Table I. Cleavage of *p*-Nitrophenoxide from DPGPNPP Vesicles at 25 °C[a]

run	additive	concn, 10^4 M	$10^4k_\psi^{f}$,[b] s^{-1}	k_ψ^{s},[c] s^{-1}
1	none		4.68	$\ll 1 \times 10^{-5}$
2[d]	none		7.08	$\ll 1 \times 10^{-5}$
3	KCl	50	6.52	$\ll 1 \times 10^{-5}$
4	n-$Bu_4N^+Br^-$	8	5.92	$\ll 1 \times 10^{-5}$
5	CTACl	1.25	8.15	$\ll 1 \times 10^{-5}$
6	CTACl	1.80	20.0	4.3×10^{-5}
7	CTACl	2.40	23.1	*e*
8	CTACl	3.60	24.4	*e*
9	CTACl	4.56	27.6	*e*
10	CTACl	5.55	32.1	*e*
11	CTACl	6.48	100	*e*
12	**2**	6.00	130	*e*
13	**3**	2.25	70[f]	$\ll 1 \times 10^{-5}$

[a] Conditions: [DPGPNPP] = 1.35×10^{-4} M in all cases, additives were cosonicated with DPGPNPP at pH 5.5. Reaction pH 11.8 ± 0.1 after addition of 0.01 M NaOH. [b] Initial "fast" pseudo-first-order cleavage of *p*-nitrophenolate ion (400 nm), ~50% of theory. [c] Subsequent "slow" cleavage; see text. [d] At 35 °C. [e] No slow reaction, the fast reaction accounted for quantitative *p*-nitrophenoxide release in a single exponential process. [f] ~60% of *p*-nitrophenoxide release was observed.

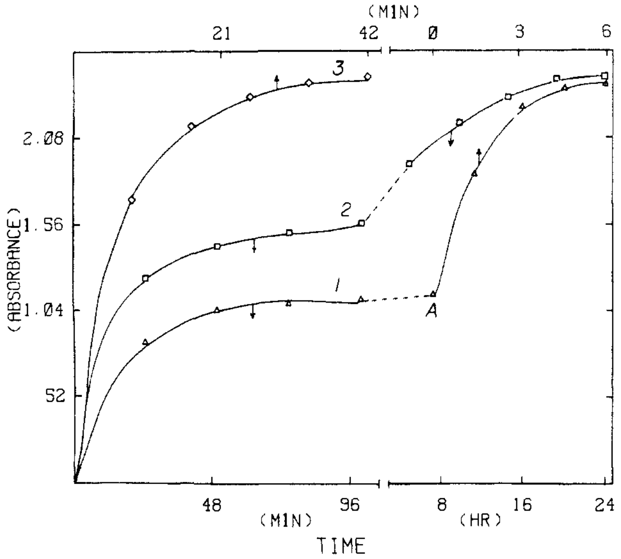

Figure 1. Absorption at 400 nm of *p*-nitrophenoxide cleaved from 1.35×10^{-4} M vesicular **1** at pH 11.8 vs. time; see text and Table I. Arrows refer to appropriate time scales. Curve 1, native vesicles; 4×10^{-3} M CTACl added at A. Curve 2, 1.8×10^{-4} M CTACl included in vesicle; note discontinuous time scale. Curve 3, 2.4×10^{-4} M CTACl included in vesicle.

In vesicles of **1** doped with CTACl or **2**, enhanced hydroxide permeation does not solely depend on the cationic head groups provided by the "foreign" surfactant. Rather, disruption of the glyceryl ester surfactant packing makes the vesicles porous:[17] note that covesicles of anionic **1** and cationic (but glyceryl ester based) **3**[18] do *not* under endovesicular PNPO$^-$ cleavage (run 13). Moreover, fluorescence from riboflavin entrapped in vesicular **3** is not quenched by OH$^-$ at pH 11.8 after 5 h.

The present work provides clear evidence for surface-specific reactions of vesicular **1**, demonstrates how the vesicles can be chemically differentiated at exo- and endovesicular sites, and suggests that glyceryl ester functional surfactants should be suitable for surface-specific vesicular chemistry.[19,20]

Acknowledgment. We thank the U.S. Army Research Office and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. We are grateful to Dr. Luis Marky and Prof. K. Breslauer for differential scanning calorimetry measurements. We thank S. Bhattacharya for synthetic assistance and Profs. P. Scrimin and L. Romsted for helpful discussions.

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(18) The synthesis of surfactant **3** will be described elsewhere. It was prepared in this laboratory by Dr. P. Scrimin and S. Bhattacharya.

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(20) A referee points out that vesicles of **1** are particularly well suited to the chemical differentiation described here because (a) the initial cleavage of PNPO$^-$ from the monoanionic disubstituted phosphate leaves behind a less reactive, dianionic monoalkylphosphate ester; (b) PNPO$^-$ is a better leaving group than a primary aliphatic alkoxide, so that the cleavage occurs at the desired P-O bond; and (c) the residual phosphatidic acid anion surfactants form stable vesicles.

Nature of the 190-nm Transition in Carbonyls: CD Measurements of Camphor Using Synchrotron Radiation

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The CD of the 190-nm transition of ketones was recently the subject of an extensive study.[1-3] The measurements extended the wavelength region to 185 nm and solvents such as hexane, acetonitrile, and trifluoroethanol were used. The second transition in simple ketones was assigned as the n → 3s Rydberg.[4] This assignment was based on the behavior of this transition under increasing pressure of a perturbing gas[5] or in solution[6] where vibronic structure is lost and substantial blue shifts are observed. Fluorine-containing solvents are especially known as strong shifters.[7]

The problem of whether a separate n valence transition exists or is being mixed with the Rydberg state was addressed in Kirk's study.[2] However, a decisive answer was not found. A second excited transition was identified in Kirk's investigation when 2,2,2-trifluoroethanol (TFE) was used.[2] This solvent causes a large blue shift to the n → 3s and exposes a second transition which was red-shifted in the latter solvent.

In this study we have measured the VUVCD of camphor in solution and in the gas phase. Two factors motivated this research. The first was Kirk's remark that it was unfortunately not possible to examine the region of the spectrum below 183 nm with available instrumentation, so the presence of a blue-shifted component of the CD could not be directly confirmed.[2] The second is that for a comprehensive characterization of excited states it is essential to compare gas and solution spectra and the lack of gas-phase data might lead to a wrong assignment. Camphor was chosen as our target molecule because of its rigid skeleton. Synchrotron radiation has been previously[8,9] employed in VUVCD studies and its ad-

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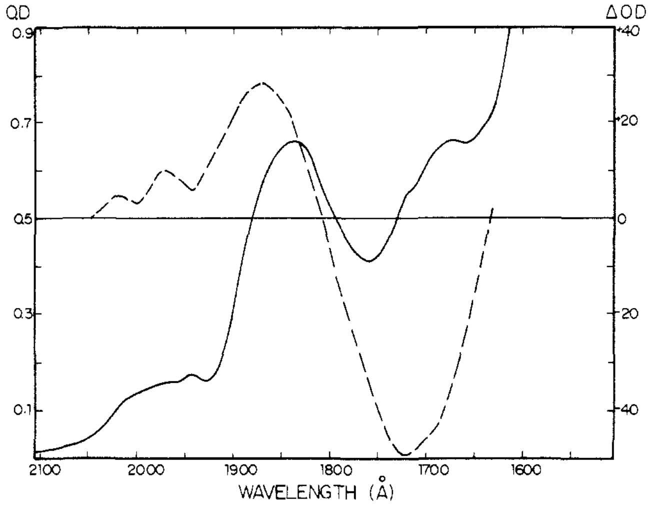

Figure 1. Absorption (—) and CD (---) spectra of (+)-D-camphor in the gas phase. The spectral resolution is 8 Å.

vantages were discussed. We have made use of its properties to yield a very collimated beam so that in gas-phase studies long-path cells can be used. This enabled us to measure compounds with a low vapor pressure or transitions having a small molar extinction coefficient. The gas-phase measurements were carried out in a 60-cm cell. Spectra were obtained at the Synchrotron radiation facility in Bonn University using a 1-m N1M monochromator in vertical mounting and were repeated at the Higity monochromator at HASYLAB, DESY Hamburg. The two instruments gave almost identical spectra except that the signal-to-noise ratio is significantly better with the HASYLAB source. The two camphor enantiomers yielded mirror-image spectra and therefore only the (+)-camphor results will be presented.

In Figure 1 we present the gas-phase absorption and CD spectra at a spectral resolution of 8 Å. The two features at 2020 and 1970 Å are better resolved in the CD spectrum than in the absorption. In Figure 2 which depicts the CD and absorption spectra of (+)-camphor in TFE there is no sign of the existence of the n → 3s because of the blue shift it undergoes in solution. The CD of (+)-camphor was also measured in hexane solution (on a CARY 60 instrument) and yielded a positive signal peaked at 1980 Å. The gas-phase spectrum is assigned as follows. The peaks at 2020 and 1970 Å belong to the n → 3s Rydberg transition. They yield a positive CD signal which is strongly blue-shifted in the TFE solution and only slightly shifted in the hexane solution. The second absorption peak in the gas phase is assigned as the n → 3p Rydberg. It is peaked at 1835 Å in absorption and at 1868 Å in the CD. This assignment is based on Robin's rule which states that the term values of 3s and 3p Rydberg reach a limit of ~23 000 and ~18 000 cm^{-1}, respectively, for molecules containing eight atoms or more.[5] An interval of 5000 cm^{-1} is thus predicted between the 3s and the 3p Rydberg states. Such an interval is observed for the proposed assignment.

The n → 3p Rydberg transition in carbonyls raises two questions. The first related to which of the 3p components of the 3p manifold is being observed.[10,11] The second is the relative intensity of the n → 3p vs. the n → 3s. This question was investigated by Udvarhazi and El-Sayed[12] who pointed out that the n → 3s is about twice as strong as n → 3p in cyclobutanone, about equal in cyclopentanone, and only half as strong in cyclohexanone. Referring to these questions, we note that in camphor the three components of the 3p manifold are not resolved. The intensity ratio of the 3s to 3p is also in agreement with the previous measurements.

The third transition in the gas-phase spectrum shows a strong negative CD band peaked at ~1725 Å. This band does not have a corresponding peak in the absorption spectrum. It appears as if the transition is electric-dipole forbidden and magnetic-dipole allowed. In the symmetric carbonyl chromophore such an excited state would have an A_2 symmetry.[13] A possible assignment is a $n_- \rightarrow \sigma^*$ where n_- is the second lone pair of the oxygen atom. This assignment is supported by the observation of a strong negative peak in the TFE solution centered at ~1920 Å. The shifts that valence transitions undergo upon solvation depend on their nature: $n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ transitions are blue-shifted in solutions whereas $\pi \rightarrow \pi^*$ is red-shifted. The fact that the transition observed in TFE is indeed red-shifted was found by Kirk[2] in an indirect way, the gas-phase data support his arguments and determine the magnitude of this red shift. The reason that the hexane solution exhibits an opposite CD signal is that in hexane the observed transition is the n → 3s, whereas in TFE due to the large shifts the $n_- \rightarrow \pi^*$ is revealed. The size of the red shift is ~5000 cm^{-1}. Theoretical random-phase approximation calculations predict[3] that the second excited valence state in saturated ketones has a large magnetic moment and a weak (stronger that the $n \rightarrow \pi^*$ but much weaker than the $\pi \rightarrow \pi^*$) electric moment. The transition is assigned as a $\sigma \rightarrow \pi^*$ excitation where σ is composed of the second oxygen nonbonding orbital (n_-), σ_{CO}, and $\sigma_{CC\alpha}$.

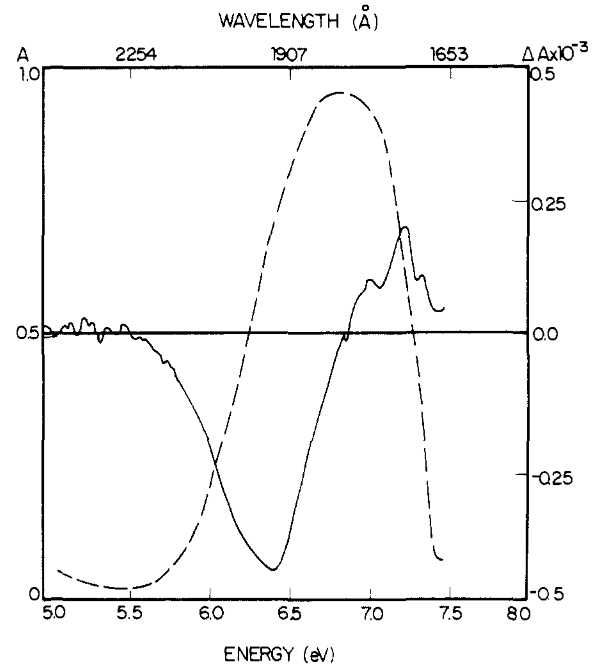

Figure 2. Absorption (—) and CD (---) spectra of a 0.065 M solution of (+)-D-camphor in TFE.

The positive band which appears at 7.4 eV in the TFE solution is attributed to the n → 3p Rydberg transition. It is well-known that the blue shift that Rydberg transitions undergo is enhanced in fluorinated compounds.[14] The n → 3s Rydberg accordingly is buried under the strong negative CD band centered at 1920 Å.

The application of the $n \rightarrow \pi^*$ octant rule to the 190-nm transition was discussed previously by Kirk.[2] However, the results of the solution CD spectrum might be a convolution of two contributions from two excited states. It is therefore important to check this rule for the n → 3s Rydberg. The three molecules for which a gas-phase spectrum with a well resolved n → 3s Rydberg is known are (1) (*R*)-(+)-methylcyclohexanone,[15] (2) (+)-D-camphor, and (3) (R)-(+)-methylcyclopentanone.[16] The first two cases show a positive CD signal for the n → 3s and the

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same sign is also observed for the n → π*. The cyclopentanone shows a negative signal opposite to the observed n → π*. It is therefore difficult to conclude whether a consignate or a dissignate octant rule is valid for the n → 3s transition.

This study provides a comprehensive assignment of the high-energy transitions observed in the CD and absorption spectra of camphor, it also explains the change in CD sign of the 190-nm band in TFE of many ketones.

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Intramolecular Shielding of Charge-Transfer Excited States of Surfactant-Active Rhenium(I) Photosensitizers

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Excited-state electron-transfer processes involving organized assemblies are currently under active study.[1] Such systems show promise for increasing the efficiency of energy-storage reactions. In particular, surfactant-active analogues of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) with long hydrophobic alkyl chains have been used to modify sensitizer chemistry and photophysics.[2]

We are studying a new series of surfactant-active Re(I) photosensitizers:

$$fac\text{-}[(bpy)Re^{I}(CO)_3L]^+ \quad (L = NC(CH_2)_nCH_3,\ n = 0,2,5,6,7,9,10,13,17)$$

These systems exhibit intense d–π* metal to ligand charge-transfer (MLCT) emissions in fluid solutions similar to the parent acetonitrile complex ($n = 0$).[3] We wish to report a dramatic example of an intramolecular perturbation of CT excited-state properties by the electronically passive alkyl chain.

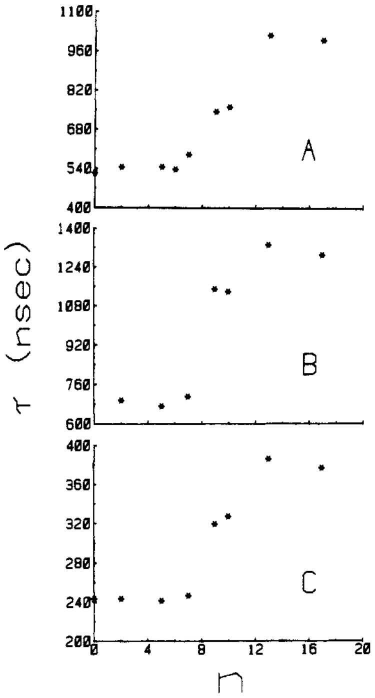

Figure 1. Excited-state lifetime of $[(bpy)Re^{I}(CO)_3NC(CH_2)_nCH_3]^+$ vs. n in deoxygenated solvents at 298 K°. (A) acetonitrile; (B) toluene; (C) pyridine.

Figure 1 shows the excited state lifetimes (τ) vs. chain length, n, for acetonitrile, toluene, and pyridine. Methanol and methylene chloride exhibit similar behavior. For the shorter alkyl chains, τ is essentially independent of chain length. There is an abrupt increase in τ over the range $6 \leq n \leq 13$, and τ then becomes essentially constant for $n \geq 13$. The differences among solvents are in the initial and final lifetimes and the ratio of these lifetimes. The ratio can exceed a factor of 3.

This dramatic change in τ must arise from changes in the radiative or radiationless rate constants. In either case, such changes may arise from perturbations of the excited-state electronic properties due to changes in molecular structure or to environmental factors.

Our lifetime changes cannot be attributed to a direct intramolecular electronic effect. The alkyl chain of the nitrile is not directly involved in the CT excited state. The nitrile does perturb the CT excited state by π-back-bonding of the CN.[4] While one might expect a small change in the degree of back-bonding on changing from CH_3CN to a $-CH_2CN$, it is inconceivable that any appreciable inductive effect could be propagated through more than one or two CH_2's. This is verified experimentally by the essential invariance of τ on going from $n = 0$ to 2 and 5. This result indicates that the radiative and radiationless rate constants are essentially invariant for the shorter chain nitriles.

We conclude that the dependence on n must reflect a change in the environment felt by the MLCT excited state. The excitation resides in the metal–bipyridine portion of the molecule, and for an environmental effect to be operative, the local environment in this region must be altered with changes in n. We propose that the observed τ dependence arises from foldback of the longer alkyl chains onto one face of the bpy ligand. The resultant displacement of the solvent from the vicinity of the excited state yields a difference in decay constants, particularly the nonradiative one, with a concomitant change in τ. Short chains cannot fold back and

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