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On the kinetics and energetics of one-electron oxidation of 1,3,5-triazines

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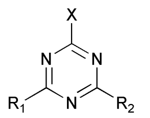
One-electron oxidation of 1,3,5-triazines is observed with both excited uranyl ion (*UO_2^{2+}) and sulfate radical anion ($SO_4^{\cdot-}$) in aqueous solution, but not with Tl^{2+}, indicating that the standard reduction potentials $E°$ of 1,3,5-triazine radical cations are ≈ 2.3 ± 0.1 V *vs.* NHE, consistent with theoretical calculations; this suggests that if triazines inhibit electron transfer during photosynthesis, they would need to act on the reductive part of the electron transport chain.

1,3,5-Triazines are among the most commonly used herbicides.[1] They are also widely used as polymer photostabilisers.[2] However, these compounds are highly toxic, stable for long periods under typical environmental conditions, and their persistence in natural waters, and specially groundwaters, is a matter of considerable concern.[3] There is an urgent need for reliable methods for removing these compounds from drinking water resources. Advanced oxidation processes (AOPs) provide a potentially important route for mineralisation of these compounds, and photocatalysed oxidation[4] is one of the most valuable of these methods. The *s*-triazines absorb at wavelengths < 270 nm, and generally only undergo direct photolysis on excitation with UVC light.[5] However, they do degrade in the presence of various photosensitisers,[5] and there is interest in the development of new processes for their photodegradation.

One-electron oxidation would seem to be particularly attractive. However, although a number of studies have been carried out on the oxidative degradation of *s*-triazines, one important parameter, the standard reduction potential of their oxidized form in aqueous solutions, is not known. Cyclic voltametry studies on 2,4-diamino-1,3,5-triazine in acetonitrile appear to show only a two-electron oxidation ($E_{1/2}$ = +1.7 V *vs.* NHE).[6] To rectify this omission, we report a study combining laser flash and steady-state photolysis, pulse radiolysis and luminescence of the reactions of a series of 1,3,5-triazines (Scheme 1) with strong one-e$^-$ oxidants produced radiolytically and photochemically (experimental details have been given elsewhere).[7]†

After steady-state 254 nm photolysis, monitored by HPLC and GC/MS, 2-hydroxyatrazine was the main organic product observed with atrazine, atraton and ametryn (Scheme 1).



	X	R1	R2
sym-1,3,5-triazine	H	H	H
2-Cl-4,6-dimethoxy-1,3,5-triazine	Cl	OCH_3	OCH_3
Atrazine	Cl	NHEt	NH*iPr*
2-OH-atrazine	OH	NHEt	NH*iPr*
Atraton	OCH_3	NHEt	NH*iPr*
Ametryn	SCH_3	NHEt	NH*iPr*

Scheme 1 Triazines used in this study.

Tl^{2+}, produced at pH ⩽ 3 by pulse radiolysis of nitrous oxide saturated aqueous solutions of Tl^+, does not react with the triazines, providing a lower limit to their redox potentials ($E°(Tl^{2+}/Tl^{+})$ = 2.22 V *vs.* NHE).[8] With the $HO^\cdot$ radical ($E°(HO^\cdot, H^+/H_2O)$ = 2.74 V *vs.* NHE),[9] produced by radiolysis of a saturated nitrous oxide aqueous solution, the reaction proceeds almost quantitatively (97%) *via* addition to the aromatic ring to form the hydroxyl radical adduct, rather than one-e$^-$ oxidation (3%), as proved by pulse radiolysis experiments at pH *ca.* 10 using conductance detection, where the increase of conductance anticipated with OH^- formation was not observed. The process showed rate constants close to the diffusion control limit (see Table 1).

In contrast, one-e$^-$ oxidation was observed with the excited uranyl (*UO_2^{2+}) ion ($E°(^*UO_2^{2+}/UO_2^{+})$ ≈ 2.6 V *vs.* NHE).[10,11] Prolonged (*ca.* 1 h) photolysis at 366 nm of aqueous solutions of UO_2^{2+} (0.01 M, pH 1.4) in the presence of 1,3,5-triazine and its derivatives atrazine, 2-hydroxyatrazine, atraton, ametryn and 2-chloro-4,6-dimethoxy-1,3,5-triazine led to a decrease in the UO_2^{2+} concentration, as seen by a reduction in intensity of its emission spectrum. In the case of *s*-triazine it was possible to detect formation of U(IV) by its absorption spectrum, confirming the photo-oxidation. The kinetics of the primary e$^-$-transfer processes were studied both by steady-state quenching of *UO_2^{2+} luminescence and by monitoring the decay of *UO_2^{2+} absorption at 570 nm following 355 or 266 nm excitation (where only UO_2^{2+} absorbs) using laser flash photolysis. In both cases, good linear dependences of the quenching on triazine concentrations were observed, showing second-order kinetics. Steady-state data were analysed using Stern–Volmer plots, and rate constants (estimated errors ±10%) determined from the slopes (K_{sv}) using the measured lifetime of *UO_2^{2+} (k_0) under these conditions. Identical values for the rate constants for reaction between *UO_2^{2+} and triazines (see Table 1) were found in steady state (k_{SQ}) and dynamic (k_{DQ}) studies. This indicates that there is no static quenching, and that only a dynamic process between uranyl excited state and the triazine is involved. This is attributed to the process [eqn. (1)]

$$^*UO_2^{2+} + \text{1,3,5-triazine} \rightarrow UO_2^{+} + [\text{1,3,5-triazine}]^{\cdot+} \quad (1)$$

The observation of the above reaction suggests triazine reduction potentials lower than *UO_2^{2+}, but higher than Tl^{2+}. To more accurately determine the reduction potential, the $SO_4^{\cdot-}$ radical anion was used as a one-e$^-$ oxidant. For this oxidant $E°(SO_4^{\cdot-}/SO_4^{2-})$ = 2.41 V *vs.* NHE when the ionic strength approaches zero,[12] being produced by photolysis of Ar-saturated aqueous $K_2S_2O_8$ or radiolysis of N_2O-saturated aqueous $K_2S_2O_8$ in the presence of an excess of the $HO^\cdot$ scavenger *tert*-butanol. The rate of decay of the characteristic absorption band[13] of $SO_4^{\cdot-}$ in the presence of different concentrations of triazines permitted determination of the rate constants ($k_{SO_4^{\cdot-}}$, see Table 1) that characterize the one-e$^-$ oxidation process. These $k_{SO_4^{\cdot-}}$ are close to the diffusion control limit.

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Table 1 Kinetic data for photophysical and photochemical processes and HOMO energies for different 1,3,5-triazine derivatives

Triazine	E_{HOMO}/eV[a]	Φ_{PI}[b]	K_{SV}/M^{-1}	k_{DQ}/M^{-1} s^{-1}[c]	k_{SQ}/M^{-1} s^{-1}	$k_{\text{HO}^\cdot}$/M^{-1} s^{-1}	$k_{\text{SO}_4^{\cdot -}}$/M^{-1} s^{-1}
sym-1,3,5-Triazine	10.4	0.005	42	2.2×10^7	2.3×10^7[d]	No reaction	No reaction
2-Cl-4,6-dimethoxy-1,3,5-triazine	10.8	—	155	9.1×10^7	9.7×10^7[e]	—	—
Atrazine	9.2	0.124		5.0×10^9	7.5×10^9[e]	2.2×10^9	1.4×10^9
2-OH-atrazine	9.1	—		[f]	[f]	—	—
Atraton	9.1	0.078				3.8×10^9	6.5×10^8
Ametryn	9.0	0.071				4.3×10^9	4.1×10^9

[a] Obtained from semiempirical calculations at the PM3 level. [b] Obtained using 193 nm laser light, by comparing the yields of e^-_{aq} immediately after irradiation of the different triazines and of Cl^- solutions of with the same absorbance, for which $\Phi_{\text{PI}} = 0.41 \pm 0.08$.[20] [c] $\lambda_{\text{exc}} = 355$ nm. [d] Taking $k_0 = (4.9 \pm 0.5) \times 10^5$ s^{-1} at $\lambda_{\text{exc}} = 413$ nm, pH = 1.30, $\tau = (1.83 \pm 0.01)$ µs, obtained from the decay of $^*UO_2^{2+}$ in the absence of *sym*-triazine. [e] Taking $k_0 = 6.2 \times 10^5$ s^{-1} at $\lambda_{\text{exc}} = 414$ nm, pH = 1.46, $\tau = 1.60$ µs, obtained from the decay of $^*UO_2^{2+}$ in the absence of the corresponding triazine. [f] It was not possible to determine accurate values because of the low solubility of the triazine. However, the observed rate constants in both steady-state and dynamic experiments are close to diffusion control (*ca.* 10^{10} M^{-1} s^{-1}).

[1,3,5-triazine]$^{\cdot +}$ is likely to be very short-lived in water. Attempts were made to observe it using 266 nm ps laser flash photolysis (7 mJ per pulse, 30 ps pulse width, using a pulsed Hamamatsu Photonics high-pressure Xe lamp providing 80 ns pulses as analyzing light) and also using 266 nm ns laser flash photolysis with IR detection (Minilite-II Continuum laser, 4 mJ per pulse, 15 Hz repetition rate, using a Nippon–Bunko dispersive spectrometer with $MoSi_2$ IR source to monitor the transient IR absorption, with a photovoltaic HgCdTe KV104-1-4-1 SMA detector and a KA020-A1 preamplifier, working at 100 Hz–20 MHz bandwidth, both from Kolmer Technologies Inc.). None of our attempts have detected any UV-Vis transient absorption above 250 nm on timescales greater than 500 ps or in the 4000–900 cm^{-1} region on ns to µs timescales. Although the observed photoionization quantum yields (Φ_{PI}) are in all cases low (see Table 1), showing there are relevant alternative ways of relaxation of the excited state, the observation of e^-_{aq} provides indirect evidence for the generation of [1,3,5-triazine]$^{\cdot +}$.

Additional information on one-e$^-$ oxidation of 1,3,5-triazines comes from their ionisation potentials. From 193, 248 and 266 nm laser flash photolysis and 254 nm steady-state photolysis experiments, all of them carried out with time-resolved UV-Vis detection, the photoionisation threshold can be estimated to be between 266 and 254 nm (4.67–4.88 eV), *ca.* 3.5 eV, being additionally supplied by the hydration energy of the products of photoionization.[14]

Theoretical values of the of HOMO energies for the different 1,3,5-triazines were also obtained by semiempirical calulations at the PM3 level, using methods similar to those reported by Danovich and Apeloig.[15] These are compiled in Table 1, and that obtained for *s*-1,3,5-triazine is in excellent agreement with the experimentally determined vertical ionisation potential[16] of 10.51 eV. Experiments are in progress to determine vertical ionisation potentials for the other triazines. Comparison of ionisation potentials with standard reduction potentials is not straightforward, since both hydration energies and the absolute value of the reference potential $E°(H^+/\frac{1}{2}H_2)$ are involved. However, these can be linearly correlated[17] as $E° = (-3.8 \pm 0.4) + (0.73 \pm 0.05)\cdot\text{VIP}$, $r = 0.97$, and from the experimental ionisation limit reported above, a value of $E°$([1,3,5-triazine]$^{\cdot +}$/1,3,5-triazine) = 2.3 V *vs.* NHE is estimated. In addition, from the calculated HOMO energies, the value of $E°$([1,3,5-triazine]$^{\cdot +}$/1,3,5-triazine) = 2.6 V *vs.* NHE can be estimated. Both values are in excellent agreement with the limits obtained from the kinetic data.

Thus, the reduction potentials of triazines can be limited to *ca.* $E°$([1,3,5-triazine]$^{\cdot +}$/1,3,5-triazine) ≈ 2.3 ± 0.1 V *vs.* NHE. Such a high value for $E°$([1,3,5-triazine]$^{\cdot +}$/1,3,5-triazine) has important implications for the mechanism of action of these compounds as herbicides. They are suggested to act by inhibiting electron transport in photosynthesis.[18,19] However, from the estimated $E°$ value, this would only be possible if they affect the reductive part of the electron transport chain.

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Notes and references

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