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# The Aqueous Photolysis of TFM and Related Trifluoromethylphenols. An Alternate Source of Trifluoroacetic Acid in the Environment

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The lampricide 3-trifluoromethyl-4-nitrophenol (TFM) is added annually to the Great Lakes (approximately 50 000 kg/y), with treatment concentrations varying from 1 to 14 mg/L at source. TFM was shown to undergo photohydrolytic degradation, at 365 nm and under actinic radiation, to produce trifluoroacetic acid (TFA). A mechanistic study for the production of TFA from TFM was conducted, and the structural parameters associated with the production of TFA from trifluoromethylated phenols were investigated. It was found that the yield of TFA is clearly dependent on the nature of the trifluoromethylated phenol. The nature of the substituents, the substitution pattern, and the pH strongly effected the photolytic half-life of the parent compound and the yield of TFA. The half-life of TFM at 365 nm was found to be 22 h (pH 9) and yielded 5.1% TFA, and 91.7 h at pH 7, yielding 17.8% TFA. Converting the nitro substituent of TFM to an amino group caused a decrease in the half-life to 2.3 min and yielded 11% TFA. The mechanism for the production of TFA from TFM was deduced from the pH dependence and the effect of altering substituents on the trifluoromethylphenol. Ultimately, the formation of trifluoromethylquinone led to the quantitative production of TFA.

## Introduction

Fluorinated chemicals are rarely observed in nature (*1*). However, the incorporation of fluorine in anthropogenic products is expanding, with fluorine present in many different types of organic materials, including agrochemicals, polymers, and pharmaceuticals (*2*). The ultimate fate of the fluorine contained within these molecules is of considerable interest. From 1958 the chemical 3-trifluoromethyl-4-nitrophenol (TFM) has been used to control the sea lamprey (*Petromyzon marinus*) in four of the Great Lakes (Superior, Michigan, Huron, and Ontario). By 1988, more than 1 million kg of TFM had been applied to these lakes, and usage since has been approximately 50 000 kg/year (*3*). TFM has also been introduced in order to control tadpole infestations in warm water ornamental fish ponds (*4*).

A possible loss mechanism for lampricides is through adsorption onto bottom sediments (*5*). However, studies have shown microbial degradation is not significant within this medium (*6, 7*). The enzymatic biodegradation of TFM was investigated under aerobic conditions in natural water sediments (*6*). No degradation of TFM was observed over a 2.5 month period. It was assumed that the trifluoromethyl substituent of the aromatic ring remained intact as no fluoride production was observed. Under anaerobic conditions, partial reduction of the TFM nitro group to an amine has been observed (*8*). TFM is almost completely ionized in most natural waters, so this is unlikely to be an important loss mechanism due to the lack of adsorption on such sediments.

It has been reported (*9, 10*) that the trifluoromethyl group contained within a phenolic ring is susceptible to hydrolytic degradation when in the ortho or para positions relative to a hydroxyl group. Conversely, when in the meta position, the trifluoromethyl group is inert to alkaline or acidic hydrolysis even at elevated temperatures. However, a photoinduced excited state may allow the cleavage of the carbon−fluorine bonds (*11*).

Trifluoromethyl aromatics, which do not contain an electron withdrawing substituent, have been shown to undergo bacterial metabolism to produce trifluoroacetic acid (TFA) (*12*). This is an unlikely mechanism for the degradation of TFM or the subsequent production of TFA due to the electron withdrawing nitro group.

The major source of TFA in the environment is believed to be the degradation of the HCFC's 123, 124, and 134a, which occurs primarily through reaction with a hydroxy radical followed by subsequent hydrolysis (*13*). From this source alone, the projected concentrations have been calculated to be $>100\ \mu g\ L^{-1}$ by the year 2010 in seasonal wetlands. However, the concentrations which have been measured in the environment cannot be accounted for based on current atmospheric sources (*14*). These levels have been shown to inhibit plant growth (*15*). TFA has also been shown to be a biliary excretion metabolite of haloethane anesthetics in infants younger than 5 months, but at greater than 5 months it has been shown to be completely retained in a enterohepatic circulation (*16*).

To date there is little evidence for the degradation of TFA. It was reported that trifluoroacetic acid was observed to degrade in both oxic and anoxic sediments (*17*), although this observation has yet to be reproduced (*18*).

The aqueous photolytic fate of TFM has been investigated by Carey et al. (*19, 20*). In the present investigation particular attention has been paid to certain key intermediates proposed by Carey et al., specifically the formation of the trifluoromethylhydroquinone, from which it was postulated that there were two competing loss mechanisms: the production of the trifluoromethylquinone or a reaction which produces the corresponding acid fluoride (2,5-dihydroxybenzoyl fluoride). Furthermore, Carey et al. hypothesized that this acid fluoride in turn leads to the formation of gentisic acid (2,5-dihydroxybenzoic acid) and hydrogen fluoride. Investigations within our laboratory have indicated that the fate of the trifluoromethyl substituent was as fluoride or trifluoroacetic acid (TFA), which had not been previously observed.

Due to the absence of naturally occurring fluorinated materials and the large spectral windows associated with fluorine, $^{19}$F NMR provides a very powerful method for the direct analysis of fluorinated materials, reaction intermediates, and degradation products (*21, 22*). Therefore this technique was adopted in the characterization of TFM degradation.

It was our hypothesis that the production of trifluoromethylquinone is of key importance to the production of TFA. Our objectives were to investigate the role of phenolic substitution patterns in the rate of degradation of the parent compound, the mechanism of TFA formation, and the influence of aromatic substituents on the yield of TFA.

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## Materials and Methods

**Chemicals and Reagents.** The chemicals 3-trifluoromethyl-4-nitrophenol (99%), 2-nitro-4-(trifluoromethyl)phenol (99%), 2-(trifluoromethyl)phenol (97%), 3-(trifluoromethyl)phenol (99%), and 4-(trifluoromethyl)phenol (99%) were purchased from the Aldrich (Mississauga, Canada). Trifluoroacetic acid (98%) was purchased from Caledon (Georgetown, Canada). All other solvents and reagents were analytical purity grade or better. All chemicals were used without further purification.

**Synthesis.** Trifluoromethylquinone was synthesized through the oxidation of 2-(trifluoromethyl)phenol using Fremy's radical in a procedure similar to that used by Zimmer et al. (*23*) for the oxidation of phenols. Synthesis of 4-hydroxy-3-trifluoromethylphenol was carried out directly using the method of Feiring et al. (*24*) in which the 3-(trifluoromethyl)-phenol was oxidized using potassium persulfate. The 4-amino-3-trifluoromethylphenol was synthesized via the reduction of the 4-nitro-3-trifluoromethylphenol using zinc metal in hydrochloric acid according to a standard procedure (*25*). All products were verified by IR, NMR, and MS.

**Photolysis Experiments.** Photolysis experiments were carried out at 365 nm (Rayonette bulbs), which also show minor lines at 334 and 313 nm. Photolysis was also confirmed under actinic radiation in a solar simulator (Suntest CPS Solar Simulator). All analytes were dissolved in buffered deionized water (Borax buffer (pH 9) and potassium dihydrogen phosphate (pH 7)) to a concentration typically in the range of 5−10 × $10^{-5}$ M and irradiated in sealed, 100 mL, quartz vessels. Samples were obtained at appropriate time intervals and analyzed using the pertinent analysis equipment.

**NMR Analysis.** $^{19}$F, $^{1}$H, and $^{13}$C NMR spectra were obtained for synthesized and degradation products when appropriate, on a Gemini 500 MHz spectrometer operating at 470.596 MHz with a broad band probe tuned to fluorine, on a Varian VXR-S 400 MHz spectrometer operating at 376.289 MHz with a Nalorac 4N probe tunable to H, F, H, and Si. Chemical shifts were reported relative to $CFCl_3$ (0.00 ppm). The internal standard 4′-(trifluoromethoxy)acetanalide (TFMAA) was used for quantification.

**Chromatographic Analysis.** HPLC analysis was carried out using either a Waters 600 pump equipped with a 486 UV/visible tunable detector, a Waters 616 pump equipped with a 996 photodiode array detector, or on a Perkin-Elmer instrument equipped with a series 200-IC pump and a diode array detector 235 C. Separation was achieved using an Alltech Econosphere C18 5U column. Mobile phases were generally AcCN/buffered water mixtures. Fluoride, nitrite, nitrate, and TFA were analyzed using a Perkin-Elmer Series 200 IC pump equipped with a Dionex Ionpac AS14 column, and an Alltech 1000 HP conductivity suppresser and conductivity detector; the mobile phase used was generally Borax buffered water. Fluoride was analyzed using an Orion ISE. High-resolution mass spectra were obtained using a Micromass 70-250S (double focusing) spectrometer in negative EI mode. Data were obtained at 10 000 (10% Valley) resolution. For GC-MS analysis aqueous samples were acidified and extracted with ethyl acetate. Derivatization, if required, was carried out using diazomethane. Samples were run on a Perkin-Elmer GC Auto System XL equipped with a Q-Mass 910 quadrupole mass spectrometer, run in EI mode, with a 30 m, 0.25 mm Simplicity 5 column. The carrier gas was helium at a flow rate of 0.5 mL/min.

**UV/vis Spectroscopy.** Molar extinction coefficients and UV/vis spectra were obtained for the analytes using an HP-diode array model 8452 spectrometer.

**Analysis of Trifluoroacetic Acid.** A new method was developed for the analysis of TFA to overcome problems such as unreliable liquid−liquid extractions and derivatization required for currently accepted procedures (*26*−*29*). Aqueous samples (100−1500 mL) of TFA ($10^{-6}$−$10^{-5}$ M) were passed through a strong anionic exchange column (SAX) at a flow rate of 5 mL $min^{-1}$. Elution was carried out using 1 mL of 2 M NaOH, or alternatively with acetone, methanol, or DMSO containing the organic base 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU). The eluents were then spiked with 300 mL of deuterated acetonitrile containing the internal standard (TFMAA), and TFA was measured directly using $^{19}$F NMR (117 ± 13% for a 500 ppb solution, and 101 ± 6% for a 120 ppb solution, $n = 3$).

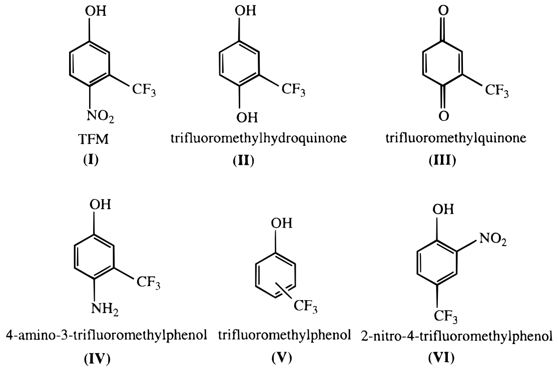

**FIGURE 1. Chemical structures used in the mechanistic fate of TFM.**

**TABLE 1. Molar Extinction Coefficients and Observed Half-Lives of Trifluoromethyl Aromatics**

| compd no. | molar extinction coefficient, $\epsilon_o$, L $mol^{-1}$ $cm^{-1}$, 365 nm, pH 9[a] | half-life, h (365 nm) |
|---|---|---|
| I | 6675 (394 nm) | 22.4 |
| II | 0.0123 (310 nm) | 0.5 |
| IV | 0.00495 (308 nm) | 0.04 |
| V | 0.0261 (298 nm) | 0.4 |
| VI | 565 (400 nm) | ∞ |

[a] Values in parentheses correspond to maximum absorption wavelength in actinic spectrum.

## Results and Discussion

Trifluoromethylated compounds used to investigate the mechanistic pathway and structural requirements for the production TFA from TFM are shown in Figure 1. The trifluoromethylhydroquinone (**II**) was selected since it is observed in the environment as a degradation product of TFM (**I**). Carey et al. (*19*) postulated that the trifluoromethylquinone (**III**) is formed from **II**, thus the degradation of this species was also investigated. The aminotrifluoromethylphenol (**IV**) and the trifluoromethylphenols (**V**) were used to investigate the influence of the nitro substituent in TFM, on the production of TFA. Finally, an isomeric form of TFM (**VI**) was studied in order to determine the substitution pattern required for the production of TFA. Molar extinction coefficients for the compounds at 365 nm and their half-lives are presented in Table 1. The rate of degradation of the parent compound is not solely dependent upon the amount of light absorbed at 365 nm. It is also dependent upon the quantum yield of the molecule. For example compound **IV** has a lower absorption at 365 nm but degrades more rapidly than **I**, indicating that it has a higher quantum yield.

**Photolysis of TFM (I).** Figure 2(a) shows the photolysis of TFM (pH 9, 365 nm). The concentration of products fluoride and TFA are shown as a function of time; nitrite was also observed as a product. Trifluoromethylhydroquinone (**II**) was observed as a short-lived intermediate based upon HPLC/UV spectral comparison with an authentic sample. These results are in concordance with work carried out by

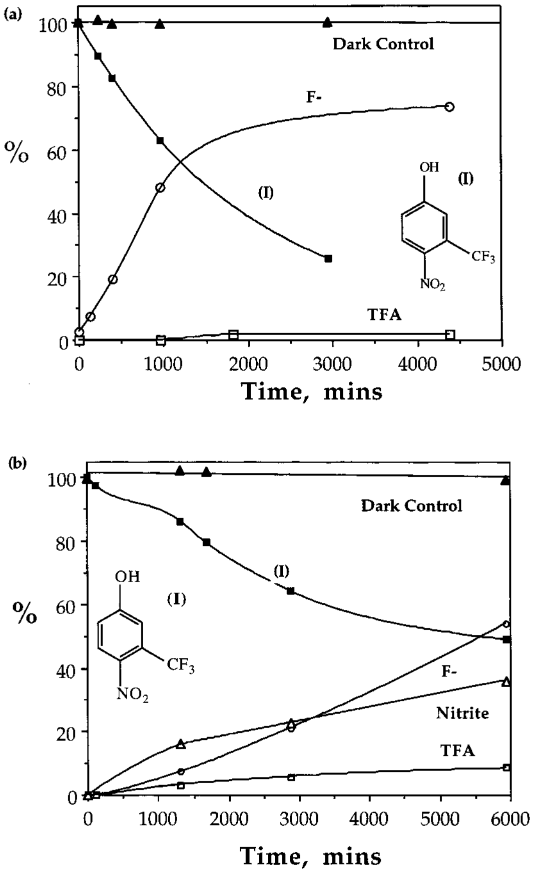

**FIGURE 2. (a) The photolysis of TFM (I) at pH 9.2. Loss of TFM and the production of fluoride and TFA. No observable loss of TFM in the absence of light. (b) Photolysis of TFM at pH 7. Loss of TFM and the production of nitrite, TFA, and fluoride. No observable loss of TFM in the absence of light.**

Carey et al. (*19, 20*), in which aqueous field samples that had contained TFM were analyzed using mass spectroscopy. Evidence was presented for an initial photoinduced nucleophilic hydroxyl displacement of the nitro group, which led to the tentative assignment of trifluoromethylhydroquinone and a trifluoromethylquinone, the latter considered to have been produced through thermal or photochemical oxidation of the hydroquinone precursor. This postulated mechanism is further supported by the observation that heteroaromatics containing a trifluoromethyl substituent undergo enhanced nucleophilic substitution (*36*).

In the present studies the observed pseudo-first-order half-life for TFM was 22.4 h. Nitrite and fluoride were produced at the time of initial irradiation, suggesting they were produced directly from TFM. Observable TFA production occurred only after irradiation for 10 h, suggesting that TFA was produced from an intermediate, rather than directly from TFM. The yield of TFA was approximately 3.9% when 76% of the parent molecule had undergone photolysis. Figure 3 shows the time-dependent $^{19}$F NMR obtained over the course of irradiation at 365 nm. The production of TFA relative to the internal standard TFMAA is shown. Photolysis of TFM using actinic radiation yielded the same photodegradation products as those observed at 365 nm. The half-life of the TFM under these conditions was observed to be 10.7 h.

TFM photolysis was also conducted at pH 7, and identical products were observed (Figure 2(b)). TFM was more persistent at pH 7, with a half-life of 91.7 h. The yield of TFA at this lower pH was 8.9%, when 50% of the parent molecule had undergone photolysis. At a lower pH there is a shift in the equilibrium toward the protonated form of TFM, overall producing a greater yield of TFA. It is hypothesized that degradation of TFM, through an excited state of the deprotonated anion, occurs more readily at higher pH and does not lead to the production of TFA. At lower pH, this type of degradation is reduced due to an increase in concentration of the protonated form. Given that the p$K_a$ of TFM is 6.1 (*7*), structure **Ib** (Figure 4) would be in a 100-fold excess at pH 9 relative to pH 7. This hypothesis is further supported by the observation that TFM absorption shifts from 297 to 394 nm as pH is changed from 7 to 9. This leads to photonucleophilic substitution occurring to a greater extent at pH 7 and producing the trifluoromethylhydroquinone intermediate (**II**), followed by subsequent degradation to TFA. It follows that, since the production of TFA is proposed to occur from the intermediate **II**, the TFA yield would increase at lower pH. This hypothesis also supported by the observation that there is an enhanced production of nitrite at pH 7 relative to pH 9. All dark control experiments showed no loss of TFM.

The photolysis of TFM was also carried out in the presence of equimolar 4-*tert*-butylphenol. The rate of reaction was observed to be identical to that in the absence of the phenol. It is known that radicals react with aromatic rings in a manner that superficially resembles that of a nucleophilic substitution (*30*), thus kinetically resembling an Sn2 type reaction. If the degradation of TFM had occurred through a radical reaction, the rate would be expected to change in the presence of the phenol due to its radical capturing ability (*31*).

The structural isomer of TFM, 2-nitro-4-trifluoromethylphenol (Figure 1, structure **VI**), was photolyzed under the same conditions. No observable degradation of the isomer was observed over time periods up to four times greater than the half-life of TFM, presumably due to the stabilizing formation of an *o*-semiquinone.

**Photolysis of Trifluoromethylhydroquinone (II).** Figure 5 shows the photolysis of trifluoromethylhydroquinone (pH 9, 365 nm). The rate of production of gentisic acid, fluoride, and trifluoroacetic acid are indicated. The half-life of the parent compound was observed to be 31 min. When complete degradation of the parent molecule had occurred, the yield of TFA was 6% and the yield of fluoride was 82%; the remaining fluoride can be accounted for in residual starting material. No degradation of the parent compound was observed in the dark. $^{19}$F NMR of the photolyzate indicated the presence of a short-lived trifluoromethylquinone ($\delta = -59$ ppm).

**Photolysis/Hydrolysis of the Trifluoromethylquinone (III).** Trifluoromethylquinone appeared to degrade rapidly (<5 min) and quantitatively at pH 9 (observed from HPLC) to TFA. To investigate the mechanism for the production of the TFA from **(III)**, the aqueous samples were extracted and derivatized with diazomethane. From mass spectral evidence the degradation structures shown in (Figure 6) were tentatively assigned. It would appear that initial hydroxylation of the quinone occurs to produce (**1**) or the 3,6-dihydroxyquinone isomer. This is followed by cleavage of the quinone ring at the 3,4-bond (**2**). The ring is then further cleaved at the 1,2-bond to yield dihydroxymaleic acid (**3**) and trifluoromethylglyoxal (**4**). Compound **4** is then presumed to decarboxylate to produce TFA, in a manner similar to that published for pyruvic acid (*32*).

**Proposed Mechanism for the Production of TFA from TFM.** The proposed mechanism for the production of TFA from TFM is outlined in Figure 7. The initial steps of this mechanism are similar to that suggested by Carey et al. (*19*). The results suggest the overall photolytic degradation of TFM occurs through the hydrolysis of the nitro substituent via a photonucleophilic aromatic substitution to produce a nitrite anion; fluoride can also be lost from the excited state of the TFM (Figure 5). The nucleophilic substitution results in the production of a trifluoromethylhydroquinone, which would then appear to undergo two competing reactions. One

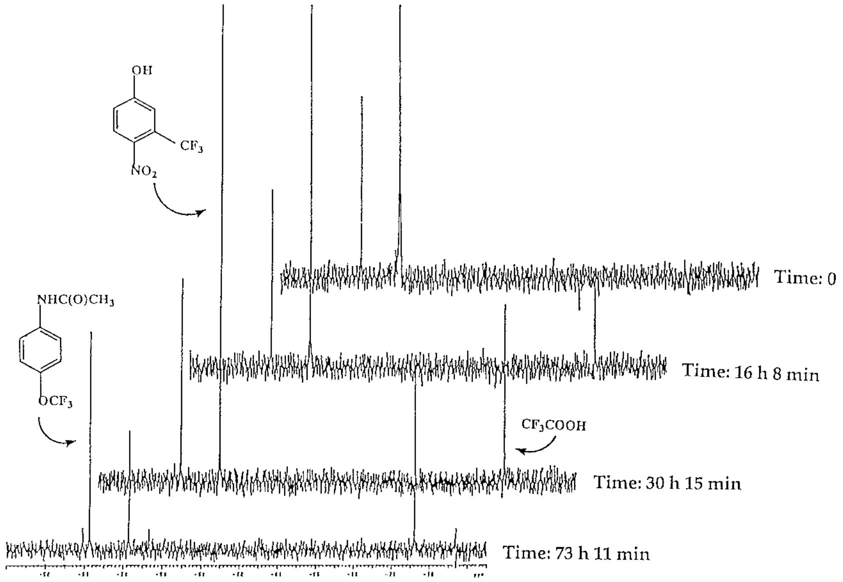

FIGURE 3. Time dependent $^{19}F$ NMR for the production of TFA (−71.2 ppm) from TFM (−56.3 ppm). The concentration is relative to the internal standard TFMAA (−54.3 ppm).

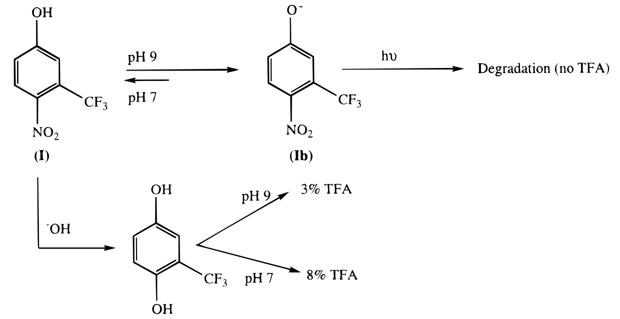

FIGURE 4. Mechanism for the enhanced production of TFA from TFM by altering the pH. Shift in equilibrium at higher pH from the production of a hydroquinone (II) toward semiquinone (Ib) which does not lead to the production of TFA.

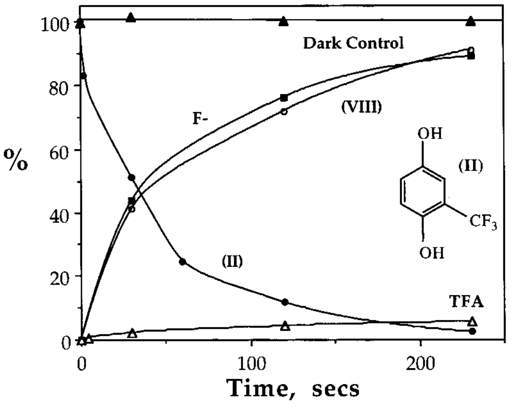

FIGURE 5. The photolysis of trifluoromethylhydroquinone (II) and the production of gentisic acid (VIII), fluoride, and TFA.

possibility is the production of an acid fluoride through the expulsion of 2 mol of fluoride. This is then followed by loss of hydrofluoric acid leading to the formation of the genistic acid. The second possibility is a photochemical oxidation of the hydroquinone to a trifluoromethylquinone. The trifluoromethylquinone then undergoes what would appear to be a hydrolytic degradation to produce trifluoroacetic acid. The mechanism of this degradation appears to be complicated due to the numerous products observed in the GC-MS. A mechanistic postulation is presented on the basis of certain key intermediates that were observed. The rate of degradation of TFM is strongly dependent upon the degree to which the compound is ionized. This is evident from the observed 4-fold increase in the half-lives of TFM from pH 9 to pH 7. As previously indicated, the production of TFA by the photonucleophilic hydroxyl substitution of the nitro group is further supported by the increased production of TFA at lower pH values due to the shift in equilibrium toward the production of the hydroquinone (Figure 4).

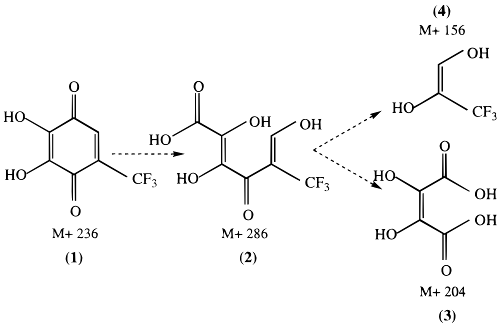

FIGURE 6. Degradation products observed from the hydrolysis trifluoromethylquinone. Parent ion mass is indicated in parentheses for the methylated product.

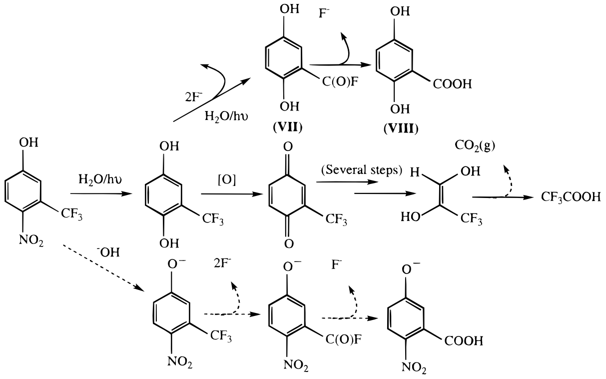

FIGURE 7. Proposed mechanism for the production of TFA from TFM (I). The alternate pathways for the degradation of TFM are also indicated.

**Possible Structural Requirements for the Production of TFA.** Trifluoroacetic acid is produced from 3-trifluoromethyl-

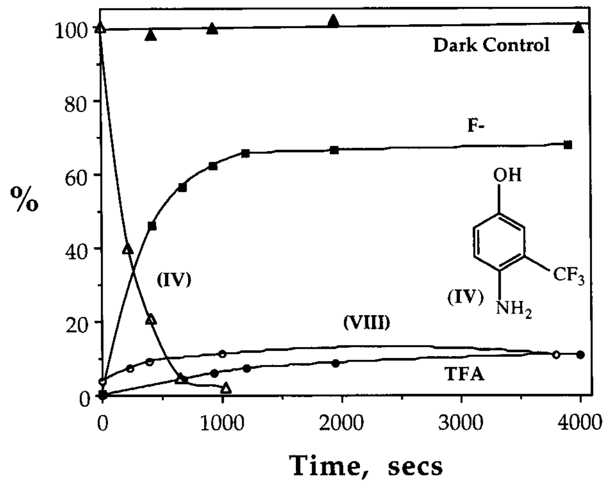

**FIGURE 8. Photolysis of 4-amino-3-trifluoromethylphenol (IV). Loss of the parent compound, production of TFA, fluoride, and gentisic acid (VII).**

4-nitrophenol (**I**). An investigation toward discovering the structural requirements within the phenol ring was carried out. An aromatic nitro group is a very strong electron withdrawing substituent that results in a p$K_a$ of 4.91 for a phenol (*33*). The role of this substituent on the production of TFA was investigated; the amount of TFA produced in the absence of this group and when it is replaced with a strong electron donating group.

**Photolysis of 4-Amino-3-trifluoromethylphenol (IV).** The strong nitro electron withdrawing substituent of the TFM was replaced with a strong electron donating amino group. Figure 8 shows the loss of the parent compound **(IV)** through photolysis and the production of fluoride, 2,5-dihydroxybenzoic acid **(VIII)**, and TFA. Approximately 11% of the expected amount of TFA was produced from the parent compound, when the parent molecule had undergone 100% photolysis. The half-life of the parent compound was 2.3 min. Mechanistically the production of TFA from the 4-amino-3-trifluoromethylphenol appears to be complicated as seen from the numerous peaks that arise in the HPLC chromatogram. Further investigations toward elucidating the mechanism will be carried out.

**Photolysis of Trifluoromethylphenols (V).** The photolysis of the three isomers *o*-, *m*-, *and p*-trifluoromethylphenol at 365 nm was executed. The relative rates of degradation, based upon the amount of fluoride that is produced, are shown in Figure 9.

As can be seen from the figure the meta isomer is stable in the dark. Both the ortho and the para isomers are not. A strong electrical interaction of electron donating substituents

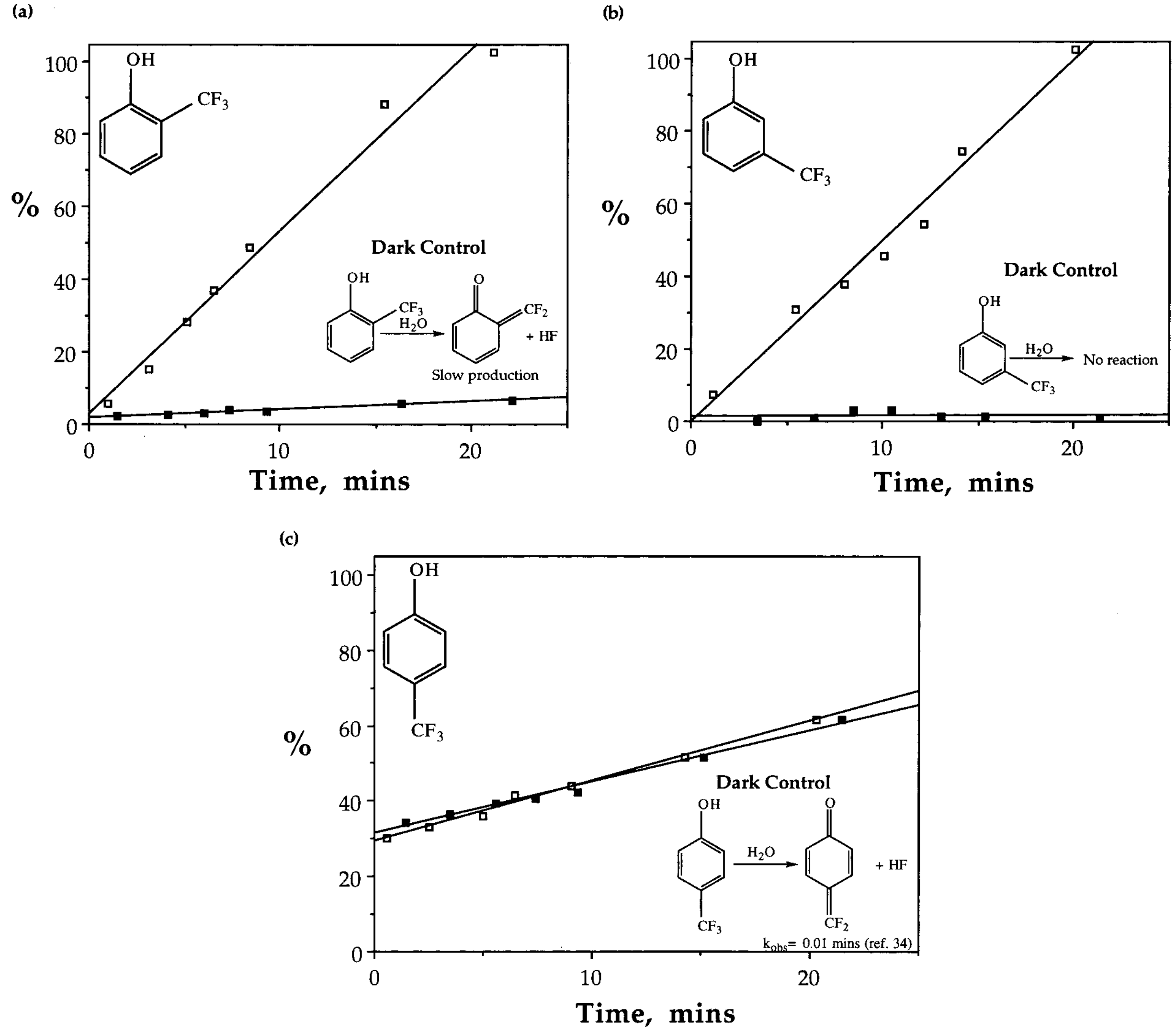

**FIGURE 9. (a–c). The photolysis of 2-, 3-, and 4-(trifluoromethyl)phenols (V) and the production of fluoride. The reaction mechanism for the hydrolysis of each of the compounds in the dark is given, along with the relative rates.**

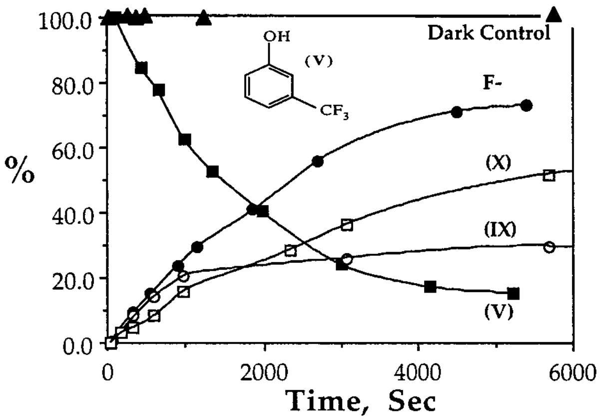

**FIGURE 10. Photolysis of 3-(trifluoromethyl)phenol and the production of fluoride, 3-hydroxybenzoyl fluoride (IX), 3-hydroxybenzoic acid (X), and fluoride.**

was initially proposed by Roberts et al. (*34*). The para isomer produces 33% fluoride immediately, after which little change is seen over time. These results are consistent with the loss of hydrogen fluoride through hydrolysis of the ortho and the para isomers to produce the semiquinones, 2-(difluoromethylene)-2,5-cyclohexadien-1-one and 4-(difluoromethylene)-2,5-cyclohexadien-1-one, respectively. The rate of hydrolysis of the para isomer is greater than the ortho isomer due to the linear conjugation produced as opposed to cross conjugation. The para isomer is then presumed to undergo polymerization as observed by Kozachuk et al. (*10*). The aqueous solution became opaque over time due to the formation of an insoluble polymer. A semiquinone is not observed for the meta isomer and, hence, is stable in the dark (Figure 9).

Further investigation into the mechanism for the degradation of 3-(trifluoromethyl)phenol is shown in Figure 10 (pH 9, 365 nm). Photolysis is observed to initiate the loss of 2 mol of fluoride to produce the acid fluoride, 3-hydroxybenzoyl fluoride **(IX)**. Assignment of this compound was based upon an $^{19}$F NMR signal at +44 ppm, which is highly indicative of an acid fluoride. The acid fluoride **(IX)** then undergoes further hydrolysis to produce 3-hydroxybenzoic acid **(X)**. The half-life of the phenol was 22 min.

Concentration of 500 mL of the photolyzed sample was carried out by passing it through a SAX column. $^{19}$F NMR and ion chromatography showed no observable TFA.

In conclusion, the photolysis of TFM under light intensities and wavelengths which would be equivalent to those found on a typical summers day in the Great Lakes region leads to the production of TFA. Based on TFM concentrations of approximately 4.6 ppm in Lake Ontario tributaries, and that the photodegradation is the primary loss mode (*19*), the average concentration of TFA produced from this source alone would be 500 ppb. Typical environmental water samples have shown a concentration in the order of 10−100 ppt (*35*), indicating that this might be an important source of TFA in the aqueous environment surrounding Lake Ontario.

It would appear that the type and sequence of substitution on a trifluoromethylphenol are of importance to the fate of the fluorine; ultimately yielding fluoride or TFA. The pH also strongly affects the production of TFA, for compounds that contain the correct structural parameters. In addition, the degree of electron donating/withdrawing of the substituent ortho to the trifluoromethyl group defines the yield of TFA. The results also indicate that the rate of decay and the nature of the products produced for trifluoromethyl phenols is dependent upon the substituents of the aromatic ring and their relative substitution.

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