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Zhou, Dapeng; Khatmullin, Renat; Walpita, Janitha; Miller, Nicholas A.; Luk, Hoi Ling; Vyas, Shubham; Hadad, Christopher M.; and Glusac, Ksenija D., "Mechanistic Study Of The Photochemical Hydroxide Ion Release From 9-hydroxy-10-methyl-9-phenyl-9,10-dihydroacridine" (2012). Chemistry Faculty Publications. 130.
https://scholarworks.bgsu.edu/chem_pub/130

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Mechanistic Study of the Photochemical Hydroxide Ion Release from 9-Hydroxy-10-methyl-9-phenyl-9,10-dihydroacridine

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Abstract: The excited-state behavior of 9-hydroxy-10-methyl-9-phenyl-9,10-dihydroacridine and its derivative, 9-methoxy-10-methyl-9-phenyl-9,10-dihydroacridine (AcrOR, R = H, Me), was studied via femtosecond and nanosecond UV–vis transient absorption spectroscopy. The solvent effects on C–O bond cleavage were clearly identified: a fast heterolytic cleavage (τ = 108 ps) was observed in protic solvents, while intersystem crossing was observed in aprotic solvents. Fast heterolysis generates 10-methyl-9-phenylacridinium (Acr+) and OH, which have a long recombination lifetime (no signal decay was observed within 100 μs). AcrOH exhibits the characteristic behavior needed for its utilization as a chromophore in the pOH jump experiment.

Photohydroxide emitters are a class of compounds that release hydroxide anions (OH) to induce a pOH jump upon UV–vis irradiation. This process is similar to the pH jump methods achieved using various photoacids.1–4 The pOH jump is generally achieved through heterolytic cleavage of the C–O bond, as is exhibited by compounds such as 9-fluorenol,5,6 9-phenylxanthen-9-ol,7 and triphenylmethane hydroxide,8,9 whose resonance structures stabilize the resulting carbocations. The application of these compounds in driving a photochemical pOH jump is mostly limited by the fast recombination of hydroxide and the carbocation.5–7 Additionally, homolytic C–O bond cleavage can complicate the chemistry with the formation of hydroxyl radical (•OH).5,7,10

Malachite green carbinol base (MGCB) has been suitable for photochemical pOH jump experiments9 because the lifetime of •OH, which is generated in 300 ps,8 is several minutes, and •OH is not formed. Upon excitation, MGCB was found to induce a jump from pH 6 to 11, making it a possible agent for studies of conformational changes in DNA/RNA11,12 and also for the release of drugs from host molecules.13

Recently, Fréchet and co-workers discovered that 9-hydroxy/methoxy-10-methyl-9-phenyl-9,10-dihydroacridine (AcrOR, R = H, Me) exhibits photochemical behavior somewhat similar to that of MGCB.14 Upon irradiation in H2O/acetonitrile (ACN) mixtures, AcrOH releases 10-methyl-9-phenylacridinium (Acr+) and OH, resulting in a pOH jump that lasts longer than that of MGCB. However, the photochemical mechanism of AcrOH has not been studied until now. This study presents a detailed investigation of the excited-state dynamics of AcrOR via femtosecond (fs) and nanosecond (ns) transient absorption (TA) spectroscopy (Scheme 1), including the varying solvent-facilitated pathways of Acr+ generation. Generation of Acr+ is obvious with protic solvation (methanol, MeOH), while an intersystem crossing (ISC) process is observed with aprotic solvation (ACN and benzene).

To evaluate the driving force for the excited-state heterolytic and homolytic C–O bond cleavage in AcrOH, a Förster energy diagram15 was constructed from pH-dependent absorption and emission measurements along with the previously known reduction and oxidation potentials of Acr+ and •OH (Figure S1 in the Supporting Information). From pH-dependent absorption measurements, the ground-state pseudobase pK of AcrOH was determined to be 11.11, which is consistent with the literature.16 On the basis of the Förster energy diagram, the driving forces for the excited-state heterolytic and homolytic C–O bond cleavages were evaluated as ΔG°hetero = −1.048 eV, ΔG°hetero = −0.263 eV, ΔG°homo = −1.513, and ΔG°homo = −0.728 eV, indicating that both heterolytic and homolytic cleavage are possible in the excited state.

Published: April 2, 2012
Published: July 5, 2012

Scheme 1. Excited-State Behavior of AcrOH in Different Solvents: MeOH (blue) and ACN or Benzene (red)†

Supporting Information

References:

dx.doi.org/10.1021/ja3031888 J. Am. Chem. Soc. 2012, 134, 11301–11303

dx.doi.org/10.1021/ja3031888 J. Am. Chem. Soc. 2012, 134, 11301–11303
The geometry of the AcrOH ground state was optimized and the characters of the AcrOH excited states were evaluated using density functional theory (DFT) and time-dependent DFT calculations, respectively (Table S1 and Figure S2). The difference density plots\textsuperscript{17,18} shown in Figure S2 indicate that the S\textsubscript{0}→S\textsubscript{1} transition exhibits π–π* character within the acridine framework, while the S\textsubscript{0}→S\textsubscript{2} transition generates a π–π* state in which an intramolecular electron transfer from the acridine framework to the phenyl moiety occurs. The laser measurements shown in this work were performed using a 310 nm excitation pulse; when compared to the calculated vertical excitations (Figure S2), this laser excitation should generate only the singlet excited (S\textsubscript{1}) state with π–π* character.

The photochemical behavior of AcrOH in different solvents (ACN, benzene, and MeOH) was investigated using the fs TA technique. In ACN, the t = 0 TA spectrum of AcrOH exhibits a broad absorbance from 350 to 800 nm with λ\textsubscript{max} at ∼780 nm that decays with a lifetime of 1.4 ns (Figure 1). This component is assigned to the S\textsubscript{1} state of AcrOH. The decay of the S\textsubscript{1} state is accompanied by the growth of a new band at ∼550 nm that does not decay within 1.5 ns (the time limit of fs TA detection). The excited-state behavior of AcrOH and AcrOMe in other aprotic solvents, such as benzene (Figure S3 and Table S3), is similar to that shown in Figure 1. If the excited-state heterolytic C–O bond cleavage occurred, the 550 nm signal could be assigned to the formation of either Acr\textsuperscript{+} (nonadiabatic process) or Acr\textsuperscript{+} (adiabatic process). However, comparison of the absorption spectra of Acr\textsuperscript{+} (λ\textsubscript{max} = 425 nm; Figure 1c) and Acr\textsuperscript{+} (λ\textsubscript{max} = 390 and 470 nm; Figure S4) to this 550 nm band shows that the heterolytic C–O bond cleavage does not occur from the S\textsubscript{1} state of AcrOH. On the basis of previous literature, this ∼550 nm peak could be postulated to arise from the acridine radical (Acr\textsuperscript{•}), which would be formed by homolytic C–O bond cleavage (AcrOR + hν → Acr\textsuperscript{•} OR). The absorption spectrum of Acr\textsuperscript{•} was obtained by a one-electron reduction of Acr\textsuperscript{+} (see the cyclic voltammogram in Figure 1d). The UV–vis spectroelectrochemical results shown in Figure 1c demonstrate that Acr\textsuperscript{•} absorbs at 500 nm, which matches well with the previously reported Acr\textsuperscript{•} spectrum obtained using chemical reduction.\textsuperscript{19} Given the large mismatch between the 550 nm band obtained in the TA spectra and the Acr\textsuperscript{•} signature band, we conclude that homolytic C–O bond cleavage from AcrOH\textsuperscript{•} does not occur. The experiments performed on the ns time scale show that the 550 nm transient is long-lived (τ\textsubscript{550 nm} = 277 ns; Figure S5) and readily quenched by molecular oxygen. Thus, this intermediate is assigned to the triplet excited (T\textsubscript{1}) state of AcrOH. These results suggest that even though the homolytic bond cleavage is thermodynamically favorable (Figure S1) and previous reports on similar systems\textsuperscript{7} demonstrate the formation of the homolytic products, the S\textsubscript{1} state of AcrOH does not undergo homolytic C–O bond breaking. This is possibly due to a competing deactivation channel of the S\textsubscript{1} state via ISC to form the T\textsubscript{1} state. Additionally, formation of the Acr\textsuperscript{•} absorbance at ∼500 nm was not observed in the ns TA measurements, showing that homolytic C–O bond cleavage on the T\textsubscript{1} state surface does not lead to separated Acr\textsuperscript{+} and OH radicals, even though the evaluated AcrOH T\textsubscript{1} energy is higher than the energy needed for the C–O bond homolysis (Figure S1). A possible scenario that can explain this absence of observable homolytic products is one in which a conical intersection between the T\textsubscript{1} and S\textsubscript{0} states exists along the C–O bond coordinate. Since the T\textsubscript{1} lifetime of AcrOH (277 ns; Figure S5e) is shorter than the T\textsubscript{1} lifetimes of most organic compounds (usually in the μs range\textsuperscript{20}), it is possible that such a mechanism operates in this case. Indeed, DFT calculations suggested that homolytic C–O bond cleavage in the T\textsubscript{1} state occurs at a C–O bond distance of 1.8 Å. This triplet transition state would lead to a pair of separated radicals at a distance of 3.0 Å. However, along the C–O distance, the ground-state singlet surface and the triplet surface cross each other at a separation of 2.8 Å. Thus, we suggest that homolytic C–O bond cleavage in the triplet state leads to a conical intersection between the S\textsubscript{0} and T\textsubscript{1} states, resulting in the recovery of AcrOH in the ground state (see Table S2 and Figures S8–S10).

On the other hand, the behavior of AcrOH in protic solvents is different (Figure 2). The initially formed S\textsubscript{1} state decay within 108 ps to generate a product that absorbs at 425 nm. This product is assigned to Acr\textsuperscript{•} by comparison to the ground-state absorption spectrum (Figure 2a inset). The protic solvation clearly has a strong effect on the energetics of the heterolysis, as schematized in Figure S1. As previously discussed by Steen,\textsuperscript{21} the protic solvation stabilizes OH by promoting the migration of the negative charge along the hydrogen-bonded solvent network. The formation of Acr\textsuperscript{•} occurs without any observable intermediate steps. To be specific, the formation of the intermediate Acr\textsuperscript{•*} via adiabatic heterolytic bond breaking along the S\textsubscript{1} surface of AcrOH was not observed in the TA spectra. The steady-state emission measurements also confirmed that Acr\textsuperscript{•*} is not formed as an intermediate during heterolytic bond cleavage (Figures S2 and S6), since no Acr\textsuperscript{•*} emission (450 to 650 nm) was observed in the emission measurements of AcrOH or AcrOMe in ACN or water.

The TA experiments on the ns time scale showed that the Acr\textsuperscript{+} signal at 425 nm is long-lived, and no signal decay was observed within 100 μs (Figure 2d). The long-lived charge...
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PhCH₂ supported by the known bond strengths of PhCH₂ the C−OH bond in MeOH. This conclusion is further supported by the known bond strengths of PhCH₂=OH and PhCH₂=OMe (78 and 68–70 kcal/mol, respectively). The lower bond energy of C=OMe also reflects the different reactivities of AcOH and AcOMe in aprotic solvents: while AcOH does not generate Ac⁺ in aprotic solvents, the TA spectra of AcOMe in ACN (Figures S3 and S5) show the formation of Ac⁺ from the singlet excited state.

In conclusion, photochemical excitation of AcOH has been shown to result solely in heterolytic cleavage in protic solvents. Since the heterolysis is fast (108 ps) and followed by slow recombination of the ions (time scale of hours15), the acidic derivatives such as AcOH show promise for use in producing fast, long-lived pOH jumps.

ASSOCIATED CONTENT

Supporting Information
Synthesis, TA laser setup, computational methods, and additional fs and ns TA results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by BGSU, the National Science Foundation (CHE-1055397 CAREER Award to K.D.G. and CHE-0743258 to C.M.H.), the Ohio Supercomputer Center, and Delta Electronics Foundation (Delta Fellowship to D.Z.). We thank Felix N. Castellano (BGSU) for help with spectroelectrochemistry measurements.

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Figure 2. (a) Femtosecond TA spectra at time delays of −6.3 ps (black), 0 ps (red), 30 ps (blue), 80 ps (green), 200 ps (gray), 400 ps (cyan), and 1487 ps (orange). The inset shows the UV–vis absorption spectrum of Ac⁺. (b) Kinetics of 1 mM AcOH in MeOH (λEX = 310 nm). (c) Nanosecond TA spectra at time delays of 60 ns (red) and 510 ns (blue). (d) Kinetics of 0.17 mM AcOH in O2-saturated MeOH (λEX = 266 nm).

dx.doi.org/10.1021/ja3031888 | J. Am. Chem. Soc. 2012, 134, 11301–11303