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Uranyl Photochemistry with Alkenes: Distinguishing between H-Atom Abstraction and Electron Transfer[†]

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Introduction

Recent studies with the uranyl ion (UO_2^{2+}) have shown that it has the potential to photocatalytically oxidize organic substrates in the presence of air.[1−3] The excited-state UO_2^{2+*} is a potent oxidant ($E° = 2.6$ V),[4] and is quenched by a variety of organic substrates.[1,5−16] The resulting U(V) species can then be oxidized back to UO_2^{2+} in the presence of oxygen.[2] Previous studies with alcohols have shown, through kinetic isotope effects, that the quenching of the uranyl excited state occurs by hydrogen atom abstraction to give UO_2H^+ and an organic radical.[1,6,7] The mechanism of quenching with alkenes has not been definitively determined.[9−16] Proposals for quenching mechanisms with alkenes have included exciplex formation, H-atom abstraction, and electron transfer. Recent work identified a U(V) species as a quenching product in the absence of oxygen, and suggested H-atom abstraction as the quenching mechanism.[1] The observation of U(V) identifies the quenching mechanism as a one-electron process, but does not discriminate between electron transfer and H-atom abstraction. Other reports show that quenching rates vary with ionization potential (IP) in the case of aromatic molecules, suggesting that electron transfer is the mechanism of quenching.[14−16] We report here on a series of quenching studies between uranyl and a variety of alkene substrates that unequivocally demonstrate quenching of the uranyl excited state with alkenes occurs by electron transfer.

Experimental Section

Materials. ACS reagent grade CH_3CN (J.T. Baker) was used as received. Water was deionized by a Millipore filtration system. The 3,3-dimethyl-1-butene was distilled prior to use to remove the inhibitor. All other alkenes were used as received (Aldrich). Uranyl nitrate (Strem) and uranyl acetate (Pfaltz and Bauer) were used as received.

Table 1. Kinetic Data for the Quenching of Uranyl by Alkenes with Literature Ionization Potential (IP) and Allylic C−H Bond Dissociation Energy (BDE) Values

alkene	k_q (M^{-1} s^{-1})	BDE[14] (kJ/mol)	IP[16,17] (eV)
3,3-dimethyl-1-butene	$(1.3 \pm 0.1) \times 10^7$	>385[b]	9.45
3-methyl-1-pentene	$(1.2 \pm 0.1) \times 10^7$	323	9.53
1-hexene	$(1.8 \pm 0.1) \times 10^7$	345[a]	9.46
trans-2-hexene	$(4.0 \pm 0.2) \times 10^7$	342[a]	9.04
2-methyl-2-pentene	$(9.6 \pm 0.3) \times 10^7$	339[a]	8.68[a]
2,3-dimethyl-2-butene	$(2.6 \pm 0.2) \times 10^8$	326	8.27
1,4-pentadiene	$(3.2 \pm 0.4) \times 10^7$	318	9.62
cis-1,3-pentadiene	$(3.0 \pm 0.2) \times 10^8$	347	8.61

[a] Values based on the structurally analogous pentene isomer. [b] Estimated C−H bond value (experimentally C−C bond cleavage occurs before C−H bond cleavage can be observed).

Measurements. Excited-state lifetimes of uranyl were determined using a Quanta Ray DCR-3 Nd:YAG laser with a R-955 PMT detector and a HP 54111D digitizing oscilloscope. Quenching studies were done in a quartz cuvette fitted with a septum to avoid any evaporation of the more volatile organics. All experiments were done in a 1:1 CH_3CN/H_2O solution (0.3 M H_3PO_4) with 2−3 mM uranyl nitrate.[17] Under the reaction conditions the uranium species in solution is a uranyl phosphate complex with a lifetime in solution of 100 μs. Solutions were deaerated by a nitrogen sparge for 5−10 min, and the cuvette was sealed with a septum. Aliquots of quencher were added until the lifetime was <3 μs, which corresponded to 1−30 mM of quencher depending on the rate constant. All of the quenching studies exhibited Stern−Volmer kinetics[18] with R^2 values >0.98.

Results and Discussion

Stern−Volmer plots of τ_0/τ vs the concentration of the alkene gave straight lines (τ_0 = lifetime of uranyl with no alkene present; τ = lifetime of uranyl at a given concentration of alkene). The slopes of the lines were used to determine the quenching rates, k_q, which are shown in Table 1 (slope = $\tau_0 k_q$). Two possible one-electron quenching processes are electron transfer and H-atom abstraction. The fundamental difference between the two processes for alkene substrates is that H-atom abstraction will occur at the allylic position to give the allyl radical, whereas electron transfer involves removing an electron from the double bond to give the cation radical product. To clearly discern between the two pathways, we investigated the quenching of the uranyl excited state with three distinct series of alkenes.

In the first series of quenching experiments, we looked at the effect of altering the substituents at the allylic position to change the bond dissociation energy (BDE) of the allylic proton without greatly affecting the IP of the alkene. H-atom abstraction of 3-methyl-1-pentene would yield a stable tertiary allylic radical, 1-hexene would give a secondary allylic radical, and 3,3-dimethyl-1-butene has no allylic hydrogen available for abstraction. The difference in the stability of the tertiary and secondary radicals can be seen in the difference in bond dissociation energies 323 and 345 kJ/mol for 1-hexene and

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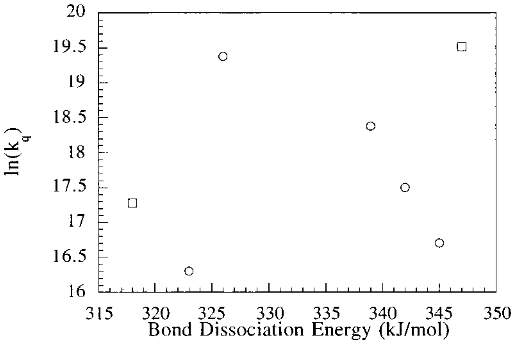

Figure 1. ln(k_q) vs the BDE of the allylic C−H bond for alkenes (○) and dienes (□).

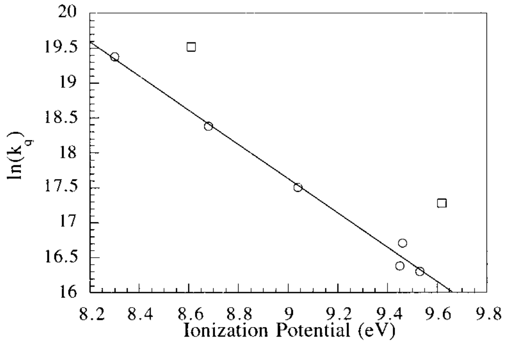

Figure 2. ln(k_q) vs the IP for alkenes (○) and dienes (□). The line represents the best fit to the hexene isomer data.

3-methyl-1-pentene, respectively.[19] The alkene 3,3-dimethyl-1-butene has no allylic proton present for H-atom abstraction, and the energy necessary for abstraction of either the vinyl proton or one of the methyl protons should be >385 kJ/mol.[20] On the basis of previous H-atom abstraction data,[1] the large difference in BDEs should lead to a variation in quenching rates of at least an order of magnitude. The observed quenching rates are all very similar and do not vary by more than a factor of 1.5, suggesting H-atom abstraction is not the quenching mechanism. These results are consistent with electron transfer as the quenching mechanism since the IPs of the three alkenes do not vary by more than 0.08 eV.[21,22]

In the second series of alkenes, 1-hexene, 2-hexene, 2-methyl-2-pentene, and 2,3-dimethyl-2-butene, the number of electron-donating methyl groups on the alkene progressively increases. As methyl groups are added to the vinyl positions, the IPs decrease, varying by 1.25 eV across the series. The allylic C−H bond strength remains relatively unchanged throughout the series. An H-atom abstraction mechanism would be expected to yield similar quenching rates for all four hexene isomers. The observed quenching rates vary by over an order of magnitude. The quenching rates increase as the ionization potential of the alkene decreases, as expected for an electron-transfer mechanism.

The final comparison is between the two diene complexes 1,3-pentadiene and 1,4-pentadiene. This comparison offers the most compelling data, because it is a rare situation in which the BDE and IP values have significant trends in opposite directions. H-atom abstraction produces identical products. Since 1,4-pentadiene lacks any stabilization from conjugated double bonds, the bond dissociation energy is much lower than that of 1,3-pentadiene (318 kJ/mol compared to 347 kJ/mol) and would quench by H-atom abstraction at a much faster rate. Ionization potentials follow an opposite trend in which 1,3-pentadiene has a much lower ionization potential than 1,4-pentadiene (8.62 eV compared to 9.61 eV) because the 1,3-pentadiene product is an allyl radical cation. The 1,3-pentadiene quenches nearly 10 times faster than the 1,4-pentadiene, once again supporting the conclusion that the quenching of the uranyl excited state by alkenes occurs by an electron-transfer mechanism.

The results can be summarized by looking at plots of ln(k_q) vs the allylic C−H bond dissociation energy (Figure 1) and ln(k_q) vs ionization potential (Figure 2). The lack of any observable correlation between the BDE of the allylic C−H bond and ln(k_q) suggests that H-atom abstraction is not the mechanism involved in quenching the uranyl luminescence. There is, however, a very good inverse linear correlation between IP and ln(k_q). Such a trend is expected on the basis of Marcus theory for electron transfer, which predicts ln(k_q) is proportional to $-\Delta G/2RT$ at low driving forces.[23] With all of the substrates the general trend of faster rates with lower IPs is clear, and within the single class of hexene isomers there is an extremely good linear correlation, demonstrating that the quenching of the uranyl excited state with alkenes occurs by electron transfer. It should be noted that the IP is a gas-phase measurement and only provides information on oxidation potential trends. Within a closely related set of compounds, solvation energies are expected to be similar and IPs should correlate well with oxidation potentials (IP will be proportional to ΔG). Compounds that are not structurally similar will have different solvation energies, and the oxidation potentials may not correlate well with IPs. Such differences between the alkenes and the dienes explain why the two diene points are displaced from the linear fit to the hexene isomer data.

The mechanism of electron transfer to give the cation radical has some implications for the type of photochemistry catalyzed by uranyl.[24,25] We have not examined products in the water/acetonitrile mixtures, but preliminary investigations into product formation in aqueous acetone mixtures show that in the case of 1-hexene the major product (>90%) is 2-nonanone. Such a saturated product would not be expected from the allylic radical formed upon H-atom abstraction, but could result from acetone addition across the cation radical.[26]

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Supporting Information Available: Figure showing the Stern−Volmer plots for 3-methyl-1-pentene and 1-hexene. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Most thermal techniques for measuring bond dissociation energies cannot be applied to 3,3-dimethyl-1-butene because C−C cleavage to give the stable tertiary radical occurs at 285 kJ/mol. We were unable to find a BDE for a C−H bond of the alkene in the literature. The BDEs for analogous methyl and vinyl C−H bonds in isopentane and ethylene are 398 and 452 kJ/mol from the *CRC Handbook of Chemistry and Physics*, 63rd ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, p F-196.

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