

Photodissociation of 1,2,3-triazine

Gad Fischer* and A.U. Nwankwoala

Department of Chemistry, The Faculties, Australian National University, Canberra 0200, N.S.W., Australia

Received 2 August 1994; accepted 18 October 1994

Abstract

The photolysis of 1,2,3-triazine in hexane and methanol solvents and in the vapour phase has been studied at a number of wavelengths in the main absorption band. For solutions of the triazine in hexane, two forms have been spectroscopically identified. They correspond to hydrogen-bonded, owing to the presence of trace quantities of water, and non-bonded species. In methanol solutions, such spectroscopic resolution was not achieved. Photodissociation quantum yields were found to decrease with increasing wavelength. For photolysis of hexane solutions conducted at the shorter wavelengths, the quantum yields were larger for the hydrogen-bonded species. The quantum yields were independent of solvent, the presence of air and the incident light intensity. The identification of acetylene and the observation of an unidentified photoproduct(s) suggest that the concerted photofragmentation mechanism cannot be the one and only photodecomposition pathway in hexane and methanol solutions. However, for the vapour the identification of acetylene and HCN suggest that it may be the mechanism.

Keywords: Photodissociation; 1,2,3-Triazine; Photolysis; Hexane solutions; Methanol solutions

1. Introduction

A considerable body of work has been devoted to the study of the electronic spectroscopy of the azabenzenes [1]. These molecules have played a fundamental role in our understanding of radiationless processes [2] and vibronic coupling [3], and they are the parent molecules for many compounds of biological significance [4].

Symmetrical triazine (1,3,5-triazine) and symmetrical tetrazine (1,2,4,5-tetrazine, the only monocyclic tetrazine to have been synthesized) have been found to undergo efficient photodissociation [5–10]. In both the gas phase and the low temperature solid state, *s*-tetrazine yields principally N_2 and 2HCN. A quantum yield of greater than unity was obtained following pumping of the lowest excited singlet state [8]. Using the method of photofragment-translational spectroscopy, Lee and coworkers [11] found that *s*-tetrazine reverts to a highly vibrationally excited state of the ground electronic state following excitation of the lowest $^1B_{3u}$ and $^1B_{2u}$ states and then converts into $N_2 + 2HCN$ via a concerted triple dissociation. Both in hexane solution at room temperature and in the gas phase, the photoreaction has been shown to occur by a single-photon process. However, in molecular crystals at low temperatures the

process involves the absorption of two photons. These results indicate that different mechanisms may be operative in the solid state at low temperature and in hexane solutions at ambient temperatures. The photochemistry of *s*-triazine shows many similarities [6].

No photolysis studies have been reported on 1,2,3-triazine and 1,2,4-triazine, but a number of investigations have been carried out on the substituted triazines. The conclusions of these studies largely follow the pattern set by the azines referred to above.

Photolysis of trimethyl-1,2,3-triazine in benzene and methylene chloride solutions gave as products, in almost quantitative yield, the fragments acetonitrile and 2-butyne [12]. Clearly the remaining fragment, N_2 , was also produced but it could not be detected owing to the experimental procedure used. Likewise, attempts to prepare trimethylazete by matrix photolysis of trimethyl-1,2,4-triazine failed and yielded only 2-butyne, acetonitrile and nitrogen [13]. A similar fragmentation was noted for the photodissociation of triphenyl-1,2,3-triazine [14]. However, in this photoreaction, some evidence in the form of the products 2,3-diphenylquinoline and hexaphenyl-1,5-diazocine was obtained for the production of a triphenylazete intermediate. Further evidence in support of the formation of an azete intermediate in some photodissociations was obtained from low temperature photolyses at 254 nm of trifluoro-1,2,3-triazine and the perfluoro-4,6-di-isopropyl deriv-

* Corresponding author.

ative [15]. On the contrary, photolysis of the perfluorotriisopropyl derivative led to fragmentation only, giving the alkyne and nitrile derivatives, and no azete intermediate [15].

Heating of 1,2,3-triazine to 130 °C caused decomposition to a tar and trace amounts of pyridine, pyridazine and pyrazole [16]. Flash vacuum thermolysis (FVT) of 1,2,3-triazines, corresponding to conditions of about 500–700 °C in a flow system caused fragmentation to an acetylene and a nitrile. Similar results had been previously obtained for the FVT of the trimethyl derivative [17].

For these azines it is clear that photodissociation can occur along a number of different pathways. In general, it may be concluded that photolysis in the gas phase results essentially in fragmentation, whereas in solution or in low temperature solids other reaction schemes also need to be entertained.

In this paper we report the photolysis of 1,2,3-triazine in solutions of methanol and hexane. Results are also reported for the gas-phase photolysis carried out on very low but constant vapour pressures of the triazine.

2. Experimental details

1,2,3-Triazine was prepared by the oxidation of 1-aminopyrazole with sodium periodate (NaIO_4) following the procedure reported by Okatani et al. [18]. The starting material, 1-aminopyrazole, was synthesized by *N*-amination of pyrazole with hydroxylamine-*O*-sulphonic acid in alkaline medium [19]. The 1,2,3-triazine crude product was purified by repeated vacuum sublimation ($\sim 10^{-3}$ mm Hg) at room temperature to give a white powder. 1,2,3-Triazine was characterized by UV-visible spectroscopy, Fourier transform IR (FTIR) spectroscopy, mass spectroscopy (MS), ^1H nuclear magnetic resonance spectroscopy and by elemental analysis. The spectroscopic data match available information on the compound [19,20]. Purity of the compound after several vacuum trap-to-trap distillations at room temperature was estimated to be greater than 98%. The compound was stable for several months when stored under vacuum in the freezer (about -20 °C).

UV spectroscopic grade hexane and methanol (SpectroSol) were used without further purification. The high solvent absorptions below 220 nm and the consequent insensitivity of the instrument made measurements in this region unreliable and were responsible for the convergence of the spectra below 220 nm in some of the figures in this paper.

Irradiations of solutions of 1,2,3-triazine in methanol and hexane in cylindrical cells of 10 cm path length were carried out at 20 nm intervals within the wavelength range 390–230 nm using the continuous output of a short-arc lamp (Varian high pressure xenon lamp

(150X8S) with Varian power supply P-150S-7) coupled to a 0.25 m Bausch and Lomb monochromator (narrow bandwidth). The bandpass was maintained at 6 nm at all irradiation wavelengths throughout the photolyses. All photolyses were conducted at room temperature (295 ± 2 K), and on both degassed and undegassed solutions. Light intensities were determined by potassium ferrioxalate actinometry [21,22].

The initial progress of the photochemical decomposition of 1,2,3-triazine was quantitatively monitored by measuring the absorbance changes at the absorption band maximum of the photolysed solution. Although possible photodecomposition products of 1,2,3-triazine were not expected to have substantial absorption in this region, photolysis was also monitored at some longer wavelengths to check for possible interference by product absorption. Irradiations were interrupted after set times and UV-visible absorption spectra of the solutions were recorded on a Shimadzu 160 and Cary 219 (Varian) UV-visible spectrophotometers. Concentrations of 1,2,3-triazine (about $\times 10^{-4}$ M) were chosen in such a way that UV spectra of the irradiated solutions could be recorded directly, without the need for further dilution.

After irradiation, some of the samples were subjected to further product analyses. The photolysis mixtures were frozen in vacuo at liquid-nitrogen temperature and degassed. The samples were then warmed to -80 °C and gases evolved at this temperature were isolated in a 10 cm gas cell and analysed by FTIR spectrometry.

The vapour-phase photolysis was carried out at a constant pressure of the vapour in equilibrium with the solid. This approach was adopted owing to the triazine's extremely low vapour pressure. Samples of triazine (about 10 mg) were placed in the side arm of a quartz cylindrical gas cell 10 cm long. The vapour was irradiated at 288 nm using the same xenon short-arc light source that was used for the solution studies. It was assumed that the vapour pressure of 1,2,3-triazine remained saturated throughout the photolysis through replenishment from the solid sample in the side arm. The photoproducts were analysed by FTIR spectroscopy.

The quantum yield measurements for 1,2,3-triazine in hexane and methanol solutions were made over the initial photolysis periods, corresponding to less than 10% loss of the 1,2,3-triazine. Experimental errors arose from sample impurity, and in the mass determination of the 1–2 mg quantities used for the preparation of the solutions (less than 5%). Additional errors were introduced through possible incomplete solution of the 1,2,3-triazine, especially in hexane, and from the absorbance measurements. The absorbance changes for the initial photolysis periods, as measured on different spectrophotometers (Cary and Shimadzu) varied by as much as $\pm 10\%$. Variations in the incident light intensities were found to be less than 5%. It is estimated

that the resulting errors in the absorption coefficients are of the order of $\pm 10\%$, and in the quantum yields of $\pm 25\%$. The values reported are the mean of some two to four measurements at each wavelength, apart from the photolysis carried out at 290 nm in methanol where some 20 measurements are included.

3. Results

3.1. Solution spectra

Solution spectra of 1,2,3-triazine in methanol and ethanol have been reported [19,20]. In both hexane and methanol solvents the absorption spectra are characterized by a broad strong band with a maximum at about 290 nm and a weaker band with a maximum at about 230 nm. The shapes of the two absorption bands and the results of the vapour-phase spectral studies suggest that transitions to more than just two states are involved. Semiempirical calculations carried out by Wormell et al. [23] support this conclusion. In hexane, both bands display some fine structure, most noticeable for the shorter-wavelength band and indicative of vibrational excitation.

The spectra are affected by the presence of water. This is most marked for the hexane solvent where, for different solutions, shifts in the more prominent longer-wavelength band of up to 17 nm, i.e. from 298 to 281 nm, were recorded, and the band shapes are different (Fig. 1). The shifts, if any, in the band at 230 nm were small and were beyond detection in our experiments. In the methanol solvent, only slight changes in the shapes of the long-wavelength band may be attributed to the presence of trace amounts of water and the occurrence of two forms of triazine: one hydrogen bonded to methanol and the other hydrogen bonded to water. However, it is to be expected that in methanol solutions most of the triazine is hydrogen bonded to

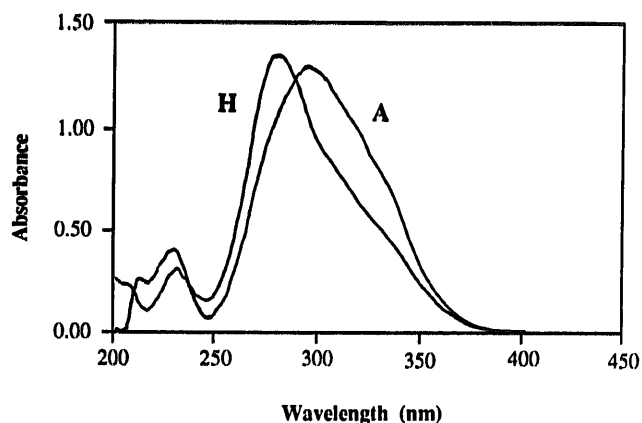


Fig. 1. Absorption spectra of the two forms (H bonded and non-bonded) of 1,2,3-triazine in hexane: A, 2.3×10^{-4} M; H, 2.1×10^{-4} M.

the methanol. At present, no firm conclusions could be reached as to the exact proportions of each form of the triazine present in the hexane solution. Rather, a measure of the relative amounts could be obtained from the shifts in the band maximum.

Apart from the shifts generated by the presence of trace quantities of water in the hexane solutions of the triazine, the intentional saturation of the hexane solutions with water led to marked reductions in the absorption intensity, apparently resulting from hydrolysis of the triazine [24,25].

3.2. Photolysis in methanol

On irradiation of 1,2,3-triazine in methanol at wavelengths corresponding to the band maximum at 290 nm ($\epsilon = 790 \pm 80 \text{ l mol}^{-1} \text{ cm}^{-1}$), the UV-visible spectrum exhibited changes as shown in Fig. 2. The spectra in Fig. 2 are for a degassed solution but are unchanged for a solution with air present. The pattern of spectral changes depicted in the figure is representative of all the photolyses conducted from 390 to 270 nm, and also at 230 nm. For the runs at 230 and 390 nm the extent of triazine conversion within the photolysis period of 380 min was too small, 17% and 9% respectively, to warrant inclusion in this report. Control samples of degassed and undegassed solutions left in the dark for times comparable with the total photolysis times and held at the same temperature experienced no measurable triazine loss.

The spectra recorded during photolysis show that with irradiation there is a decrease in both band maxima, but that the 290 nm maximum decreases much more rapidly than does the 230 nm maximum. Furthermore, for the long-wavelength photolyses there appear to be two isosbestic points evident between the two band maxima (Fig. 3). The two points approach one another as the wavelength of irradiation is reduced, such that,

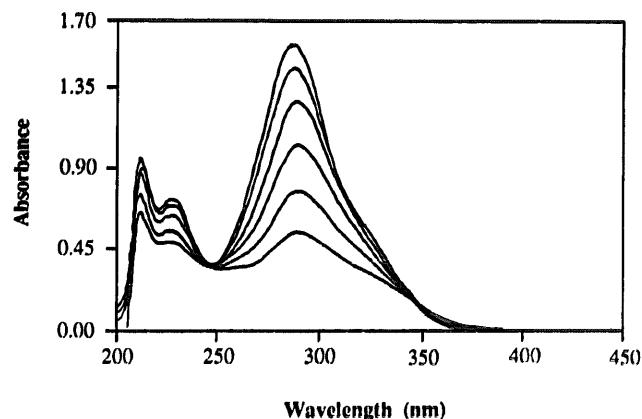


Fig. 2. Changes in the absorption spectra with irradiation at 290 nm for a degassed solution of 1,2,3-triazine in methanol. The curves, from the top down, refer to photolysis times of 0 min, 10 min, 40 min, 100 min, 190 min and 310 min.

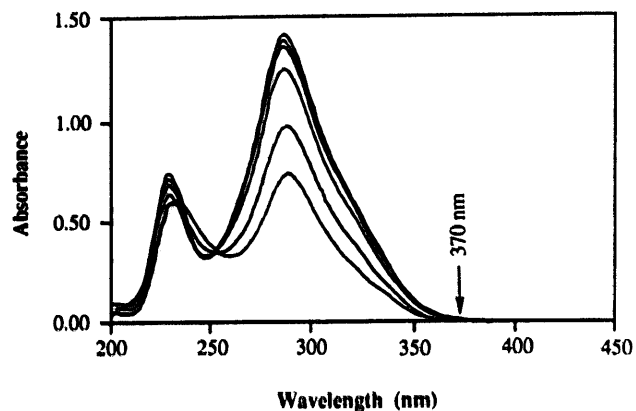


Fig. 3. Changes in the absorption spectra with irradiation at 350 nm for a solution of 1,2,3-triazine in methanol. The curves, from the top down, refer to photolysis times of 0 min, 5 min, 20 min, 65 min, 200 min and 380 min.

for photolysis at 310 nm, one rather extended isosbestic point is obtained at about 248 nm. For photolyses conducted at 290 and 270 nm the isosbestic point is less well defined and is better described as a wavelength region in the vicinity of 250 nm for which there is a small yet real decrease in absorption with continuing irradiation. This becomes more evident when longer photolysis times are used. Thus, in the case of photolysis carried out at 290 nm and for times greater than 380 min, the entire absorption decreases so that after 1030 min the reactants and products remaining are characterized by a low, broad and almost structureless absorption contour. That this is a photochemical and not thermal process is demonstrated by the observation that cells left in the dark for protracted times after completion of photolysis and during photolysis runs showed no changes in the absorption spectra. It was also observed that a relatively larger loss in absorption occurs for the region about the wavelength of irradiation. Thus, for irradiation at 350 nm for 380 min, the 290 nm band maximum is very considerably reduced while the 230 nm band maximum is almost unchanged (19% and 97% respectively remain of their starting values), whereas for irradiation at 270 nm the band maxima are more evenly reduced (42% and 64% respectively remain).

3.3. Photolysis in hexane

The photolysis behaviour in hexane is very similar to that observed in the methanol solvent. However, a complication is introduced owing to the spectral resolution of two forms, hydrated (H bonded) and anhydrous, of the triazine. The two forms, designated H and A respectively, are characterized by different absorption band shapes and consequently different absorption coefficients (see Fig. 1). At the band maxima

the molar absorption coefficients are $\epsilon_{281 \text{ nm}} = 750 \pm 75 \text{ l mol}^{-1} \text{ cm}^{-1}$, and $\epsilon_{297 \text{ nm}} = 600 \pm 60 \text{ l mol}^{-1} \text{ cm}^{-1}$ respectively.

The spectra presented in Fig. 4 record the changes in absorption following photolysis at 310 nm for the two forms of triazine in hexane. The overall similarity to the methanol spectra is evident in the following features. With irradiation both absorption bands were seen to decrease, the longer-wavelength band more rapidly. An isosbestic or quasi-isosbestic point is observed at about 250 nm. Photolysis runs when interrupted and left in the dark for 12–24 h showed no measurable change and, as for the methanol solutions, control samples of degassed and undegassed solutions left in the dark for times up to 14 days and held at the same temperature experienced no measurable triazine loss. Very long photolysis times resulted in low, very broad absorption bands with well-defined peaks at 266, 273, 298 and 304 nm, and some broader peaks at 321, 330 and 335 nm. The absorption bands continued to decrease at relatively very slow rates with continuing irradiation. No measurable effect on the photolysis rate or products

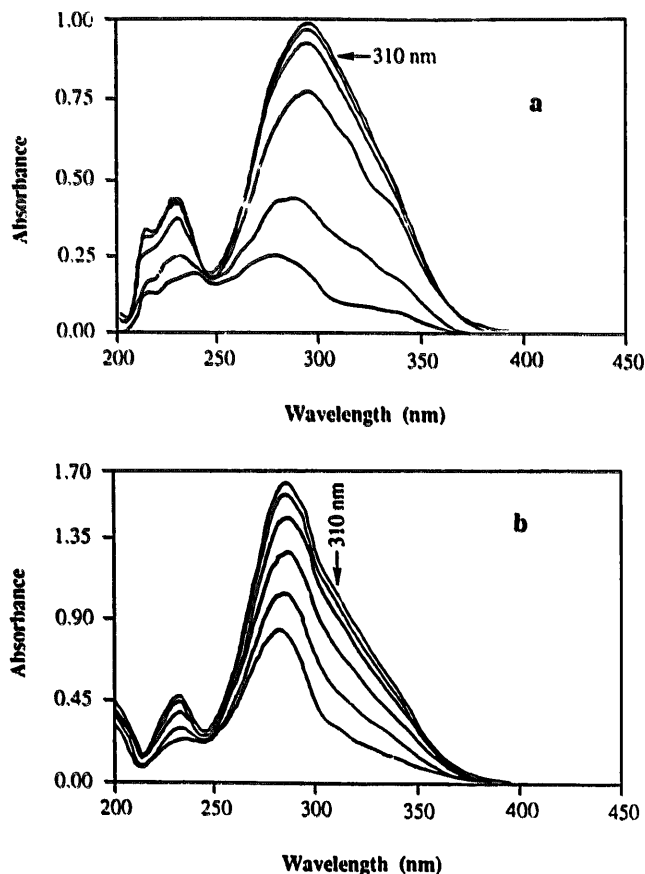


Fig. 4. Changes in the absorption spectra with irradiation at 310 nm for a solution of 1,2,3-triazine in hexane: (a) A form, from the top down for photolysis times of 0 min, 5 min, 20 min, 65 min, 200 min and 380 min; (b) H form, from the top down for photolysis times of 0 min, 10 min, 40 min, 100 min, 190 min and 310 min.

was detected as a result of the presence or absence of air.

The photodissociation behaviour of the two forms of triazine in hexane, although different initially, approached one another with increasing photolysis times, for each wavelength of irradiation studied. As was the case with the methanol solutions, irradiation at the longer wavelengths caused a more rapid decrease in the longer-wavelength absorption, while irradiation at the shorter wavelengths tended to reduce the absorption more uniformly.

Careful consideration of the spectral changes during irradiations shows that the initial photolysis rates for irradiation at 270 and 290 nm differed significantly for the H and A forms but were similar for photolyses of the two forms conducted at the longer wavelengths. This is borne out by the quantum yields determined for the first few per cent photodecomposition, and listed in Table 1. For longer times of irradiation, similar fractional losses of the triazine were obtained.

3.4. Photolysis products

Only acetylene was identified from the FTIR spectroscopic analysis of the gases isolated from the photolyte at -80°C . However, the isolation of acetylene from the methanol and hexane solutions was not quantitative and hence absolute quantum yields for the production of acetylene could not be obtained in this work. HCN was expected to be formed via the same process as acetylene but was not identified in the IR spectrum. The absence of HCN bands in the IR spectrum can be rationalized by noting that, at -80°C , acetylene has a vapour pressure of more than 1 atm while that of HCN is less than 1 Torr. The absorbance in the IR for such a small pressure of HCN in a cell of 10 cm path length is insufficient for observation with our spectrometer. The use of higher temperatures to obtain increased pressures of HCN was unsuccessful owing to obscuring absorption by the solvent vapours.

The photolytes were also subjected to vacuum distillation at room temperature. No solid residues were obtained. Hence, any products formed during the pho-

Table 1
Photolysis quantum yields ($\pm 25\%$) for 1,2,3-triazine in hexane and methanol at a number of irradiation wavelengths

Solvent	Quantum yield for the following irradiation wavelengths					
	270 nm	290 nm	310 nm	330 nm	350 nm	370 nm
Hexane A	"	0.70	0.87	0.68	0.66	"
Hexane II	2.45	1.91	1.18	0.68	0.47	
Methanol	2.35	1.18	0.98	0.42	0.71	

" Change in triazine concentration was minimal.

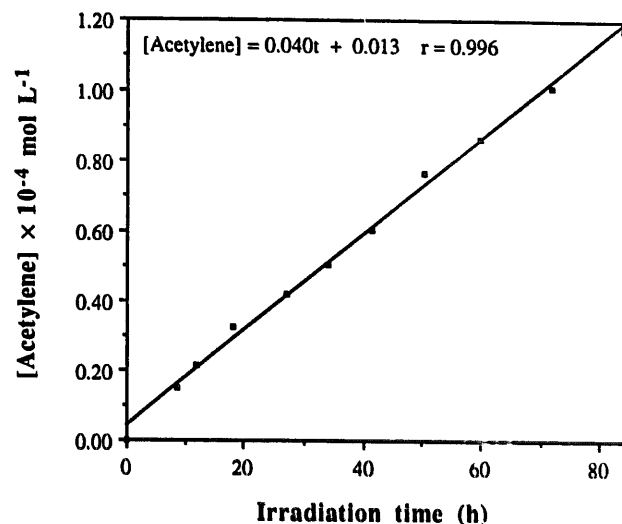


Fig. 5. The production of acetylene as a function of time in the vapour-phase photolysis at 290 nm of a constant pressure of 1,2,3-triazine.

tolyses, which may be responsible for absorption in the UV, were not identified.

3.5. Vapour photolysis

The vapour-phase photolysis of 1,2,3-triazine gave both acetylene and hydrogen cyanide, identified by their characteristic IR bands. No attempt was made to search for nitrogen, although stoichiometrically it was expected to complement the other two products. A typical plot of acetylene formation during irradiation at 290 nm of a constant pressure of the triazine is shown in Fig. 5. A similar plot was obtained for the production of HCN. The plots are linear, indicating that the rates of formation of acetylene and HCN were constant for the constant pressure of triazine, and that the products did not interfere with nor take part in the triazine photodecomposition process.

Unirradiated solid samples of triazine, in equilibrium with the vapour and kept in the dark and under vacuum, were stable for times longer than the total photolysis period.

4. Discussion

The blue shift observed in methanol as well as that induced by the addition of trace quantities of water to the hexane solutions suggests that the 290 nm band may be assigned to a $\pi^* \leftarrow n$ transition. This is in conformity with predictions from semiempirical calculations [23]. Since no changes were observed in the methanol spectra on addition of water, it can be argued that in methanol the triazine is already hydrogen bonded and so the replacement of an H bond due to methanol by one due to water is not expected to result in large

energy changes. In contrast, hexane is not expected to be H bonded to the triazine and the presence of water can induce significant energy changes as evident in the large blue shift.

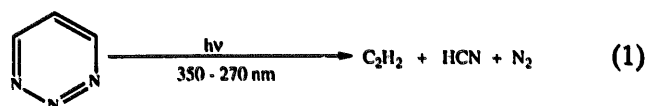
As more water is added to the hexane solvent, hydrolysis of the molecule accompanies H bond formation. The triazine ring is sufficiently π -electron deficient to be readily attacked by nucleophiles. The ultimate result of the attack of water molecules on the π -electron-deficient carbons is opening of the ring and destruction of the molecule. The high stability of the solutions of triazine in hexane when left in the dark, even those that displayed an absorption spectrum corresponding to the hydrated form, strongly suggests that the trace quantities of water initially present in the solutions were insufficient to produce measurable hydrolysis.

One explanation for the initially different pattern of spectral changes obtained in hexane upon photolysis is based on the different absorption coefficients for the hydrated and anhydrous forms of the triazine (Fig. 1), and also on the different quantum yields (Table 1). The solutions with band maxima at 281 nm and denoted H accordingly have greater relative amounts of H present than those with band maxima at 297 nm and denoted A. Thus irradiation at 350 nm of either category of solution caused more rapid photodecomposition of A, leading to a relative increase in H. The same behaviour was obtained for photolysis at 310 nm but to a smaller degree. For photolyses conducted at 290 and 270 nm, however, the reverse was true. In addition the high relative quantum yields for photodecomposition at 290 and 270 nm of H meant that for both solutions the H form was quickly removed, and the subsequent photolysis involved the A remained. This explains why the spectra became so similar once some 50% of the triazine had been photodecomposed.

All spectra, in methanol and in hexane, display one or more isosbestic or quasi-isosbestic points at about 250 nm. The occurrence of an isosbestic point is an indication that the decomposition of the triazine is accompanied by the appearance of a product whose rate of production is fixed to the rate of disappearance of the triazine. The gradual drop in absorbance at the isosbestic point with continuing irradiation, which occurred once almost all the triazine had been photodecomposed, can be reconciled with the production of a photoproduct that is itself photolabile. This is further supported by the observation that the relative reductions in the heights of the two band maxima depended on the wavelength of irradiation. Thus the photoproduct had greater absorption in the vicinity of the 230 nm band maximum and consequently was more readily photolysed by irradiation at 270 nm than at 350 nm. It had been demonstrated that in the absence of irradiation the photoproduct is stable. The identity of

the photoproduct, giving rise to the absorption, has not been determined. Neither acetylene nor HCN has significant absorption at 230 nm, nor in the vicinity of the isosbestic point, and hence cannot account for the formation of the isosbestic point nor for the observed absorption. The electronic spectra of the molecules pyridine, pyridazine and pyrazole, detected in trace amounts in the thermolysis of neat 1,2,3-triazine [16], do not appear to correspond to the spectrum of the photoproduct. A possible candidate for the photoproduct is discussed below.

The detection of both acetylene and the unidentified photoproduct(s) that has (have) an absorption band in methanol and hexane solutions at about 230 nm, would appear to exclude the concerted photofragmentation into N_2 , HCN and C_2H_2 as the sole decomposition pathway in solution:



Thus one or more other photodecomposition channels must be open, which lead to photoproducts having absorption near 230 nm. In the vapour both acetylene and HCN have been identified and concerted photofragmentation may be the mechanism.

The quantum yields listed in Table 1 show a similar pattern for both solvents insofar as their magnitudes and trends are concerned. The results for photolysis of hexane solutions conducted at 270 nm are revealing. At this wavelength, absorption by the A form is small and considerably less than that by the H form. It is for this reason that only a very small absorbance change of the A form was measured for the initial photolysis period, less than experimental error, and consequently a quantum yield could not be estimated with any degree of reliability. It also suggests that the so-called A form contains little of the other form. On the contrary a large absorbance change was measured for the H form. A large difference between the quantum yields for the two forms in hexane was also determined at 290 nm. The quantum yield for the H form had decreased from its value at 270 nm while that of the A form was similar to the values obtained at longer wavelengths.

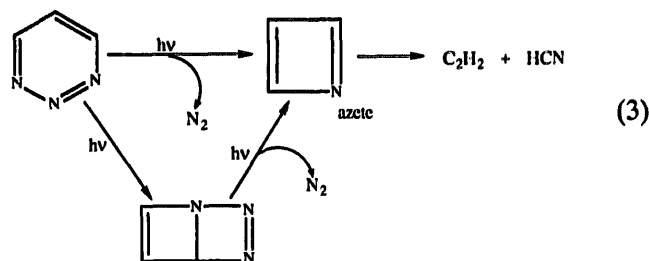
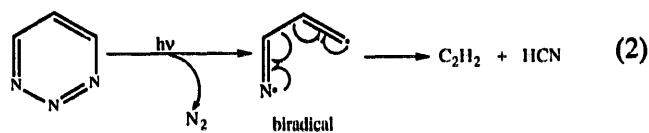
When account is taken of the large errors associated with the quantum yield determinations (25%), the quantum yields at the longer wavelengths may be viewed as similar for the two forms and also for the methanol solutions. For both solvents there appears to be a trend of decreasing quantum yield with increasing wavelength. In so far as hexane is concerned, the values listed in the table suggest that the origin of this trend may lie in a decreasing quantum yield with increasing wave-

length for the H form only. For methanol, more than one form could not be spectrally resolved.

Although there are differences between the photolysis behaviours of the two forms of the triazine in hexane, no clear effect of the solvent on the quantum yields was noted. The solvent behaviour observed is indicative of a decomposition mechanism that does not involve initial formation of radicals. Photodecomposition reactions involving radical intermediates tend to exhibit a solvent effect because of the involvement of solvent cages, the so-called "cage effect". *n*-Hexane and methanol have appreciably different viscosities, 3.13×10^3 P and 5.93×10^3 P at 20 °C respectively [22]. Accordingly, a radical mechanism would be expected to give rise to higher quantum yields of triazine photodecomposition in hexane than in methanol. This is not observed. The spectral changes and the photolysis quantum yields for the air-saturated solutions did not differ significantly from those of the corresponding degassed solutions. These observations are also consistent with a photodecomposition mechanism not involving radicals since, for a mechanism involving radicals, oxygen, a radical trapping agent [22], would be expected to play a significant role.

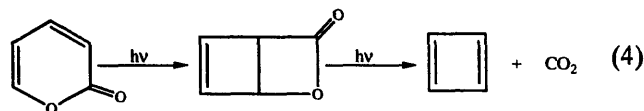
The quantum yields were also found to be independent of the incident light intensity. Such an invariance in yield with light intensity is indicative of a photochemical process involving single-photon excitation. Similar observations were made for the room-temperature photochemical decomposition of *s*-tetrazine in hexane and in the vapour [9].

The overall products identified (acetylene in solution, both acetylene and HCN in vapour) are in addition to the concerted photofragmentation also consistent with a decomposition mechanism proceeding through biradical or azete intermediates:



Apart from the possibility of generating an azete by direct photo-elimination of nitrogen from 1,2,3-triazine, an initial photorearrangement of the 1,2,3-triazine to the triaza bicyclo compound could also lead to an azete intermediate. Analogues of the triaza bicyclo compound (e.g. the bicyclic lactones as in the following equation)

are known to be fairly stable and have indeed been isolated [26]:

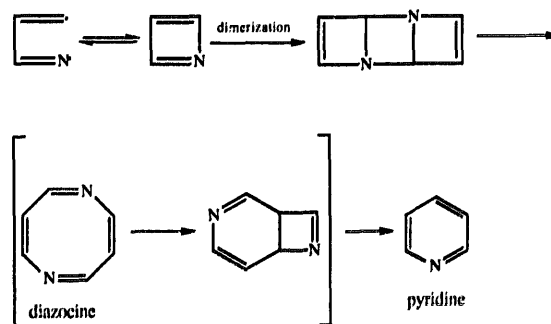


The triaza bicyclo compound is a possible candidate for the photosensitive photoproduct observed in the UV spectra but neither isolated nor identified.

The behaviour of the quantum yields with variations in some of the photolysis parameters, such as changes in solvent and the presence of oxygen, do not, however, support a biradical mechanism. Similarly, support for an azete or biradical intermediate is lacking in that one of the expected end products was not detected. An azete or biradical intermediate would also have undergone dimerization, leading to the formation of diazocine (Scheme 1). The ultimate product of the reaction sequence, pyridine, would have been detected in the UV spectra since it is expected to be stable at the irradiation wavelengths used in this study. Apart from the significant difference between the quantum yields at the shorter irradiation wavelengths no other evidence was obtained to suggest that different mechanisms apply to the photolysis of the A and H forms of the triazine in hexane.

The electron impact mass spectrum of 1,2,3-triazine shows that the most abundant ion (the base) peak is at 25 (C_2H^+), with other significant fragment ions at 53 ($M^+ - N_2$), 52 ($C_3NH_2^+$), 27 (HCN^+) and 26 ($C_2H_2^+$). The molecular ion peak, 81 (M^+), appeared relatively weak, suggesting that the molecule readily fragments to acetylene, HCN and nitrogen on electron impact. Similar fragmentation patterns have been observed during FVT of substituted 1,2,3-triazines to yield an alkyne, a nitrile and nitrogen [16]. In the vapour phase photolysis the detection of acetylene and HCN is in accord with the fragmentation route.

In solution, two factors have hindered our attempts to identify unambiguously the photolysis mechanism. They are the failure to isolate and identify the products



Scheme 1. Formation of pyridine through an azete or a biradical intermediate.

which gave rise to the observed new absorption during the photolyses, and the confusion generated by the presence of two forms of triazine in the solutions studied. Nevertheless, it can be concluded that the concerted photofragmentation into acetylene, HCN and nitrogen cannot be the one and only photodecomposition pathway.

Acknowledgment

We are grateful to Dr. M. Rasmussen and Dr. P. Wormell for critical reading of the manuscript.

References

- [1] K.K. Innes, I.G. Ross and W.R. Moomaw, *J. Mol. Spectrosc.*, **132** (1988) 492.
- [2] J. Kommandeur, *Adv. Chem. Phys.*, **70**(1) (1987) 133.
- [3] G. Fischer, *Vibronic Coupling*, Academic Press, London, 1984.
- [4] A.R. Katritzky and C.W. Rees (eds.), *Comprehensive Heterocyclic Chemistry*, Vol. 3, Pergamon, Oxford, 1984.
- [5] R. Bersohn, G. Ondrey, S. Kanfer, P. Brewer and S. Yang, *J. Photochem.*, **17** (1981) 257.
- [6] G.S. Ondrey and R. Bersohn, *J. Chem. Phys.*, **81** (1984) 4517.
- [7] D.M. Burland and F. Carmona, *Mol. Cryst. Liq. Cryst.*, **50** (1979) 279, and references cited therein.
- [8] J.H. Meyling, R.P. van der Verf and D.A. Wiersma, *Chem. Phys. Lett.*, **28** (1974) 364.
- [9] D.M. Burland, F. Carmona and J. Pacansky, *Chem. Phys. Lett.*, **56** (1978) 221.
- [10] R.M. Hochstrasser and D.S. King, *J. Am. Chem. Soc.*, **97** (1975) 4760; B. Dellinger, D.S. King, R.M. Hochstrasser and A.B. Smith III, *J. Am. Chem. Soc.*, **99** (1977) 3197, 7138.
- [11] X. Zhao, W.B. Miller, E.J. Hintska and Y.T. Lee, *J. Chem. Phys.*, **90** (1989) 5527.
- [12] G.L. Closs and A.M. Harrison, *J. Org. Chem.*, **37** (1972) 1051.
- [13] G. Maier and U. Schafer, *Justus Liebigs Ann. Chem.*, (1980) 798.
- [14] E.M. Burgess and J.P. Sanchez, *J. Org. Chem.*, **39** (1974) 940.
- [15] R.D. Chambers, T. Shepherd, M. Tamura and P. Hoare, *J. Chem. Soc., Perkin Trans. I*, (1990) 983.
- [16] T. Itoh, M. Okada, K. Nagata and A. Ohsawa, *Heterocycles*, **34** (1992) 1183.
- [17] R.F.C. Brown, *Pyrolytic Methods in Organic Chemistry*, Academic Press, New York, 1980.
- [18] T. Okatani, J. Koyama and K. Tagahara, *Heterocycles*, **29** (1989) 1809.
- [19] H. Neunhoeffer, M. Clausen, H. Votter, H. Ohl, C. Kruger and K. Angermund, *Justus Liebigs Ann. Chem.*, (1985) 1732.
- [20] A. Ohsawa, H. Arai, H. Ohnishi, T. Itoh, T. Kaihoh, M. Okada and H. Igeta, *J. Org. Chem.*, **50** (1985) 5520.
- [21] G.C. Hatchard and C.A. Parker, *Proc. R. Soc. London, Ser. A*, **235** (1956) 518.
- [22] J.G. Calvert and J.N. Pitts Jr., *Photochemistry*, Wiley, New York, 1966.
- [23] P. Wormell, A.R. Lacey, L.I.K. Ryan and D.M. Wynn-Hatton, *Chem. Phys. Lett.* in press.
- [24] H. Neunhoeffer, 1,2,3-Triazines and their benzo derivatives, in A.R. Katritzky and C.W. Rees (eds.), *Comprehensive Heterocyclic Chemistry*, Vol. 3, Pergamon, Oxford, 1984, p. 369.
- [25] T. Itoh, M. Okada, K. Nagata, K. Yamaguchi and A. Ohsawa, *Chem. Pharm. Bull.*, **38** (1990) 2108.
- [26] R.N. Warrener, G. Kretschmer and M.N. Paddon-Row, *J. Chem. Soc., Chem. Commun.*, (1976) 806.