

GAS PHASE PHOTOLYSIS OF PROPYLENE AT 8.4 AND 10.0 eV

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Summary

The photolysis of gaseous propylene was carried out in a static system using the krypton (10.0 eV) and xenon (8.4 eV) resonance lines at pressures in the range 1 - 700 Torr. Only decomposition processes were studied and no attempt was made to establish the pattern of free-radical reactions.

The primary decomposition channels were established. With increasing energy the contribution of the processes involving molecular elimination increases at the expense of simple scission of the C—C and C—H bonds. A comparison of the present data with those obtained by Collin and coworkers at 7.6 eV reveals that in the range 7.6 - 10.0 eV the mechanism for dissociation changes completely. At 7.6 eV atomic hydrogen is formed, while at 10.0 eV this process is virtually absent being replaced by the formation of molecular hydrogen. Both processes occur at an intermediate energy of 8.4 eV. The energy distribution among the products of the primary decomposition exhibits marked deviations from statistical randomization.

1. Introduction

The photolysis of propylene has been studied extensively. At low photon energies (up to 7.6 eV) the photoexcited molecule usually undergoes simple scission of the C—C and C—H bonds (reactions (1) and (2)) and yields free radicals [1 - 4]:



The processes involving molecular elimination (reactions (3) - (5)) are of little importance at low energies. The contribution of hydrogen molecule elimination (reaction (5)) has been reported to increase markedly at higher photon energies (up to 8.4 and 10.0 eV) [5 - 7]. The purpose of the present investigation was to obtain more details on the photolysis in the energy range 8.4 - 10.0 eV. These data, together with the results of extensive studies by Collin *et al.* [4] at a photon energy of 7.6 eV, are expected to clarify some outstanding problems concerning the mechanism. Both scavenged and unscavenged experiments are reported over a range of pressures (1 - 700 Torr) that is wide enough to distinguish between the primary and secondary processes. The effect of pressure is due to the competition between dissociation and collisional stabilization.

2. Experimental details

The experimental techniques were the same as those described previously [8, 9]. In the photolysis at 10.0 eV the actinometry was based on $\phi(\text{C}_2\text{H}_2) = 0.17$ in the krypton photolysis of 1-butene [8], and in the photolysis at 8.4 eV $\phi(\text{C}_2\text{H}_2) = 0.12$ in the xenon photolysis of 1-butene was used [9]. The hydrogen was analysed using an argon ionization detector developed in this laboratory [10]. The actinometry was based on $\phi(\text{H}_2) = 0.39$ in the xenon photolysis of ethylene [11]. Only low molecular weight products up to and including C_6 hydrocarbons were determined. The conversion was kept below 1% to avoid any secondary effects.

3. Results

The dependence of the quantum yields of the major molecular products on the pressure and the presence of scavengers is shown in Figs. 1 - 3.

The quantum yield of acetylene was found to be independent of pressure and the presence of scavengers (within the limits of experimental error) and was almost the same at both photon energies ($\phi = 0.24$ at 8.4 eV and $\phi = 0.23$ at 10.0 eV). The quantum yield of molecular hydrogen, determined over the range 10 - 140 Torr, was independent of pressure and was equal to 0.45 at 10.0 eV and 0.25 at 8.4 eV.

The quantum yields of the main hydrocarbon products at pressures of 1 and 500 Torr are summarized in Table 1.

4. Discussion

4.1. C_3H_4 hydrocarbons at 10.0 eV

The pressure dependence of the yields for these hydrocarbons is markedly different at the two photon energies used. The initial increase in the yield with increasing pressure at 10.0 eV indicates the formation of

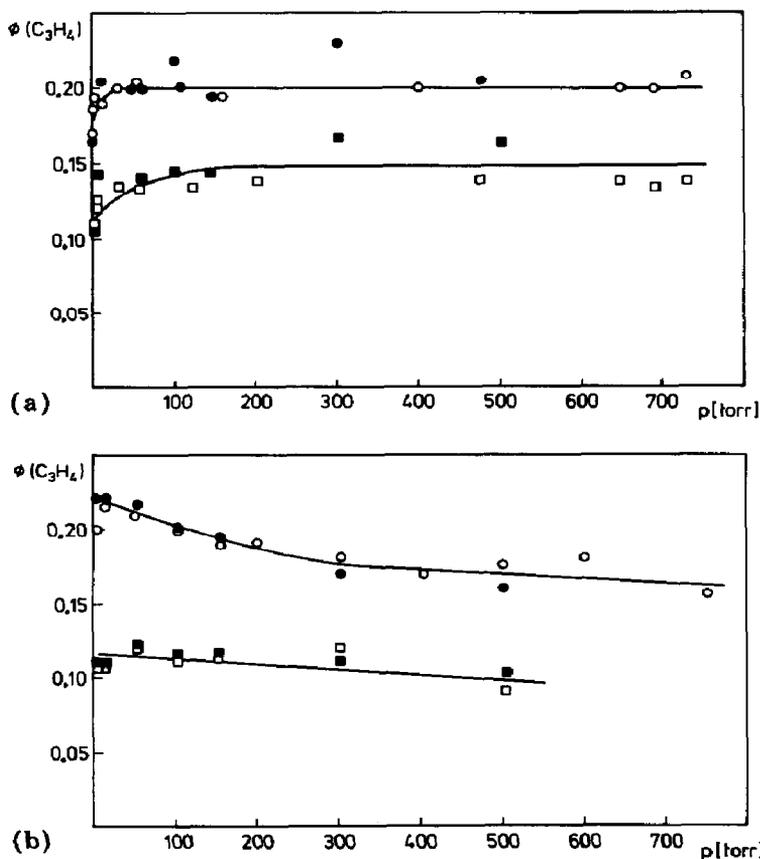


Fig. 1. Pressure dependence of the yields of allene and propyne in the photolysis of propylene at (a) 10.0 eV and (b) 8.4 eV: ●, allene; ○, allene in the presence of 6% O₂; ■, propyne; □, propyne in the presence of 6% O₂.

excited C₃H₄ molecules followed by the competitive reactions of fragmentation and collisional stabilization:



The occurrence of reaction (6) is confirmed by the presence of 1-butyne, which is believed to be the product of the recombination of the CH₃ and C₃H₃ radicals, among the photolytic products (see Table 1). Once the occurrence of reaction (6) is established, it follows that allene and propyne are formed by the detachment of molecular hydrogen (process (5)) as already suggested by Becker *et al.* [5]. The alternative mechanism



involving the consecutive elimination of two hydrogen atoms (process (1) and reaction (8)) should be rejected.

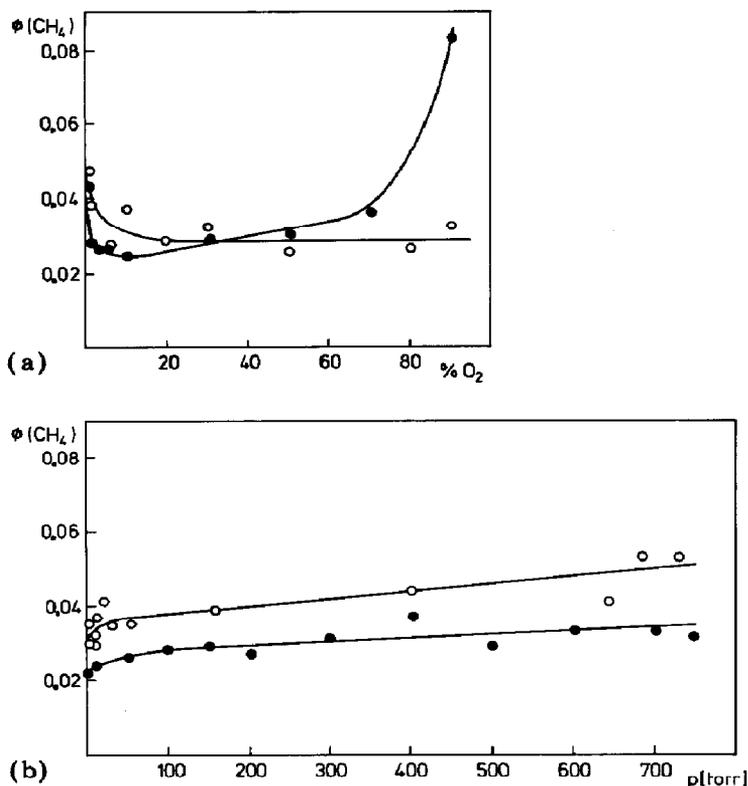


Fig. 2. Dependence of the yield of methane in the photolysis of propylene on (a) the oxygen concentration and (b) the pressure of a mixture of propylene and 6% O_2 : ●, photolysis at 8.4 eV; ○, photolysis at 10.0 eV.

The excess energy of C_3H_4 molecules ($\Delta E = 86 \text{ kcal mol}^{-1}$) is insufficient to make the subsequent fragmentation possible ($\Delta H_1 \approx 86.6 \text{ kcal mol}^{-1}$). A comparison of the total yield of allene and propyne ($\phi(\Sigma\text{C}_3\text{H}_4) = 0.34$ at $p > 50$ Torr) with that of molecular hydrogen ($\phi(\text{H}_2) = 0.45$) provides additional evidence for the occurrence of process (5). The greater value of $\phi(\text{H}_2)$ may be due to either incomplete stabilization of excited C_3H_4 molecules (even at pressures as high as 500 - 700 Torr) or abstraction of hydrogen atoms from propylene by hot hydrogen atoms. Of course the outright rejection of process (1) and reaction (8) is not justified; these processes are likely to contribute to some extent to the formation of C_3H_4 hydrocarbons. The observed pressure independence of $\phi(\Sigma\text{C}_3\text{H}_4)$ over the range 50 - 700 Torr may be due to the superposition of reaction (7), leading to enhancement of the yield, with the collisional stabilization of C_3H_5 cancelling this effect. However, the contribution of process (1) is definitely small. A rough estimate based on the relationship shown in Fig. 1(b) shows that the rate constant for dissociation of excited C_3H_4 molecules is of the order of $10^7 - 10^8 \text{ s}^{-1}$. The corresponding values of the excitation energy calculated by Rice-Ramsperger-Kassel-Marcus (RRKM) methods [12, 13] assuming

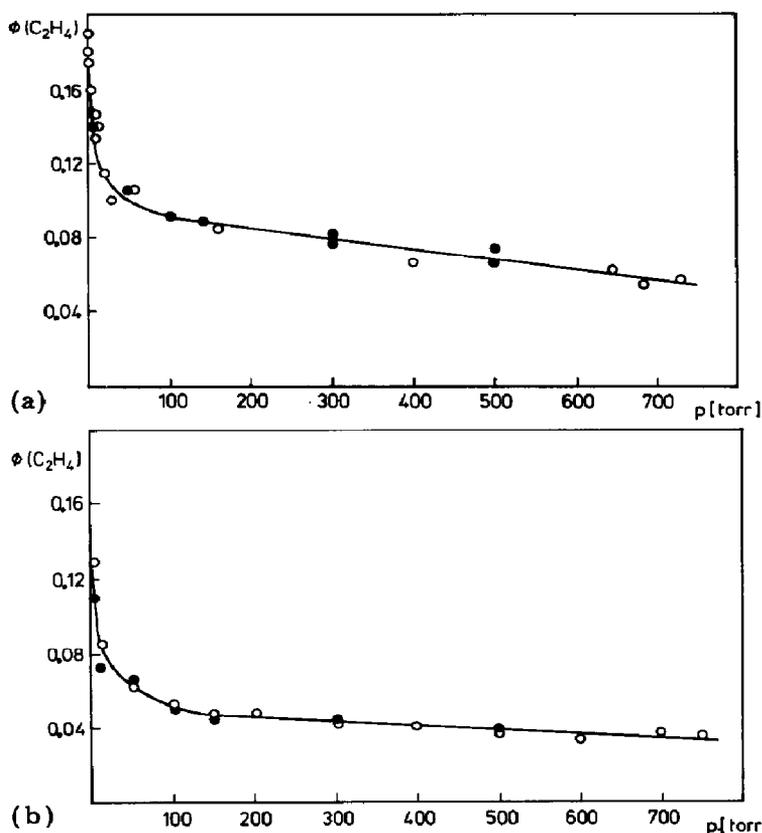


Fig. 3. Pressure dependence of the yield of ethylene in the photolysis of propylene at (a) 10.0 eV and (b) 8.4 eV: \circ , in the presence of 6% O_2 ; \bullet , pure propylene.

TABLE 1

The effects of pressure and the presence of oxygen on the products of propylene photolysis at 8.4 and 10.0 eV

Product	8.4 eV			10.0 eV		
	1 Torr	500 Torr	500 Torr (6% O_2)	1 Torr	500 Torr	500 Torr (6% O_2)
Methane	0.050	0.048	0.029	0.055	0.044	0.040
Acetylene	0.24	0.24	0.24	0.23	0.23	0.23
Ethylene	0.11	0.038	0.037	0.19	0.067	0.063
Ethane	0.062	0.032	—	0.076	0.032	—
Allene	0.22	0.16	0.175	0.165	0.205	0.20
Propyne	0.11	0.10	0.090	0.11	0.16	0.14
Isobutane	0.165	0.098	—	0.15	0.090	—
<i>n</i> -butane	0.001	0.020	—	0.0023	0.018	—
1-butene	0.021	0.032	0.0020	0.033	0.080	0.011
1-butyne	0.040	0.016	—	0.11	0.040	—
2-methylpentane	0.0043	0.041	—	0.0037	0.045	—
2,3-dimethylbutane	0.068	0.155	—	0.105	0.155	—
4-methyl-1-pentene	0.023	0.14	—	0.033	0.048	—
1,5-hexadiene	0.001	0.0052	—	0.002	0.005	—

different activated complex configurations ($\log A_{300} = 14.3 - 15.6$) are in the range 90 - 100 kcal mol⁻¹ for both allene and propyne. This value is much smaller than the difference between the photon energy and the enthalpy for process (1) ($E_{h\nu} - \Delta H_1^{300} \approx 190$ kcal mol⁻¹ for both allene and propyne). Hence, an energy of about 90 kcal mol⁻¹ remains as the oscillation energy of the hydrogen molecule and the kinetic (translational and rotational) energy of both fragments. This result indicates that elimination of the hydrogen molecule involves a deviation from the statistical energy distribution. The mechanism of this reaction is uncertain. According to Becker *et al.* [5] elimination from the CH₃ group contributes two-thirds of the total yield of process (5); an intermediary product CH₂CHCH undergoes isomerization and rearranges to either the allene or the propyne structure. Another mechanism involving the isomerization of the excited propylene molecule prior to any elimination is also possible; analogous processes are discussed by Evleth and Sevin [14] for the case of ethylene [14]. Mutual unimolecular isomerization of allene and propyne is also known [15 - 17].

4.2. C₃H₄ hydrocarbons at 8.4 eV

The quantum yields of C₃H₄ hydrocarbons decrease markedly with increasing pressure (Fig. 1(b)). A two-step mechanism appears to be involved; process (1) is followed by competing reactions (8) and (9). As *p* approaches zero, $\phi(\Sigma C_3H_4)$ approaches 0.34. According to Collin *et al.* [4] such a mechanism is the only source of allene in photolyses at 163 and 174 nm. The increase in the yield of 4-methyl-1-pentene with increasing pressure, which indicates an increase in the yield of the stable C₃H₅ radical, is another argument in favour of this mechanism. However, in contrast with the photolyses with photons of lower energies, this mechanism cannot be exclusive at 8.4 eV because significant (although less than the total yield of allene and propyne) amounts of molecular hydrogen are formed ($\phi(H_2) \approx 0.25$). These results are in agreement with those of Tschuikow-Roux [6]. An accurate estimation of the contribution of molecular hydrogen elimination to the mechanism is not feasible because the hydrogen may originate from other reactions (*e.g.* abstraction reactions involving hot hydrogen atoms). Further evidence for the occurrence of process (5) is provided by the presence of C₃H₃ radicals (determined as 1-butyne) in the photolysis products.

These considerations lead us to conclude that the total change in the mechanism of primary dissociation occurs over the energy range 7.6 - 10.0 eV: elimination of atomic hydrogen at low energies, elimination of molecular hydrogen at 10.0 eV and an intermediate situation at 8.4 eV where both processes occur.

4.3. The formation of molecular methane

Molecular methane may be formed by process (3); however, the occurrence of abstraction reactions involving methyl radicals should not be neglected. If the methyl radicals are hot, the addition of small concentrations of scavengers would not be able to suppress these reactions entirely. The

yield of process (3) was determined for a wide range of oxygen concentrations (see the data in Fig. 2(a) for $p = 10$ Torr). At 10.0 eV a slow decrease in $\phi(\text{CH}_4)$ with increasing oxygen concentration up to about 20% was observed, followed by levelling off to a constant value corresponding to $\phi \approx 0.03$. The dependence was very different at 8.4 eV where the initial decrease was followed by a sharp increase in the yield. Since some other products, *e.g.* ethylene, exhibit the same dependence, it may be due to the absorption of 8.4 eV photons by the oxygen followed by secondary processes such as the transfer of excitation energy and reactions of excited oxygen molecules and atoms with propylene. Extrapolation gives $\phi \approx 0.02$ for the yield of process (3) at 8.4 eV.

The distribution of energy between the methane and the acetylene also requires comment. The difference between the photon energy and the enthalpy for process (3) is $162 \text{ kcal mol}^{-1}$ at 8.4 eV and $200 \text{ kcal mol}^{-1}$ at 10.0 eV. An excess energy of this magnitude should result in further fragmentation of methane and acetylene, particularly at high photon energies. Since the number of vibrational degrees of freedom is small, the decomposition would be too fast to be quenched effectively by increasing the pressure. Nevertheless a marked collisional quenching effect can be seen in Fig. 2(b). Thus the high pressure values for the methane yield (0.05 and 0.03 at 10.0 eV and 8.4 eV respectively) represent only the lower limit of the contribution from process (3). Despite these reservations molecular elimination is more likely at 10.0 eV than at 8.4 eV; the trend is the same as that described for the elimination of the hydrogen molecule.

4.4. The elimination of the methylene radical

It is particularly difficult to establish the yield for process (4) because the methylene radicals react strongly with propylene, producing different C_4H_8 hydrocarbons. The yield of ethylene is not a good indication of the contribution of this process because ethylene can be formed in other reactions. At pressures above 300 Torr the ethylene yield reaches a constant value (independent of the presence of oxygen) of 0.04 at 8.4 eV and 0.06 at 10.0 eV. These yields can be assumed to represent the yields for process (4), with the following two provisos: first the excess energy of the fragments is great enough to make possible the subsequent fragmentation of ethylene, particularly at 10.0 eV; second, the reaction of atomic hydrogen with propylene provides another channel for ethylene formation.

4.5. The formation of acetylene

The yield of this product is substantial (0.24 and 0.23 at 8.4 eV and 10.0 eV respectively) and is independent of the pressure and the presence of oxygen. It is formed by the elimination of molecular methane as described above. Another pathway involves the simple rupture of the C—C bond (process (2)) followed by the dissociation of the excited vinyl radical:



Our RRKM calculations, based on the assumption of a plausible model of the activated complex ($\log A = 14.0$), reveal that the rate constant for the dissociation of the vinyl radical is very large even when the energy is only slightly greater than the threshold value. Thus the effect of pressure on reaction (10) is insignificant, in agreement with the experiments.

It is of interest to examine the statistical distribution of energy between the vinyl and the methyl radicals (the assumption that the propylene molecule undergoing decomposition is vibrationally excited but is in the ground electronic state is inherent in our RRKM calculations). The calculations indicate that stable vinyl radicals should be formed with a yield of 0.18 at 8.4 eV and 0.045 at 10.0 eV. The experimental values for $\phi(\text{C}_2\text{H}_3)$, determined as the difference between the yields of ethylene in the presence of 20% H_2S and in the presence of 6% O_2 , are approximately a factor of 2 lower than the calculated values (about 0.06 at 8.4 eV and 0.025 at 10.0 eV). Obviously the vinyl radical possesses excess energy over that due to the random distribution. Two explanations can be offered: first, the electronically excited state undergoes cleavage of the C—C bond; second, owing to the large amounts of excess energy, the dissociation following the rapid internal conversion to the ground electronic state may become so fast that it will occur prior to the statistical randomization over all accessible degrees of freedom, and since the π electrons of the double bond are expected to be excited by photon absorption the excess energy will be localized in the vinyl fragment. The yield for process (2) is estimated to be 0.26 at 8.4 eV and 0.20 at 10.0 eV.

4.6. *The formation of ethylene*

The ethylene yield depends strongly on pressure (Fig. 3). This product is formed partly as a result of the elimination of methylene as described above and partly from the dissociation of *n*-propyl radicals formed by the addition of hydrogen atoms to propylene. The contribution of the non-terminal addition is substantial (about 20%) in the case of hot hydrogen atoms [18]. The *n*-propyl radicals formed in such a process are energized, and their excess energy is the sum of their enthalpy of formation and the energy of the hydrogen atoms. The additional energy contributed by the hot hydrogen atoms enhances the rate constant for the decomposition of the *n*-propyl radical.

5. Conclusions

A fragmentation scheme for the photoexcited propylene molecule and approximate yields for the individual decomposition channels are shown in Table 2. The yields of the molecular products increase with increasing photon energy at the expense of the yields of products originating from simple rupture of the C—C or C—H bonds. The total yield is much less than unity: $\phi = 0.68$ at 8.4 eV and $\phi = 0.66$ at 10.0 eV. It should be remembered,

however, that the products of extensive destruction of the molecule (such as C_3H_3 and possibly others) are not accounted for in the material balance. The quantum yields for ionization should also be taken into account in the krypton photolysis.

TABLE 2

Primary fragmentation of the photoexcited propylene molecule at different photon energies^a

Process	Products	Quantum yield			
		6.7 eV	7.6 eV	8.4 eV	10.0 eV
(1)	$C_3H_5 + H$	0.41	0.565	} ≥ 0.34	≥ 0.34
(5)	$C_3H_4 + H_2$	0.02(?)	—		
(2)	$C_2H_3 + CH_3$	0.40	0.335	0.27	0.21
(3)	$C_2H_4 + CH_2$	0.03	0.02	0.04	0.06
(4)	$C_2H_2 + CH_4$	0.04	0.05(?)	≥ 0.03	≥ 0.05

^aThe data reported in the literature for photon energies of 6.7 eV [3] and 7.6 eV [4] are included for comparison.

Acknowledgments

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