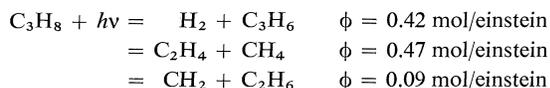# The Photolysis of Propane at 123.6 nm
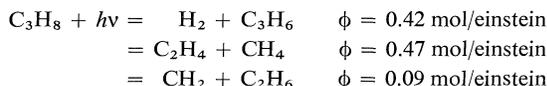
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Propane has been photolyzed at 123.6 nm, in the presence and absence of O_2, at pressures from 2–380 Torr. All products except ethane exhibit a pressure dependence which is attributed to secondary dissociation of the primary fragments, H_2, CH_4, C_2H_4, and C_3H_6. It is assumed that the range of energies carried by these fragments is broad enough that some will not dissociate even at low pressures while others of the same species cannot be stabilized even at high pressures. An internally consistent analysis rationalizes the entire observed product spectrum, with some uncertainty arising from an ambiguity in the source of acetylene. The following primary quantum yields, prior to secondary dissociation, are estimated:

$$
\begin{aligned}
C_3H_8 + h\nu = \quad & H_2 + C_3H_6 & \phi &= 0.42 \text{ mol/einstein} \\
= \quad & C_2H_4 + CH_4 & \phi &= 0.47 \text{ mol/einstein} \\
= \quad & CH_2 + C_2H_6 & \phi &= 0.09 \text{ mol/einstein}
\end{aligned}
$$

Le propane a été soumis à une photolyse à 123.6 nm, en présence et en absence de O_2, à des pressions de 2–380 Torr. Tous les produits, excepté l'éthane, manifestent une dépendance, par rapport à la pression, laquelle est attribuée à la dissociation secondaire des fragments primaires, H_2, CH_4, C_2H_4, et C_3H_6. On admet que l'étendue des énergies entraînées par ces fragments est suffisament large de sorte que certains ne se dissocieront pas même à de faibles pressions alors que d'autres de la même espèce ne peuvent être stabilisés même à de hautes pressions. Une analyse intérieurement cohérente coordonne le spectre obtenu des produits entièrement, avec certaines incertitudes provenant d'une ambiguité dans la source d'acétylène. Les premiers rendements quantiques qui suivent, précédant la seconde dissociation, ont été estimés:

$$
\begin{aligned}
C_3H_8 + h\nu = \quad & H_2 + C_3H_6 & \phi &= 0.42 \text{ mol/einstein} \\
= \quad & C_2H_4 + CH_4 & \phi &= 0.47 \text{ mol/einstein} \\
= \quad & CH_2 + C_2H_6 & \phi &= 0.09 \text{ mol/einstein}
\end{aligned}
$$

[Traduit par le journal]

Introduction

The photochemistry of propane has been studied a good deal in the last decade (1–14) and the primary photolytic steps have been largely determined. Isotopic studies have identified precisely the origins of fragments within the molecule. Notably lacking, however, has been a measurement of quantum yields for each primary process. Two reasons for this are the uncertain actinometry in the vacuum u.v. and the extensive secondary reactions which make measurement of the yields of primary processes difficult.

While we have not improved our absolute actinometry, we have developed a two-windowed lamp which allows direct comparison of yields to those of an external standard. Thus, while absolute quantum yields may not be determined directly, yields relative to the standard may be, and the direction and magnitude of the changes in product yields may now be followed as a function of experimental conditions.

Secondary reactions are identified from the pressure dependence of all products. We sum the yields of these reactions in an attempt to estimate the overall quantum yield of the various primary processes. Yields of free radicals are obtained directly from radical combination product yields.

Experimental

Materials

Phillips research grade propane was used. After purification by gas chromatography using a silica gel column, impurity levels were below 5 p.p.m. The purified propane was dried over Drierite and vacuum distilled to a storage bulb. Linde C.P. oxygen was used without further purification.

Lamps and Cells

A krypton resonance lamp, similar to those described by Gorden *et al.* (15), was used for the photolysis. The lamp was filled on a mercury free vacuum line capable of achieving pressures less than 1×10^{-6} Torr (Veeco discharge gauge) and was gettered with a titanium gettering assembly. The chromatic purity was greater than 98%

in the region between 105 and 165 nm (McPherson 0.3 m vacuum monochromator). MgF_2 windows were attached to the lamp with Ag–AgCl seals. MgF_2 was chosen because it has a very weak dependence of its transmission properties on temperature (16). Moreover, MgF_2 is apparently less affected by irradiation history than LiF (17). Both properties were very important, as constant window properties were required for the successful use of the two-windowed lamp described in the next paragraph. The light intensity, calculated from the yield of acetylene from the photolysis of ethylene (18), was $1.7 \pm 0.1 \times 10^{14}$ quanta/s.

A "T"-shaped lamp with windows at each end of the crossbar was used to study the photolysis. The lamp was powered by a microwave generator through a tuned Evenson cavity placed on the base of the "T" nearest the crossbar. Each window looked into individual sample cells. Each cell had a 2.5 cm i.d. with a path length of 2.5 cm. The ratio of light intensities entering the two cells was determined by measuring the relative amounts of products formed in the photolysis of equal pressures of oxygen-scavenged propane. This ratio was constant throughout this work. Thus, one cell with constant sample conditions was used as an external standard to which runs made in the other cell could be compared.

The yield of methane from the photolysis of oxygen-scavenged propane at a pressure of 20 Torr was used as the external standard. The rate of formation of methane in the standard was found to be constant over the range 0.05–4% decomposition of parent to product (2).

All scavenged photolyses were conducted with 5% oxygen added to intercept free radicals and triplet methylene. No products which could be ascribed to these species were found. Except for conversion dependence runs, photolysis was carried to 0.1% conversion of parent to product. All analyses were done by gas chromatography (FID) on a 25 ft × 1/4 in. o.d., 35% (w/w) squalene column for the products containing four carbon atoms or less and a 25 ft × 1/4 in. o.d., 3% (w/w) squalene column for the product containing five or six carbons. Both columns were maintained at room temperature.

Results

Photolysis products observed in the presence of 5% oxygen at 123.6 nm include hydrogen, methane, ethane, ethylene, acetylene, propylene, and iso- and normal butane. Very small amounts of doubly unsaturated three-carbon molecules and butenes may also be observed under proper conditions. A summary of major product yields in the presence of oxygen at pressures from 2–380 Torr is given in Table 1.

As ethane was the only product found to be pressure invariant over the range investigated, all yields in Table 1 are normalized to the yield of ethane. Ethane yield serves as an internal standard and was compared directly to our external standard. The quantum yield of 0.086 reported for ethane in Table 1 was determined relative to the yield of acetylene from the

TABLE 1. Quantum yield* of nonscavengeable products in the photolysis of propane at 123.6 nm as a function of pressure

Product	Pressure (Torr)					
	2	10	20	50	100	380
CH_4	0.167	0.165	0.163	0.160	0.159	0.152
C_2H_2	0.151	0.140	0.135	0.122	0.100	0.092
C_2H_4	0.423	0.427	0.431	0.438	0.448	0.448
C_2H_6	0.086	0.086	0.086	0.086	0.086	0.086
C_3H_6	0.237	0.250	0.248	0.263	0.259	0.283

*Determined relative to the quantum yield of acetylene from ethylene equal to 0.90 at 123.6 nm.

photolysis of ethylene at the same wavelength, 123.6 nm, assumed equal to 0.90, as suggested by Meisels (18).[1] We make no claims for the validity of this assumption and use this number primarily for convenience. The sum of the quantum yields for the proposed primary processes in propane is near unity when the above assumption is made.

Acetylene exhibits a striking pressure dependence. The acetylene quantum yield drops from 0.151 at 2 Torr to 0.092 at 380 Torr. The quantum yield of methane also decreases with pressure. Ethylene and propylene quantum yields increase with increasing pressure.

It is relevant to point out, in light of the recent work of Tanaka and co-workers (1), that the sum of the acetylene and ethylene yields is not independent of pressure. The difference between the ethylene yield at 380 and 2 Torr is only 50% of the difference between acetylene yields at the same pressures.

Table 2 compares the yields of products in the presence and absence of oxygen at 380 Torr. The multitude of products ascribable to radical combination in the latter case attests dramatically to the radical intercepting ability of oxygen at the levels used. Acetylene yields were not affected by the presence of oxygen. Thus, a convenient internal standard is available for comparing yields in the presence and absence of oxygen.

One may compute quantum yields of each radical relative to isopropyl by correcting the appropriate combination product for disproportionation. These products are isobutane (methyl-isopropyl) isopentane (ethyl-isopropyl),

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[1]In this paper, the quantum yield of C_2H_2 from C_2H_4 is measured as 0.90.

TABLE 2. Quantum yield of all products observed in the photolysis of propane at 380 Torr

Product	No O_2	O_2, 5%	Product	No O_2
CH_4	0.181	0.152	1-Pentene	0.003
C_2H_2	0.092	0.092	Isopentane	0.029
C_2H_4	0.445	0.448	n-Pentane	0.006
C_2H_6	0.167	0.086	4-Methyl-1-pentene	0.026
C_3H_6	0.328	0.283	2,4-Dimethylbutane	0.080
1-Butene	0.020	—	2-Methylpentane	0.029
Isobutane	0.151	0.015	1,5-Hexatriene	trace
n-Butane	0.063	0.036	1-Hexene	0.005
3-Methyl-1-butene	0.003	—	n-Hexane	0.004

TABLE 3. Quantum yield of free radicals in the photolysis of propane at 380 Torr

Radical	Base product	$1 + k_d/k_c$*	Yield relative to isopropyl radical	Quantum yield of radical
Methyl	Isobutane†	1.22	0.616	0.339
Vinyl	Isopentene	1.2	0.010	0.006
Ethyl	Isopentane	1.27	0.126	0.069
Allyl	4-Methyl-1-pentene	1.3	0.124	0.068
i-Propyl	2,4-Dimethylbutane	1.68 ($\times 2$)	1.0	0.551
n-Propyl	2-Methylpentane	1.40	0.167	0.093

*Values selected from ref. 19.
†Corrected for isobutane formed by CH_2 insertion.

isopentene (vinyl-isopropyl), 4-methyl-1-pentene (allyl-isopropyl), 2-methylpentane (n-propyl-isopropyl), and 2,4-dimethylbutane (isopropyl-isopropyl). The sum of all products involving isopropyl radical corrected for disproportionation provides its quantum yield, 0.551. The quantum yields for all other radicals are then computed by multiplying the radical yields relative to isopropyl times the quantum yield of isopropyl radical (see Table 3).

Vinyl and allyl radicals show striking pressure dependence, both decrease with increasing pressure. The pressure dependence of allyl radical has been discussed in an earlier communication (3). It clearly results from a secondary reaction. Vinyl radical behaves similarly.

Figure 1 demonstrates the conversion dependence of the radical products i-pentane and 2,3-dimethylbutane over the range of 0.06% to 0.87% conversion (% conversion = (products)/ (propane)$_0$ × 100). 2,3-Dimethylbutane, the product of isopropyl radical combination, increases by approximately 30% of its lowest observed yield in this range. i-Pentane increases by 100% over this same range. The more striking conversion dependence of i-pentane must arise

from the conversion dependence of ethyl radical production. This result is not unanticipated in a system where both hydrogen atoms and ethylene are produced. The ratio of concentration of ethylene to propane ranges from 6×10^{-4} to 8.7×10^{-3} at these conversions. Since the ratio of the rate constants for H addition to ethylene relative to H abstraction from propane (19) is approximately 5×10^2, ethylene may compete effectively with propane for hydrogen atoms. As suggested in the discussion, the addition of H atoms to ethylene appears to provide the only "important" source of ethyl radicals as far as computing overall yields of products is concerned.

Discussion

Of many possible primary processes in the photolysis of propane, only the following have been directly demonstrated to exist (1, 9, 12, 13)

[1] $C_3H_8 + h\nu = C_3H_6 + H_2$

[2] $C_3H_8 + h\nu = C_2H_4 + CH_4$

[3] $C_3H_8 + h\nu = CH_2 + C_2H_6$
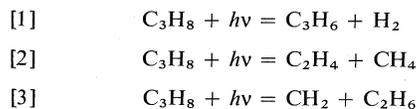
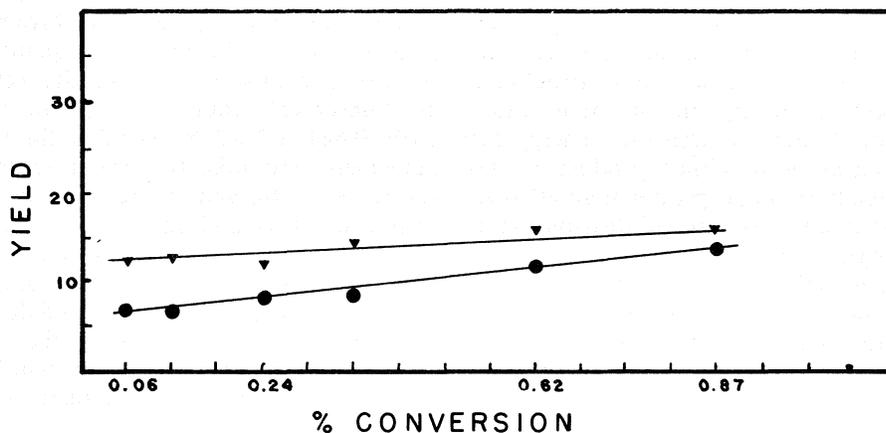The inequity of yields between hydrogen and propylene, and methane and ethylene, as well as

FIG. 1.   The yield of isopentane, ●, in arbitrary units, as a function of percent conversion of propane to photolysis products. The actual quantum yields of isopentane at the highest and lowest conversions are 0.018 and 0.007 mol/einstein, respectively. The data were obtained in an oxygen free system of 20 Torr total pressure. For contrast the conversion dependence of 2,3-dimethylbutane is also plotted, ▼.
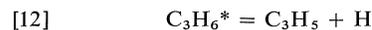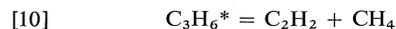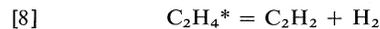
the appearance of acetylene, allene, and a number of products of a higher molecular weight than propane, require that other processes occur than those written as eqs. 1–3. Whether these other processes are subsequent to reactions 1–3, where any one of the fragments produced may further dissociate; or whether these other processes correspond to distinctly different processes such as reactions 4 and 5 has not been conclusively demonstrated.

[4] $C_3H_8 + h\nu = C_3H_7 + H$

[5] $C_3H_8 + h\nu = C_2H_5 + CH_3$
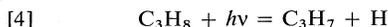
Photolysis of propane at 123.6 nm supplies enough energy that subsequent dissociation of any of the polyatomic fragments listed is energetically possible. Furthermore, secondary products from the dissociation of the fragments of reaction 1 are indistinguishable from the secondary products from the dissociation of fragments of reaction 4 if both occur at such a rate that they may not be quenched simply by increasing sample pressure. For example, $C_3H_6 +$ H + H may result from propyl radical dissociation in reaction 4 or from H_2 dissociation in reaction 1. The same total energy is available to each sequence as both would be initiated by a photon from the same source. It has also been demonstrated that energy is not necessarily statistically partitioned in a primary process in the photolysis of propane (20). Therefore, one cannot invoke the usual arguments regarding the

number of oscillators "available" to the energy deposited by the incoming photon.

Since very rapid secondary reactions cannot be distinguished from primary processes, we will *arbitrarily* view the mechanism for the photolysis of propane as follows. The primary processes in the photolysis of propane can be generally classified as reactions 1–3. Each fragment in the primary process is generated with a broad distribution of energy. This implies that each primary fragment will have species falling into three different reactivity categories: low energy species where no further dissociation can occur; middle energy species where there will be a competition between dissociation and collisional deactivation over the pressure range studied; and high energy species which will always dissociate. "Secondary" unimolecular dissociations which must be considered are then:

[6] $H_2^* = 2H$

[7] $CH_4^* = CH_3 + H$

[8] $C_2H_4^* = C_2H_2 + H_2$

[9] $C_2H_4^* = C_2H_3 + H$

[10] $C_3H_6^* = C_2H_2 + CH_4$

[11] $C_3H_6^* = C_3H_4 + H_2$
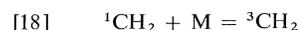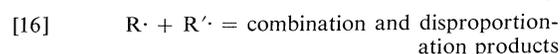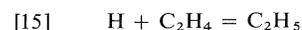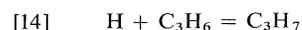
[12] $C_3H_6^* = C_3H_5 + H$

The asterisk indicates energy in excess of the activation energy of that reaction.

Secondary dissociations of the fragments of eq. 3 are not included since ethane did not show

a pressure dependence. This lack of pressure dependence of the yield of ethane is reasonable in the framework of our assumptions. Reaction 3 is considerably more endothermic than either reaction 1 or 2, and the activation energy for further dissociation of either product of reaction 3 is relatively high (greater than 80 kcal/mol). The assumption of a broad distribution of energies suggests that some ethane molecules indeed have enough energy to further dissociate, but the fraction of ethanes having this energy would be too small for us to detect in the pressure range we have studied (20). (The maximum internal energy in the distribution of energies for any of the fragments is, of course, the energy of the photon, 10 eV, less the endothermicity of the reaction and less energy distributed to external degrees of freedom.) On the other hand, because of the large energies available and the relatively small endothermicities of [1] and [2], it may occur that high pressure limits to yields of primary products lose their meaning. Other processes, such as cage effects, may become important before pressures become sufficiently high to quench all secondary dissociation of propylene or ethylene.

The following equations show the most probable reactions of the intermediates generated in reactions 3–12.

[13] $H + C_3H_8 = C_3H_7 + H_2$

[14] $H + C_3H_6 = C_3H_7$

[15] $H + C_2H_4 = C_2H_5$

[16] $R\cdot + R'\cdot$ = combination and disproportionation products

[17] $^1CH_2 + C_3H_8 = C_4H_{10}$

[18] $^1CH_2 + M = {}^3CH_2$

Reactions 17 and 18 have been discussed for this system in a recent series of papers (21) and we will not discuss them in detail here. Reaction 17 does make a significant contribution to the overall butane yield, however, and this contribution must be considered when assigning radical yields based on observed butane. Reaction 16 is assumed to be the only important reaction of all free radicals except H and the CH_2 discussed above.

Relative rate constants for reactions 13–15 are available in the literature (19). At 380 Torr and 0.1% final conversion of propane to produce the relative yields of reactions [15]/[14] + [13]

(ethyl to total propyl) is calculated from reported rate constants to be 1:9.9. The quantum yields of radicals computed in the results section show an "observed" ratio of ethyl to propyl of 0.069:0.644 or 1:9.3. We consider this to be good agreement and take this result to imply that reactions 13, 14, and 15 are the only important source of ethyl and propyl radicals. Thus, if reactions 4 and 5 are actually primary processes, the polyatomic radical fragments are not substantially stabilized at 380 Torr and do not make an important contribution to the ethyl and propyl radical yields. Similar conclusions have been reached by previous investigators (1, 5, 11[2]).

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[2]Ausloos and Lias (11) would agree that stable propyl radicals are formed only in very low yields in a primary process. However, they report a yield of C_2D_5H relative to methane of 0.27 for the photolysis of 29.4 Torr of C_3D_8 in the presence of 12.9% H_2S. They interpret this product as arising from the scavenging of C_2D_5 by H_2S. Obtaining a quantum yield of C_2D_5H by comparing the relative yield to the measured quantum yield of methane in our system at a similar pressure, this implies a quantum yield of primary ethyl radicals (ostensibly from reaction 5) of 0.04 or greater than 50% of our total measured ethyl radical yield. If it were indeed the case that the C_2D_5H did arise from ethyl radicals produced in a primary process, our conclusion that such radicals make a negligible contribution to the overall ethyl radical yield would obviously be false. The simple consideration of the appropriate energetics presented below, however, shows how unlikely it is that the measured C_2D_5H could actually arise from ethyl radicals produced in a process such as reaction 5. One may compute an upper limit to the total possible quantum yield of ethyl radicals produced in reaction 5 by summing the quantum yields of acetylene, ethylene and all pentanes (measured at 30 Torr in the absence of O_2) and subtracting the yield of "molecular" methane (the quantum yield of methane in the presence of oxygen) to be 0.33. At a similar pressure the measured quantum yield of C_2D_5H has already been computed to be 0.04. Of the total possible ethyl radicals, then, 12% are stabilized at 30 Torr and 88% decompose. This is obviously a limiting case since the total ethyl radical yield computed is an upper limit on the actual possible yield. In the notation of Rabinovitch and Setser (22), $D/S = 0.73$. To obtain such a ratio for the number of ethyl radicals decomposing to the number collisionally stabilized requires that greater than 80% of the ethyl radicals produced in reaction 5 carry as vibrational energy 50 kcal or less. The reader convinces himself of the veracity of this last statement using the energy dependence of the microscopic rate constant curve presented by Rabinovitch and Setser, a critical energy of decomposition of ethyl radicals of 39.8 kcal/mol, and a specific deactivation rate of $2 \times 10^8 \, s^{-1}$ (at 30 Torr). The total energy deposited in the photolyzed propane is 231 kcal. The endothermicity of reaction 5 is 84 kcal. The energy remaining to be partitioned among the various degrees of

As a means of organizing the available data we consider all photolysis products to arise from primary processes 1, 2, and 3 and secondary reactions 6–18. The contribution of each primary process will be assessed by independently considering each of the two fragments for each process 1–3. Agreement between these individual assessments will be interpreted as evidence for the completeness of our analysis.

To the yield of molecular hydrogen in the presence of a radical scavenger must be added the hydrogen which formally does not appear as H_2 because of reaction 6. This hydrogen does not appear because it reacts as H atoms. The total quantum yield of H atoms may be determined by summing the yields of propyl and ethyl radicals because only reactions 13–15 will be important H atom reactions in this system. From the total yield of H atoms must be subtracted those which arise from reactions 7, 9, and 12 as these do not represent a contribution from primary process 1. The total H atom quantum yield attributable to process 1 is then halved and added to the observed H_2 yield. Finally, H_2 arising from reactions 8 and 11 must be subtracted from the total. This last step places uncertainties on the quantum yield of reaction 1 as calculated from the hydrogen yield. Experimental difficulties prevented us from routinely determining the quantum yield of C_3H_4, reaction 11. However, this yield is small. The major uncertainty arises in determining what fraction of the observed acetylene arises from reaction 8 and what fraction arises from reaction 10. This could possibly be determined from an isotopic analysis of acetylenes produced from selectively labeled propanes; however, such an analysis has not been done at present. Thus, our estimate of the overall quantum yield for reaction 1 based on hydrogen originating products must remain in uncertainty by the observed acetylene yield. This

freedom of the product methyl and ethyl radicals is 147 kcal. It would be an intriguing process indeed that partitioned only 1/3 of this energy to the internal degrees of freedom of the more complex ethyl radical while the remaining 100 or so kcal went into the methyl radical and external degrees of freedom. If such considerations have any validity, it is difficult to believe that the observed C_2D_5H has primary ethyl radicals as its source, even though no obvious alternative exists. The strong conversion dependence of products arising from ethyl radical as a precursor, pentanes, reinforces our conclusion that reaction 15 is the most important source of stable ethyl radical in this system.

estimate, then, has the range of 0.403–0.495 mol/einstein.

The quantum yield of reaction 1 may also be estimated by examining the propylene related fragments. To the quantum yield of propylene observed in a scavenged system one must add the yields of reactions 10, 11, and 12, all of which remove propylene in secondary unimolecular reactions. Reaction 14 need not be considered since it will not occur in a scavenged system. The same uncertainty in assigning the yield of reaction 10 occurs as was discussed in the previous paragraph. We are thus left with the estimate of the quantum yield of reaction 1 of 0.351–0.443 mol/einstein based on propylene related product yields.

Similar analyses may be accomplished for the methane and ethylene fragments expected in primary process 2. To the observed methane yield must be added the yield of methyl radicals formed in reaction 7. The methane produced in reaction 10 must be subtracted from this total. As explained above the yield of methane from reaction 10 cannot be directly determined from presently available data. Thus we are left with the range of 0.399–0.491 mol/einstein as the quantum yield of primary process 2 based on methane related reactions. To the quantum yield of ethylene observed in a scavenged system must be added the yield of acetylene resulting from reaction 8. The same uncertainty regarding the relative importance of reactions 8 and 10 still plagues us here. A range of quantum yields of 0.448–0.540 mol/einstein is thus obtained for process 2 from ethylene related reactions.

Primary process 3 is determined in a straightforward fashion. It is simply the observed ethane yield in a scavenged sample. Since ethane does not exhibit a pressure dependence, no secondary reactions of ethane need be considered. The quantum yield of reaction 3 is thus 0.086 mol/einstein. The sum of the butane yields in an oxygen scavenged system must be less than this value since all methylenes produced in reaction 3 do not survive as singlets to undergo reaction 17. The observed butane yield is 0.051 mol/einstein. The calculations of the last three paragraphs are summarized in Tables 4 and 5, where the appropriate numbers are given.

The proposed reaction scheme, [1]–[3], [6]–[18], is seen in the previous paragraphs to lead to internally consistent results. The calculated quantum yield of each of the primary processes

TABLE 4. Assessment of the yields of important secondary reactions at 380 Torr and 0.1 % conversion

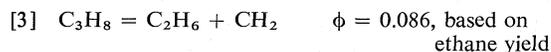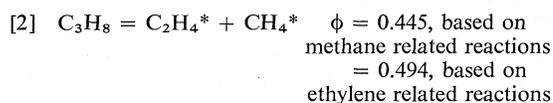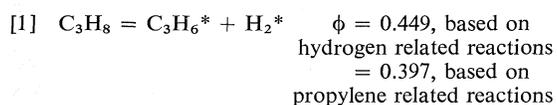| Reaction	Product measured	ϕ 380 Torr
[7]	CH_3	0.339
[8] + [10]	C_2H_2	0.092
[9]	C_2H_3	0.006
[11]	C_3H_4	Not determined
[12]	C_3H_5	0.068
[13] + [14]	$C_3H_7\cdot$	0.644
[15]	C_2H_5	0.069
[17]	C_4H_{10}	0.051
[6] ϕ_H	$(C_3H_7\cdot + C_2H_5 - C_3H_5 - C_2H_3 - CH_3)$	0.299

TABLE 5. Summary of computation of quantum yield of primary processes for the photolysis of propane

Primary reaction	Fragment considered	Important yields and secondary reactions	Quantum yield
[1]	H_2	$H_2^{*,\dagger} + [6] - [8] - [11]$	0.403–0.495
	C_3H_6	$C_3H_6^* + [10] + [11] + [12]$	0.351–0.443
[2]	CH_4	$CH_4^* + [7] - [10]$	0.399–0.491
	C_2H_4	$C_2H_4^* + [8]$	0.448–0.540
[3]	C_2H_6	$C_2H_6^*$	0.086

*Quantum yield of this product in a scavenged system at 380 Torr.
†Yield estimated from data in refs. 9 and 13.

1–3 is found to be similar when calculated by considering each of its fragments individually. The major uncertainty which pervades may be traced to the acetylene forming reactions. Although we do not have direct evidence for the relative importance of reactions 8 and 10, we may speculate as to the relative importance of these two reactions. The increase in ethylene over the pressure range studied, Table 1, accounts for only 50% of the observed decrease in acetylene yield. If we assume that both reactions 8 and 10 are quenched at similar rates, then we may estimate that the observed acetylene receives approximately equal contributions from reactions 8 and 10.

If we estimate that reaction 8 contributes 50% of the observed acetylene yield at 380 Torr and reaction 10 contributes about 50%, then the following quantum yields are determined for the three postulated primary processes.

[1] $C_3H_8 = C_3H_6^* + H_2^*$ $\phi = 0.449$, based on hydrogen related reactions
= 0.397, based on propylene related reactions

[2] $C_3H_8 = C_2H_4^* + CH_4^*$ $\phi = 0.445$, based on methane related reactions
= 0.494, based on ethylene related reactions

[3] $C_3H_8 = C_2H_6 + CH_2$ $\phi = 0.086$, based on ethane yield

In each case the quantum yields based on individual determinations of the two fragments associated with each process overlap with a $\leqslant 5\%$ uncertainty. Considering the rather complex analysis necessary, this is most gratifying. Summing the average value for each primary process gives a total quantum yield for disappearance of propane of 0.979 mol/einstein.

Summary

Using an experimental system in which it is possible to determine quantum yields relative to an external standard for all products in the photolysis of propane, we found that all molecules observed in a scavenged system varied with pressure except ethane. This pressure dependence of product yields strongly suggests that second-

ary reactions involving primary fragments are important in determining the observed product distribution. We have postulated a scheme in which three primary processes, reactions 1–3, are the source of all unimolecularly reactive species. Secondary dissociations of H_2, C_3H_6, CH_4, and C_2H_4 provide all other reactive intermediates. The major difficulty in determining the quantum yields of each of the three primary processes lies in assessing the relative contributions to the observed acetylene yield from reactions 8 and 10, the secondary dissociation of ethylene and propylene, respectively. If indirect evidence is used to determine the relative contributions of each of these reactions, one estimates the following quantum yields for the primary processes: $\phi_1 = 0.42$; $\phi_2 = 0.47$; $\phi_3 = 0.09$. This corresponds to 43% of total primary reaction giving propylene plus hydrogen, 48% giving ethylene plus methane, and 9% giving ethane plus methylene.

Reactions 4 and 5 may be primary processes, but it has been concluded here and by previous investigators that the propyl and ethyl radicals produced in these reactions continue to dissociate by elimination of an H atom. Such sequences are not experimentally distinguishable from reaction 1 followed by 6 and reaction 2 followed by 7 and thus have not been explicitly considered. Their omission has not led to any glaring inconsistencies in our analysis.

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