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Photocatalysis for the Destruction of Aqueous TNT, RDX, and HMX

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Abstract

The photo-destruction of the high explosives HMX, RDX and TNT was investigated using two systems (ozone versus titanium dioxide), two reactors (pot vs annular reactor), and two types of lamps (1000 Watt Hg-Xe vs 25 Watt LP Hg). A mass balance was performed on reactions executed under pseudo-solar conditions, and relative reaction rates and products were compared for ozone and titanium dioxide based processes. The ratios of relative product formation is also discussed. Results show that there was little difference in the reactions performed in the annular reactor when either ozone or titanium oxide were used. The chemistry of RDX and HMX are very similar, as expected. Future work involving the mechanism is also discussed.

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Introduction

We have been investigating TiO_2 photocatalysis for a number of years for applications involving waste water remediation.^{1,2} Recently, our attention has become focused on the problems of aqueous munitions waste.^{3,4}

Aqueous waste containing dissolved high explosives originates from numerous munitions processes including load and pack operations, explosives machining, cutting and hogging out operations, as well as demilitarization activities. Water containing 2,4,6-trinitrotoluene (TNT) that has been exposed to light is commonly referred to as "pinkwater". This "pinkwater" contains not only TNT (and its degradation

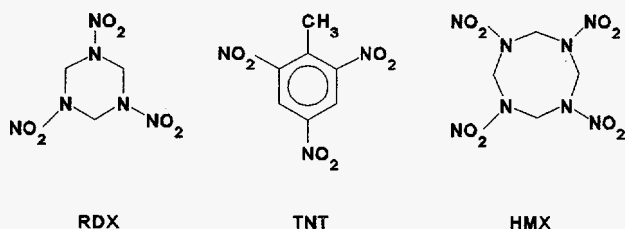


Figure 1 Structure of HE Test Materials.

byproducts), but may also contain other explosives and contaminants as well (High melt explosive, HMX, or research development explosive, RDX). The actual makeup of the waste water is dependent on the type of process the effluent is from. These dissolved materials make the water highly toxic and therefore untreatable via classic biological water purification systems. Hence treatment is required before the materials can be discharged to the environment or municipal sewage streams. Traditionally the water is treated by filtration to remove suspended solids, then passed over activated carbon to remove the organics. This, however, has some disadvantages. The practice of using the carbon only once can be expensive and contribute to air pollution since the spent material is openly burned.⁵ Carbon regeneration

is feasible in some cases, although ultimately the carbon is again disposed of through open burning. Changing environmental regulations indicate that open burning will be prohibited within a number of years. Furthermore, newly proposed environmental discharge criteria will not be met through carbon adsorption systems. Thus, new, low-cost technologies that do not generate secondary waste are being sought for the treatment of this "pinkwater" waste.

We are currently investigating two technologies to achieve this goal: titanium dioxide (TiO_2) photocatalysis and photolytic degradation through the action of ultraviolet light (UV) and ozone (O_3). Photocatalysis with TiO_2 semiconductor occurs when light causes the formation of electron/hole (e^-/h^+) pairs in particles suspended in solution. The e^-/h^+ pairs can react independently at the surface of the catalyst particle with solvent or contaminants, or

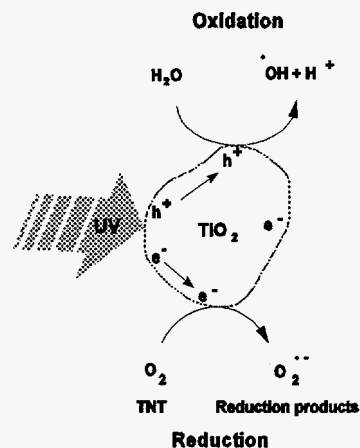


Figure 2 Oxidation and Reduction on TiO_2 .

can recombine internally to generate heat. The holes react with water to produce hydroxyl radicals (OH^\cdot) which are capable of oxidizing organic contaminants to carbon dioxide, water and dilute mineral acids. The electrons can react with either dissolved oxygen to generate further OH^\cdot or can directly reduce some species in solution such as metals or organics (ie. nitrogroups to amines).

Titanium dioxide is the most commonly used photocatalyst due to its stability, low toxicity, low cost, and effectiveness under near UV light (< 390 nm). Since near UV is present in normal sunlight, TiO₂ can be used without the requirement of electrically powered lamps. Semiconductor catalysts have an advantage in that both oxidation and reduction can be performed on the surface of the same material.

Ozone can be typically produced using 185 nm light in the presence of oxygen. Decomposition of the O₃ molecule can be initiated by either a collision with a surface or absorption of 254 nm light. These reactions produce oxygen radicals, which in the presence of water will generate hydroxyl radicals. Ozone can also react directly with organic contaminants, however due to its normally low concentration and short lifetime, this is not the primary pathway of ozone decomposition. Drawbacks of ozone treatment are the need for artificial lamps, no reduction chemistry, and the toxicity of the active molecule.

Experimental

Samples of synthetic and actual explosives-contaminated water were used in a series of treatability tests. Laboratory synthetic wastewater was prepared from deionized water and the appropriate high explosive. The concentrations of the high explosives approached their saturation limits in water: TNT (90 mg/L), RDX (40 mg/L) and HMX (4 mg/L). All of our simulated solutions are colorless to begin with and stored in amber glass away from light. Actual pinkwater was obtained from the Louisiana Army Ammunition Plant (LAAP), Thiokol Corporation, Shreveport, LA. This contained 63 mg/L of TNT, 51.5 mg/L RDX and a number of UV created photointermediates. The color in this case is deep pink or orange.

Three types of experimental setups were used in these reactions. The first involved 400

mL batch reactions in a glass pot reactor (capacity 1.5 L) illuminated with a 1000 Watt Hg-Xe ozone free arc lamp (see Figure 3). The resulting spectrum of light from this lamp is very similar to sunlight.⁶ All optics employed were constructed of quartz in order to allow low-loss passage of both visible and UV light. The pot was sealed with a quartz lid and a Viton O-ring. Anaerobic reactions were carried out by sparging the reactor with nitrogen gas through a fritted glass tube. All reactions were stirred using a magnetic stirrer and samples were withdrawn from a sealable sampling port. Titanium dioxide was used in this setup to simulate sunlight acting on a photocatalyst.

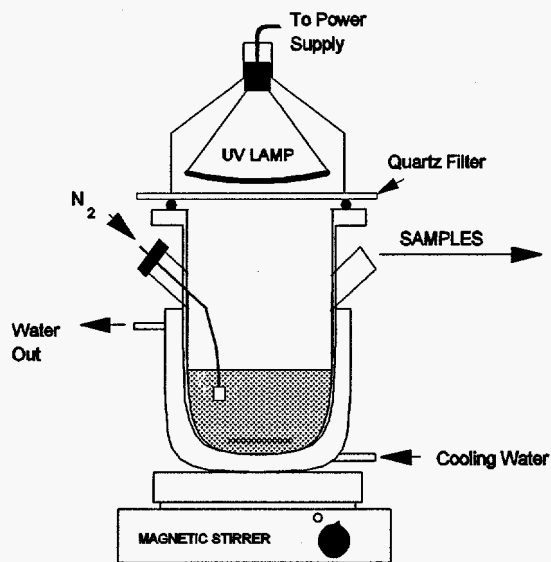


Figure 3 1000 Watt Pot Reactor.

The second apparatus was an annular core recirculation reactor with 1 L of solution passing in front of a low pressure 25 Watt quartz jacketed Hg arc lamp (see Figure 4).⁷ This lamp was constructed of fused quartz and emitted primarily at 254 nm (ca. 95-98%), with a small amount of emission at 185 nm. The space between the walls of the reactor and lamp were blanketed with argon. The interior wall of the

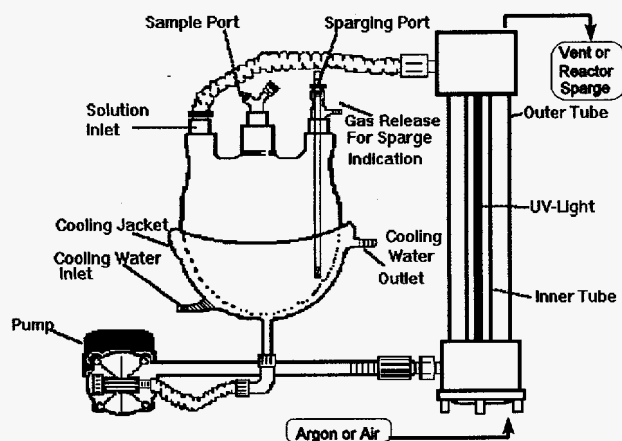


Figure 4 NREL Continuous Flow Reactor.

reactor was composed of fused quartz and the balance of the system was built of Pyrex and teflon tubing. This reactor was used with titanium dioxide.

The third reaction was also performed in the annular reactor but with a change in the setup so that a stream of air at 60 mL/min passed between the wall of the reactor and the lamp. This gas stream was then bubbled into the solution. No catalyst was used in this last reactor, since here our desire was to simulate ozone photodegradation in the absence of catalyst. Reactions were run for 5 hrs and cooled to 20° C with a water jacket. Reactions involving TiO₂ were filtered before analysis using a 10 mL disposable syringe and a 0.25 µm Teflon syringe filter.

The photocatalyst was anatase TiO₂ Tioxide Tilcom HACS (210 m²/g) powder suspended at 1 g/L in the 1000 Watt case and 0.25 g/L in the 25 Watt case. The lower loading was used in the annular reactor based on results from the National Renewable Energy Laboratory (NREL) where the reactor was designed and built.⁸

All reactions were sampled and analyzed using high performance liquid chromatography (Waters HPLC with 231 nm UV detector), ion chromatography (Dionex IC with conductivity detector), and total organic carbon analysis (Shimadzu TOC). UV/Visible spectroscopy was used to provide qualitative information on

reaction progress in the case of the "pinkwater" reactions.

Results and Discussion

Carbon and nitrogen mass balances were performed independently on all three explosives in the 1000 Watt reactor under aerobic and anaerobic conditions (see Tables 1,2,3).

In the case of TNT, the destruction of the explosive was less complete under nitrogen than in air (Table 1). This is to be expected if the initial reaction is oxidative in nature. However, a smaller amount of soluble intermediates, as well as a lower overall number of individual species (5 vs. 3) are formed under reducing conditions. This may have the added benefit of reducing the toxicity of the solution (Table 4).

At the end of the anaerobic reaction the catalyst is coated with a brown substance (60% deposited carbon, 45% nitrogen) or a 3/1 by mass ratio of carbon to nitrogen. This result when compared to a 2/1 ratio of carbon to nitrogen in the parent compound shows that this is definitely not TNT, but rather some decomposition product. Analytical techniques have yet to positively determine the nature of this coating, but early results point towards a poly-aniline analogue produced through the reduction of nitrogroups to amines or diazo linkages.^{9,10} We have also found that the surface of this coating, as observed with X-ray photoelectron spectroscopy (XPS), differs from the bulk, indicating that there is a change in the deposited species over the course of the reaction.¹¹

The catalyst from the aerobic reaction also has some detectable amounts of carbon and nitrogen (15% and 2% respectively, with a ratio of 15/1 by mass), however no color is evident on the surface. Here it would seem that decomposition of the nitrogroups would be an important step in the destruction of TNT under oxidative photocatalytic conditions.

Significant mineralization of the high explosive is realized under these conditions by looking at the amount of unaccounted for carbon (45% of total carbon).

Table 1 TNT Mass Balance Pot Reaction Results

	TNT, N ₂	TNT, Air
Products	%	%
Unaccounted C	4.48	47.57
HE C	0.34	0.00
C on TiO ₂	61.81	14.67
Inorganic C	0.45	0.00
C Intermediates	32.93	37.76
Unaccounted N	35.49	69.74
HE N	0.72	0.00
N on TiO ₂	44.60	2.03
N as NO ₃ ⁻	0.69	12.36
N as NO ₂ ⁻	2.35	0.16
N as NH ₄ ⁺	16.15	15.71

Experiments using cycling of first reductive and then oxidative conditions in TNT wastewater have shown this to be an effective way to clean off the catalyst, while producing fewer intermediate species. This does have the drawback of increasing the reaction time, but may prove useful in decreasing the overall toxicity of the treated water, if biotreatment is determined to be a useable end treatment for this waste.^{3,4,5} Further experiments will determine quantitatively the degree of toxicity/mutagenicity for the two methods.

The reactions involving RDX also had a higher conversion percentage under air than under nitrogen (Table 2). However, the overall conversion is disappointing under the best conditions (35% with N₂, 70% with air). The amount of material deposited on the catalyst is independent of the presence of air and is entirely carbon based. The number of intermediates

formed under aerobic conditions is 4 times that created under anaerobic conditions (2 vs 8), although this could be a function of the much lower conversion under nitrogen and corresponding lower side product reactions.

Reactions involving TNT and RDX in the same pot reactor have shown that the use of anaerobic conditions accelerate the degradation of RDX (vs RDX alone) while still completely decomposing TNT in 300 minutes. This is assumed to be related to the presence of having a co-reactant in solution to electrochemically balance the e⁻/h⁺ pairs in titanium dioxide. The rate of the TNT decomposition is unaffected by this addition. Only five detectable intermediates

Table 2 RDX Mass Balance Pot Reaction Results

	RDX, N ₂	RDX, Air
Products	%	%
Unaccounted C	0.00	41.76
HE C	65.26	30.66
C on TiO ₂	34.78	27.20
Inorganic C	3.33	0.00
C Intermediates	3.76	0.38
Unaccounted N	29.94	6.55
HE N	65.26	30.30
N on TiO ₂	0.00	0.00
N as NO ₃ ⁻	0.21	48.10
N as NO ₂ ⁻	0.25	0.45
N as NH ₄ ⁺	4.33	14.61

are observed in the final sample, vs seven intermediates for the two reactions independently (Note: there was no observable overlap of intermediates).

The HMX reactions indicate that aerobic conditions are the best in effecting mineralization with 40% conversion under N₂ and 100% under air (Table 3). Very few intermediates are formed that are detectable, but this is

understandable given that the HMX reactions are based on only 4 mg/L of explosive and that the intermediates may not be present in high enough concentrations to be detectable. The material deposited on the catalyst is almost exclusively carbon in both cases. This is in agreement with the RDX data. We expect that the chemistry between these two will be very similar under the same conditions.

Table 3 HMX Mass Balance Pot Reaction Results

	HMX, N ₂	HMX, Air
Products	%	%
Unaccounted C	31.42	80.75
HE C	61.92	0.00
C on TiO ₂	1.94	1.52
Inorganic C	0.38	1.64
C Intermediates	4.35	16.09
Unaccounted N	29.88	57.14
HE N	61.92	0.00
N on TiO ₂	0.28	0.00
N as NO ₃ ⁻	0.12	19.54
N as NO ₂ ⁻	0.00	0.00
N as NH ₄ ⁺	7.81	23.33

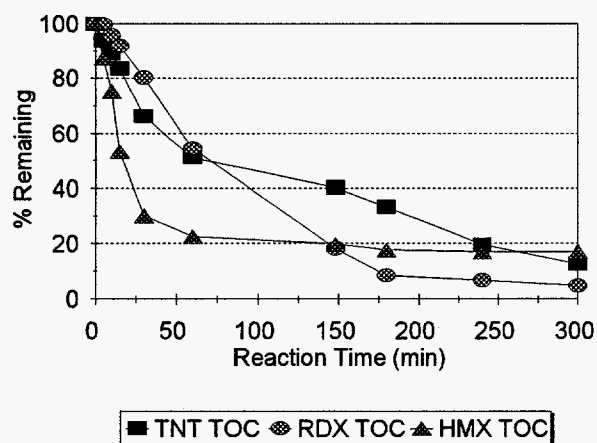


Figure 5 Normalized TOC for HE with TiO₂.

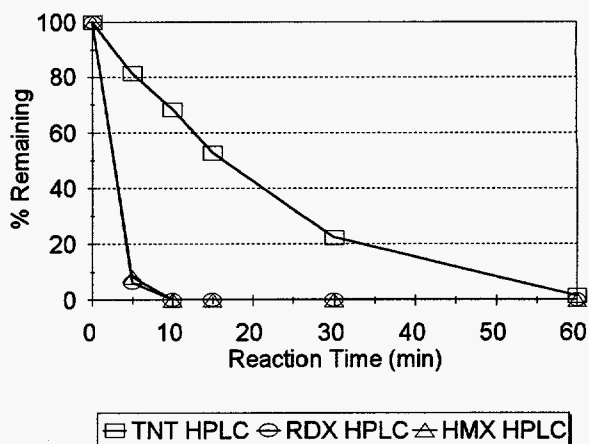


Figure 6 Normalized HPLC for HE with TiO₂.

It would be desirable, based on the above results, to employ cycling of the reaction between oxidative and reductive conditions to obtain the most effective destruction of mixed waste involving the three listed explosives. This is based on the acceleration of destruction of RDX with TNT under anaerobic conditions, while the catalyst is maintained in a more useful form when it is used under oxidative conditions. In order to determine that the results were not reactor/lamp specific and to have the freedom of using ozone as an oxidant, we also used a second reactor system. This modified 25 Watt National Renewable Energy Laboratory (NREL) annular core reactor was continuously recirculated mechanically, rather than being stirred with a magnetic stirrer. The reactions in this system were performed for comparison purposes of the reactivity of titanium dioxide vs. ozone. The reaction results were all very similar when comparing ozone generation in-situ against titanium dioxide photocatalysis with this system (Figures 5-8). In the reactions involving TNT, there is a slight difference in the amount of carbon in solution at the end of the reaction (85% drop in TiO₂ vs 78% drop in ozone, Figures 6 and 8). This is attributed to adsorption of the carbon onto the surface of the

catalyst. The ozone reaction is slightly faster, but four intermediates are present at the end of the reaction, while only two are present when titanium dioxide was used (Table 4).

Table 4 Conversion and Intermediates of HE Reactions in Different Apparatus

Conditions	Lamp/Reactor	% HE Conv.	# of Inter.
TNT/N ₂ /TiO ₂	Hg-Xe/Pot	99.3	5
TNT/Air/TiO ₂	Hg-Xe/Pot	100	3
TNT/Air/TiO ₂	Hg/Annular	100	2
TNT/Air/O ₃	Hg/Annular	100	4
RDX/N ₂ /TiO ₂	Hg-Xe/Pot	34.8	2
RDX/Air/TiO ₂	Hg-Xe/Pot	69.7	8
RDX/Air/TiO ₂	Hg/Annular	100	1
RDX/Air/O ₃	Hg/Annular	100	1
HMX/N ₂ /TiO ₂	Hg-Xe/Pot	38.1	3
HMX/Air/TiO ₂	Hg-Xe/Pot	100	2
HMX/Air/TiO ₂	Hg/Annular	100	1
HMX/Air/O ₃	Hg/Annular	100	1

In both cases, the clear solution turned immediately red following ignition of the lamp and then slowly changed to lighter orange and yellow colors over the course of the reaction. The RDX and HMX reaction rates,

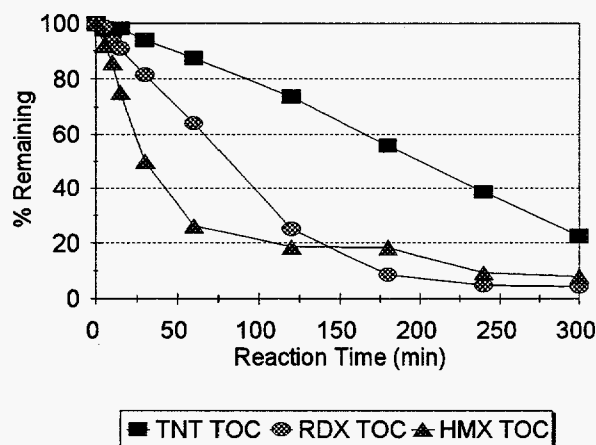


Figure 7 Normalized TOC for HE with Ozone.

intermediates, and final total carbon were insensitive to the type of oxidation method used. This demonstrates, as shown in the Xe-Hg lamp pot reactions, that RDX destruction is relatively insensitive to reductive chemistry. Based on the similarity of the molecule HMX with RDX, the chemistries should be analogous and we find that indeed this is the case. One of the problems of working with HMX is that most of our analysis techniques become limited after the first few minutes of the reaction. Since RDX and HMX seem to behave similarly, in future work we plan to use RDX and extend the work to HMX though extrapolation. This is valid because RDX is a much larger problem than is HMX based on its greater solubility in water and use in explosive components.

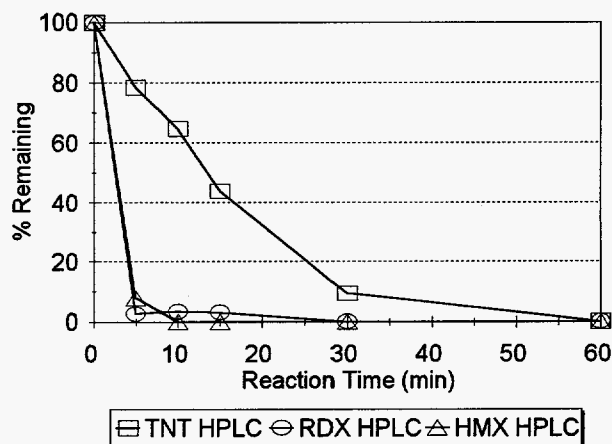


Figure 8 Normalized HPLC for HE with Ozone.

Another reaction was performed to compare the lab results of pure samples to those using actual wastewater. These reactions involving LAAP pinkwater were all performed in the annular reactor so that the color changes could be more closely monitored visually. The TNT and RDX were gone after 2 hrs of reaction as shown by HPLC analysis. There were 8 identifiable byproducts at the start of the reaction and 6 following 13 hrs of reaction under

ozone. The pH remained basic throughout the reaction at ca. 8.2.

A similar reaction was attempted with TiO_2 but with important differences. In the first reaction, a large quantity of inorganic carbon was measured (carbonate from hard water). We believe that this can have a detrimental impact on the mineralization of the HEs. We also were taxing the limits of our TOC analyzer with the amount of carbon in solution. Therefore, we diluted the solution volume by half with deionized water and acidified the solution (with 1% HNO_3 until a pH of 6.0 was reached) under mixing to counteract these problems.

A direct comparison can not now be made between the two reactions but we plan on repeating the experiment at zero dilution in titanium dioxide and acidification with half dilution using ozone treatment. As expected, the number of intermediates with the catalyst and acid treatment was much lower than that with ozone (start of 7, and ending with 2). The destruction of RDX was complete after 15 minutes and the TNT was gone after 1 hr. The acidification removed ca. 30% of the carbon present initially.

The use of acid to remove inorganic carbon in order to increase the rate of destruction of HEs is viable, however the dilution would have to be investigated with toxicological methods before being promoted as a way to increase the rate of reaction. The production of 100 gallons of highly toxic waste from 20 gallons of slightly toxic waste is a situation that must be avoided.

Conclusions

The chemistry of HMX and RDX are very comparable in photoreaction products and rates. Based on the similarity of the molecules this is not surprising but is useful since the development of a technique of removal of RDX can be easily applied to one containing HMX as well. The chemistry of TNT is much more complicated than either of these molecules and is

primarily related to the greater complexity of the molecule and the presence of aromaticity.

Photoremediation can be a viable option in the destruction of high explosive contaminated groundwater. The issues center on cost and speed of destruction in either a lamp based or solar based operation.

Solar photocatalysis can be of use in remote areas with high average insolation. The use of lamp driven phototreatment when employing either ozone or titanium dioxide was similar with a few exceptions. The ozone reactions seem to create more intermediates that may require longer treatment to lower the toxicity to a dischargeable level but at the same time lack the mechanical difficulty of dispersing and separating a catalyst in a batch process.

Future Work

Future work will involve the measurement of toxicity/mutagenicity of the products of these different oxidation techniques. The use of bioremediation has not been thoroughly examined, but we feel this may offer faster cleanup times if it follows initial destruction of the parent compounds using the techniques described herein.

We also are looking at the mechanism of the oxidation reactions based on product formation. Our labs are in the development stages for the detection of intermediates using a high performance liquid chromatography instrument. We are currently obtaining the experimental UV/Visible spectra of intermediates and plan to obtain representative theoretical spectra of likely candidates using semi-empirical quantum mechanical methods. Early results with aqueous TNT are promising and work with known compounds will be used to determine if this will be a viable method, or whether another semi-empirical method will give better matches to experimentally obtained data. This will be a case where the use of a theoretical quantum chemistry method can be validated at

the same time that it is applied to a known chemical problem.

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