PHOTODEGRADATION OF 4-CHLORO-3-NITROBENZOTRIFLUORIDE IN AQUEOUS MEDIA

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ABSTRACT

4-Chloro-3-nitrobenzotrifluoride dissolved in water was irradiated ($\lambda \geq$ 300 nm) in the presence of suspended TiO_2 (2.0 ± 0.1 g/l). The illumination energy was 28.1 ± 0.7 W/m^2. The disappearance of the chemical as a function of the irradiation time was monitored with a gas chromatographic technique. The disappearance rate was initially higher, as the concentration diminished by 50 % within the first 45-60 min of irradiation, but it decreased with increasing length of irradiation. No chemical loss was observed in pure water, or when TiO_2 was replaced with aqueous 2 % cetylpyridinium chloride alone or mixed with 2 % cetylpyridinium chloroiodide. Keywords: aqueous photodegradation, benzotrifluorides, photodegradation modelling, environmental reclamation.

INTRODUCTION

4-Chloro-3-nitrobenzotrifluoride (NCTT; Figure 1) and some other benzotrifluorides were detected in a groundwater system used for private and agricultural supplies in northern Italy.[1] Contamination had been provoked by improper disposal of a chemical waste coming from a local factory producing intermediates for pharmaceutical products and agrochemicals.

As we are currently investigating sunlight-based photochemical techniques for detoxification of environmentally-important halogenated aromatics, we thought it of interest to use NCTT in a pilot study to set up specific investigation methods and criteria.

EXPERIMENTAL

Chemicals Analytical-grade n-hexane was obtained from Carlo Erba (Milan, Italy) and used after distillation in a glass apparatus. Carlo Erba also provided analytical-grade anhydrous sodium chloride, sodium hydroxide, sodium sulfate, and potassium permanganate. High-purity titanium dioxide (anatase) powder, for use as a semiconductive catalytic support[3,4] for NCTT, was from Aldrich Chimica (Milan, Italy). Cetylpyridinium chloride was furnished by Chemical Market Research Service (Eschen, FRG); cetylpyridinium chloroiodide was made in the laboratory.[5]

High-purity water was obtained by first refluxing alkalinized distilled water in the presence of permanganate for several hours in a glass apparatus; refluxed water was then distilled off.

NCTT (from Rimar Engineering, Trissino (Vicenza), Italy) was >95 % pure, as confirmed by NMR (main impurity: 4-chloro-3-nitrotoluene). NCTT spectral features (Figure 1) and solubility in water (174 ± 12 mg/l at 20 °C; N = 12) were investigated in the laboratory.[6]

Glassware Pyrex glassware was used throughout. Items were carefully cleansed with detergent and water, rinsed with distilled water, and kept at 250 °C overnight prior to use.
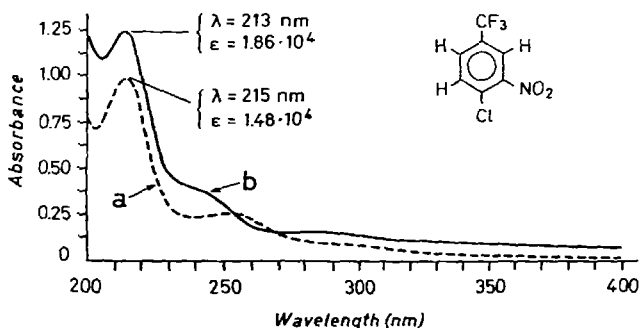
Figure 1 UV spectra of NCTT (15.0 mg/l) in high-purity water (a) and n-hexane (b) were record-
ed with a Hewlett-Packard (Palo Alto, California, USA) Model 8452A spectrophotometer and a
standard 1-cm cell. Absorbance of both solvents was <10^{-3} over the full spectral range (190-
820 nm). NCTT exhibits absorption bands only below 400 nm. NCTT is a stable chemical which has
a moderate acute toxicity in laboratory animals[1] and a mutagenic potential (UDS test).[2]

The vials for irradiation were dark, flat-bottomed cylinders (i.d., 3.0 cm; volume,
20 ml) with an open, flanged top to accomodate a transparent quartz disk (o.d., 3.5 cm; thick-
ness, 2.0 ± 0.1 mm), later sealed with high-vacuum sealant for preventing volatilization
losses.[6]

Apparatus A Hewlett-Packard (Palo Alto, California, USA) Model 5710 gas chromatograph, equip-
ped with an electron capture detector (GC/ECD) and an HP-5 10-m-long 0.53-mm-i.d. fused silica
column, was used for analytical assessment. GC conditions were: (a) injection block, 200 °C;
(b) oven, 130 °C; (c) detector, 300 °C; (d) carrier and makeup (for both, argon-10 % methane
mixture) flow rates, 2.0 and 25 ml/min, respectively.

A "solarbox"-type photoreactor was purchased from CO.FO.ME.GRA. (Milan, Italy). The
apparatus mounted a 1.5-kW low-pressure xenon lamp and a filter system to cut off light
<300 nm. Illumination energy was monitored with a gauge (CO.FO.ME.GRA.) responding to 295-
400-nm light. When the lamp was on, the irradiation chamber was ventilated to disperse heat;
samples, irradiated singly, were kept at 15 °C by partially immerging the vials in water
cooled by a Haake (Karlsruhe, FRG) Model F3 heat exchanger.

NCTT assessment A portion (0.50 ± 0.01 ml) of the aqueous matrix containing NCTT was pipetted
out and dissolved in 50-ml n-hexane. The organic mixture was combined with a 5-g sodium
chloride-sodium sulfate (1:4) mixture and allowed to dry overnight. GC/ECD determination was
carried out with the external standard technique.

RESULTS AND DISCUSSION

NCTT volatilization loss from TiO_2-added aqueous media was checked by irradiating samples
in vials top-blinded with aluminum foil. Irradiation conditions and lengths (up to 240 min) in
the different checks were the same as those later adopted in photodegradation trials. Since
the NCTT concentration in unexposed samples (60.1 ± 3.2 mg/l; N = 10) was undistinguishable
from the check samples (59.7 ± 3.4 mg/l; N = 10), the vials proved to be satisfactorily
vapor-tight.

				IRRADIATION TIME (min)					
	0.0	15	30	45	60	90	120	180	240
Mean (mg/1)	60.1	47.6	38.1	29.6	27.7	25.4	22.1	17.7	12.5
SD (mg/1)	3.2	2.1	2.4	2.3	2.3	0.6	1.1	1.2	1.1
VC (%)	5.25	4.34	6.17	7.77	8.16	2.30	4.86	6.66	8.77
N	10	10	7	3	7	3	3	3	5*
Normalized mean	1.000	0.792	0.634	0.493	0.461	0.423	0.368	0.295	0.208
SD	0.074	0.054	0.051	0.046	0.045	0.024	0.026	0.025	0.020
VC (%)	7.42	6.81	8.10	9.38	9.70	5.73	7.15	8.48	10.6

(*) From original seven-datum set, two outliers (Chauvenet's rule).

During photodegradation trials, which took several days, the stability of illumination energy was spot checked at different irradiation times (from 0 to 240 min) by placing the gauge head at a fixed position next to the sample where illumination was optimized. When all readings were compared, it was found that the energy had remained constant (28.1 ± 0.7 W/m^2; N = 20) throughout the study.

A summary of photodegradation results is presented in Table 1. Experimental conditions were as described above; independent trials were replicated three to ten times. In the table, the upper four data lines show direct concentration measurements (mg/1), whereas the lower three lines represent the above data normalized against the mean concentration value of unexposed (t = 0) samples; standard deviation of normalized values was estimated via the error propagation method.[7]

Experimental points are shown in Figure 2, where regression curves are reported. 50 % of the initial NCTT disappears within the first 45-60 min; however, the disappearance rate becomes less with increasing irradiation time. Although no specific study on the order of reaction had been carried out, four mathematical models were used to fit the data: (a) an exponential function, I, and the linear combinations of (b) I and a steady-state function, II, (c) I and a linear function, III, and (d) two Is, IV. Aside from the latter, which did not
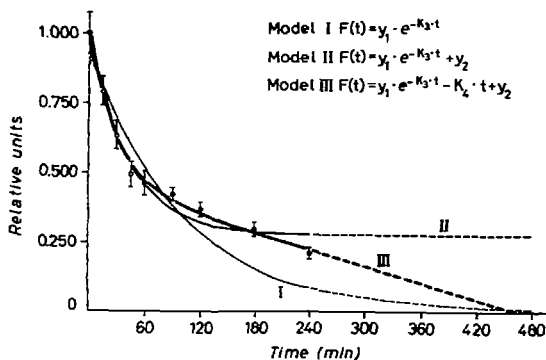

Model I $F(t) = y_1 \cdot e^{-K_3 \cdot t}$

Model II $F(t) = y_1 \cdot e^{-K_3 \cdot t} + y_2$

Model III $F(t) = y_1 \cdot e^{-K_3 \cdot t} - K_2 \cdot t + y_2$

Figure 2 Photodegradation induced by simulated sunlight of aqueous NCTT in the presence of suspended TiO_2. Normalized experimental data and regression curves of Models I, II, and III (see Table 2) are shown. With reference to Model III (mean estimates), it might be predicted that NCTT photodegrades by 90, 99, or 99.9 % after 360-, 450-, or 460-min irradiation times, respectively. Fitting was performed with the derivative-free nonlinear regression BMDP-AR Program (BMDP Statistical Software, Inc., 1987, Los Angeles, California, USA).

TABLE 2. Regression analysis data of TiO_2-catalyzed photodegradation kinetics of 4-chloro-3-nitrobenzotrifluoride exposed to simulated sunlight in aqueous medium (see Figure 2).

MODEL I	REGRESSION CONVERGENCE CRITERION:		SATISFIED	
	RESIDUAL SUM OF SQUARES:		2.17E-03	
	CHI-SQUARE OF REGRESSION:		3.69E-01 (DOF= 6)	
	MEAN SQUARE ERROR:		3.10E-04	
	PARAMETER	STANDARD DEVIATION	COEFFICIENT OF VARIATION	
y1	0.932419	0.052596	0.056408	
k3	0.009980	0.001619	0.162265	

MODEL II	REGRESSION CONVERGENCE CRITERION:		SATISFIED	
	RESIDUAL SUM OF SQUARES:		3.17E-04	
	CHI-SQUARE OF REGRESSION :		3.67E-02 (DOF= 5)	
	MEAN SQUARE ERROR:		5.28E-05	
	PARAMETER	STANDARD DEVIATION	COEFFICIENT OF VARIATION	
y1	0.721305	0.036920	0.051185	
y2	0.276397	0.031402	0.113613	
k3	0.023138	0.002830	0.122330	

MODEL III	REGRESSION CONVERGENCE CRITERION:		SATISFIED	
	RESIDUAL SUM OF SQUARES:		1.37E-04	
	CHI-SQUARE OF REGRESSION:		7.68E-03 (DOF= 4)	
	MEAN SQUARE ERROR:		2.74E-05	
	PARAMETER	STANDARD DEVIATION	COEFFICIENT OF VARIATION	
y1	0.542964	0.059433	0.109459	
y2	0.463933	0.059677	0.128633	
k3	0.035038	0.006729	0.192062	
k4	0.001001	0.000339	0.338789	

provide a converging regression, the other models reached convergence yielding significant fittings (Chi-square test; Table 2). From Figure 2, it is evident that only III fits the experimental points closely, while the other models do not, especially for long irradiation times.

NCTT photochemical behavior was studied also in different media. As could be predicted from Figure 1, no NCTT loss was observed in pure water. Similarly, losses were not observed when TiO_2 was replaced with 2 % cetylpyridinium chloride or with a mixture of 2 % cetylpyridinium chloride and 2 % cetylpyridinium chloroiodide,[5] both producing micellar matrices. As to the latter, this finding was expected.[5] Additional data will be reported soon.[6]

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