

Infrared Laser Multiple Photon Dissociation of Thiophene in Gas Phase

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Abstract. Infrared laser multiple photon excitation/dissociation of Thiophene (Th) was studied as a function of Th pressure, laser pulse energy, pulse duration and added buffer gas. While the excitation process was probed via optoacoustic technique, the stable reaction products were analyzed by IR spectroscopy and mass spectrometry. Although C_2H_2 and $CH_3C\equiv CH$ were the major hydrocarbon products under all experimental conditions, the distribution of these, as well as higher hydrocarbons of lower yield, was found to be very much dependent upon the experimental conditions. The laser induced reaction under dielectric breakdown conditions with either high substrate pressure or laser energy produced significant amount of CS_2 and unidentified polymer as well. We propose a mechanism involving breakage of the C–S bond in Th to form an unstable 1,5-diradical which further decomposed via different channels. However, at higher substrate pressures, radical-Th reactions complicated the overall chemistry of the system. Evidences for collisional energy-pooling and rotational hole-filling were also obtained.

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The photochemistry of heterocyclic compounds in general has attracted great interest in recent years. Various reviews [1–3] have appeared on the subject of wide variety of transformations of these compounds under electronic excitation. In particular the photo-rearrangements of five-membered heteroaromatics and their probable mechanisms based on various valence isomers have been investigated [4–7]. All of the five-membered diolefin heterocycles possess a conjugate diene ring, somewhat modified by the presence of different hetero-atom, which renders them an aromatic-like stability (6π ring). The aromaticity increases in the following order:

pyrrole < furan < thiophene < benzene.

Thiophene absorbs very strongly below 240 nm and the transition is probably of (π, π^*) type. The photochemistry is very complex, but thorough investigations of the effects of irradiation wavelength, temperature, light intensity and inert/scavenger gas has shown that at least three intermediate lead to the observed pro-

ducts [8,9]. The UV photolysis products were identified as C_2H_2 , $CH_2=C=CH_2$, $CH_3C\equiv CH$, CS_2 , $CH_2=CHC\equiv CH$ and polymer. A few transient intermediates have also been identified in flash-photolysis work [10].

On the contrary, no work on IR photochemistry of this compound is reported to the best of our knowledge. Thiophene has several strong IR absorption features [11] of which the bands at 1083 and 1036 cm^{-1} (C–H in-plane bending ν_5 and ν_6 mode respectively) can conveniently be used to study its dissociation using TEA CO_2 laser. In the present study, we attempt to use IR laser induced chemistry for better understanding of this complex photodissociation process. The multiple photon excitation process in this molecule was probed with optoacoustic spectroscopy. The stable reaction products have been identified by IR spectroscopy and mass-spectrometry. Effect of various experimental parameters have been studied and a probable mechanism of the dissociation process is discussed.

1. Experimental

A Lumonics 103-2 grating tuned TEA CO₂ laser operating at 0.5 Hz with a multimode output was used as the irradiation source. The irradiations were carried out in 10.4 cm long pyrex cell of 2.5 cm diameter fitted with polished KCl windows. After passing through an aperture 1.5 cm in diameter the laser pulse was suitably attenuated in energy by polythene sheets whenever necessary and was focussed at the centre of the reaction cell using a BaF₂ lens ($f=25$ cm). The pulse energy was measured by a calibrated pyroelectric detector (Lumonics 20D). The energy fluence at the focus was estimated from the laser beam divergence of 1.7 mrad and the laser input energy. The temporal profile, as monitored by a photon drag detector (Rofin) consisted of a 100 ns initial spike followed by ≈ 1 μ s tail. For avoiding the tail, N₂ lean mixture was used for the laser.

A greaseless glass vacuum system was used for gas handling. Thiophene (City Chemicals Ltd., New York) was used as such after degassing by freeze-pump-thaw technique. Concentrations of thiophene and various products were determined from quantitative IR spectroscopy (Perkin-Elmer 180). At 1081 cm⁻¹, we measured an extinction coefficient of 1.055×10^{-3} cm⁻¹ Torr⁻¹ for thiophene. After the IR analysis the sample was analysed by a mass spectrometer (VG Micromass 7070 F) and compared with that of a reference sample.

The multiple photon excitation (MPE) spectrum of thiophene was measured by optoacoustic (OA) technique as described in [12]. Briefly, the non-resonant aluminium OA cell had an overall length of 10 cm and a radius of 1.5 cm. A Knowles BT-1759 electret microphone (sensitivity 1 mV/ μ bar) was centrally mounted at about 1 cm from the long axis of the cell. All measurements were made with a collimated (cross sectional area 0.8 cm²) laser beam. The microphone output was recorded by a Biomation 8100 transient digitiser and transferred to a Nicolet 1170 signal averager for repetitive measurements.

2. Results

2.1 Multiple Photon Excitation Spectrum

Essential to a better interpretation of IRMPD process is characterization of the absorption process. Specifically, determinations of the average number of photons absorbed per molecule $\langle n \rangle$ is an important prerequisite to a study of this type. The OA signal obtained from the irradiation of 1.3 Torr Th at 40 mJcm⁻² fluence was plotted as a function of exciting frequency (Fig. 1). It can be seen that the MPE spectrum of Th appears to follow the small signal

absorption spectrum, however, with some apparent broadening when the laser fluence was increased. The absence of any observable "red shift" in the MPE spectrum indicates that anharmonicity does not play any important role in the pumping of ν_5 and ν_6 modes of Th. Irradiation with *R*-branch lines of 9.6 μ m band of CO₂ laser yielded better OA signal than with *P*-branch. On the basis of this measurements, 9R(24), 1081.08 cm⁻¹ was chosen as the exciting frequency in the subsequent dissociation experiments.

Calibration of OA signal with conventional energy absorption measurement indicated that the value of $\langle n \rangle$ at a given fluence remained constant, within experimental error, over the entire pressure range up to 10 Torr. At an energy density of 1.35 Jcm⁻² and 4 Torr Th, $\langle n \rangle$ was found to be 2 and was linearly dependent on fluence over the range of 0.2–2 Jcm⁻². Quantitative comparison of multiple photon absorption in polyatomic molecules by Judd et al. [13] have indicated that $\langle n \rangle(\phi)$ can be represented by the function: ϕ^γ where $\gamma=1$ for $[\sigma\phi/\langle f \rangle] < 1$ and $\gamma=2/3$ for $[\sigma\phi/\langle f \rangle] \gg 1$ where σ is the spectroscopic absorption cross section and $\langle f \rangle$ is the effective fraction of molecules that interact with radiation field. In the fluence range up to 2 Jcm⁻², $\sigma\phi \approx 1$, however, $\langle f \rangle$ for larger polyatomic could be close to unity; thereby the linear relationship of $\langle n \rangle(\phi)$ with ϕ is maintained.

2.2 Effect of Pulse Energy and Duration

The dissociation yield of Th was seen to increase with the pulse energy and can be related to 3/2 power dependence of energy. The 3/2 power law can be attributed to the conical geometry of the focussed laser beam where only the reaction volume change is taken into consideration. However, with shorter pulse duration (100 ns) the yield was found to be more with same pulse energy. This can be understood as the energy in the short pulse is more effective than the conventional long pulse (1 μ s) where the energy content in the subsequent tail is insufficient for up-pumping the molecule to dissociation threshold.

2.3 Effect of Number of Pulses

The dissociation of Th was followed by IR, spectroscopy as a function of the number of laser shots at various pressures. A plot of $\ln(P_0/P_n)$ with number of pulses, where P_0 was the initial pressure and P_n was the pressure after "n" pulses, did not fit a straight line. From the Fig. 2, it can be seen that the yield decreased with more number of pulses as the system was progressively photolysed. The conventional picture of MPD relates the reactant disappearance by a first order kinetic process whereas the result in the present

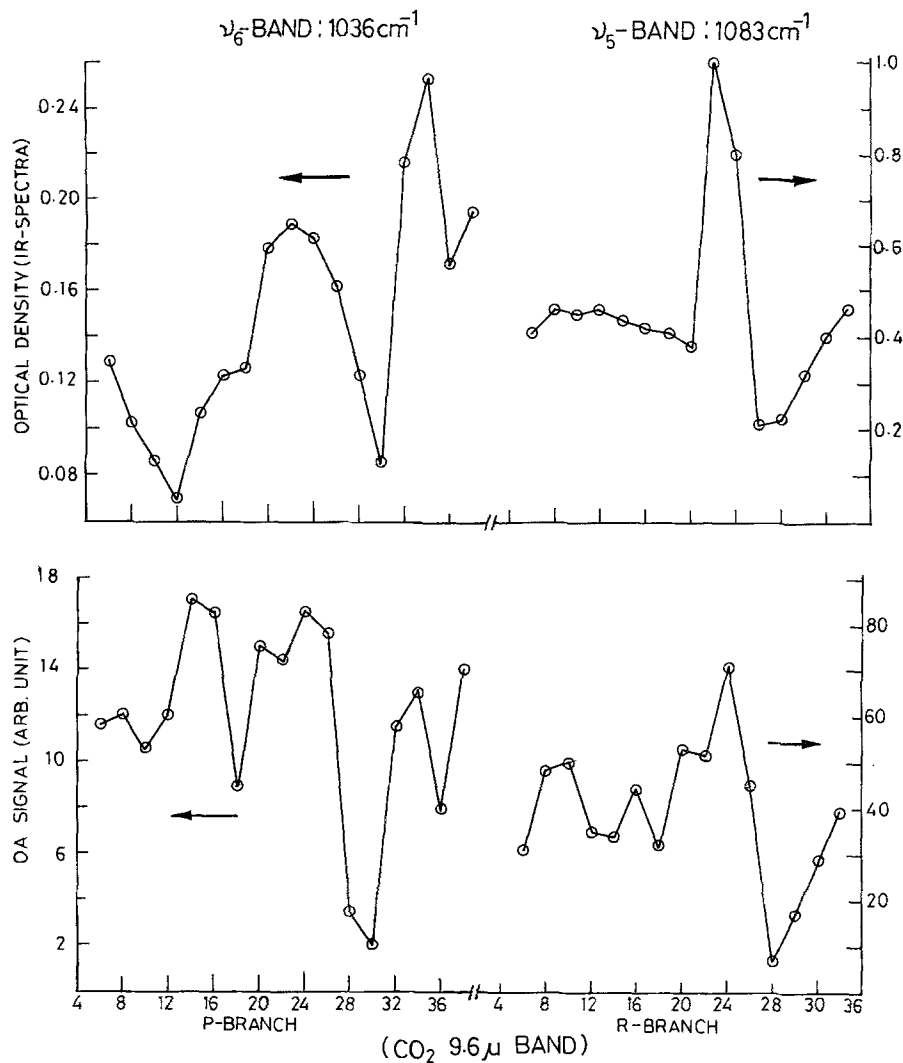


Fig. 1. Frequency dependence of multiple photon excitation of ν_5 and ν_6 band of Thiophene (1.3 Torr) at 40 mJ cm^{-2} fluence. For comparison, the small signal absorption in Thiophene is also shown

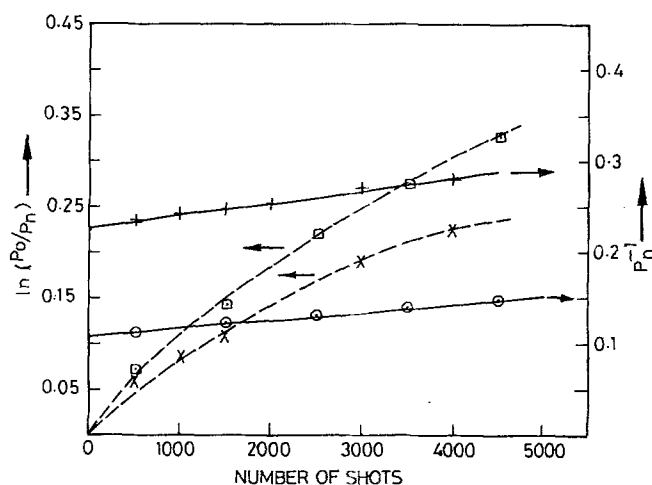


Fig. 2. Plot of $\ln(P_0/P_n)$ vs. the number of laser pulses (dashed curve) for irradiation at two different pressures; (x): 4.5 Torr, (\square): 9.5 Torr. The right-hand ordinate shows the reciprocal of P_n , the pressure of Th remaining after "n" laser pulses; (+): 4.5 Torr, (\circ): 9.5 Torr

case follows a second order kinetics which is evident from the linear plot of $(P_n)^{-1}$ vs. number of pulses. However, for 50% conversion at two different pressures of 4.5 and 9.5 Torr required approximately similar number of pulses. Thus the standard kinetic theory analogy could not explain the system behaviour with the extent of the reaction.

2.4 Pressure Dependence

The pressure dependence of laser induced decomposition of Th was studied from 1.5–9.5 Torr. At each pressure 1500 laser pulses with energy 0.6 J were used. The yield was found to increase with higher pressure. When the dissociation yield was plotted vs. Th pressure, two linear regimes were apparent with an abrupt change in the yield at around 3 Torr (Fig. 3). However, further increase in system pressure to around 12 Torr resulted in dielectric breakdown with large yield of CS_2 and unidentified brown polymer. Above 3–4 Torr of

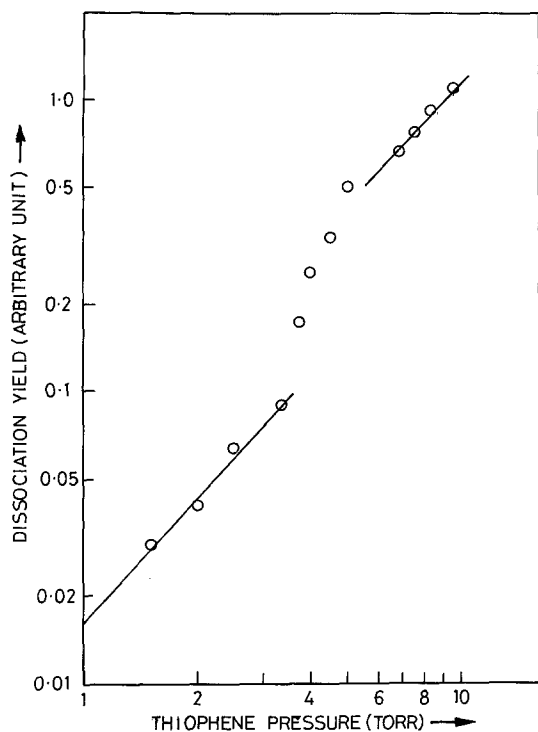


Fig. 3. Log-log plot of reactant depletion vs. reactant pressure. Each irradiation run consisted of 1500 laser pulses at 600 mJ pulse energy

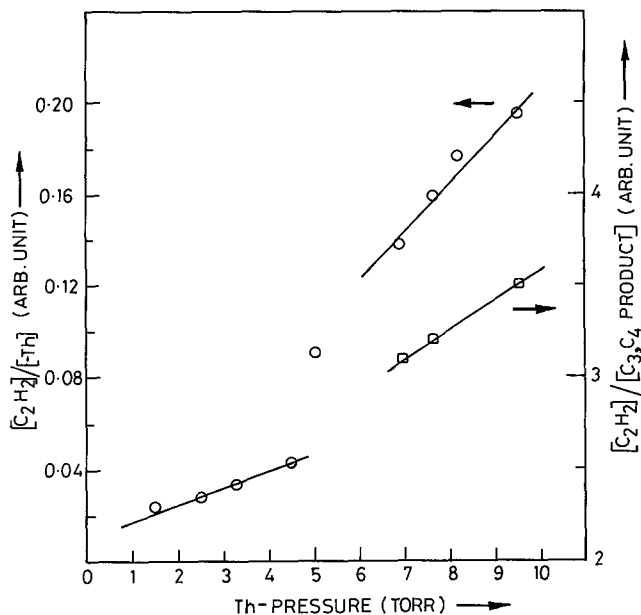


Fig. 4. Plot of the ratio of $[C_2H_2]$ and depletion of Th vs Th pressure. The right hand ordinate shows the variation of the ratio of $[C_2H_2]$ and $[C_3, C_4 \text{ product}]$ with thiophene pressure

Th, the character of laser-induced decomposition changes. In part this change arises from the increasing importance of the radical attack on Th as explained later in the discussion section. But primarily the increased yield is due to collisional mechanisms involv-

ing both rotational hole-filling and collisional energy pooling reactions.

When the decomposition was monitored as a function of the number of laser shots at various pressures of Th, the data was fitted to a second order kinetic equation (cf. Sect. 2.3). We believe that the kinetic complexity of Th reaction does not explain the failure to observe a linear relationship between $\ln(P_0/P_n)$ and the number of laser shots. The most speculative explanation could be the involvement of collisional up-pumping leading to accumulation of sufficient energy for dissociation. Also the observed effect of increasing yield when argon buffer gas was progressively added to Th system suggests that rotational hole-filling as well as collisional energy pooling is involved.

In Fig. 4, the yields of various products C_2H_2 , $CH_3C\equiv CH$, and $HC\equiv C-C\equiv CH$ were shown with variation of the system pressure. Below 3–4 Torr system pressure the yield of C_2H_2 increased, although slowly, with increase in Th pressure. However, increasing the pressure further C_2H_2 yield increased significantly. This can be understood in terms of increased dissociation of Th due to collisional mechanisms (cf. Fig. 3) and also increased secondary reaction of $:C=CH-CH=CH\cdot$ radical leading to additional C_2H_2 formation. But this reaction produces more diacetylene as well. However, the relative yield of C_2H_2 compared to the total C_3, C_4 products increased at higher pressures (Fig. 4) which can be explained by reaction of CS radical with $\cdot CH=CHS\cdot$ biradical. Though most of the $\cdot CH=CHS\cdot$ and CS polymerised normally, under high concentration of these species, some of them may react together to produce more of C_2H_2 to give the observed effect. Also there is indication that CS_2 is beginning to appear at high pressure photolysis because of the "hot" CS radical reaction.

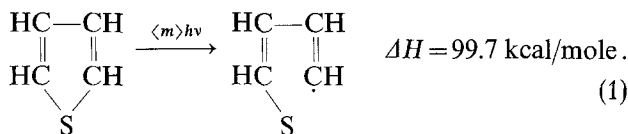
3. Discussion

From the close similarities of the hydrocarbon products obtained in the UV photolysis and CO_2 laser induced decomposition of Th, it can be assumed that many of the mechanistic features may be common to both of them. Although UV photolysis via an electronically excited state and IRMPD through vibrational levels of the ground electronic state are uniquely two different processes, the initial bond breaking step in both cases is consistent with breakage of C–S bond in Th. Differences could be due to higher concentrations of radicals produced by the focussed IR laser beam. The higher level of excitation with UV photons in the excited electronic (singlet or triplet) state could lead to more fragmentation of the Th molecule. Nevertheless, in IR excitation the vi-

brationally excited species formed can also decompose directly or absorb subsequent IR photons to dissociate producing further fragmented products. Following the CO₂ laser pulse, $V \rightarrow T/R$ relaxation may also result in considerable temperature jump and can introduce thermal features especially at high pressures.

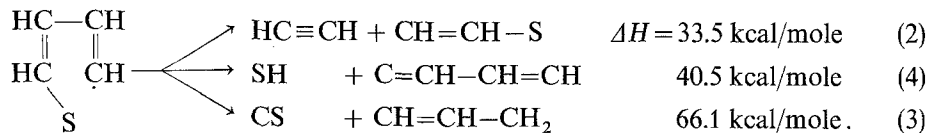
Following the general observation of the decomposition of most of the heterocyclic compounds (5 membered diolefins), it is the weakest C-S bond in Th that determines the primary bond scission. Using a thermochemical cycle it is possible to estimate the C-S bond strength in Th. The cycle starts with 1,3-butadiene-thiol where the S-H and a terminal C-H bond are broken and then H₂ is reformed. From this the heat of formation of the resulting biradical $\cdot\text{CH}=\text{CH}-\text{CH}=\text{CHS}\cdot$ can be estimated to be 127.4 kcal/mole [14, 15]. When combined with ΔH_f° for Th, the C-S bond strength in Th is estimated to be 99.7 kcal/mole. Thus at 1081 cm⁻¹, a minimum of ≈ 33 photons must be accumulated before it dissociates.

After absorbing sufficiently large number of IR photons, the C-S bond breaks:



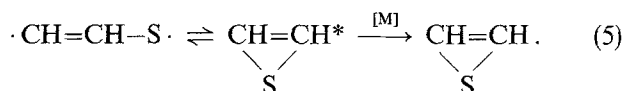
From the prevailing wisdom of IRMPD process, the energy at or above dissociation threshold is statistically distributed among the Th vibrational degrees of freedom and RRKM theory can be applied. Assuming that most of the molecules dissociate within the laser pulse duration, RRKM theory indicates that the molecule with 21 vibrational degrees of freedom must have enough internal energy in excess of the bond strength. Following the breakage of the C-S bond, any excess internal energy will reside in the biradical leading to further decomposition.

The transient biradical can further decompose via three different pathways by breakage of different possible bonds:

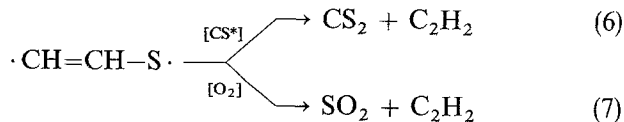


The reaction (2) is the acetylene channel which requires 133.2 kcal/mole while other products come from the subsequent rearrangement/reaction of the transient radicals via other routes. Hence C₂H₂ is thermodynamically favoured product in the system. We now consider the fate of the radicals produced in reactions (2), (3), and (4).

The transient $\cdot\text{CH}=\text{CH}-\text{S}\cdot$ can close to form episulphide. As the reaction is highly exothermic ($\Delta H = 56.3$ kcal/mole), unless collisions are effective in stabilizing, it will revert back to original species.

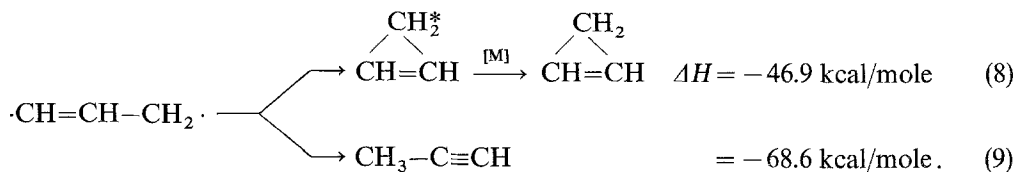


Under the present condition, collisions were not very effective in stabilizing the episulphide and, in fact, such product was not obtained as a product. However, such an episulphide was obtained as a minor product in 213.9 nm photolysis of tetra(trifluoromethyl)thiophene [9]. Formation of thioketene from the biradical is also highly improbable because of the exothermicity of the reaction. Although thioketene is stable as monomer at -80°C, it polymerises on warming. Furthermore, this biradical can react with hot CS radical or even with traces of O₂, if present in the system:



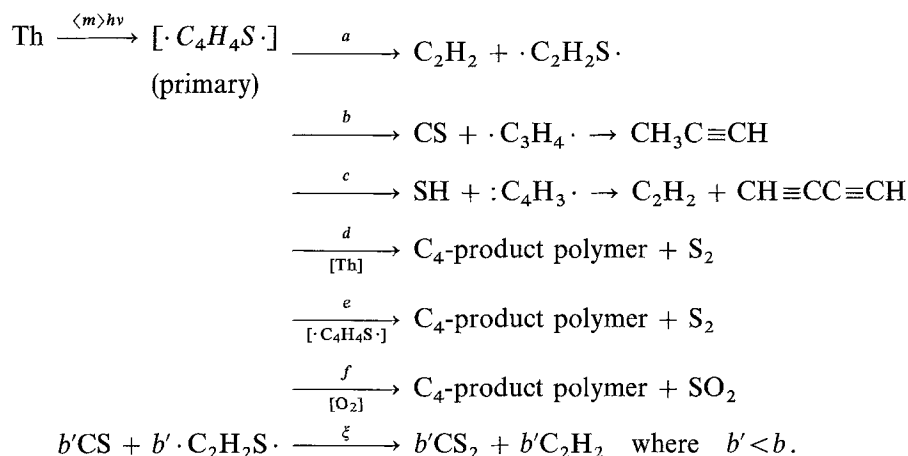
In the UV photolysis work [8], it has been postulated that two kinetically indistinguishable routes, i.e. polymerisation or production of C₂H₂, exist for this radical. From the ratio of C₂H₂/[-Th] and very little CS₂ yield in our experiments, it is likely that most of the C₂H₂S underwent polymerisation and did not contribute to C₂H₂ yield.

The transient $\cdot\text{CH}=\text{CH}-\text{CH}_2\cdot$ can react in much the same way as $\cdot\text{CH}=\text{CH}-\text{S}\cdot$ biradical, but the energetics are different. The $\cdot\text{CH}=\text{CH}-\text{CH}_2\cdot$ can close to form hot cyclopropene or rearrange to propyne:

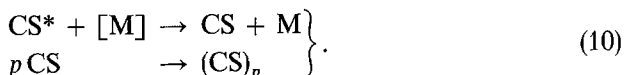


However, the possibility of the hot cyclopropene, in absence of stabilizing, decomposes to yield propyne can not be ruled out. Small amounts of C_6H_8 , 1-hexen-5-yne, found in the product could come from the dimerisation/rearrangement of the above biradical. The intermediate CS produced in step (3) should have excess energy to react further with different species present in the system. The hot CS reacts with the primary biradical to form CS_2 and C_4 -product, $CH_2=CH-C\equiv CH$. For a higher conversion of Th and with time it has been observed that C_4 -products also

of hot CS radical to form additional C_2H_2 and CS_2 as well [reaction (6)]. The second channel [reaction (3)] generates hot CS and another biradical $CH=CH-CH_2$ which leads to stable product propyne, $CH_3-C\equiv CH$ after rearrangement [reaction (9)]. The third route [reaction (4)] produces SH radical which polymerises and $\cdot CH=CH-CH=C:$ radical which undergoes β -scission followed by dimerisation [reaction (11)] to produce C_2H_2 and diacetylene. In summary, the essential features of the scheme is as follows:

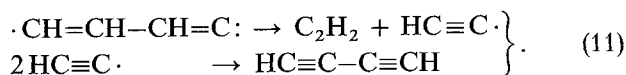


get polymerised [8]. In the same work, it has been shown that all of CS did not have sufficient energy to produce CS_2 , even if it was not deactivated. On deactivation, CS is removed from the system as polymer:



In addition, even traces of O_2 present in the system can remove CS and $\cdot CHCHCHHS\cdot$ very efficiently to quench the CS_2 and C_4 -product yield.

In the flash photolysis work on thiophene, the transient spectra of the species like SH and C_4H_3 radical have been observed [10] i.e. via the reaction step (4). The fate of SH radical presumably ends up in polymerisation while the C_4 -radical can undergo β -scission to form C_2H_2 and $C\equiv CH$ radical which dimerises to yield diacetylene, C_4H_2 :



The mechanism presented above proposes that Th decomposes via three channels through a common precursor $\cdot CH=CH-CH=CHS\cdot$ biradical. Thermodynamically most favourable channel [reaction (2)] produces C_2H_2 as the major product and a biradical $CH=CHS$ which mostly undergoes polymerisation. However, at higher concentration it reacts with some

The major product C_2H_2 comes from channels a , c , and g while C_3 , C_4 -stable products propyne and diacetylene originates through channels b and c . A small amount of CS_2 is produced from channel g . The primary biradical is scavenged and polymerised via routes d , e , and f whereas the route d indicates additional decomposition of Th in the system. Using this scheme and from the relative yields of various products at 9.5 Torr of Th, i.e.

$$[\text{propyne}] : [\text{diacetylene}] : [CS_2] = 1 : 0.1 : 0.05,$$

a preliminary estimation of the contributions of various channels were made. It was found that scavenging routes were major pathways with combined 60% contribution. The other contributions were $a=30\%$, $b=8.5\%$, and $c=1.5\%$.

4. Conclusions

We have shown that thiophene undergoes multiple photon dissociation under the irradiation of 9.6 μm TEA CO_2 laser, the nature of the multiple photon excitation process was probed by OA technique and a suitable exciting frequency was located. The dominant reaction products were found to be acetylene and propyne with little yield of diacetylene and CS_2 . The yield and distributions of various products were observed to be dependent upon most of the parameters investigated with substrate pressure and laser energy

being most important. The photochemistry of the system is not as complicated as UV photolysis where at least three intermediate electronically excited species were invoked. Nevertheless, it gets fairly complicated at high pressure because of secondary reactions originating from high concentrations of transient radicals. But at lower pressures, the dissociation is governed mostly by the multiple photon process.

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