

MULTIPHOTON-INDUCED CHEMISTRY OF THIIRANE

ROBERT P. GUIGLIANO and JOSEPH J. BELBRUNO[†]

Department of Chemistry, Dartmouth College, Hanover, NH 03755 (U.S.A.)

(Received July 11, 1986)

Summary

The visible multiphoton photolysis of thiirane is examined at pressures of 1 to 20 Torr. The effect of experimental variables such as total pressure, sample pressure, laser wavelength and laser energy on the photochemistry is explored. The confirmed products, S₂, C₂H₄ and CS₂, are used to postulate a simplified mechanism for the reaction involving a thiirane ion in the initiation and rate-determining step. Measurements of the efficiency of the process are also reported.

1. Introduction

Multiphoton techniques have become standard tools for the physical chemist [1]. The wavelengths employed in the technique allow for a convenient method of obtaining spectroscopic data at energies normally accessible only by UV irradiation. UV-visible laser excitation has been shown to result in multiphoton ionization (MPI) and/or multiphoton dissociation (MPD) [2]. IR multiphoton pumping has long been recognized as a tool for the deposition of the requisite energy for photochemical processes to become active (see, for example, ref. 3). Recently, reports involving similar experiments using UV-visible MPD have begun to appear in the literature [4]. In this respect, the MPI/MPD photochemistry resembles the typical radiation chemistry experiment. Radiolysis of organic samples yields significant quantities of ions and radicals which proceed to interact with each other and neutral components of the reaction mixture resulting in the production of species which arise from high energy pathways [5]. MPI/MPD at pressures of 1 - 10 Torr represents an intermediate technique with respect to photochemistry and radiolysis. Radicals can be minimized while significant concentrations of ions are produced which are then allowed to interact via secondary processes. This technique should prove useful in unraveling the combination of ionic- and radical-initiated chemistry in the radiation chemistry experiments. We have recently demonstrated [6, 7] that collisional

[†] Author to whom correspondence should be addressed.

effects and secondary reactions in MPI/MPD open reaction channels not accessible to either unimolecular or conventional photochemical experiments.

Michelsen *et al.* [6] report, in the first of a series of papers on non-linear effects in small heterocyclic molecules, that *N*-isopropylidimethyl-oxaziridine, at pressures of 1 - 2 Torr, was found to yield acetone as the exclusive carbonyl fragment when the sample was subjected to MPI/MPD. This is in marked contrast to the conventional photochemical experiment which produces predominately the substituted acetamide. The different products were attributed to ionic pathways in the multiphoton-induced decomposition. Greenfield and BelBruno [7] have reported that gas phase octafluorocyclo-octatetraene (OFCOT) may be photolyzed to perfluorobenzene, tetrafluoroethylene and carbon atoms upon multiphoton ionization at 308 nm. In this case, the conventional experiment yields a tricyclic C_8F_8 isomer as the primary product [8]. The large amount of energy deposited by the multiphoton excitation led to rearrangements in the multiphoton channel which were not energetically allowed in the one-photon reactions.

As part of our continuing study of "high pressure" (*i.e.* 1 - 20 Torr of target gas) multiphoton-induced chemistry, we report on the fragmentation of multiphoton ionized thiirane. The neutral photolysis is well known and reported to yield sulfur plus ethylene with minor amounts of hydrogen sulfide and acetylene [9]. For a two-photon resonant, three-photon ionization process, we find that, in addition to those products resulting from photolysis via a neutral intermediate, a significant quantity of carbon disulfide is produced. This is consistent with a previously published mass spectrometric (MS) kinetic study which invoked the formation of two different $C_2H_4S_2^+$ intermediates to explain the observed rate data. The additional product is assumed to represent the ultimate fate of the second intermediate which is not produced in the neutral photolysis.

2. Experimental details

The MPI spectra were recorded in a cylindrical gas cell of the type which has become the standard design [10]. Details of the cell construction have already been reported [6], so that only a brief description is given here. A stainless steel cell, equipped with a cylinder/wire electrode system, contains the sample at a pressure monitored by a Baratron capacitance manometer. The output (about 15 ns) of either a XeCl excimer laser or an excimer pumped dye laser (Lumonics Model T-861S/EPD-330) is coupled to the cell by means of a lens of focal length 15 cm and the resulting photocurrent is recorded by a Keithley Model 625 Electrometer and stored in a laboratory microcomputer for later processing. Dye laser wavelengths are monitored by means of an optogalvanic effect cell for absolute calibration.

Photolysis experiments were carried out in a Pyrex cross cell fitted with 1.75 in NaCl and 1 in Suprasil windows. The laser photolysis path

length is 7 cm and the IR detection path length is 10 cm. Samples were admitted to the cell via a stainless steel and Teflon vacuum line. IR spectra were recorded on either a Perkin-Elmer Model 599 Grating or a Digilab Model FTS-40 Fourier Transform Spectrometer. The same lens, of focal length 15 cm, used for the recording of MPI spectra was employed in the photolysis. The laser power density in these experiments was difficult to measure exactly, but was estimated from known parameters to be of the order of $1 - 5 \text{ MW cm}^{-2}$. IR spectra were recorded as a function of laser photolysis time (or, equivalently, the number of laser pulses) for a 15 Hz repetition rate. The laser pulse energy was recorded by means of a Scientech power meter and stored with the spectroscopic data.

Additional analyses were performed using mass spectrometry. These methods were intended to aid in the absolute identification of the photolysis products and were not used in the kinetic studies.

An attempt was made to follow the course of the photolysis using MPI spectroscopy. This technique has been successful in at least one of our earlier studies [6]; however, the major products, ethylene and carbon disulfide, have extremely small cross-sections for multiple photon ionization via the three-photon process and could not be easily quantized.

Thiirane was obtained from Aldrich Chemical Co. and purified by trap-to-trap distillation prior to use. Argon was Air Products High Purity grade and used without further purification. Ethylene, used for qualitative analysis purposes, was purchased from Matheson Gas Products and employed directly in the reported experiments. Experiments were run with thiirane pressures between 0.1 and 20 Torr, both in the presence and the absence of background gases up to a total pressure of as much as 300 Torr.

3. Results and discussion

The major photolysis products were identified by mass spectrometric (MS) and IR analysis. Low energy (20 eV) MS analysis indicated the presence of parent ions of m/e ratios 60, 64, 76 and 92, corresponding to molecules with the empirical formulae $\text{C}_2\text{H}_4\text{S}$, S_2 , CS_2 and $\text{C}_2\text{H}_4\text{S}_2$. The remaining mass peaks were readily assigned to electron impact dissociation products created from these precursors in the mass spectrometer. Ethylene could not be detected in our spectrometer owing to an inherent limitation at the low end of the mass scale. The presence of C_2H_4 , CS_2 and $\text{C}_2\text{H}_4\text{S}$ was confirmed by IR analysis of the photolyzed mixture. S_2 , of course, does not have any IR-active bands and the absorptions due to sulfur stretches in either of the plausible $\text{C}_2\text{H}_4\text{S}_2$ structures (see below) would be weak and occur at the limits of the range of the IR spectrometer employed in the study. The combination of the two analytical techniques allows an identification of the major photolysis products as C_2H_4 , S_2 , CS_2 and $\text{C}_2\text{H}_4\text{S}_2$.

Figure 1 shows an example of the time evolution of a segment of the IR spectrum as a function of the number of 308 nm laser pulses. The decrease

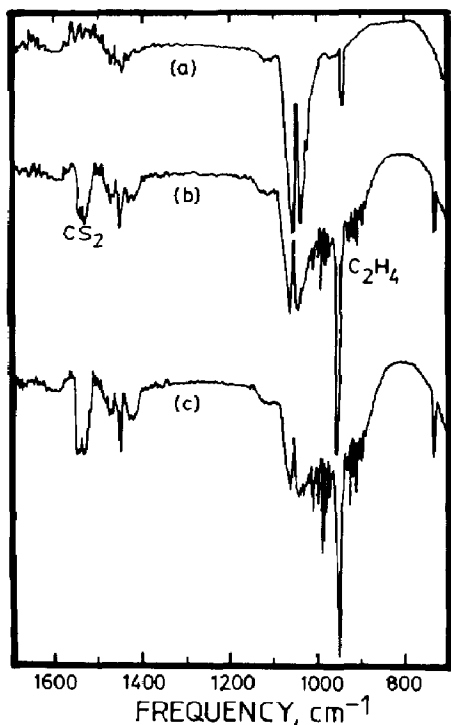


Fig. 1. IR spectrum of thiirane as a function of the laser photolysis time (number of laser pulses). The lines assigned to thiirane, ethylene and carbon disulfide are noted. The photolysis wavelength was 308 nm and the laser energy was $4.5 \text{ mJ pulse}^{-1}$. The sample pressure was 4.8 Torr. Spectra labeled (a), (b) and (c) are the result of 0, 18 000 and 36 000 laser pulses.

in the intensity of the CH_2 bending transition of thiirane at 949 cm^{-1} and the corresponding increase in the intensity of the ethylene absorption, which belongs to a partially rotationally resolved bending transition, is obvious with the increase in photolysis time. The slowly increasing band at 1535 cm^{-1} , assigned to the asymmetric CS_2 stretching motion, is also visible in Fig. 1.

We have employed quantitative IR analysis using the thiirane bending vibration to follow the decrease in reagent concentration with time. The procedure permits the reaction to be monitored until approximately 50% completion, at which time the weaker ethylene rotational structure becomes relatively more significant and begins to interfere with the analysis at 949 cm^{-1} . Analysis of the thiirane concentration as a function of the number of laser pulses (time) indicates that the decrease in concentration follows first-order kinetics. These experiments were run with initial thiirane concentrations between 3 and 20 Torr and laser pulse energies from 0.3 to 20 mJ pulse^{-1} . Implications of the first-order behavior are discussed in a subsequent section, but are indicative of a mechanism in which excitation and/or unimolecular decomposition following excitation is the rate-limiting step. The rate constant for this process has, therefore, been expressed in terms of an

efficiency per pulse rather than the customary units of inverse time. Conversion to the customary units requires only division by the laser pulse width (15 ns). The value obtained for 308 nm radiation at 4.5 mJ pulse⁻¹ was 2.5×10^{-6} pulse⁻¹. This type of rate constant is more appropriate since the time between laser pulses is much longer than the reaction time and our data indicate that the excitation step or unimolecular reaction following excitation is the rate-limiting process, so that the net result of any given number of pulses is the result per pulse multiplied by the number of pulses.

The effect of laser pulse energy, excitation wavelength and added background gas pressure has been explored. The rate constant, as is the case for all non-linear photoprocesses, is very sensitive to the laser pulse energy. When all other parameters, including gas pressure, laser wavelength and focusing, are kept constant while increasing the laser pulse energy from 4.5 mJ to 16 mJ the rate constant increases from 2.5×10^{-6} pulse⁻¹ to 38×10^{-6} pulse⁻¹. This increase is consistent with a process that depends on the square of the laser power, an indication that the ionization step from the resonant intermediate may be saturated. Increasing the laser energy increases the concentration of ions by increasing the number of molecules pumped to the Rydberg level. The non-linear nature of the excitation causes the rate of the photolysis to be sensitive to the excitation wavelength as well. As discussed below, the photolysis is initiated via a two-photon resonant, three-photon ionization (2 + 1). Attempts to initiate the process through a 3 + 1 ionization were unsuccessful. This was attributed to the large decrease (typically 10^{-18}) in cross-section [11] which was not compensated by a concurrent increase in laser power density. Additional non-linear photolyses were attempted at about 385 nm and about 500 nm without success.

A portion of the resonantly enhanced multiphoton ionization (REMPI) spectrum is presented in Fig. 2. The spectrum shown was taken from the 3 + 1 region of thiirane and includes the Rydberg transition at 462 nm. This is the three-photon equivalent of the 308 nm two-photon band used in the photochemical pumping. Thiirane is unique, in the sense that a Rydberg transition occurs at exactly twice the frequency of the XeCl laser. The result is that a substantial number of molecules may be pumped to the resonant intermediate level and the usual low ionization yield from a non-resonant process is avoided. Most of the spectroscopic transitions observed in this study have been previously assigned via the vacuum UV experiments of Basco and Morse [12].

Molecules have been classified by Gedanken *et al.* [13] into three divisions depending upon whether ionization occurs before or after molecular dissociation. The competition between ionization and dissociation from the resonant level is a reflection of the relative magnitudes of the up pumping rate ($=\sigma I$, the product of the ionization cross-section and the laser photon density) and the unimolecular decomposition rate ($=\gamma$, independent of the laser photon density). Based upon this scheme and the REMPI spectrum shown in Fig. 2, thiirane is a Class A molecule. These species are characterized by insignificant decomposition from the resonant level and ioniza-

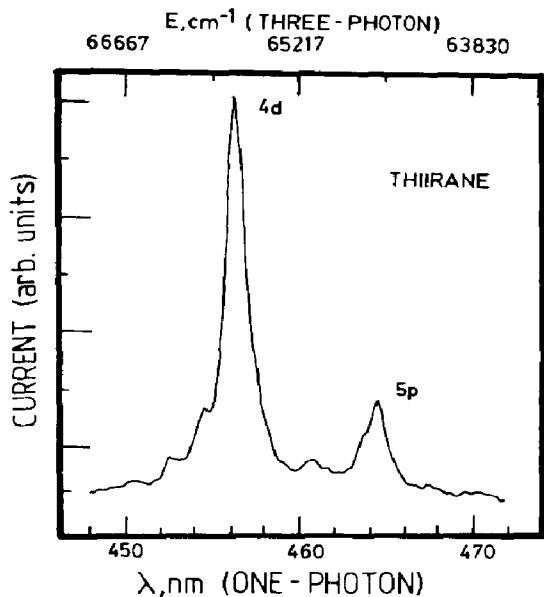
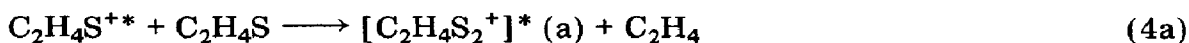


Fig. 2. A portion of the resonantly enhanced multiphoton absorption spectrum of thirane. The spectrum shown is three-photon resonant, four-photon ionization. The transition at 462 nm is the three-photon equivalent of the two-photon transition at 308 nm used in the photochemical studies. This spectrum represents the range of a single laser dye (C460). The signal is uncorrected for laser intensity, since we are concerned with peak position rather than intensity. Assignments are from ref. 12.

tion prior to any dissociation. Typically, this behavior is a reflection of the accessibility of Rydberg levels in the intermediate state rather than valence states [13]. After ionization, the parent ion may absorb additional photons and, under collisionless conditions, be observed to unimolecularly fragment into products which may then undergo similar processes. This has been referred to as the ladder switching mechanism in detailed studies of REMPI [14].

Thiirane has been examined under low sample pressure conditions (10^{-5} Torr) in a mass spectrometer [15]. The major product observed in these studies was due to sulfur-atom transfer from the bimolecular collision of the ion with a neutral thiirane, a result similar to that reported in neutral photochemistry. However, Baykut *et al.* could not explain the ion yields without invoking the existence of two different $C_2H_4S_2^+$ ions, designated "reactive" and "unreactive". The reactive ion was postulated to accept more sulfur atoms from neutral molecules, forming addition products containing as many as four sulfur atoms. The unreactive $C_2H_4S_2^+$ ions represented terminal products in the reaction mechanism. Based upon the data generated in the current work and that reported in the low pressure experiment, we *speculate* that the mechanism for the high pressure reaction at 308 nm may be that shown in Scheme 1.



Scheme 1.

Of course, any number of reaction mechanisms consistent with the observed results may be generated. While the proposed mechanism is certainly a simplification of the complex chemistry taking place in our reaction vessel, it does satisfy the requirements demanded by the kinetic data recorded during this work. The basis for support of Scheme 1 is outlined below.

Reactions (1) and (2) are confirmed by the MPI spectrum. As discussed below, essentially all of the thiirane molecules in the focal path of the laser are ionized. Reaction (3) is speculative; however, this is the usual process following ionization for a Class A molecule [13]. The value of n can only be estimated and this will be done in the discussion that follows, but clearly the total energy input into the activated ions in reactions (4) is represented by the sum of the energy in n photons of 308 nm radiation and the energy of the neutralization, step (5). The total energy required is determined by the final step in which the activated $\text{C}_2\text{H}_4\text{S}_2$ molecules rearrange into products. The neutralization step has been arbitrarily written as reaction (5). We cannot be certain which of the many intermediates actually undergoes neutralization and, in fact, the interpretation of the kinetic data would not be altered if $\text{C}_2\text{H}_4\text{S}^{++}$ or the ionic final products were the species to be neutralized. The activated ionic sulfur addition products labelled (a) and (b) in reactions (4) are the reactive and unreactive ions described in the MS ion-molecule experiments [15]. Finally, the observed products are produced in reactions (6) and (7) via unimolecular fragmentation or collisional dissociation (not shown in Scheme 1).

The mechanism shown above is consistent with the observation that the disappearance of thiirane follows first-order kinetics. The rate of the reaction should be governed by reaction (4), assuming a rapid unimolecular decay to products, but the concentration of ions is extremely low and these reactions are best described as pseudo first order with the neutral thiirane in excess. This interpretation is confirmed by the linear increase in the observed rate constant resulting from an increase in the thiirane concentration and

also by estimating the concentration of ions created in the reaction mixture. The latter may be obtained by converting from the observed ionization current in an MPI cell. The recorded current is approximately 10^{-11} A pulse⁻¹, corresponding to 10^8 ions created per laser pulse. At sample pressures of 1 - 10 Torr, the concentration of neutral thiirane would be of the order of 10^{16} - 10^{17} cm⁻³ and, given that the cell volume is 450 cm³, the number of neutral thiirane species is approximately 10^{11} greater than the ions, clearly fulfilling the conditions for a pseudo-first-order process. This number of ions represents approximately all of the thiirane molecules in the laser focal region. This concentration of ions is consistent with the magnitude of the pseudo-first-order rate constant described above.

As noted earlier, the $[\text{C}_2\text{H}_4\text{S}_2^+]$ species labelled (a) and (b) correspond, in our model, to the reactive and unreactive ions reported in the MS experiments [15]. The structures of these ions were never determined; however, the authors speculated that the reactive ion was a thiosulfoxide. Other workers have shown that the insertion of sulfur atoms into ring systems such as thietane is possible [16]. Further extending the speculative mechanism, a plausible structure for the unreactive ion could be a 1,3-dithietane molecule. Indeed, this structure was suggested as an alternative in the low pressure studies [15]. One might then imagine a fragmentation/rearrangement process from this species to yield CS₂, just as the thiosulfoxide would be expected to yield S₂ and C₂H₄ by an elimination step. We stress, again, that both the mechanism and the structures are speculative, but are consistent with the kinetic data and the observation of a novel pathway in the photochemical process.

The energetics of the photolysis are complicated, but a simplistic analysis based on Pauling's rule is instructive [17]. Both overall reactions (*i.e.* two thiirane molecules yielding either CS₂ or S₂) are endoergic, the former by about 37 kcal mol⁻¹ and the latter by about 17 kcal mol⁻¹. Ignoring any barrier to reaction (clearly an arbitrary assumption), this is the energy that must be supplied by the absorption of additional photons in reaction (3). A single photon at 308 nm supplies about 93 kcal mol⁻¹. Therefore, multiphoton absorption by the ion, while possible, is unnecessary in accounting for the energy requirements of the reaction. Indeed, the single photon could easily supply the energy required to surmount a typical reaction barrier.

In conclusion, we note that the MPI/MPD initiation of photochemical reactions is a simple means of opening novel, high energy reaction channels normally closed to conventional photolysis. Since the ionic species created by multiple-photon absorption can and do absorb additional photons from the intense laser field applied to the system, up pumping is faster than decomposition and it is possible to create ions with significant excesses of internal energy. We have applied this technique to the photolysis of thiirane and observed the presence of a new reaction pathway yielding CS₂.

Acknowledgments

The authors wish to thank G. A. Raiche for his assistance with the MPI experiments, R.P.G. acknowledges financial assistance in the form of a Xerox Undergraduate Research Grant.

References

- 1 S. H. Lin, Y. Fujimura, H. J. Neusser and E. W. Schlag, *Multiphoton Spectroscopy of Molecules*, Academic Press, New York, 1984.
- 2 P. M. Johnson and C. E. Otis, *Ann. Rev. Phys. Chem.*, **32** (1981) 139.
- 3 V. N. Bogratashvili, V. S. Letokhov, A. M. Makarov and E. A. Ryabov, *Multiple Photon Infrared Laser Photophysics and Photochemistry*, Harwood Academic, New York, 1984, and references cited therein.
- 4 J. J. Yang, M. A. El-Sayed and F. Rebentrost, *Chem. Phys.*, **96** (1985) 1.
- 5 J. W. T. Spinks and R. J. Woods, *An Introduction to Radiation Chemistry*, Wiley, New York, 1964.
- 6 H. A. Michelsen, R. P. Guigliano and J. J. BelBruno, *J. Phys. Chem.*, **89** (1985) 3034.
- 7 S. R. Greenfield and J. J. BelBruno, *J. Am. Chem. Soc.*, submitted for publication.
- 8 A. C. Barefoot, W. D. Saunders, J. M. Buzby, M. W. Grayston and D. M. Lemal, *J. Org. Chem.*, **45** (1980) 4292.
- 9 F. Fowles, M. deSorgo, A. J. Yarwood, O. P. Strausz and H. E. Gunning, *J. Am. Chem. Soc.*, **89** (1967) 1056.
- 10 P. M. Johnson, *J. Chem. Phys.*, **64** (1976) 4143.
- 11 P. M. Johnson, *Acc. Chem. Res.*, **13** (1980) 20.
- 12 N. Basco and R. D. Morse, *Chem. Phys. Lett.*, **20** (1973) 404.
- 13 A. Gedanken, M. B. Robin and N. A. Keubler, *J. Phys. Chem.*, **86** (1982) 4096.
- 14 S. W. Stiller and M. V. Johnston, *J. Phys. Chem.*, **89** (1985) 2717.
- 15 G. Baykut, K. P. Wanczek and H. Hartmann, *Adv. Mass Spectrosc. A*, **8** (1980) 186.
- 16 M. Green, E. M. Lown and O. P. Strausz, *J. Am. Chem. Soc.*, **106** (1984) 6938.
- 17 F. T. Wall, *Chemical Thermodynamics*, W. H. Freeman, San Francisco, 1974, 3rd edn., p. 63.