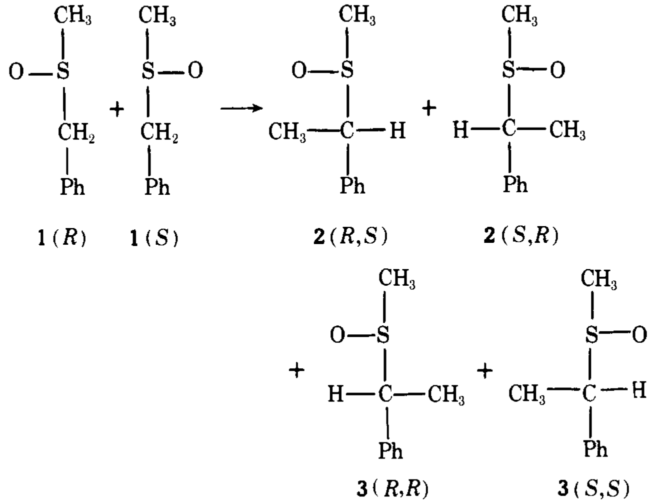

methyl iodide vapor and nitrogen was passed over the dispersed solid at 25 °C, one single diastereoisomer was formed which was shown by ^1H NMR to be identical with the major isomer (*R,S* and *S,R*) formed above and in solution (in THF at 25 °C, the ratio *r* was 5).[20] If the solid is not dispersed, a liquid phase appears and most likely the reaction with methyl iodide occurs in this liquid phase; the ratio *r* was 5. When methyl iodide was added to the mother liquors at −78 °C or to the solid dissolved in THF at −78 °C, the ratio *r* was found to be 15. This is because equilibration of the diastereoisomeric carbanions has taken place in solution. When the solid was treated with heavy water or O-deuterated ethanol as liquids, there was only very slight preference for one diastereoisomer.

Thus the reaction of methyl iodide vapors with the dispersed solid occurs stereospecifically. The stereoselectivity was lost with chelating reagents like deuterium oxide and ethanol. This is reminiscent of the effect of lithium halides on the stereoselectivity of the reaction in solution[21] and could be due to catalysis by lithium cation.[16] Quite clearly, in the solid state, one diastereoisomer is present and its reactivity is highly stereoselective with a nonchelating reagent.

This now opens up the possibility of investigating the stereochemical course of an electrophilic substitution by the structural analysis of this solid. In the solid state, asymetric induction may be intramolecular as in the present case, or intramolecular in the presence of an asymetric ligand. This line of work is worthy of further investigation.

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J. F. Biellmann,* J. F. Blanzat, J. J. Vicens
Laboratoire associé au CNRS, Institut de Chimie
Université Louis Pasteur, 1 Rue Blaise Pascal
67008 Strasbourg, France
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Light-Induced Charge Separation by Functional Micellar Assemblies

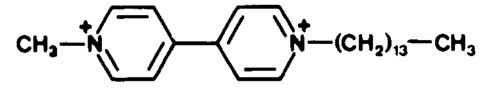
Sir:

In the field of photochemical energy conversion, particular attention has been paid to the reduction of methylviologen by the charge-transfer excited state of $Ru(bpy)_3^{2+}$:

$$^*Ru(bpy)_3^{2+} + MV^{2+} \rightarrow MV^+ + Ru(bpy)_3^{3+} \quad (1)$$

This reaction was first investigated by Whitten et al.[1] after Gafney and Adamson[2] discovered that the excited ruthenium complex can serve as a powerful one-electron reductant. Important with respect to light energy conversion is that the reaction products MV^+ and $Ru(bpy)_3^{3+}$ are capable of producing hydrogen[3] and oxygen[4] from water. Moreover, simultaneous H_2 and O_2 generation from water by visible light has recently been observed with the same redox system.[5] To improve the quantum efficiency of this device, it is necessary to retard the back-reaction between MV^+ and $Ru(bpy)_3^{3+}$ which in water occurs at a rate of 2.4×10^9 M^{-1} s^{-1}.[6] A micellar system which achieves this goal is now described in detail.

Instead of simple methylviologen, we employed the amphiphilic derivative $C_{14}MV^{2+}$ as an electron acceptor. This



$C_{14}MV^{2+}$

surfactant micellizes at concentrations above ~(7) × 10^{-3} M as determined from surface tension measurements.[7] Throughout the work it was employed at concentrations considerably below the cmc. A frequency doubled Nd laser (λ 530 nm, pulse width 15 ns) was used for excitation and the behavior of transient species monitored by kinetic spectroscopy.[8]

The oxidative quenching process

$$^*Ru(bpy)_3^{2+} + C_{14}MV^{2+} \rightarrow C_{14}MV^+ + Ru(bpy)_3^{3+} \quad (2)$$

was found to occur with a specific rate of (8 ± 0.8) × 10^8 M^{-1} s^{-1} at 10^{-4} M $Ru(bpy)_3^{2+}$ and 5 × 10^{-4} M $C_{14}MV^{2+}$ (ionic strength 1.4 × 10^{-3} M). This is somewhat faster than the reduction[3b] of MV^{2+} in water (k_1 = (2) × 10^8 M^{-1} s^{-1}). The kinetic salt effect induces a slight acceleration of the reaction with increasing ionic strength. For example, in the presence of 10^{-2} M NaCl (total ionic strength 1.14 × 10^{-2} M) the rate constant is (1.1 × 10^9) M^{-1} s^{-1}.

Cationic micelles do not affect the kinetics of reaction 2. This was carefully checked by measuring the quenching rate in the presence of increasing amounts (up to 5 × 10^{-2} M) of cetyltrimethylammonium chloride (CTAC) in solutions containing 5 × 10^{-4} M $C_{14}MV^{2+}$ and 10^{-4} M $Ru(bpy)_3^{2+}$. Fluctuations in the k_2 values were within 10% of (8) × 10^8 M^{-1} s^{-1} over the whole concentration range. In particular no systematic change in k_2 was observed when the CTAC concentration passed

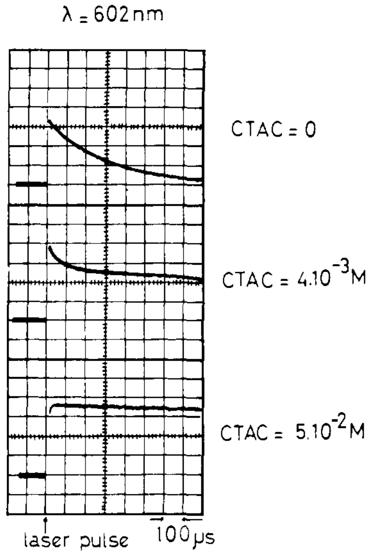


Figure 1. Effect of CTAC concentration and micelle formation on the decay of reduced functional viologen: $[C_{14}MV^{2+}] = 5 \times 10^{-4}$ mol/L; λ(excitation) 530 nm, λ(observation) 602 nm.

through its cmc value. Such a finding is not compatible with the formation of mixed $C_{14}MV^{2+}$/CTAC micelles, which should produce a pronounced decrease of the reaction rate due to electrostatic repulsion of $Ru(bpy)_3{}^{2+}$ from the surface of the aggregates. Rather, it must be concluded that $C_{14}MV^{2+}$, despite its tetradecyl chain, is mainly present in the aqueous phase.[9] This may be a consequence of the strongly hydrophilic nature of the bipyridinium head group.[10] A minor fraction of $C_{14}MV^{2+}$ could still associate with CTAC micelles, the resultant small decrease in the reaction rate being compensated for by the kinetic salt effect discussed above.

The lack of micellar effects on the quenching reaction 2 contrasts sharply with the kinetic phenomena observed for the backward electron transfer:

$$Ru(bpy)_3{}^{3+} + C_{14}MV^{+} \rightarrow Ru(bpy)_3{}^{2+} + C_{14}MV^{2+} \quad (3)$$

These are illustrated in Figure 1, which shows the temporal behavior of the characteristic absorbance of $C_{14}MV^{+}$ at 602 nm. The signal of $C_{14}MV^{+}$ is deflected upward immediately after the laser pulse indicating that the quenching reaction is too fast to be resolved on the time scale employed. The features of the subsequent decay of the 602 absorbance are strongly affected by the CTAC concentration. In the absence of CTAC, $C_{14}MV^{+}$ disappears rapidly with $k_3 = (4 \pm 0.4) \times 10^9\ M^{-1}\ s^{-1}$ (ionic strength 1.4×10^{-3} M[11]). At 4×10^{-3} M CTAC the decay occurs in two steps: the first part is fast and resembles the kinetics observed in CTAC-free solution while the second component is much slower and hardly noticeable over a time period of 1 ms. If the CTAC concentration is increased above 10^{-2} M, only the slow component remains. Experiments carried out at 453 nm where $Ru(bpy)_3{}^{2+}$ has an absorption maximum showed that the ground-state bleaching of $Ru(bpy)_3{}^{2+}$ behaves as the exact mirror image of the 602 decay. From these results, we infer that the back-reaction 3 is strongly retarded in the presence of micellar aggregates leading to a drastic stabilization of the intermediates $C_{14}MV^{+}$ and $Ru(bpy)_3{}^{3+}$. The rate constant for back electron transfer is at least 100-fold smaller in the micellar solution than in water, $k_3 \leq 2 \times 10^7\ M^{-1}\ s^{-1}$.[12]

The retardation of the back-reaction by CTAC micelles may be rationalized in terms of a significant shift in the hydrophylic-lipophylic balance of the surfactant electron acceptor occuring upon reduction. $C_{14}MV^{+}$ has a much more hydrophobic character than its mother ion $C_{14}MV^{2+}$, and hence shows a high affinity for the micellar pseudophase. It will be entrapped into CTAC micelles immediately after the electron transfer has occurred. The subsequent back-reaction is blocked by strongly repulsive interactions of $Ru(bpy)_3{}^{3+}$ with the cationic aggregates.

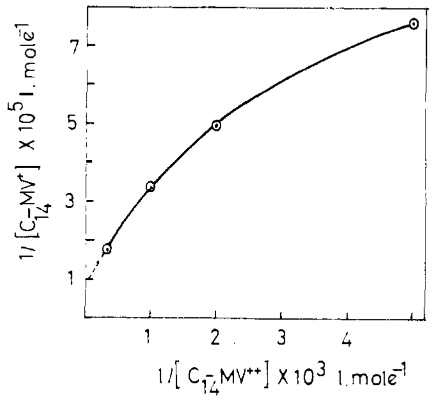


Figure 2. Effect of $C_{14}MV^{2+}$ on the yield of reduced viologen ($C_{14}MV^{+}$): $[CTAC] = 5 \times 10^{-2}$ mol/L.

A final point concerns the yield of redox products from reaction 2. This was investigated as a function of $C_{14}MV^{2+}$ concentration (2×10^{-4} to 3×10^{-3} M) while maintaining the CTAC at 5×10^{-2} M. Data are shown in Figure 2. The extrapolated ordinate intercept gives for the efficiency of the redox reaction η_{re} = 30% which agrees closely with the value observed for simple methylviologen.[3b] From simple homogeneous solution kinetics, one would expect a linear relation:

$$\frac{1}{[C_{14}MV^{+}]} = \frac{\eta_{re}}{{}^0Ru(bpy)_3{}^{2+}\ (CT)} + \frac{\eta_{re}}{{}^0Ru(bpy)_3{}^{2+}\ (CT)} \times \frac{k_0}{k_2} \times \frac{1}{[C_{14}MV^{2+}]} \quad (4)$$

Here ${}^0Ru(bpy)_3{}^{2+}$ (CT) designates the initial excited-state concentration produced by the flash while k_0 is the specific rate of deactivation in the absence of quencher and k_2 is the quenching rate constant. However, the points in Figure 2 show deviations from linearity. This effect is attributed to a decrease of the apparent value of k_2 due to an augmentation of the micelle bound fraction of $C_{14}MV^{2+}$ as its concentration increases.

In conclusion, the present paper illustrates the case of micellar inhibition of back-electron transfer in an important photoredox reaction. The general nature of the charge separation mechanism has meanwhile been established with other sensitizers such as water-soluble porphyrins. Our approach is different from previous work[13] in that the earlier investigations used a surfactant derivative of $Ru(bpy)_3{}^{2+}$ which through its hydrocarbon chain is anchored to the micelle. In this case back-transfer is very rapid unless a third component is added to the solution which reduces $Ru(bpy)_3{}^{3+}$. The advantage of the present system is its simplicity, charge separation being accomplished by proper organization of the reactants on the molecular level and a fortunate interplay of hydrophobic and electrostatic forces. Studies to combine this system with catalytic H_2 and O_2 production from water are now underway.

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(7) The details of this measurement as well as the synthesis carried out by Dr. A. M. Braun in our laboratory will be published in a forthcoming full paper.
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(10) 3-Carboxyamidpyridinium surfactants show a similarly low affinity for cationic micelles: C. A. Bunton, private communication.
(11) The back-reaction is accelerated by increasing the ionic strength. For example, addition of 10^{-2} M NaCl produces ~30% augmentation of k_3.
(12) Owing to low frequency noise interference with measurements on relatively long time scales, only an upper limit for the rate constant can be given.
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Pierre-Alain Brugger, Michael Grätzel*
Institut de Chimie Physique
Ecole Polytechnique Fédérale de Lausanne
CH-1015 Lausanne, Switzerland

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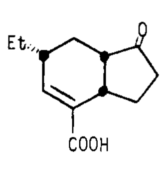
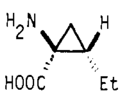
Total Synthesis of (±)-Coronafacic Acid: Use of Anionic Oxy-Cope Rearrangements on Aromatic Substrates in Synthesis

Sir:

Coronafacic acid (**1**) has been isolated directly from the culture broth of *Pseudomonas coronafacience* var. atropurpurea.[1] The amide of coronafacic acid (**1**) with coronamic acid (**2**) is also produced by the same phytopathogenic bacterium.[1]



1



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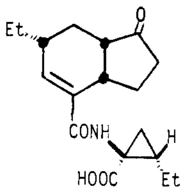
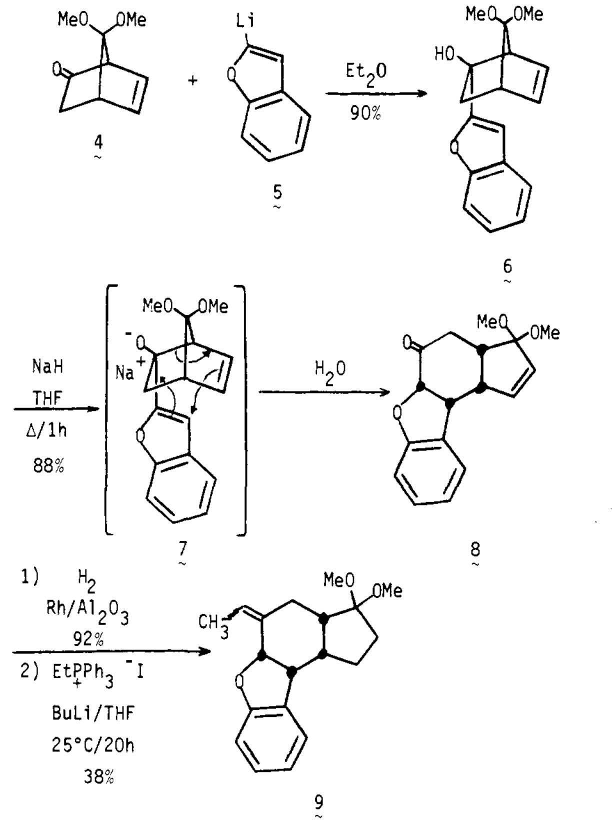


3

This natural phytotoxin, coronatine (**3**), induces chlorosis on the leaves of Italian rye grass and promotes the expansion of potato cells at very low concentrations.[2] Herein is reported an efficient total synthesis of coronafacic acid which employs as a key step an anionic oxy-Cope rearrangement on an aromatic substrate, a synthetic process developed recently in our laboratory.[3] In addition, a novel silicon-based alternative to an ethylidene Wittig reaction is described.

The only known total synthesis of coronafacic acid utilized a Diels-Alder reaction between cyclopentenone and a substituted butadiene to construct the 1-hydrindanone skeleton.[4] It was envisioned that the anionic oxy-Cope rearrangement of a suitably substituted norbornenyl alcohol would produce a hydrindan intermediate which could be easily transformed into the desired natural product (Scheme I). To this end, the highly functionalized enone **4**[5] was treated with 2-lithiobenzofuran (**5**, prepared from benzofuran[6] by treatment with *n*-butyllithium) to furnish a 90% yield of the crystalline exo alcohol **6**[7] (mp 116-117 °C, IR 3500 cm^{-1}).[8] The stereochemistry of the product was assigned both by analogy to our earlier work in these norbornenyl systems[3] and by the effect of the shift reagent, $Eu(fod)_3$, on the chemical shifts of the various protons in the molecule, especially those of the *syn*-7-methoxy group, which undergo a very large downfield shift.

Scheme I



Refluxing a solution of **6** and sodium hydride in tetrahydrofuran (THF) for 1 h afforded the crystalline rearranged product **8** in 88% yield (mp 146-147 °C; IR 1735, 1600, 1460 cm^{-1}). This reaction proceeds by the presumed intermediacy of the anion **7** which would be expected to undergo facile oxy-Cope rearrangement.[3,9] The stereochemistry of the four asymmetric centers in **8** are assumed to be all cis based both on analogy to our previous work[3] and on the similarity of the chemical shifts and coupling constants of the protons in **8** and those of **12**, the structure of which was proven unambiguously by an X-ray analysis. Although catalytic hydrogenation of **8** proceeded in high yield, the subsequent Wittig reaction gave only a fair yield of the ethylidene mixture **9**[7] under all conditions tried. A large amount of starting ketone is recovered so that enolization of the ketone by the very basic ylide is the probable source of difficulty. The use of other solvents, e.g., DME or Me_2SO, for the production of the ylide did not significantly improve the reaction. Since the highest yield for this process was only 38% (68% on unrecovered ketone), we sought alternatives to the Wittig route.

Encouraged by the widely reported successes of the silyl-Wittig reaction of Peterson[10] for methylene formation, we attempted to extend this approach to the formation of an ethylidene unit. Reaction of the Grignard reagent formed from commercially available α-chloroethyltrimethylsilane with the ketone **8** afforded simple reduction of the carbonyl in 85% yield with no evidence for addition. This result is not due to the steric bulk of the carbonyl in **8** since both benzophenone and cyclohexanone also give nearly quantitative yields of the corre-

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