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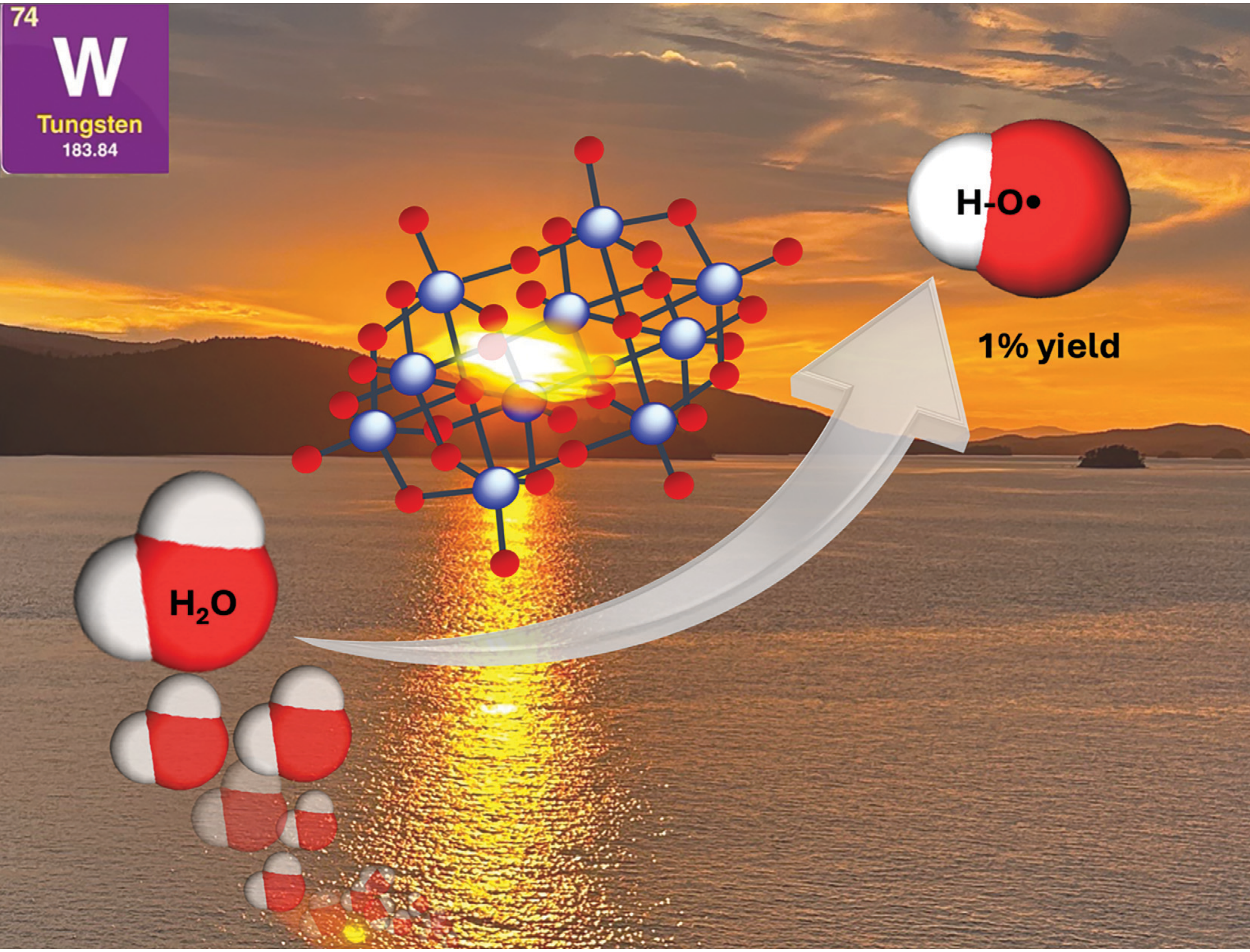

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Can excited decatungstate abstract hydrogen from water? New results and thoughts on this unusual reaction

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Excited decatungstate (DT) abstracts hydrogen atoms from water with a quantum yield of ∼0.01 which means only 1 out of 100 photons absorbed yields hydroxyl radicals. This was calculated using laser flash photolysis. Our results exclude the triplet state of DT as a viable pathway for hydrogen atom transfer (HAT) due to its insufficient energy, but rather HAT is mediated by a higher electronic state, likely a singlet with charge transfer characteristics. We also approximate the BDE of O–H in DTH· using the thermodynamic data available.

Excited decatungstate, $[W_{10}O_{32}]^{4-}$ (DT), a potent photocatalyst, exhibits remarkable ability to initiate reactions through hydrogen atom transfer (HAT).[1–8] While its HAT chemistry is extensively documented with organic substrates featuring C–H bonds, some research suggests that excited decatungstate can also interact with water, leading to the cleavage of O–H bonds and the formation of highly reactive hydroxyl radicals (·OH).[9,10]

This finding has been experimentally verified using techniques such as EPR spin trapping. The formation of ·OH radicals implies that the excited decatungstate possesses the unusual capability to break the strong O–H bond in water molecules.

The recent demonstration that the triplet state of decatungstate, ^{3}DT*, possesses a triplet energy of only ∼21 kcal mol^{-1} (ref. 11) makes it an unlikely precursor for a reaction that involves the cleavage of the robust (118 kcal mol^{-1}) O–H bond in water. Earlier work, before the energetics of ^{3}DT* were established, suggested this species as the active HAT reagent.[10] In fact, the precise mechanistic details of how excited decatungstate interacts with water to generate hydroxyl radicals remain an active area of research, even if the reaction outcome aligns with a process involving the homolytic cleavage of the water O–H bond.

Given the potential of decatungstate triplet as a possible hydrogen abstractor for water,[9,10] we decided to re-examine the ideas and thermodynamics behind reaction (1) to explore this concept further.

$$\mathrm{DT^* + H_2O \rightarrow DTH\cdot + HO\cdot} \qquad (1)$$

To investigate this, we used coumarin as a reporter for the hydroxyl radicals that should be formed after hydrogen abstraction from water.[9] This fluorescent probe allows us to monitor the formation of these radicals through a fluorescence technique. However, it is worth noting that this method might not be precise for the total hydroxyl radical production and shows only the fraction that forms the fluorescent hydroxylated product.[12] Additionally, we examined the laser flash photolysis (LFP) of decatungstate to observe the formation of its reduced transient form, 'DTH·' which helped us to measure the quantum yield for its formation.

The results presented here lead us to conclude that while decatungstate is capable of abstracting hydrogen from water, the excited state involved cannot possibly be the triplet state. Therefore, we propose that a higher energy excited state, likely a singlet or a charge transfer excited state, is responsible for the hydrogen transfer. DTH· is readily detectable in LFP experiments. However, its formation could not be time-resolved in an instrument with a 7 ns rise time, supporting the idea that the triplet state DT* (τ ∼ 40 ns in water)[11] cannot be responsible for the hydrogen transfer.

We chose NaDT as the precursor to ensure the absence of C–H bonds in the system. We conducted two types of experiments. First, aqueous NaDT solutions (containing 0.2 mM NaDT) were irradiated in the presence of 0.2 mM coumarin. A characteristic fluorescence of 7-hydroxycoumarin is observed at 454 nm. Second, LFP experiments were performed to measure DTH·, which would serve as a clear

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reporter of hydrogen transfer from water as this transient species exhibits a characteristic absorbance in the red region.

While we present our own results demonstrating the scavenging activity of coumarin against HO·, there is literature precedent for this type of experiments.[9] The main findings are presented in Fig. 1, which includes H/D isotope effects, with an initial slope ratio of 2.4. We note that for reference solutions of 7-hydroxycoumarin its intensity of emission is the same in water and in D_2O (see SI-Fig. S1).

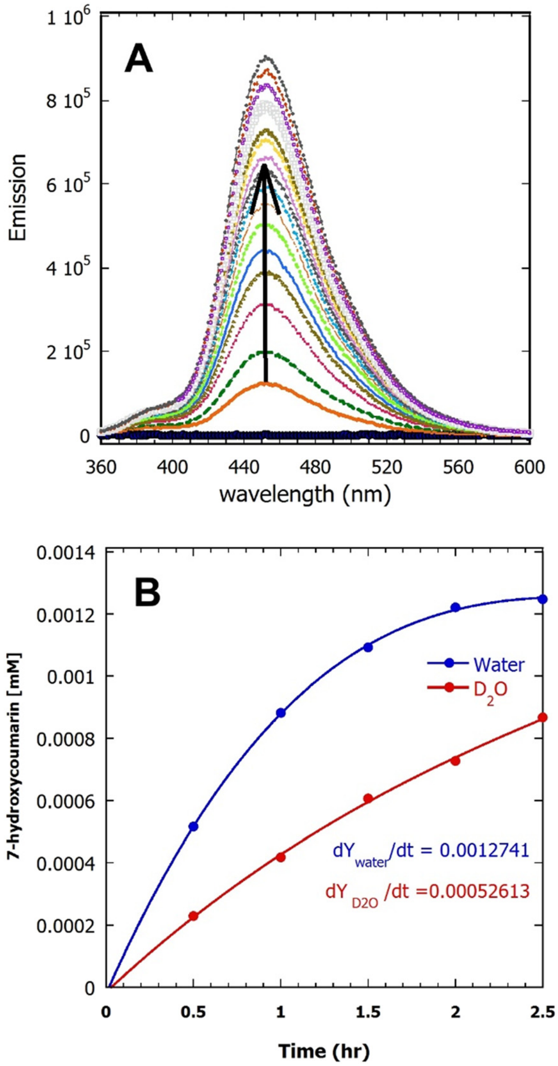
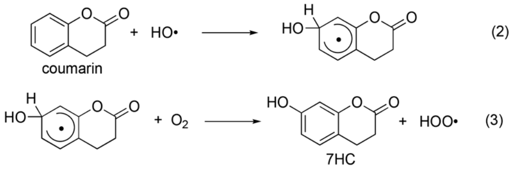


Fig. 1 UVA photolysis of aqueous 0.2 mM NaDT containing 0.2 mM coumarin under air. Spectra were recorded every 5 minutes for the first hour and every 10 minutes later. The excitation wavelength was 340 nm. Panel A: emission spectra due to 7-hydroxycoumarin formed as a product and displayed every 10 minutes. Panel B: in a separate experiment the emission at 450 nm was converted to concentrations (see SI Fig. S2 for calibration) and plotted against irradiation time for data in water and D_2O. The ratio of initial slopes is 2.4. Emission spectrum and UV-vis absorbance of samples before and after irradiation are presented in SI Fig. S3. The slopes displayed in panel B are slopes at the origin (time → 0). The spectrum of Kessil UVA lamp and the UV-vis absorbance of samples and control tests for emission are shown for comparison in SI Fig. S5 and S6 respectively.



Scheme 1 Generation of 7HC from coumarin.

Surprisingly, we found that the strong emission is only observed in aerated samples, while under argon, most of the fluorescence is suppressed (see SI Fig. S4). Scheme 1 below shows the radical scavenging mechanism proposed, including reaction (3) which is responsible for the requirement of oxygen for the fluorescence enhancement to take place. Reaction (3) is similar to that for cyclohexadienyl radical interacting with oxygen.[13] While H_2O_2 is a likely product, it would take about one hour to generate 1 μM H_2O_2, a concentration that we are unlikely to detect with standard techniques, and with a sample under continuous UV irradiation.

The isotope effect observed is indicative of a primary isotopic effect and is unlikely to reflect reaction (2), as HO· additions are extremely fast[14] and the proton is not at the main reaction center; thus we assume that the main H or D atom transfer from excited DT is sensitive to isotopic substitution. The pH during these studies was ~6. While some pH effects may be anticipated,[15] this aspect was not pursued.

Our second set of experiments involved LFP studies. It was our purpose to determine if the decay of $^3DT^*$ led to, or was concurrent with, the formation of DTH·, as this would be evidence for HAT from water. While we observed residual absorbance following $^3DT^*$ decay, we notice that these residual ΔOD values were small, but highly reproducible. This experiment was repeated several times in two separate laser systems for laser pulses with energy of 60 mJ per pulse and 18 mJ per pulse, the results for the latter are presented in SI Fig. S7–S10. We compared the yield and spectra for DTH·, generated in pure water, or in the presence of 10% isopropanol in water; the latter, with some calculations, serve as an actinometer for the formation of DTH· in pure water, which is demonstrated in Fig. 2.

Spectra recorded immediately after the traces of Fig. 2 confirm the assignment of the transient to DTH· and are included in the SI Fig. S13. The choice of 680 nm as the monitoring wavelength for radical yields is based on the excellent system response at this wavelength. Fig. S8 shows that monitoring at 780 nm also gave small but positive values of ΔOD; however, given the poor performance of our photomultiplier tube in this region, the 780 nm data was regarded as qualitative-only information. The reaction of $^3DT^*$ with 10% isopropanol was used as an actinometer to quantify the yield of DTH·. The transient absorbance in the plateau region was 0.223. In an earlier publication we estimated the quantum yield of DT intersystem crossing, Φ_{ISC} as 0.55 ± 0.10, while the lifetime of $^3DT^*$ in water as recorded

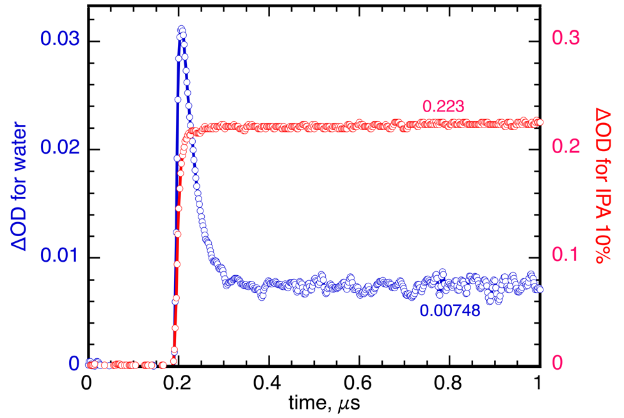


Fig. 2 Results from an LFP study of 0.2 mM DT in water under air after 355 nm excitation with approximately 60 mJ per pulse and monitored at 680 nm, where DTH· exhibits good absorbance. The blue trace represents pure water as the solvent, while the red trace contains 10% isopropanol. Note that in this double-Y graph, the two scales differ by a factor of 10. The plateau absorbances (determined statistically from the last 300 points) are displayed in the graph. The red trace represents an average of two laser shots, while the blue one represents an average of 10 shots. Screen captures of the traces as obtained from the software are presented in SI (Fig. S11 and S12).

in the same experiment was 32 ns and the rate constant for ^{3}DT* reaction with isopropanol is 2.9 × 10^7 M^{-1} s^{-1}.[11] Considering a concentration of isopropanol of 1.31 M, 55% of the triplets, ^{3}DT*, will be trapped by isopropanol; combining these numbers the quantum yield of DTH· generation in 10% isopropanol is $\Phi_{DTH\cdot} = 0.30$. In the case of ^{3}DT* in water, the residual signal in the plateau region averages to ΔOD of 0.00748 from Fig. 2. That is a ratio of 29.8 times more signal when isopropanol was added. When these numbers are taken into account (see SI) the quantum yield for DTH· formation in water is, $\Phi_{DTH\cdot} \sim 0.010 \pm 0.003$.

Attempts to detect a resolvable growth for DTH· in water failed across the 600 to 840 nm region. This is perhaps not surprising considering the very low quantum yield; in any event, it is consistent with our conclusion (*vide infra*) that in water DTH· does not originate from a ^{3}DT* reaction.

While it is tempting to assign the fate of DTH· to reaction (4), earliest studies from our laboratory suggest that this is a very slow reaction,[13] and more likely DTH· disproportionates as shown in reaction (5),[16] ultimately leading the recovery of DT *via* reaction (6). In any event we anticipate that DT, as a catalyst, will also be recovered and confirmed as no blue color characteristic of DTH$_2$ has been observed.

$$\mathrm{DTH\cdot + O_2 \rightarrow DT + HOO\cdot\ (very\ slow)} \tag{4}$$

$$\mathrm{2DTH\cdot \rightarrow DTH_2 + DT} \tag{5}$$

$$\mathrm{DTH_2 + O_2 \rightarrow DT + H_2O_2\ (slow)} \tag{6}$$

It is important to understand the kinetics associated with reaction (1), both for the ground states of DT and potentially for any excited states involved. Interestingly the redox potential required are all available in the literature.[17] Thus, for the ground state reaction at pH 7:

$$\Delta G_r^0 = E^0_{DT/DTH\cdot} - E^0_{HO\cdot/H_2O} \tag{7}$$

$$\Delta G_r^0 = -0.279 - (-2.3) = 2.021\ \mathrm{V} \tag{8}$$

which converted represents +46.6 kcal mol^{-1}. Clearly a very unfavorable reaction from the DT ground state. Even allowing for 21 kcal mol^{-1} triplet excitation the value of ΔG_r^0 would be an unfavourable +25.6 kcal mol^{-1}. In fact, given the thermodynamic barrier of eqn (8), we would estimate that a DT excitation energy of at least 50 kcal mol^{-1} would be required for the reaction to be viable.

Enough rate constants are known for HAT by ^{3}DT* to plot the rate constant against bond dissociation energy (BDE) for this excited state, as illustrated in Fig. 3. While the plot exhibits significant scatter, it is evident that the rate constant decreases dramatically as BDE increases, making the reaction essentially impossible when BDE exceeds ~98 kcal mol^{-1}, presumably the point where the reaction of ^{3}DT* becomes endergonic Given that the first BDE in water is 118.8 kcal mol^{-1}, HAT by ^{3}DT* is essentially impossible.

Examining again Fig. 3, we see that the BDE of water is 20 kcal mol^{-1} higher than the limit estimated for viable ^{3}DT* HAT processes, or (subtracting the ^{3}DT* triplet energy), about 41 kcal mol^{-1} endergonic for the ground state, in line with the +46.6 kcal mol^{-1} estimated above from electrochemical measurements, given the uncertainty associated with both values.

If not ^{3}DT*, then which is the state responsible for the generation of hydroxyl radicals? The spectrum of NaDT shows a clear maximum at 324 nm, corresponding to a

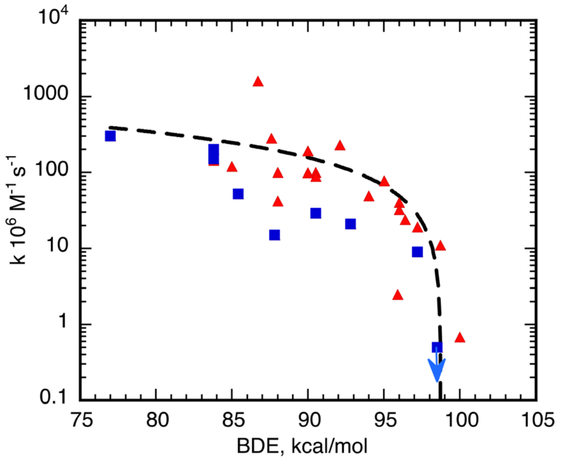


Fig. 3 Reported rate constants for HAT reactions involving ^{3}DT. Blue points are from our laboratory. While plotted in a semi log graph, the fit was made in a linear space. The analysis is similar to that usually made for Rehm–Weller plots.[18] The point with a down arrow corresponds to 1,1,2,2-tetrachloroethane for which only an upper limit of the rate constant could be determined (see SI Fig. S14 and S15).

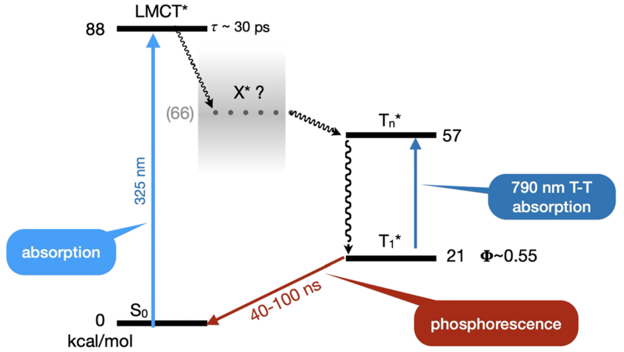
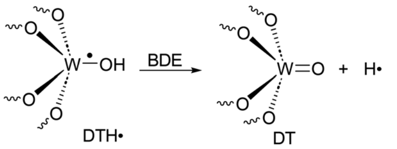


Fig. 4 Jablonski-type diagram summarizing the known information about the excited states of DT. Given various reports on the picosecond dynamics of the system, we speculate that a state, *X** may be involved in HAT from water and possibly in the path to ^{3}DT*.

transition at 88 kcal mol^{-1}. This is assigned to the excited singlet state, believed to be 'Ligand-to-Metal Charge Transfer State', LMCT.[19,20] There are various reports on this very short lived excited state, sometimes regarded as a 'hot' state, that relaxes to another excited state. This information is usually inferred from femtosecond and picosecond studies and our data do not provide additional information on this issue. However, for a DT state to react with water it must be below the 88 kcal mol^{-1} initial excitation, and at least 50 kcal mol^{-1} above the ground state based on both electrochemical and thermodynamic considerations. In Fig. 4 we include this state as *X** (dotted line) and all we can state is that its energy must be 66 ± 15 kcal mol^{-1} and shown with a grey gradient reflecting the uncertainty discussed above. On the triplet manifold T_1* is 21 kcal mol^{-1} above the ground state and its triplet–triplet absorbance (TTA) at 790 nm requires a T_n* state 57 kcal mol^{-1} above S_0. This state may be T_2* but this is not conclusive as other undetected TTA may remain hidden in the NIR region.

In any event, either S_1* or *X** is capable of HAT from water with low efficiency, but the process happens with fast kinetics, given the sub-nanosecond lifetime of the excited state involved.

While admittedly speculative, our thermochemical data, combined with the triplet energy of DT allows us to estimate the apparent bond dissociation energy (BDE) of the O–H bond in DTH·, as shown in reaction (9). If we assume from Fig. 3 that 98 kcal mol^{-1} corresponds to a thermoneutral reaction for ^{3}DT*, then correcting for a triplet excitation energy of 21 kcal mol^{-1}, the Δ*H* for reaction (9) is 77 kcal mol^{-1}. We refer to this as an 'apparent' BDE, as the process is compensated by the formation of the W=O double bond.



(9)

In the context of HAT reactions involving water, it is evident that the BDE in water is too strong for ^{3}DT* to successfully abstract a hydrogen atom. Consequently, the formation of hydroxyl radicals must be attributed to a higher singlet or CT excited state. This process occurs inefficiently, as it must compete with the short lifetime of this excited state.

Conclusions

This work presents an insight into the photocatalytic activity of decatungstate (DT), demonstrating the formation of hydroxyl radicals *via* hydrogen atom transfer (HAT) directly from water. Our experiments, including a clear kinetic isotope effect observed with deuterium oxide, establish that a HAT event from the O–H bond of water occurs. By using the absorbance of the DTH· species at 680 nm and using the reaction of DT triplet state with isopropanol as an actinometer, we determined a quantum yield of approximately 0.01 for this water-derived HAT. Interestingly, thermodynamic and redox potential arguments reveal that the triplet excited state of DT (^{3}DT*) is not energetically poised to directly abstract a hydrogen atom from water to form ·OH. Instead, our findings compel us to propose that the singlet state or a charge transfer excited state is probably the actual active species responsible for this observed HAT. This revised mechanistic understanding significantly challenges established views on decatungstate reactivity with strong O–H bonds.

Conflicts of interest

There are no conflicts to declare.

Data availability

Supporting information: Fluorescence and isotope effect data, experimental details, quantum yield calculations and laser flash photolysis representative data. See DOI: **https://doi.org/10.1039/D5CY00785B**.

The data supporting this article have been included as part of the SI.

Acknowledgements

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