hibiting β-phenyl quenching in either probe may indeed be the same as applies for BCCN (ECCN is one carbon shorter than **1**), it is also possible that ECCN forms a different type of smectic phase than does BCCN.[7] This solvent does, however, provide a model isotropic solvent against which to compare the behavior of **1** and **2** in BCCN. Such comparisons indicate that nematic order may as well have some effect, albeit small, on the energetics of β-phenyl quenching in **1** and **2**. The magnitude of the effect (1–2 kcal/mol in E_a) is similar to those reported for other cyclization reactions in nematic and cholesteric solvents.[2]

In conclusion, our results indicate that smectic liquid-crystalline order can drastically inhibit the intramolecular mobility and reactivity of a rodlike solute, provided that the solute is of an appropriate length to fit within the solvent layers. Experiments to better define the interrelationship between solute and solvent molecular length and the effects of smectic order on solute mobility are currently in progress.

Photoactivated Oxidation of Alcohols by Oxygen

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Primary and secondary alcohols can be converted to the corresponding aldehyde or ketone by using O_2 and visible light. The process is catalyzed by the presence of H_2PtCl_6 and $CuCl_2$.[1] This

$$RCH(OH)R' + {}^1/_2O_2 \xrightarrow[h\nu]{\substack{H_2PtCl_6, \\ CuCl_2}} RC(=O)R' \qquad (1)$$
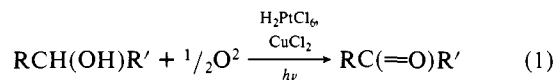
photoassisted catalytic reaction occurs at room temperature under 1 atm of O_2 in neat alcohol. The mild reaction conditions coupled with the ability to employ high substrate concentrations favors good product yields with high selectivity compared to more standard oxidation methods. For example, both aliphatic and allylic primary alcohols are oxidized to aldehyde without overoxidation to the carboxylic acid. The catalytic cycle is stable for several days when using primary or secondary substrate alcohols. Further, the consumption of expensive reagents is avoided. The concept of using H_2PtCl_6 in this reaction extends from the observation that $[PtCl_6]^{2-}$ can be photoreduced first to Pt(II) and then to Pt–metal in the presence of alcohols with visible light.[2] A catalytic process is possible if a lower oxidation state of platinum can be intercepted and reoxidized prior to conversion to Pt–metal. On thermodynamic grounds O_2 should be capable of this oxidation under acidic conditions; however, experimentally we do not find this to occur. Addition of $CuCl_2$ to the reaction mixture as a

Table I. Two-Electron Oxidation of Alcohols[a,h]

alcohol	product	time, h	equiv formed[e]	Φ^P [g,h]
ethanol[b]	acetaldehyde	20	25	0.05
benzyl alcohol[d,f]	benzaldehyde	24	27	0.03
cinnamyl alcohol[d]	cinammaldehyde	24	13	0.02
n-hexyl alcohol[b,d]	*n*-hexanal	24	10	0.02
isopropyl alcohol	acetone	24	45	0.06
cyclopentanol[c]	cyclopentanone	18.5	23	0.04
cyclohexanol[c]	cyclohexanone	24	11	0.02

[a] Unless otherwise noted, a solution of 0.009 M H_2PtCl_6 in neat alcohol with 2 equiv of $CuCl_2$ was purged with O_2. The reactants were then irradiated with 488-nm (85 mW) illumination from an Ar$^+$ laser while O_2 was passed over the stirred solution. [b] 3 equiv of $CuCl_2$ were used. [c] 0.006 M H_2PtCl_6 was used. [d] A 50% by volume mixture of alcohol and acetone was used. [e] Equivalents were determined using FID GC[4] and internal standards and are relative to moles of H_2PtCl_6 initially. The values reported here do not reflect limiting values. [f] 0.007 M H_2PtCl_6. [g] Quantum yields, Φ^P, were measured in terms of product (ketone, aldehyde) appearance as follows: Carbonyl product yields were ascertained by GC analysis[4] by using a Perkin-Elmer Sigma 3B, FID gas chromatograph with H.P. 3390A integrator. Photon yield was determined by using a beam-expanded argon ion laser (488 nm) adjusted to low intensity as the light source. The photon flux was monitored by a NRC model 815 radiometer. The accuracy of the radiometer is ±5% NBS traceable. Data were obtained as a function of time. Only yields that were time independent over the course of the reaction are reported. In carrying out these experiments a neat alcohol solvent was employed of which only a few percent was converted to product. [h] See ref 3a.

charge-transfer mediator, however, does cause the reaction to become catalytic in Pt(IV); although, $CuCl_2/O_2$ in the absence of H_2PtCl_6 does not produce organic products with visible-light photolysis.

As can be seen from the data in Table I this system is capable of carrying out the specific two-electron oxidation of a variety of alcohols. For example, ethanol is converted to acetaldehyde in 94% yield under the conditions reported in Table I. Even low redox potential alcohols such as benzyl alcohol show no tendency to be overoxidized to the acid. Further, reactivity is not influenced by the presence of sites of unsaturation near the alcohol functionality. Thus, as demonstrated by using cinnamyl alcohol, (Table I) conjugated aldehydes can be generated in good yield. There does appear to be a steric effect on the turnover rates obtained, with larger substrates being oxidized more slowly. Presumably, this steric effect can be related to the ease with which the substrate coordinates to the Pt complex.

In a typical synthetic procedure a 10-mL solution containing H_2PtCl_6 (8 mmol, 0.06 mol %) and $CuCl_2$ (16 mmol, 0.12 mol %) in neat alcohol was purged with O_2 prior to irradiation (5 min). The solution was then statically maintained under 1 atm of O_2 using an oil bubbler while being irradiated with a tungsten–halogen source.[3a] In the case of isopropyl alcohol after 37 h of irradiation a solution that was 0.18 M in acetone (by GC analysis[4]) was obtained. As an alternative procedure the reactants were diluted with acetone. For example, photolysis[3b] of cyclopentanol in a solution consisting of alcohol (70 mmol), H_2PtCl_6 (3.5 mmol, 5 mol %), and $CuCl_2$ (7 mmol, 10 mol %) and O_2 purged as described above provided a 98% yield[4] of cyclopentanone.

In order to ascertain overall reaction parameters the oxidation of isopropyl alcohol to acetone has been studied in detail. At room

(1) This process is stoichiometrically similar to the recently published[8] $O_2/CuCl_2$ oxidation of alcohols using 2,2,6,6-tetramethylpiperidinyl-1-oxy as an electron mediator with the exception that secondary alcohols that are unreactive in that system produce good product yields in the current case. Thus, a more general catalytic oxidation scheme is possible.

(2) That this reaction is occurring is proven by ^{195}Pt NMR studies and parallel GC analysis of the ketone formed. These studies indicate that prior to metal formation a large fraction of $[PtCl_6]^{2-}$ has been converted to $[PtCl_4]^{2-}$ and $[PtCl_3(ROH)]^-$ with concomitant formation of ketone. $[PtCl_6]^{2-}$ yields a singlet in its ^{195}Pt spectrum which we have employed as the reference signal. The NMR spectrum of $[PtCl_4]^{2-}$ is composed of a singlet 16 016 ppm upfield of $[PtCl_6]^{2-}$.

(3) (a) A variety of light sources have been employed to carry out this reaction, in the case of white light sources such as tungsten–halogen lamp or a xenon lamp a UV cutoff filter was employed to avoid photolysis of the product. An IR filter ensured the solution remained at 25 °C. An argon ion laser running at low power was employed as an alternate source to simplify quantum yield determinations (Table I). (b) For this particular reaction a low-power, beam-expanded argon ion laser (90 mW) operating at 488 nm was employed.

(4) Gas chromatography analysis was carried out on a Perkin-Elmer Sigma 3B FID instrument with a 3% Carbowax 20 M chromosorb WHP column. The inlet temperature was maintained at 180 °C and a ramp rate of 2 °C/min was employed (initial temperature 35 °C). All solutions were analyzed prior to irradiation and appropriate dark controls were also executed.
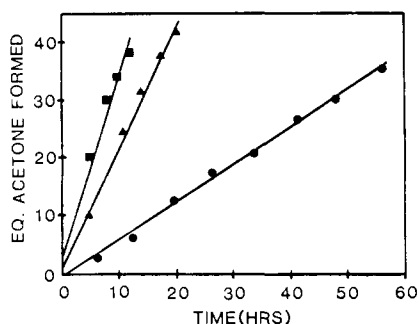
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Figure 1. Equivalents of acetone formed (with respect to moles of H_2-$PtCl_6$ used) vs. time for three intensities of 488-nm light. (0.046 (●), 0.138 (▲), and 0.276 W (■)) from an Ar^+ laser. All trials contain 7 mM H_2PtCl_6 and 7 mM $CuCl_2$ in 5 mL of neat isopropyl alcohol, with a slow stream of O_2 passing over the reaction mixture. The solutions were maintained at room temperature. Catalyst stability is indicated by the linearity of these curves ($\Phi^P = 0.05$).

temperature, there does not exist a thermal pathway to acetone formation in the presence of $H_2PtCl_6/CuCl_2/O_2$. The reaction can be easily driven, however, by visible light. The reaction is found to proceed with wavelengths of light as low as 514 nm when a monochromatic source is employed. This corresponds to the lowest energy absorption band in the $[PtCl_6]^{2-}$ complex. the absorption in this region has previously been assigned to a triplet ligand field transition ($^1A_{1g} \rightarrow {}^3T_{2g}$)[5]; although there are strong indications in the $[PtCl_6]^{2-}$ photochemistry literature that there exists a component of ligand → metal charge-transfer character in this region of the spectrum.[6] Product quantum yields as high as 0.1 have been observed for this reaction (at 488 nm), with values of ~0.05 (Figure 1 and Table I) being more standard. Turnover numbers in excess of 150 have been observed when white light[3] is employed with only a slight decrease in catalytic activity at the end of the reaction period. Catalyst stability is further indicated by the data in Figure 1 which shows a linear relationship between turnover number and reaction time over a 60-h period. Note that the slopes of the lines in Figure 1 change linearly with light intensity demonstrating a constant value of the product quantum yield over the intensity regime employed and a turnover rate that is directly proportional to the light intensity. The linearity of these data with respect to both time and light intensity further substantiates the high product specificity noted earlier.

The reaction is found to be fairly sensitive to the amount of $CuCl_2$ present. If either the $CuCl_2$ or O_2 is omitted from the reaction, then Pt–metal is observed to form along with a stoichiometric amount of organic products. As the $CuCl_2$ concentration is increased the turnover rate is observed to increase linearly. This phenomenon appears to saturate at an ~2:1 ratio of $CuCl_2$ to $[PtCl_6]^{2-}$. Addition of an excessive amount of $CuCl_2$ causes the solution to turn brown with a concomitant loss of catalytic activity. ^{195}Pt NMR studies demonstrate that Cu^{2+} cannot oxidize $[PtCl_4]^{2-}$. This result, taken along with a consideration of standard redox potentials which indicates that $CuCl_2$ cannot thermodynamically oxidize $[PtCl_4]^{2-}$, can be best explained by assuming that Cu^{2+} is oxidizing a Pt(III) chloride complex to regenerate $[PtCl_6]^{2-}$. The presence of a Pt(III) intermediate is consistent with previous photoaquation results[6,7] and suggests that alcohol oxidation may be occurring via a free radical mechanism. Support for this mechanism is provided by the observation that extensive irradiation of the isopropyl alcohol system yields trace amounts of acetaldehyde suggesting methyl free radical loss from the free radical alcohol. The exact details of the total catalytic cycle are currently under investigation.

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Chiral Pyrene Excimer in the γ-Cyclodextrin Cavity

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Several multicomponent complexes of cyclodextrins have recently been reported.[2-15] The formation of the 2:1 and/or 2:2 complexes of pyrene with γ-cyclodextrin (γ-CDx) have been proved by the pyrene excimer fluorescence.[16-18] In this paper, we report the formation of a chiral pyrene excimer in the cavity of γ-CDx, which shows extremely intense circular polarization in fluorescence.

A dilute aqueous solution of pyrene showed only monomer fluorescence whose lifetime was 127 ns under aerobic conditions. Upon addition of γ-CDx, a broad excimer fluorescence band centered at 474 nm appeared at the expense of the monomer fluorescence. The fluorescence maximum of the pyrene excimer in the γ-CDx solution shifted to longer wavelength compared with those in organic solvents (462–467 nm). A fluorescence decay curve of the excimer in the aqueous γ-CDx solution consisted of two rise and one decay components: $\tau_1 =$ very fast ($f_1 =$ ca. –0.7), $\tau_2 = 24$ ns ($f_2 =$ ca. –0.3), and $\tau_3 = 112$ ns ($f_3 = 1.00$). The fast rise component may be due to the pyrene dimer in the CDx cavity which yields an excimerlike state immediately after exciting. Interestingly, parts of the pyrene molecules form the excimer state through a relatively slow dynamic process, a rise time being 24 ns.

An extremely intense circularly polarized fluorescence (CPF) signal was measured at the excimer region in the γ-CDx solution (Figure 1).[19] The ordinate in Figure 1 is Kuhn's dissymmetry factor, $g_{em} = 2(I_L - I_R)/(I_L + I_R)$.[20] No or very weak CPF signal was measured at the monomer region, which is in good agreement with the results for (+)- and (−)-1-(1-hydroxyhexyl)pyrenes in methanol[21] and N-acetyl-D- and N-acetyl-L-pyrenylalanines in

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