

FLASH PHOTOLYSIS OF PROPENE: APPLICATION OF A GARTON LAMP AS A PHOTOLYSIS SOURCE OPERATING IN THE VACUUM ULTRA-VIOLET

D. R. A. CUFF, G. R. JOHNSTON* and D. PRICE

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT (Gt. Britain)

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Summary

A Garton lamp has been used to flash photolyze propene in the vacuum ultra-violet region. Analysis of the end-products obtained is reported and mechanisms for product formation discussed.

Introduction

A relatively recent development in the flash photolysis technique has been the extension of the photolyzing wavelength region into the vacuum ultra-violet. The associated technology involved has recently been reviewed [1].

One source of monitoring light used for such experiments is the Garton-type flash lamp [2] which emits high intensity light in the form of a continuum extending from the vacuum ultra-violet to the visible region. This paper describes the first application of a Garton-type flash tube as a photolysis source in the vacuum ultra-violet region. This application of the Garton lamp was investigated by undertaking a study of the flash photolysis of propene which has strong absorption bands below 190 nm [3]. Analysis of the end-products obtained in these experiments is reported and discussed with reference to previous studies of the photolysis of propene in a static system [4 - 8].

Experimental

The experimental arrangement is shown in Fig. 1. The Garton flash lamp (Chelsea Instruments Ltd) was operated with an air pressure of 5 N/m² and energized by a 10 μ F condenser charged to 8 kV. The lamp was fired by means of a pulse transformer connected to the trigger electrode, the flash

* Australian Defence Scientific Service, Dept. of Supply, Defence Standards Laboratories, Maribyrnong 3032 (Australia).

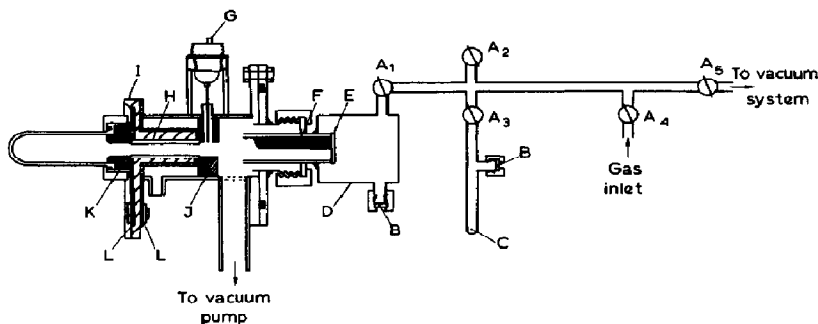


Fig. 1. Garton flash lamp and end-product analysis system. $A_1 - A_5$, Greaseless stopcocks; B, septum plug; C, 2 ml sampling tube; D, reaction vessel; E, LiF window; F, Pyrex capillaries; G, trigger electrode; H, ceramic capillary; I, epoxy resin insulation; J, negative electrode; K, positive electrode; L, transmission lines.

duration being $2 \mu\text{s}$ at $1/e$ peak height. Changing the gas filling, *e. g.* argon, helium, has no effect on the radiation emitted but decreases the opacity of the system in the vacuum ultra-violet region.

Deposition of debris, from the discharge, onto the lithium fluoride window between the lamp and the reaction vessel, necessitated frequent cleaning of the window [2b, 9]. Insertion of thin-walled Pyrex capillary tubes between the discharge tube and the window markedly reduced the frequency of cleaning without significantly reducing the intensity of the light entering the reaction cell.

The 25 ml reaction vessel was evacuated and filled in the conventional manner and flash photolyses of propene were performed in the pressure range $50 - 200 \text{ N/m}^2$. Samples of the end-products were then removed for gas chromatographic analysis in the following manner. The reaction cell was let up to atmospheric pressure with air, by piercing the septum plug with a hypodermic needle. After allowing sufficient time for adequate mixing of the gases, 0.5 ml samples were removed for analysis *via* the septum plug.

An alternative method, involving concentration of the reaction products prior to analysis, was used for the determination of products present in trace amounts. The reaction products were condensed into a 2 ml sampling tube (C, Fig. 1) which was cooled with liquid nitrogen. Stopcock A_3 was closed and the tube and contents were allowed to equilibrate to room temperature. The sampling tube was then let up to atmospheric pressure and samples were removed for analysis *via* the septum plug as described previously.

Gas chromatography

Gas chromatographic analyses were performed using a Perkin-Elmer 880 Gas Chromatograph equipped with flame ionization detection and a Kent Chromalog Peak Integrator. The hydrocarbon products were separated on matched 2 m (4 mm o.d.) stainless-steel columns packed with Squalane-Alumina H (3:97). Nitrogen, at a flow rate of 0.5 ml/s, was used as the carrier gas

and the columns were operated in the 60 - 80 °C region. The hydrocarbon products were identified by comparing their retention times with those of pure hydrocarbons and synthetic mixtures of known composition. Quantitative data were obtained by calibration of the gas chromatographic response to each hydrocarbon with reference to propene.

Materials

Propene and calibration gases were obtained from E. D. T. Supplies Ltd. Gas chromatographic analysis of the propene indicated the presence of ethylene (0.05%) and propane (0.045%) as impurities. These impurities were not removed prior to use but were allowed for in the calculation of the results.

Results

A comparison of the averaged data obtained in this work with those of previous studies of the steady state photolysis of propene are shown in Table 1. The product yields are expressed as a percentage of the total products, excluding hydrogen which was not quantitatively determined in our studies. Our results were found to be independent of the number of flashes, up to 30 flashes, and of the pressure of propene over the pressure range studied. Approximately 0.5% of the propene was decomposed per flash. If it is assumed that each molecule of propene decomposed absorbed one quantum, then at least 4×10^{15} photons were absorbed by the propene per flash. The lamp output is obviously greater than this since only that portion of the emitted light with wavelength below 190 nm was absorbed by the propene [3]. A carbon/hydrogen balance for the detected products is $C_3H_{5.6}$ and is independent of the number of flashes. The hydrogen deficit is presumed to be due to the undetermined free hydrogen generated by the production of unsaturated hydrocarbons. Some experiments were carried out with up to 12.5% added oxygen. These showed that oxygen reduced the overall hydrocarbon yield. The relative yield of acetylene decreased by a factor of three in the presence of oxygen whilst those of butene-1 and isobutane increased two- to three-fold. The relative quantities of the other products were essentially unaffected by the presence of oxygen.

Discussion

In flash photolytic decomposition studies much greater concentrations of free radicals or primary photochemical decomposition species are instantaneously generated than in static photolysis experiments. Consequently the results (Table 1) obtained in this study may be expected to reflect the increased importance of radical-radical reactions over radical-substrate reactions in direct contrast to the situation which is pertinent to the static photolysis studies.

TABLE 1

Hydrocarbon yields^a obtained by flash photolysis of propene. Recalculated^b data from previous static photolysis studies given for comparison

Reference	4	5	7	10 ^g	This work
Photolysis	Static	Static	Static	Static	Flash
Propene pressure (kN/m ²)	1.33	2.6	5.3	1.3	0.2
Conversion (%)	0.2	-	0.6	-	0.5
Wavelength (nm)	147	185	147	185	Continuum
Product:					
Methane	3.2	7.2	5.5	7.0	4.5
Ethane	6.8	6.2	5.1	5.0	9.5
Ethylene	11.3	9.9	7.7	9.0	18.1
Propane	6.8	10.7	13.4 ^c	7.0	6.1
Acetylene	35.5	10.7	28.3	8.0	28.5
Isobutane	10.7	7.9	16.8	10.0	7.4
Allene	6.8	2.1	17.8	2.0 ^c	14.0
Butene-1	3.3	13.9	3.0 ^d	17.0	2.9
<i>trans</i> -Butene-2	6.7	-	0.2	-	-
<i>cis</i> -Butene-2	1.8	-	0.1	-	0.1
Isobutylene	3.3	-	e	-	-
1,3-Butadiene	-	-	-	-	0.4
Methyl acetylene	6.8	4.3	f	h	8.4
Isopentane	-	-	0.2	-	0.2
n-Butane	-	-	1.7	-	-
2-Methylpentane	-	7.8	-	-	-
4-Methylpentane-1	-	19.3	-	16.0	-

^a Expressed as a percentage of the total hydrocarbon products.

^b Hydrogen yields excluded.

^c Includes methyl acetylene.

^d Includes isobutylene.

^e See butene-1.

^f See propane.

^g Percentages estimated from quantum yield data.

^h See allene.

The formation of large yields of ethylene and acetylene (~ 46% of total products) is in agreement with the relatively high quantum yield of 0.31 determined for primary process (1) by Borrell and co workers [8]:



Vinyl radicals formed in this reaction subsequently undergo the disproportionation reaction to yield the two products, *viz.*:

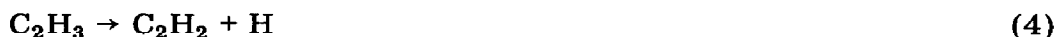


Studies involving the generation of vinyl radicals *via* flash photolytic conditions [10, 11] have indicated that the disproportionation reaction of vinyl radicals is of far greater importance than the recombination reaction:



Thus, the observation of small yields of 1,3-butadiene in our experiments is further evidence for the formation of large amounts of vinyl radicals.

If it is considered that reaction (2) is the major route to the formation of acetylene and ethylene as a result of primary process (1), then approximately equal yields of the two products should be observed. The results in Table 1 show that the acetylene yield is about 1.6 times the ethylene yield and this may be mainly attributed to the fragmentation of vinyl radicals which enhances the relative acetylene yield:



This reaction has been postulated by several authors [5, 7, 10] and recent experiments in this laboratory, on the generation of vinyl radicals by flash photolysis [11], have also indicated that the acetylene yield is about 1.5 times the ethylene yield in support of reaction (4).

The enhanced formation of ethane in the flash photochemical system (Table 1) compared to the static photolysis results may also be considered as a reflection of the generation of large concentrations of methyl radicals which undergo the recombination reaction:

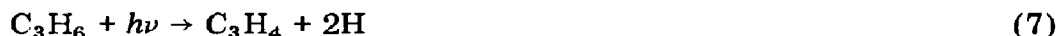


This reaction is probably the sole route to ethane formation as indicated by Becker *et al.* [4].

In their static photolysis study at 147 nm, Becker *et al.* [4] proposed the molecular elimination of hydrogen as a second major primary process:



Alternatively C_3H_4 formation (*i. e.* methylacetylene + allene) has been attributed to the alternative primary process [7]:



which is considered to make an additional contribution to reaction (6) although Borrell has shown that the quantum yield for reaction (7) at 185 nm is only 0.02. Assuming that all of the reaction products from the flash photodecomposition of propene have been indentified in this investigation, then the carbon-hydrogen balance of $\text{C}_3\text{H}_{5.6}$ indicates that the yield of molecular hydrogen is 3.3% of the products whilst the total C_3H_4 yield is ~ 22.4%. Clearly reaction (6) is not of major importance in the flash photolytic decomposition. The alternative routes to allene, *via* reaction (7) in either one or two stages:



may consequently lead to the formation of an excited C_3H_4 moiety which rearranges to form allene or methylacetylene *viz.*:



At 185 nm, reaction (8) is considered to be the major primary process in the photolysis of propene [8], the quantum yield being 0.41. However, as the wavelength of the incident absorbed radiation is decreased the amount of vibrational degraded photochemical energy which is carried away in the C_3H_5 fragment may well favour the fragmentation reaction (9), such that effectively reaction (7) may be a major primary process at lower wavelengths. Alternative routes to the formation of C_3H_4 may occur as a result of radical reactions with the allyl radical formed in reaction (8) *e. g.*



Further evidence for the presence of allyl radicals in the system is indicated by the formation of butene-1 which is attributed to the reaction with methyl radicals [5, 7, 8]



The hydrogen atoms formed in reactions (4) and (7) - (9) will most probably be scavenged by propene molecules *viz.*:



as indicated by previous investigators. These C_3H_7 radicals are responsible for the appreciable yields of isobutane formed in the reaction system *via* recombination with methyl radicals [8]:



The lack of involvement of ethyl radicals in our system is well demonstrated by the absence of n-butane in the hydrocarbon products. The hydrogen atoms may also combine with methyl radicals to produce methane [4].

The generation of C_3H_7 radicals is probably also the precursor for propene formation *via* the disproportionation reaction:



although it is surprising that traces of the recombination product C_6H_{14} were not detected [8].

As large concentrations of allyl radicals are indicated by the total C_3H_4 and the low value of the molecular hydrogen yield, a further source of propene may well be the reaction between allyl and propyl radicals:



In the static photolysis investigations [5 - 7], a further primary process:



has been considered to be important. In these investigations, CH_2 radicals were considered to react with propene to form "activated" methylcyclopropane which could be deactivated or alternatively isomerized to produce a mixture of butene isomers. The absence of methyl cyclopropane, isobutylene and significant amounts of butene-2 isomers under the present conditions, indicates that reaction (19) is not important in the flash photolysis of propene.

In conclusion it may be stated that the flash photolysis of propene results in the generation of large concentrations of CH_3 , C_2H_3 and C_3H_5 radicals together with H atoms. The observed reaction products are consistent with radical-radical reactions of these species plus the hydrogen scavenging reaction by the parent molecule which generates propyl radicals which further react with the photochemically produced free radical species.

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