond to the leaving group cleaves in the rate-limiting step, which is not consistent with a tetrahedral mechanism and favors the contention that this reaction follows a concerted $A_ND_N$ displacement. This isotope effect is within the range of those found for the phosphoryl-transfer reactions of phosphate diesters and triesters of p-nitrophenol,[8] reactions known to occur by concerted nucleophilic displacement at phosphorus. Using the value of 1.0028 to represent a fully broken bond,[8] the acyl-transfer reaction with phenolate has a transition state with about 35% bond cleavage to the leaving group.

Comparison of the present data with those from studies of phosphoryl-transfer reactions indicates that, in terms of leaving group departure at the transition state, the reaction of p-nitrophenyl acetate with phenoxide most resembles phosphoryl-transfer reactions with neutral phosphate esters of p-nitrophenol. For these substrates (a triester or a protonated diester), transition-state bond cleavage was about 25–32%, whereas for anionic phosphodiesters of p-nitrophenol, transition-state bond cleavage was higher, about 55%.[8,9]

Further isotope effect studies are under way to better characterize the present reactions, particularly that with hydroxide, and to examine the nature of this acyl-transfer reaction with different nucleophiles. It will be of interest to determine whether the apparent concertedness of acyl-transfer reactions between phenoxides arises from their $pK_a$ values or is due to some other characteristic specific to phenoxides.

**Determination of Isotope Effects.** Aqueous solutions of p-nitrophenyl acetate were made by prolonged stirring. The isotope effect reactions were run on 100-μmol samples of p-nitrophenyl acetate and allowed to run to about 50% completion. The p-nitrophenol product was separated from the residual starting material, and each was assayed to determine the exact fraction of reaction. The nitrogen from both was separately converted to $N_2$, and the isotopic composition was determined by an isotope ratio mass spectrometer, as previously described.[9] The isotopic composition of unreacted starting material was separately determined. Isotope effects were calculated from the isotope ratios

of the unreacted starting material and the residual starting material after partial reaction and, independently, from those of the unreacted starting material and product.[10] Six separate isotope effect experiments were run, giving 12 independent measurements of each isotope effect.

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## Color Benzyloxyl, Cumyloxyl Orange, and 4-Methoxycumyloxyl Blue. Unexpected Discovery That Arylcarbinyloxyl Radicals Have Strong Absorptions in the Visible[1]

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The pioneering application of nanosecond laser flash photolysis (LFP) to "real time" studies of tert-butoxyl chemistry by Small and Scaiano[3] in 1978 opened an exciting new era in free radical kinetics. Because the tert-butoxyl radical had no absorption band in the visible and showed only a weak "tail-end" absorption in the near UV[4] (see Figure 1A), Small and Scaiano developed a competitive kinetic "probe" technique to monitor the evolution in time of the tert-butoxyl concentration as this radical reacted with different substrates following the laser flash.[3,5] The probe chosen was a compound that, on reaction with tert-butoxyl, yielded a radical with a strong and characteristic absorption in the visible, e.g., diphenylmethanol which yields $(C_6H_5)_2\dot{C}OH$, $\lambda_{max} = 545$ nm.[6,7] In subsequent LFP kinetic studies on other alkoxyls,[8–10] including benzyloxyl[9] and cumyloxyl,[10] it appears to have been implicitly assumed that these radicals have the same UV–visible spectral characteristics as tert-butoxyl. This assumption is incorrect. Benzyloxyl, cumyloxyl, and p-methoxycumyloxyl exhibit strong, broad absorptions in the visible with $\lambda_{max} = 460$, 485, and 590 nm, respectively (see Figure 1).

Cumyloxyl radicals were generated at room temperature by direct 308-nm and (where solvent permitted) 266-nm LFP of dicumyl peroxide[11] and by direct 266-nm LFP and xanthone triplet ($E_t = 74.1$ kcal/mol, $\lambda_{max} = 630$ nm) photosensitized 355-nm LFP of dicumyl hyponitrite.[11] The visible and UV absorptions were observed to grow-in "instantaneously" in $CCl_4$, $CH_3CN$, $CH_3CO_2H$, $(CH_3)_3COH$, c-$C_6H_{12}$, $C_6H_6$, and $C_6H_5Cl$, with no significant shift in the visible absorption maximum from 485 nm over this range of solvents. Of course, the rates of cumyloxyl radical decay do depend on the solvent. However, in all cases, the rates

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(2) Summit Postdoctoral Fellow, 1990–1991.
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(9) Mendenhall, G. D.; Stewart, L. C.; Scaiano, J. C. J. Am. Chem. Soc. 1982, 104, 5109–5114. Note the precautionary statement in the experimental section.
(10) Baignée, A.; Howard, J. A.; Scaiano, J. C.; Stewart, L. C. J. Am. Chem. Soc. 1983, 105, 6120–6123.
(11) Purified by triple crystallizations from methanol.

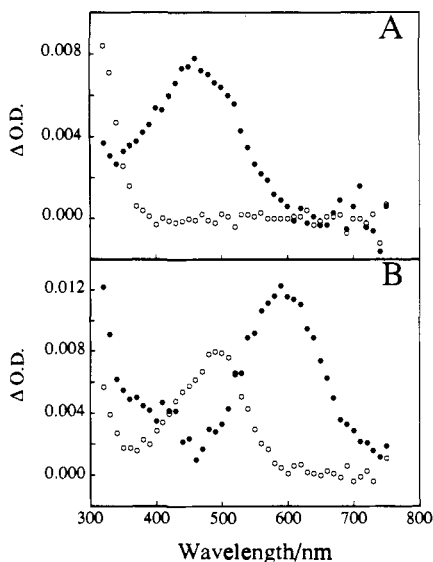(9) Hengge, A. C.; Cleland, W. W. J. Am. Chem. Soc. 1991, 113, 5835–5841.

**Figure 1.** Absorption spectra of (A) *tert*-butoxyl (O) and benzyloxyl (●); (B) cumyloxyl (O) and *p*-methoxycumyloxyl (●). The spectra were obtained by 266-nm LFP of di-*tert*-butyl peroxide, dibenzyl hyponitrite, dicumyl peroxide, and bis(4-methoxycumyl) hyponitrite in CH₃CN, 56, 70, 63, and 61 ns, respectively, after the laser flash. Spectra were recorded under similar, but not standardized, conditions.

of decay of the visible and UV absorptions were equal (within experimental error), which demonstrates that they arise from a common transient (or, less probably, from two species in rapid equilibrium). The ratios of the 485-nm to 320-nm absorption intensities were found to be slightly dependent on the solvent, varying from a high of 1.35 in CCl₄ to a low of 0.72 in CH₃CN.[12] The absolute intensities immediately after LFP of both absorptions showed a linear dependence on laser flux, which implies that the transient(s) responsible for the two absorptions is formed by a monophotonic process. The intensities and decay rates of the visible and UV absorptions were unaffected by oxygen, as would be expected for an oxygen-centered radical but not for a carbon-centered radical or excited triplet.[13,14] For all of these reasons, we confidently assign both the UV and the visible absorptions to the cumyloxyl radical (Figure 1B).

$$[C_6H_5C(CH_3)_2O]_2 \xrightarrow{h\nu} C_6H_5C(CH_3)_2O^{\bullet} \xleftarrow{h\nu} [C_6H_5C(CH_3)_2ON]_2$$
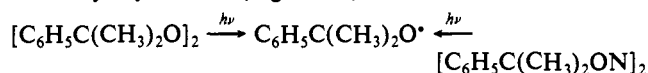
Similar experiments involving the direct LFP and the xanthone photosensitized LFP of dibenzyl hyponitrite[9] "instantaneously" gave transient visible ($\lambda_{max}$ = 460 nm) and UV absorptions (see Figure 1A). Application of all of the tests described above indicated that both absorptions were due to a single oxygen-centered radical, viz., to the benzyloxyl radical.

In a preliminary exploration of potential substituent effects on these "new" absorption bands, we subjected bis(4-methoxycumyl) hyponitrite[9,15] to 266-nm LFP in CH₃CN. A transient having a UV and visible absorption was produced "instantaneously" (Figure 1B). The 4-methoxy substituent shifts the unsubstituted cumyloxyl radical's absorption maximum by a dramatic 105 nm into the red, i.e., $\lambda_{max}$ shifts from 485 to 590 nm.

The arylcarbinyloxyl radicals' visible absorptions are obviously fairly strong (Figure 1). The extinction coefficient of the visible cumyloxyl absorption was determined in a pair of carefully matched experiments involving the 308-nm LFP of 0.126 M

dicumyl peroxide in CH₃CN. In one experiment, diphenylmethanol was added at a concentration of 1.0 M (which was found to be sufficient to react with ca. 92% of the cumyloxyl radicals and generate benzophenone ketyl radicals, $\epsilon_{545}$ = 3220 M⁻¹ cm⁻¹,[6] within 110 ns). From the ratio of the absorption intensities at 485 nm in the absence and 545 nm in the presence of the diphenylmethanol (appropriately corrected for the small absorption of the alcohol at the excitation wavelength), we estimate that $\epsilon_{485}$ ≈ 1300 M⁻¹ cm⁻¹ for cumyloxyl.

The intriguing difference between the absorption spectra of alkoxyl and arylcarbinyloxyl radicals suggests that there may be some internal charge transfer in the latter radicals:[16]

$$\left[ \begin{array}{cc} \delta^{\bullet} & \delta^{-} \\ \multicolumn{2}{c}{C_6H_6CH_2O} \end{array} \right]^{\bullet}$$
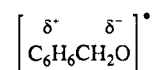
In reference to this, it is worth noting that, in a pair of carefully matched experiments involving 308-nm LFP of dicumyl peroxide in CCl₄ and CH₃CN, there was no measurable difference in either the intensity of the visible absorption immediately after the laser pulse or in the position of $\lambda_{max}$.

In conclusion, we note that the intensity and band width (e.g., ca. 120 nm at half-height for cumyloxyl) imply that arylcarbinyloxyl radicals should be visible to the naked eye under certain conditions. In such a case, benzyloxyl and cumyloxyl will be a rose pink in color and 4-methoxycumyloxyl will be a beautiful dark blue.

(16) The possibility of homoconjunction in (incipient) arylcarbinyloxyl radicals (produced by the thermal decomposition of hyponitrites) has been raised.[17]

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# Lithium–Tin Exchange Reaction.[1] Stereochemistry at Tin

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The lithium–tin transmetalation reaction proceeds with retention of configuration at carbon.[2,3] This observation provides important mechanistic information, but even more important in this context is the stereochemistry at tin, which has been examined in only one rather unusual case.[4] In that case, exchange proceeded with

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(12) It was not possible to determine the UV $\lambda_{max}$ for any of these radicals. Measurements at 320 nm correspond to ΔOD on the (steep) "side" of the UV absorption. The change in the 485-nm/320-nm absorption intensity ratios may therefore be due either to solvent effects on the relative intensities of the two absorption bands or to a shift in the $\lambda_{max}$ of the UV absorbance.

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