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Short Communication

TNT photolysis quantum yield

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2,4,6-Trinitrotoluene (α-TNT) in water is photolyzed in sunlight giving "pink water" [1]. An approximate value of 0.001 for the quantum yield in cyclohexane has been reported with no measurable effect of oxygen [2]. No value in aqueous solution has been reported, and this is a value of some importance for environmental considerations.

1. *Experimental*

Aqueous solutions of α-TNT (100 μM) were irradiated by a low pressure mercury lamp whose main output is at 253.7 nm. The irradiance was adjusted between runs by changing the cell–lamp distance or by using a narrow band-pass filter. A cylindrical 1 cm quartz absorption cell (volume = π cm^3; window area = π cm^2) was used for both photolysis and actinometry runs. Photolyses were carried out in distilled water saturated with air at about 700 Torr. TNT decomposition was monitored at intervals by UV analysis as shown in Fig. 1. Thin layer chromatographic analyses of reaction products were qualitatively the same as those observed by Kaplan *et al.* [1].

2. *Quantum yield calculations*

The disappearance of spectral absorption at 233 nm was followed to monitor the photolysis at 253.7 nm. The formula for quantum yield is

$$q = \frac{(\mathrm{d}A_{233}/\mathrm{d}t)_{t=0} V_c N f_p}{E_{253.7} \epsilon_{233} l_c A_c \{1 - 10 \exp(-A_{253.7})\}} \quad (1)$$

where $(\mathrm{d}A_{233}/\mathrm{d}t)_{t=0}$ is the rate of disappearance of TNT as measured at 233 nm and as extrapolated to zero time determined graphically as shown in Fig. 2. ϵ_{233} converts A_{233} to molar values and is 19 500 M^{-1} cm^{-1}. The path length l_c of the cell is 1 cm. The volume V_c of the cell is $\pi \times 10^{-3}$ l. The area A_c of the cell window is π cm^3. N is Avogadro's number. f_p is the correction factor to account for absorbance by the products at 233 nm, since

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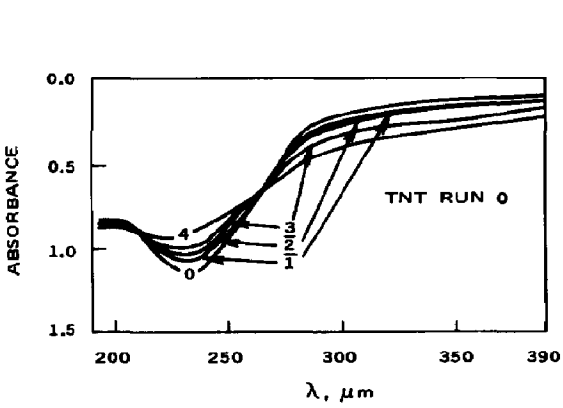

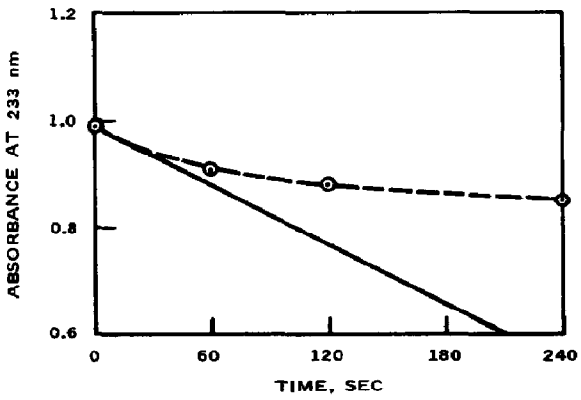

Fig. 1. Spectrograms taken at intervals during the photolysis of TNT. Spectra were taken after 0, 1, 2, 4 and 10 min irradiation. Run 3 of Table 2.

Fig. 2. Decrease of A_{233} during photolysis. The rate at zero time is 1.784×10^{-3} s^{-1}. Run 3 of Table 2.

long runs to complete photolysis of TNT showed some remaining absorbance at 233 nm. Further photolysis made A_{233} larger. Table 1 shows values of A_{233} after long irradiation times. We used the lowest value of A_∞/A_0 to generate $f_p = 1.33$. This factor introduces the largest uncertainty in our measurement of q. $1 - 10 \exp(-A_{253.7})$ is the fraction of light absorbed in 1 cm. In practice we measured A_{233} and used an average value of the ratio $A_{253.7}/A_{233} = 0.72 \pm 0.02$. $E_{253.7}$ is the irradiance at the cell window and was determined using potassium ferrioxalate actinometry [3, 4].

TABLE 1

Absorbance at 233 nm of a 100 μM TNT solution before irradiation and after 4.5 h full irradiation

Run	1	2	3
A_0	1.19	1.19	1.19
A_∞	0.46	0.42	0.39
A_∞/A_0	0.39	0.35	0.33

Absorbances in a 0.5 cm cell.

3. *Results and discussion*

Table 2 gives the pertinent data for calculating the quantum yields. The irradiances are averages of two or three runs in each position. The precision of the data is good. There is some indication of an increase in q at lower irradiances. The quantum yield is given for 253.7 nm but it is likely that it is the same across the 233 nm absorption band of α-TNT in aqueous solution. The solar spectrum [5] goes to zero energy at about 295 nm where TNT absorbs very weakly. The rapid formation of pink water from TNT solutions

TABLE 2

Quantum yield data

	Run			
	1	2	3[a]	4
[TNT] (μM)	39.2	50.0	52.6	43.8
$A_{253.7}$	0.547	0.706	0.734	0.612
Fraction absorbed at 253.7 nm	0.72	0.80	0.82	0.755
Distance (cm)	4.6	4.6	2.5	9.2
E (photon s^{-1} cm^{-2} $\times 10^{-15}$)	11.3	11.3	2.52	3.4
$(dA_{233}/dt)_0$ ($s^{-1} \times 10^3$)	1.65	1.78	0.442	0.593
q (molecule $photon^{-1}$)	0.0083	0.0081	0.0090	0.0095

[a]In this run a narrow band-pass filter (Corning) was employed.

is due to the fairly large quantum yield as measured here, as well as to quite large irradiance values in direct sunlight. Our values in distilled water are several times as large as those reported in cyclohexane [2]. It seems likely that other conditions such as pH will also affect the quantum yield as well as the products.

Acknowledgments

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