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Stability of Cyanuric Acid to Photocatalytic Degradation

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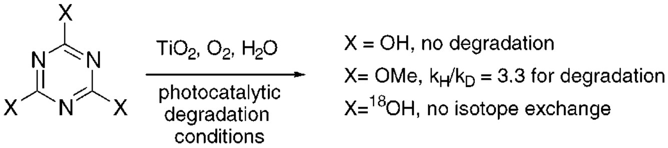
ABSTRACT



Cyanuric acid is unique among organic molecules in being resistant to photocatalytic degradative conditions by TiO_2 in oxygenated water. Trimethyl cyanurate shows an isotope effect of 3.1–3.3 on degradation selectivity when the methyl groups are deuterated, and cyanuric acid enriched in ^{18}O does not exchange hydroxyl groups with bulk water under these conditions. Thus, the tolerance of cyanuric acid to photocatalysis is not due to rapid and reversible addition to the aromatic nucleus.

Semiconductor photocatalysis and photocatalytic degradation has been the subject of an intense research effort over the past 20 years. In fact, since 1981 there have been over 2000 papers published on the topic.[1] A very large number of these have concentrated on the application of photocatalysis to the degradation of common organic water pollutants and the detailed physical and organic chemistry of the degradations. In general, exhaustive exposure of aqueous solutions of organic molecules containing TiO_2 and oxygen to light results in the complete oxidation (or mineralization) of the compound to CO_2, H_2O, and various inorganic ions. Some of the most attractive targets for this technology are agricultural chemicals, and thus reports have appeared on the degradation of atrazine (Figure 1), a common broadleaf herbicide, and other triazine herbicides. All of the ring substituents are mineralized, but the resulting cyanuric acid remains unaffected, resistant to further degradation.[2]

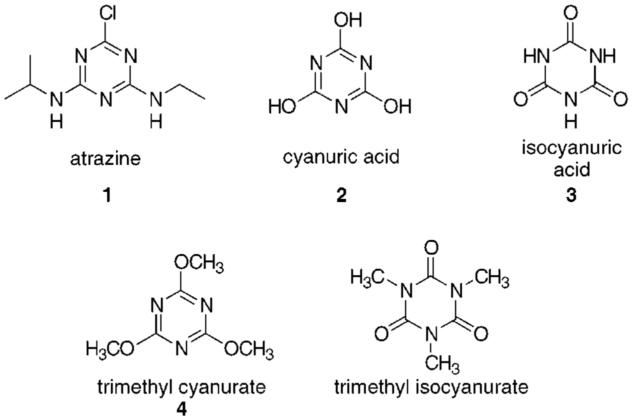


Figure 1. Cyanuric acid derivatives.

Though the acute and chronic toxicity of cyanuric acid is modest[3] and cyanuric acid is known to be generally difficult to hydrolyze or oxidize,[4] its tolerance of photocatalytic conditions is of fundamental interest because it is the only organic molecule known to be resistant to TiO_2-mediated degradation. In cyanuric acid, the carbon is formally at the same oxidation state as CO_2, but the nitrogens may be further oxidized. Indeed, control experiments analogous to those described below showed that urea is degraded under our conditions. Thus, the resistance of cyanuric acid is not due simply to the carbon oxidation state. In this letter we address that resistance using isotopic probes designed to look for reversible reactions that might account for its unique properties.

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[1] Mills, A.; Le Hunte, S. *J. Photochem. Photobiol. A: Chem.* **1997**, *108*, 1−35.

[2] Pelizzetti, E.; Maurino, V.; Minero, C.; Carlin, V.; Pramauro, E.; Zerbinati, O.; Tosato, M. L. *Environ. Sci. Technol.* **1990**, *24*, 1559−1565.

[3] Canelli, E. *Am. J. Public Health* **1974**, *64*, 155−162.

[4] Wojtowicz, J. A. *Cyanuric and Isocyanuric Acids*, 4th ed.; Kroschwitz, J. I., Ed.; Wiley: New York, 1991; Vol. 7, pp 835−851.

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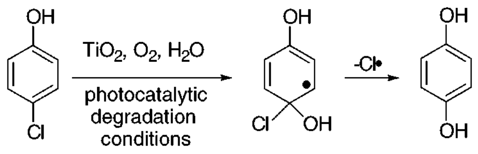
Cyanuric acid (**2**) is in equilibrium with its tautomeric form isocyanuric acid (**3**), the latter of which often predominates.[4] (The term cyanuric acid is often applied to both tautomers.) Measured pK_a values are 6.9, 11.4, and 13.5. The trianion is best described as fully deprotonated **2**.[5] Analogous and intermediate tautomeric forms have been proposed for various mono- and disubstituted cyanurates. The effect of adsorption on TiO_2 on the equilibrium is not known, but it might be expected that O-adsorption would be favored, giving more enolic form on the TiO_2 surface than in bulk solution. It is presumed here that both tautomers may be relevant to the experiments described below, but no direct attempt is made to separate out their contributions.

On the assumption that photocatalytic conditions generate surface-bound hydroxyl radicals that are the major potential oxidizing agents for cyanuric acid, three reasonable hypotheses may be given to account for its resistance. (1) Hydroxyl radical does not react with cyanuric acid fast enough in any fashion to compete with its other decomposition pathways. (2) Reaction occurs exclusively by N−H and/or O−H hydrogen abstraction. The resulting radical is sufficiently stable to avoid further oxidation until another H atom can be obtained from $HOO^\bullet$ or other sources. (3) Reaction occurs by addition but is reversible and yields only the original cyanuric acid.

The third possibility is plausible for **2** in that substitution of chloroarenes to hydroxyarenes occurs by addition−elimination. Such substitution occurs in 4-chlorophenol and related derivatives despite phenolic OH groups that are potential hydrogen atom donors (Scheme 1).[6] Two approaches were used to probe for such an addition−elimination reaction; the second is also applicable to **3**. We report here that there is no evidence for reversible $HO^\bullet$ addition to cyanuric acid.

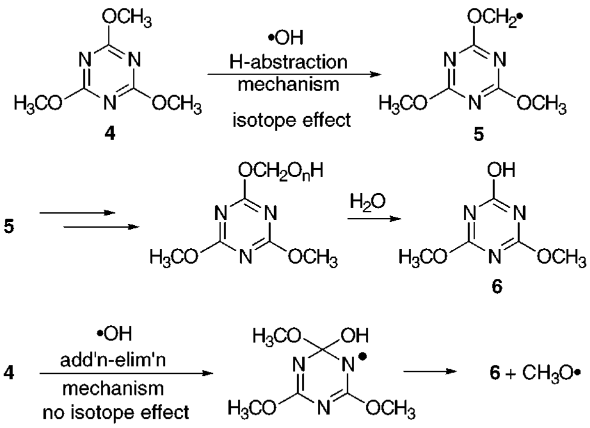
Scheme 1



Results and Discussion. Solutions of trimethyl cyanurate **4**[7] in oxygen-saturated, phosphate-buffered (pH 6.2) water containing TiO_2 were irradiated with the 350 nm bulbs of a Rayonet minireactor at ambient temperature.[8] When the reaction progress was monitored either by HPLC or by evaporation, silylation, and GC,[9] it was found that **4** sequentially loses its methyl groups to give cyanuric acid. The mono- and dimethyl cyanurates were confirmed by comparison to authentic samples.[7,10] Control experiments showed that neither dark hydrolysis nor direct photolysis was significant on the time scale of the experiment. The methylated cyanurates did not tautamerize to methylated isocyanurates.

d_9-Trimethyl cyanurate was prepared[7] to examine whether a hydrogen abstraction mechanism was involved in the initial degradation to dimethyl cyanurate (Scheme 2). If so, then a primary isotope effect in the selectivity for degradation of isotopomers would be expected. In contrast, an addition−elimination mechanism in which $HO^\bullet$ substituted for $CH_3O^\bullet$ would not be expected to show a measurable isotope effect. Competitive photocatalytic degradations of h_9-**4** and d_9-**4** (3 mM each) were carried out to low conversion, such that only the first demethylation was observed. The silylated derivatives of h_6- and d_6-dimethyl cyanurate were separable on GC. The selectivities (±10%) observed at pH 3.9, 6.2, and 7.9 were 3.3, 3.1, and 3.3, respectively. This result is in line with previous reports of kinetic isotope effects for hydrogen abstraction by $HO^\bullet$ from alkanes, which range from 2 to 5.[11] As a result, it is concluded that attack of $HO^\bullet$ on the methyl hydrogens is the kinetically important route to demethylation of the methyl cyanurates.

Scheme 2



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(5) Ito, M. *Bull. Chem. Soc. Jpn.* **1953**, *26*, 339−341.

(6) Stafford, U.; Gray, K. A.; Kamat, P. V. *Heterog. Chem. Rev.* **1996**, *3*, 77−104.

(7) Dudley, J. R.; Thurston, J. T.; Schaefer, F. C.; Holm-Hansen, D.; Hull, J. H.; Adams, P. *J. Am. Chem. Soc.* **1951**, *73*, 2986−2990. This material is free of trimethyl isocyanurate. d_9-Trimethylcyanurate was similarly prepared, using d_4-methanol.

(8) The phosphate buffer was 30 mM, the initial concentration of **4** was 4.5 mM, and TiO_2 was DeGussa P-25. Solutions were continuously bubbled with oxygen. Water was from a Millipore Milli-Q Plus water purification unit. All irradiations were carried out using the 350 nm bulbs of a Rayonet minireactor (Southern New England Ultraviolet Co.). These put out a fairly broad spectrum of light, mainly from about 320 to 390 nm. The reactor has been modified to contain both a fan and magnetic stirring. All irradiations used a 0.2 wt % suspension of TiO_2.

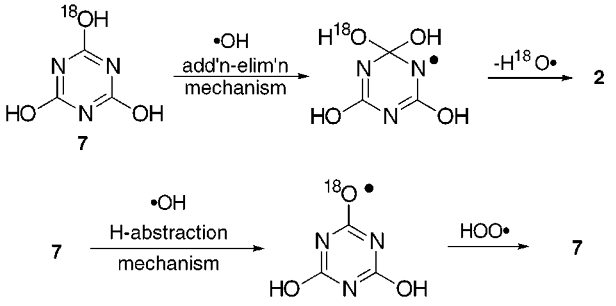
(9) Samples to be analyzed by GC-MS were first filtered to remove TiO_2. The water was evaporated under reduced pressure. To the residual solid was added 0.5 mL of pyridine, 0.1 mL of hexamethyldisilazane, and 0.05 mL of chlorotrimethylsilane. After 5 min, the solution was centrifuged and the supernatant analyzed. Silylated buffer was always a component of the analyte.

(10) (a) Copp, J. D.; Cronin, J. S.; Ginah, F. O.; Murray, A. R. *Synth. Commun.* **1996**, *26*, 3491−3494. (b) Kaminski, Z. J.; O'Leary, M. H.; Paneth, P. *J. Org. Chem.* **1991**, *56*, 5716−5718.

(11) (a) McCaulley, J. A.; Kelly, N.; Kaufman, F. *J. Phys. Chem.* **1989**, *93*, 1014−1018. (b) Tully, F. P.; Droege, A. T. *J. Phys. Chem.* **1986**, *90*, 1949−1954. (c) Tully, F. P.; Droege, A. T. *J. Phys. Chem.* **1986**, *90*, 5937−5941. (d) Tully, F. P.; Droege, A. T. *J. Phys. Chem.* **1987**, *91*, 1222−1225. (e) Tully, F. P.; Hess, W. P. *J. Phys. Chem.* **1989**, *93*, 1944−1947.

To investigate the parent system, where the tautomerization and adsorption may play a greater role, cyanuric acid enriched with ^{18}O (53.7 ± 3.5%) was prepared by acid-catalyzed hydrolysis of cyanuric chloride.[12] An addition−elimination mechanism onto **7** (a representative isotopomer) would result in incorporation of ^{16}O hydroxyl groups from the bulk water (Scheme 3).

Scheme 3



Pulse radiolysis experiments in water have shown that some H-atom migrations to hydroxyl groups occur on the microsecond time scale by an unknown mechanism.[13] This might provide for an isotope exchange mechanism for attack of hydroxyl on the carbonyl of **3**, though this is speculative. Hydrogen abstraction from either **2** or **3** is expected to lead to no exchange.

Solutions containing 4 mM ^{18}O-enriched cyanuric acid, phosphate buffer, and 0.2 wt % TiO_2 were photolyzed and analyzed as above, using the parent M, M + 2, M + 4, and M + 6 EI-MS peaks of the silylated derivatives to determine ^{18}O incorporation. Dark control experiments ensured that ordinary acid- or base-catalyzed exchange was insignificant. The steady-state quantity of adsorbed cyanuric acid is also very small relative to bulk concentration. Photolyses were carried out for up to 14 h and at pH 3.9, 6.2, and 7.8.[14] In all cases, the measured ^{18}O content of the cyanuric acid was identical with that of the starting material, within experimental error.

Conclusions. Taken in combination, the isotope effect on the degradation of trimethyl cyanurate and lack of ^{18}O exchange in cyanuric acid under photocatalytic degradative conditions strongly argue that reversible addition of $HO^{\bullet}$ to cyanuric acid is not a kinetically important process. The resistance of cyanuric acid to photocatalytic degradation is thus not due to this reaction as a rapid and reversible process. It remains possible that hydrogen abstraction is rapid and does not lead to degradation and that cyanuric acid is simply unreactive to the oxidative species produced by excitation of TiO_2.

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[12] Zobrist, F.; Schinz, H. *Helv. Chim. Acta* **1952**, *35*, 2380−2388. Into a flame-dried flask and condenser were charged 0.882 g of cyanuric chloride and 15 mL of dry THF. After 5 min of stirring, 0.4 mL of $H_2{}^{18}O$ (95% enrichment) was added, followed by 0.2 mL of concentrated sulfuric acid. The solution was heated to reflux with stirring for 1 h. After the solution was cooled, the resultant white precipitate was filtered and washed with cold THF. A 48% yield of cyanuric acid was recovered. The content of ^{18}O was determined to be 53.7 ± 3.5% by MS.

[13] von Sonntag, C.; Schuchmann, H.-P. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1229−1253.

[14] Using otherwise identical solutions, 14 h was sufficient to convert trimethyl cyanurate completely to cyanuric acid.