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PRIMARY PROCESSES IN THE PHOTOLYSIS OF PROPANE: THE USE OF HI AS A RADICAL SCAVENGER

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SUMMARY

The photolysis of C_3D_8 has been investigated with 8.4, 10.0, and 11.6–11.8 eV photons, using HI to scavenge the radicals through the reaction: $R_D + HI \rightarrow R_DH + I$ (where R_D is a fully deuterated alkyl or alkenyl radical). Comparison of the results with the results of analogous experiments using H_2S as a scavenger leads to the conclusion that HI is a more efficient radical scavenger than H_2S. The results are discussed with particular emphasis on determining whether the primary processes include direct C–C and C–H bond cleavage. An examination of the effects of HI concentration, conversion, and pressure on the yield of ethyl radicals intercepted indicates that the ethyl radicals are formed in the primary process: $C_3D_8^* \rightarrow C_2D_5 + CD_3$. It is noted that the relative importances of this process and the other primary processes involving breaking of the C–C bond ($C_3D_8^* \rightarrow CD_4 + C_2D_4$ and $C_3D_8^* \rightarrow C_2D_6 + CD_2$) do not change with energy, and it is thus suggested that they all occur from an excitation in the C–C bond, and that RRKM considerations relating to equipartition of energy are not applicable to the dissociations of electronically excited alkanes. It is pointed out that, as in the photolysis of ethane, the dissociation leading to the formation of a molecule of hydrogen (deuterium) ($C_3D_8^* \rightarrow D_2 + C_3D_6$), which apparently occurs as a result of an excitation in a C–H (C–D) bond, predominates in the 8.4 eV photolysis, but diminishes sharply in importance with respect to the C–C bond cleavage processes when the energy is increased. The insertion of methylene into a primary C–H bond of C_3H_8 to give n-butane is examined, and information concerning the internal energy of the CH_2 species is derived and discussed in terms of the primary dissociation of propane.

INTRODUCTION

The photolysis of propane has been investigated many times with 8.4, 10.0, and 11.6–11.8 eV photons (the xenon, krypton, and argon resonance lines)[1,2].

The quantum yields of the products have been determined, and the overall photolytic mechanism leading to the formation of these products has been explored through experiments utilizing deuterium labelling. Although several of the primary processes occurring in the photolysis of propane are firmly established, a recent study[2h] has called into question the occurrence of primary processes involving direct C–C or C–H (C–D) bond cleavage:

$$C_3D_8^* \rightarrow C_3D_7 + D \qquad (1)$$

$$\rightarrow C_2D_5 + CD_3 \qquad (2)$$

A complete understanding of all the details of the photolytic mechanism requires an accurate determination of the yields of both the molecular products and the free radicals produced in primary and secondary dissociative processes. In the case of propane, the determination of radical yields has been based on a measurement of product yields in the absence of a radical scavenger, interpreted through known combination/disproportionation ratios for the various radicals[2h], as well as on the yields of partially deuterated products produced in C_3D_8/H_2S mixtures[2a,3] through the radical-scavenging reaction:

$$H_2S + R_D \rightarrow R_DH + HS \qquad (3)$$

where R_D is a D atom or a fully deuterated alkyl or alkenyl radical.

The purpose of this paper is two-fold. First, we want to ascertain the efficacy of HI as a free radical scavenger in a system which has already been fairly well characterized. Like H_2S, HI interacts with alkyl and alkenyl radicals to give neutral hydrocarbon products whose yields can be readily determined, especially if deuteration is used:

$$HI + R_D \rightarrow R_DH + I \qquad (4)$$

Secondly, this paper represents an attempt to reaffirm certain details of the primary dissociative processes of excited propane molecules originally proposed in earlier studies from this laboratory.

The results obtained here will demonstrate that HI is a more effective free radical and H(D) atom scavenger than H_2S, and will also present evidence that direct bond cleavage process (2) does occur in excited propane.

EXPERIMENTAL PROCEDURE

The experimental procedure is identical to that described in recent studies from this laboratory[4,5].

A gradual decrease in the transmission of the LiF window was noted after each experiment. The actual drop in intensity depended on the wavelength, and the composition of the mixture, the total pressure and the number of photons passing through the window. In the course of this study the minimum decrease in light flux was of the order of 1% (147 nm, 5.5 Torr C_3D_8, 0.2 Torr HI, 10^{16} photons transmitted through window). The maximum decrease in transmission was 12% (104.8–106.7 nm, 317 Torr C_3D_8, 12.7 Torr HI, 10^{17} photons transmitted through window). The output of the xenon and krypton resonance lamps could be restored to their original value by wiping the window with CCl_4. In the case of the argon resonance experiments F-center formation contribute to the decrease in transmission, so that bleaching in the manner suggested before[6] was necessary in order to regain full transmission.

The quantum yields given in the Tables are based on the ion current intensity before and after the experiment[4,6]. The accuracy of the quantum yields reported in this paper is estimated to be somewhere between 5 and 10%. The larger error limits apply to those products formed with quantum yields of less than 0.1.

DISCUSSION

Free radical scavenging by HI and H_2S

In the photolysis and radiolysis of hydrocarbons, the use of H_2S or HI as a radical scavenger with a fully deuterated compound provides, through the occurrence of scavenging reactions (3) or (4), a simple straightforward method for the determination of a complete distribution of molecular and radical products. That is, dissociation processes leading to the direct formation of a product molecule as well as fast bimolecular processes (hot radical reactions, carbene insertion reactions) will give fully deuterated products, while thermal alkyl and alkenyl radicals will react with the scavenger to give partially deuterated hydrocarbon products.

In the past, H_2S has generally been favored over HI as a radical scavenger, largely because it was feared that complications would arise due to radical scavenging by the I_2 which would accumulate in the system[3]. (In the radiolysis, it was also assumed that the neutralization mechanism would be modified because of electron-scavenging by HI.) Actually, if experiments are performed in such a way that products such as I_2 are not allowed to build up to concentrations high enough to interact with radicals—and with the present sensitive analytical techniques this is feasible—the use of HI as a radical scavenger presents no particular difficulties[5]. Hydrogen sulfide, on the other hand, does have some drawbacks for use as a radical scavenger. On a practical level, the use of H_2S presents the difficulty that the window of a lamp becomes coated with sulfur during an irradiation[3], so that the transmission drops. On a scientific level, simple consideration of the relative bond strengths of HS–H and R–H would lead us to expect that when the R–H bond being formed in reaction (3) has a strength less than about 90 kcal/mol (the HS–H bond strength)[7], the activation energy for the reaction should become significant enough that radical scavenging will not be efficient. On this basis, it should be expected that the efficiency of scavenging by H_2S will be low for many radicals larger than C_3 or C_4. It has, for instance, been shown[3] that allyl radicals [$D^0(CH_2{=}CHCH_2{-}H){=}85$ kcal/mol) are not effectively scavenged by H_2S.

In HI, the H–I bond strength is 70.4 ± 0.1 kcal/mol, or 20 kcal/mol lower than the HS–H bond strength[8]. Therefore, one might expect reaction (4) to be considerably faster than reaction (3), and efficient for the interception of higher hydrocarbon radicals[9]. Furthermore, HI has an extinction coefficient which is lower than that of the higher hydrocarbons, at least at 8.4 eV ($\varepsilon = 50 \pm 20$ atm^{-1} cm^{-1})[5].

Table 1 shows the quantum yields of the deuterated and partially deuterated products formed in the photolysis of C_3D_8 in the presence of varying amounts of HI and 10% H_2S, in the photolysis with 8.4, 10.0, and 11.6–11.8 eV photons. In the first place, we can point out that there is no change in the yields of the products when the concentration of HI is increased from 0.3% to 10%, demonstrating that even at an HI concentration of 0.3%, the radicals, including C_3D_5, are effectively scavenged. For the smaller radicals, the agreement with the earlier C_3D_8/H_2S photolysis results (Table 1) is good. The quantum yields of D atoms scavenged by HI (*i.e.* the yields of HD) are somewhat higher than the yields scavenged by H_2S.

Since it is necessary[3] to add 10% H_2S to a system to insure quantitative scavenging of the radicals while 0.3% of HI sufficies, it must be concluded that HI is superior to H_2S as a scavenger of H (D) atoms and alkyl or alkenyl radicals.

As mentioned above, conversions should be kept low when HI is used as a scavenger, since I_2 formed by combination of I atoms (from reaction 4) will intercept radicals to form iodides if allowed to build up in the system. However, at conversions below about 0.2%, no effect of conversion can be discerned, as the results given in Table 2 show. This is in part due to the fact[5] that most of the I_2 is removed by the silver of the LiF–AgCl–Ag–AgCl seal which is used in the resonance lamp construction[6].

Primary processes in the photolysis of propane

General comments

In a number of studies carried out at 8.4, 10.0, and 11.6–11.8 eV, with C_3H_8, C_3D_8 (and mixtures of the two) as well as $CD_3CH_2CD_3$ and $CH_3CD_2CH_3$, it has been demonstrated that excited propane dissociates to form molecular hydrogen and propylene:

$$C_3D_8^* \rightarrow D_2 + C_3D_6 \tag{5}$$

methane and ethylene:

$$C_3D_8^* \rightarrow CD_4 + C_2D_4 \tag{6}$$

TABLE 1

QAUNTUM YIELDS OF PRODUCTS OF THE PHOTOLYSIS OF C_3D_8/HI AND C_3D_8/H_2S MIXTURES AS A FUNCTION OF HI CONCENTRATION

Pressure in all experiments = 33 Torr

	Scavenger	Quantum yields										
		D_2	HD	CD_4	CD_3H	C_2D_6	C_2D_5H	C_2D_4	C_2D_3H	C_3D_6	C_3D_5H	C_2D_2
I 8.4 eV	0.3% HI	0.80	0.41	0.08	0.19	0.020	0.018	0.165	0.032	0.51	0.09	0.014
	1.6% HI	0.85	0.50	0.07	0.20	0.020	0.020	0.165	0.034	0.51	0.09	0.022
	3.0% HI	0.80	0.42	0.07	0.18	0.021	0.019	0.165	0.032	0.51	0.07	0.018
	10.0% HI	0.83	0.42	0.07	0.20	0.021	0.021	0.165	0.033	0.53	0.08	0.022
	10.0% H_2S†	n.d.	n.d.	0.08	0.20	0.031	0.021	0.165	0.046	0.43	—	n.d.
II 10.0 eV	3.4% HI	0.54	0.92	0.21	0.43	0.085	0.058	0.35	0.082	0.12	0.044	0.10
	10.0% H_2S†	0.35	0.51	0.19	0.36	0.085	0.049	0.32	0.065	n.d.	n.d.	0.086
III 11.6–11.8 eV*	3.7% HI	0.44	0.83	0.19	0.54	0.060	0.060	0.28	0.086	0.10	0.039	0.16
	10.0% H_2S†	0.39	0.67	0.17	0.56	0.042	0.059	0.28	0.090	n.d.	n.d.	0.20

† Ref. 3. Because no quantum yields were determined in earlier studies, the relative yields reported have been normalized taking C_2D_4 as base.

*At this energy, $C_3D_8{}^+$ ions (which do not dissociate at pressures above ~ 10 Torr) are formed with a quantum yield of 0.25. Therefore, in order to ascertain the probability that the superexcited $C_3D_8{}^*$ molecules will give a certain product (M/N_{ex}), these quantum yields should be multiplied by 1.33.

TABLE 2

THE EFFECT OF CONVERSION ON QUANTUM YIELDS OF PRODUCTS IN THE 8.4 eV PHOTOLYSIS OF A C_3D_8/HI (1:0.03) MIXTURE

Pressure = 33 Torr

Conversion	Quantum yields				
(%)	Methane	Ethane	Ethylene	Propylene	Acetylene
0.03	0.25	0.043	0.20	0.57	0.019
0.09	0.25	0.044	0.20	0.57	0.017
0.16	0.25	0.041	0.20	0.58	0.018

and ethane:

$$C_3D_8^* \rightarrow C_2D_6 + CD_2 \qquad (7)$$

Experiments with $CD_3CH_2CD_3$ and $CH_3CD_2CH_3$ have demonstrated[10] that process (5) involves the elimination of a hydrogen molecule primarily from the center carbon atom, *i.e.*:

$$CD_3CH_2CD_3^* \rightarrow H_2 + CD_3CCD_3 \rightarrow H_2 + CD_3CDCD_2 \qquad (8)$$

The methane elimination process (6) primarily involves the initial formation of ethylidine at these energies (*i.e.* the methane is formed from a methyl group and a H from the adjacent carbon atom):

$$CD_3CH_2CD_3^* \rightarrow CD_3H + CD_3CH^* \rightarrow CD_3H + CD_2CDH \qquad (9)$$

although a small fraction of the methane formed in $CD_3CH_2CD_3$ consists of CD_4, suggesting the possibility that the process:

$$CD_3CH_2CD_3^* \rightarrow CD_4 + CD_2CH_2 \qquad (10)$$

also occurs. However, the yield of the minor CD_4 product shows a decrease with increasing pressure[3], a fact which suggests that some or all of the CD_4 may actually originate in a secondary dissociation of another product, such as the propylene product formed in reaction (5).

Singlet methylene formed in the dissociation process (7) will insert into propane to form n-butane and isobutane:

$$^1CD_2 + C_3D_8 \rightarrow C_4D_{10}^* \qquad (11)$$

or will undergo a collision-induced conversion to the triplet state[2b,f,11]:

$$^1CD_2 + C_3D_8 \rightarrow {}^3CD_2 + C_3D_8 \qquad (12)$$

The $^3CD_2$ will not insert into propane; its fate in the C_3D_8/HI is unknown. The excited butane molecules formed by insertion reaction (11) will dissociate to give methyl, ethyl, and propyl radicals:

$$\text{(n- or iso-) } C_4D_{10}^* \rightarrow CD_3 + C_3D_7 \tag{13}$$

$$n\text{-}C_4D_{10}^* \rightarrow 2C_2D_5 \tag{14}$$

or, will undergo collisional stabilization:

$$C_4D_{10}^* + C_3D_8 \rightarrow C_4D_{10} + C_3D_8 \tag{15}$$

Some of the fragments formed in the primary processes (5), (6), and (7) may undergo further dissociation to give smaller molecules such as acetylene, or radicals. It has been shown[2a] that as the energy is increased, radical formation becomes more important. On the basis of a number of observations which will be reviewed below, it was concluded that the increased radical formation could be attributed not only to an increased importance of secondary dissociation of the molecular products, but also to an increased importance of primary fragmentations involving direct C–C or C–H (C–D) bond cleavage, reactions (1) and (2).

Formation of stable ethyl radicals; *C–C cleavage processes*

In a recent publication[2h] it was assumed that secondary dissociations of the hydrogen and methane formed in primary processes (5) and (6) respectively were important, and primary processes (1) and (2) did not have to be invoked to explain the relative yields of the observed products. Because of this contention, it is worthwhile to review the evidence for the occurrence of processes (1) and (2).

First, it has been shown in the past, as well as in the results reported here, that ethyl radicals are intercepted by H_2S and HI, even at pressures high enough that all butanes formed by insertion reaction (11) will be stabilized, and process (14) cannot contribute (in the fully deuterated system, more than 90% of the C_4D_{10} molecules are stabilized at pressures above about 5 Torr as demonstrated below). These ethyl radicals cannot originate in the reaction:

$$D + C_2D_4 \rightarrow C_2D_5 \tag{16}$$

as suggested recently[2h], since (1) all D atoms are effectively removed by the H_2S or HI (Table 1), and (2) the yield of C_2D_5H in the presence of HI is essentially invariant with HI concentration (Table 1) or conversion (Table 2). Thus, it is impossible to explain the presence of ethyl radicals in these experiments by any process involving reaction of an accumulated product. Furthermore, as shown in Table 3, the yield of C_2D_5 radicals intercepted by HI does not diminish when the pressure is increased, demonstrating that the ethyl radicals do not originate in a secondary dissociation of a larger radical or molecular product. The results given in Table 4 provide further corroborative evidence for the occurrence of process (2) (and/or 1). These results show that at 10 eV about half of the ethylene formed in $CD_3CH_2CD_3$ consists of CD_2CH_2. Not more than 10% of this can be explained by the occurrence of process (10), since the quantum yield of CD_4 is very low; it could be argued[2h] that the CD_4 formed in this process actually dissociates further:

TABLE 3

THE EFFECT OF PRESSURE ON THE QUANTUM YIELDS OF PRODUCTS IN THE PHOTOLYSIS OF C_3D_8/HI (1:0.04) MIXTURES AT 8.4, 10.0, AND 11.6–11.8 eV

	P (Torr)	D_2	HD	CD_4	CD_3H	C_2D_6	C_2D_5H	C_2D_4	C_2D_3H	C_3D_6	C_3D_5H	C_2D_2
I 8.4 eV	5.7	0.8	0.4	0.07	0.20	0.021	0.020	0.15	0.047	0.39	0.13	0.028
	32.8	n.d.	n.d.	0.07	0.18	0.021	0.019	0.165	0.032	0.50	0.08	0.018
	72.7	0.82	0.4	0.07	0.20	0.022	0.023	0.17	0.025	0.58	0.07	0.016
	166.6			0.07	0.20	0.022	0.026	0.18	0.018	0.62	0.05	0.014
II 10.0 eV	5.7	n.d.	n.d.	0.21	0.46	0.090	0.061	0.35	0.094	0.16	0.16	0.11
	11.6	0.45	0.83	0.21	0.44	0.086	0.061	0.34	0.082	0.12	0.044	0.10
	34.3	0.55	0.92	0.21	0.43	0.085	0.058	0.35	0.082	0.16	0.16	0.10
	168.4	n.d.	n.d.	0.21	0.41	0.089	0.060	0.35	0.082	0.17	0.17	0.095
	243.8	0.40	0.86	0.20	0.40	0.088	0.063	0.35	0.082	0.16	0.036	0.095
III 11.6–11.8 eV≠	5.7	0.45	0.92	0.19	0.51	0.072	0.071	0.21	0.0072	0.07	0.03	0.19
	11.6	0.52	1.03	0.19	0.54	0.067	0.071	0.26	0.086	0.08	0.03	0.18
	33.3	0.44	0.83	0.19	0.54	0.060	0.069	0.26	0.089	0.08	0.03	0.19
	168.7	0.47	1.06	0.18	0.54	0.060	0.075	0.35	0.085	0.09	0.04	n.d.
	329.7	0.46	1.10	0.18	0.55	0.065	0.090	0.30	0.099	0.10	0.04	0.16

≠ At this energy, $C_3D_8^+$ ions (which do not dissociate at pressures above ~ 10 Torr) are formed with a quantum yield of 0.25. Therefore, in order to ascertain the probability that the superexcited $C_3D_8^*$ molecules will give a certain product (M/N_{ex}), these quantum yields should be multiplied by 1.33

TABLE 4

YIELDS* OF METHANE, ETHYLENE, AND PROPYLENE ANALOGUES FORMED IN THE PHOTOLYSIS OF $CD_3CH_2CD_3/NO$ (1:0.05) MIXTURES

	CD_4	CD_3H	C_2D_3H	$C_2D_2H_2$	C_3D_6	C_3D_5H
I 8.4 eV	0.007	0.063	0.09	0.06	0.32	0.18
II 10.0 eV	0.016	0.19	0.16	0.18	0.046	0.073
III 11.6–11.8 eV**	0.013	0.17	0.10	0.16	0.015	0.065

* Assumed quantum yields derived from isotopic analyses reported in ref. 2a and the quantum yields of molecular products measured in C_3D_8/HI mixtures (Tables 1, 2 and 3).

** At this energy, $C_3D_8^+$ ions (which do not dissociate at pressures above ~ 10 Torr) are formed with a quantum yield of 0.25. Therefore, in order to ascertain the probability that the superexcited $C_3D_8^*$ molecules will give a certain product (M/N_{ex}), these quantum yields should be multiplied by 1.33

$$CD_3CH_2CD_3^* \rightarrow CD_4 + CH_2CD_2 \rightarrow D + CD_3 + CH_2CD_2 \tag{17}$$

but this can be ruled out on the ground that the yield of CD_4 actually decreases with an increase in pressure[3]. Also, if process (17) were to occur, it would mean that essentially all of the excess energy available goes into the CD_4 fragment, in sharp contrast to the analogous process (9), where the ethylene product but not the methane undergoes further dissociation[3]. It follows that the ethylene CD_2CH_2 (Table 4) must be formed in the overall process:

$$CD_3CH_2CD_3^* \rightarrow CD_3 + CH_2CD_2 + D \tag{18}$$

and that the actual mechanism for this may be through a reaction analogous to process (1):

$$CD_3CH_2CD_3^* \rightarrow CD_3CH_2CD_2 + D \rightarrow CD_3 + CD_2CH_2 + D \tag{19}$$

and/or through a reaction analogous to process (2):

$$CD_3CH_2CD_3^* \rightarrow CD_3CH_2 + CD_3 \rightarrow CD_3 + CD_2CH_2 + D \tag{20}$$

Evidence that reaction (1) (or reaction 19) is not very important in the photolysis of propane at these energies will be presented later in our discussion of C–H bond cleavage processes.

It is interesting in this regard to note that the relative abundances of the C_2D_5 (process 2), C_2D_6 (process 7), CD_4 (process 6), and ethylene resulting from the dissociation of ethyl radicals (*i.e.* the CD_2CH_2 in $CD_3CH_2CD_3$ experiments, Table 4) are the same at 8.4 eV, at 10.0 eV, and at 11.6–11.8 eV. This curious observation, illustrated in Table 5 suggests that all the C–C cleavage processes may be associated with an excited propane species having energy excitation in one C–C bond; according to this picture, the dissociation of such an excited species will always involve cleavage of the C–C bond, but there is a certain probability, independent of energy, that the cleavage will be accompanied by the move-

TABLE 5

RELATIVE ABUNDANCES OF PHOTOLYTIC FRAGMENTS IN PROPANE AT 8.4, 10.0, AND 11.6–11.8 eV, DETERMINED FROM C_3D_8/HI MIXTURES AND $CD_3CH_2CD_3$/NO MIXTURES

	CD_4[a]	C_2D_6[a]	C_2D_5[a]	CH_2CD_2[b]	D_2[a]	C_2D_2[a]
8.4 eV	41	12	12	35	470	13
10.0 eV	39	16	11	34	84	19
11.6–11.8 eV	39	14	14	33	92	37

[a] Relative yields from 11.6 Torr experiments with C_3D_8/HI mixtures given in Table 3. (At 8.4 eV, 5.7 and 32.8 Torr experiments were used.)

[b] Relative yield derived from quantum yield of CH_2CD_2 formed in $CD_3CH_2CD_3$/NO mixtures, given in Table 4.

ment of an H species across the bond, from a center carbon to the methyl group [process (6), 40%], or from the methyl group to the center carbon [process (7), 14%]. It has been correctly pointed out[2h] that if one applies the usual RRKM considerations about equipartitioning of energy, ethyl radicals formed by direct C–C cleavage in propane would all be expected to dissociate at atmospheric pressures, even after allowing for the fact that quantitative parameters given in the RRKM calculations on C_2H_5[12] have to be adjusted for the fully deuterated ethyl radical for which all our results apply. Our hypothesis, based on the observation presented in Table 5, suggests that the theories relating to equipartition of energy are not applicable to the dissociations of electronically excited alkanes, and that one or the other fragment of a dissociation process may carry away an amount of energy in excess of that which would be predicted by RRKM theory.

Assuming that the stable C_2D_5 radicals are only observed when they carry away less than about 2.5 eV, on the average (the threshold energy for the dissociation process:

$$C_2D_5 \rightarrow C_2D_4 + D \tag{21}$$

is 1.8 eV), the methyl radicals formed in process (2) must contain ~2.5–4.3 eV excess energy in the 8.4 eV experiments, ~ 4.1–5.9 eV at 10.0 eV, and ~ 5.9–7.6 eV at 11.6–11.8 eV. The lowest excited state of the methyl radical is the $\tilde{B}\ {}^2A_1$ state, 5.7 eV above the ground state[13]. Electronic excitation of the methyl radical is, thus, excluded in the 8.4 eV experiments, where the excess energy in the methyl radical must be in the form of vibrational energy. However, at 11.6–11.8 eV, electronically excited methyl radicals may be formed. Also, at this energy, the methyl radicals have abundant energy to dissociate to give either CH or CH_2 species, the formation of which would require 4.8 eV[14]. Little can be said about whether or not these processes occur in propane. However, it has been demonstrated that CH species are formed in the photolysis of methane[15] and ethane[16]. If such species are indeed formed in the 11.6–11.8 eV experiments, they would insert into propane to form isobutyl and n-butyl radicals, which at the pressures of our experiments would be expected to dissociate to give methyl and ethyl radicals, respectively. Such processes would account for at least some of the stable ethyl radicals at 11.6–11.8 eV. An analysis of the ethylene formed in a $C_3D_8/C_3H_8/NO$ mixture in the experiments at 8.4 and at 10.0 eV, however, confirmed that at the lower energies, the insertion process:

$$CH + C_3H_8 \rightarrow (C_4H_9)^* \rightarrow C_2H_4 + C_2H_5 \qquad (22)$$

does not contribute to ethylene or ethyl radical formation. Concerning the possibility that methyl radicals may dissociate at 11.6–11.8 eV to give excess methylene species, it is true[2g] that the ratio of molecular ethane (process 7) to the n-butane formed by methylene insertion (process 11) is lower at 11.6–11.8 eV than at the lower energies (Fig. 1), a fact which suggests that there is an additional source of CD_2. However, there is an alternate explanation for this observation, discussed below.

C–H excitation processes

A corollary of the hypothesis that processes (2), (6), and (7) all occur through excitation in a single C–C bond is that the $H_2(D_2)$ elimination process (5) occurs when the excitation is localized elsewhere than in a C–C bond. In ethane, it has been suggested that the elimination of H_2 occurs through excitation of a C–H bond[2g]. The $H_2(D_2)$ elimination process (5) predominates in the 8.4 eV photolysis; the occurrence of this process through C–D(C–H) bond excitation is, thus, consistent with recent interpretations[17] of the electronic spectra of saturated hydrocarbons which suggest that in methane, ethane, and propane, the first singlet–singlet transitions involve an electron taken from a molecular orbital mainly populated in the C–H bonds. This is also consistent with the prediction[18] that in the lowest excited state, ethane should have a stronger C–C bond and weaker C–H bonding than in the ground state. The yields of molecular hydrogen are also listed in Table 5. Some of this originates in process (5), and some comes from secondary decompositions, such as:

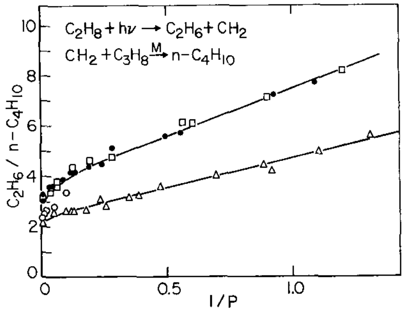

Fig. 1. Plots of $C_2H_5/n\text{-}C_4H_{10}$ *vs.* $1/P$ (Torr). ●, 8.4 eV; □, 10.0 eV; △, 11.6–11.8 eV. The circles (○) correspond to experimental points (10.0 eV) taken from ref. 2f.

$$C_2D_4^* \rightarrow C_2D_2 + D_2 \qquad (23)$$

The yields of acetylene are also listed, they demonstrate that secondary decompositions become more important as the energy is increased even though the overall hydrogen yield diminishes, thus demonstrating the diminishing importance of process (5). Accepting this, the molecular hydrogen yields summarized in Table 5 indicate that C–H bond excitation and C–C bond excitation vary in relative importance when the photon energy is changed, with C–H bond excitation apparently predominating at 8.4 eV, and diminishing in importance as the photon energies are increased. This is in agreement with the trends observed in ethane for the analogous processes[16].

The yields of propylene corroborate the interpretation that process (5) diminishes in importance as the photon energy is raised. At 8.4 eV, in the photolysis of the C_3D_8/HI mixture, C_3D_6 is the main product. At this energy, it should be noted, the C_3D_6 species could be formed with up to 6.9 eV excess energy, so that secondary decomposition might be expected to occur. Indeed, when the pressure of the system is increased in the 8.4 eV experiments, the yield of C_3D_6 increases (Table 3), due to collisional deactivation[2d]. As the yield of C_3D_6 increases (Table 3), that of C_3D_5H decreases, demonstrating that as suggested before[2c] one of the modes of decomposition of the internally excited propylene is:

$$C_3D_6^* \rightarrow C_3D_5 + D \qquad (24)$$

There is another mode of decomposition of the excited propylene molecule, $C_3D_6^*$, which should be considered:

$$C_3D_6^* \rightarrow CD_3 + C_2D_3 \qquad (25)$$

If one examines the effect of increasing pressure on the yields of C_3D_5H and C_2D_3H, (Table 3) it is seen that their yields both decrease in the same way. That is, the quantum yield of C_3D_5 and C_2D_3 both decrease by 60% when the pressure is raised from 5.5 Torr to 160 Torr (Table 3). This would suggest a common precursor for these two radicals at 8.4 eV. An approximate dissociative lifetime of 5×10^{-9} s can be estimated for the excited propylene molecule formed in process (5) in the 8.4 eV photolysis from the data given in Table 3. However, the fact that the increase in the yield of C_3D_6 is not entirely compensated by the decrease in the yields of C_3D_5H and C_2D_3H suggests that there are other modes of fragmentation. One plausible mode is:

$$C_3D_6^* \rightarrow C_3D_4 + D_2 \qquad (26)$$

The yield of C_3D_4 could not be measured with the chromatographic column used in this study, but it is relevant to note that the sum of the quantum yields of methane and propylene (or of C_2 products plus propylene) is 0.79 at a pressure of 5 Torr, and 0.94 at a pressure of 160 Torr in the 8.4 eV experiments. It follows that the yield of C_3D_4 decreases by 0.15 over this pressure range due to stabilization of its precursor.

When the photon energy is raised to 10.0 eV, it is seen that the yields of C_3D_6 are lower, as one would expect if the overall importance of process (5) decreases as a function of energy. It might be expected that the excited $C_3D_6^*$ species would undergo increased fragmentation at the higher energy, but this obviously does not explain the decrease in C_3D_6 observed, since the yield of C_3D_5 (formed in process 24) is much lower at a given pressure in the 10.0 eV results than in the 8.4 eV experiments (Table 3). In contrast, the yield of the vinyl radical is higher at 10.0 eV than at 8.4 eV, suggesting that at this energy process (27) may be occurring to some extent:

$$C_2D_4 \rightarrow C_2D_3 + D \qquad (27)$$

The formation of C_2D_3 in the photolysis of C_2D_6 has been attributed[16] to such a decomposition mode.

We have not yet presented any definite evidence for the occurrence of process (1), which would also be expected to occur through C–H bond excitation. Firm conclusions about the occurrence or non-occurrence of this process cannot be obtained from the results presented here. However, if this process (process 19) did occur in $CD_3CH_2CD_3$, the abundance of CH_2CD_2 relative to methane, ethane, and ethyl radicals might be expected to change as a function of energy, and it does not (Table 5). Further corroborative evidence that direct C–H cleavage [processes (1) for C_3D_8, (19) for $CD_3CH_2CD_3$] is not important in the photolysis of propane at energies between 8.4 and 11.8 eV is obtained from the isotopic composition of the ethylene formed in the photolysis of $CD_3CH_2CH_3$[2d]; in this molecule, one would expect that C–H cleavage would predominate over C–D cleavage, so that the final ethylene product formed by dissociation of the resulting propyl radical should consist of C_2H_4 and CH_2CD_2, with the C_2H_4 predominating. The other ethylene-producing processes [reactions analogous to (6) and (2)–(21)] should not show an isotope effect and would therefore lead, respectively, to equal amounts of C_2H_4 and C_2D_3H, and C_2H_4 and $C_2D_2H_2$. It has been reported that C_2D_3H and $C_2D_2H_2$ are formed in approximately equal yields, and the yield of C_2H_4 is only slightly ($\sim$ 10%) greater than the sum of the two partially deuterated ethylenes. Thus, process (1) may occur in propane, but only to a slight extent at these energies. Furthermore, in the experiments with $CD_3CH_2CD_3$ in the presence of a radical scavenger (Table 4), some C_3D_5H is formed. A fraction of this product may be formed in the process:

$$CD_3CH_2CD_3^* \rightarrow CD_3CHCD_2 + HD \qquad (28)$$

If one makes the reasonable assumption that the relative importances of process (28) and process (8) do not change significantly with a change in photon energy, we can state from the results in Table 4 that the maximum value for the ratio of [process (28)/process (8)] is 0.56, and therefore at 10.0 and at 11.6–11.8 eV, some C_3D_5H must be formed in the process:

$$CD_3CH_2CD_3^* \rightarrow CD_3CHCD_3 + H \rightarrow CD_3CHCD_2 + H + D$$

The maximum quantum yield which could be attributed to this process at these energies is about 0.05.

Methylene insertion reaction

The relative product abundances summarized in Table 5 show that the relative probabilities of processes (2), (6), and (7) (*i.e.* the relative yields of CD_4, C_2D_6, and C_2D_5) are apparently the same in the HI-scavenged experiments at all energies. This result is somewhat unexpected, since in an earlier study[2g] of the photolysis of propane (carried out with H_2S and NO as radical scavengers) it was reported that the ratio C_2H_6 (molecular)/CH_4(molecular), as well as the pressure-dependent ratio C_2H_6/n-C_4H_{10} was the same for experiments with 8.4 and 10.0 eV photons, but decreased significantly when 11.6–11.8 eV photons were used. The n-C_4H_{10} is formed in the methylene insertion reaction (11). It was concluded that at 11.6–11.8 eV, a fraction of the ethane molecules formed in process (7) underwent further dissociation. (The ratio C_2H_6/n-C_4H_{10} and the ratio C_2H_6/CH_4 change by the same fraction in going from the lower energy results to the 11.6–11.8 eV results, as they should if the change involves a change in the relative yield of C_2H_6 rather than that of methane or butane.) That is, the yield of C_2H_6 seems to have changed relative to the yields of CH_2 species which insert, or relative to the molecular methane. The onset of excitation for ethane to a forbidden state occurs at an energy of 7.0–7.1 eV[19]. In the photolysis with 11.6–11.8 eV photons, there is 7.4–7.6 eV to be distributed between the two fragments of process (7). If one proposes a hypothesis that the change in the yield of ethane relative to methane and butane observed in the presence of H_2S or NO scavengers is due to the formation of excited ethane species which dissociate or are otherwise removed from the system, then one must explain why this loss of ethane apparently does not occur when HI is used as a radical scavenger. A plausible explanation for this would be that the loss of ethane observed in the presence of NO or H_2S at 11.6–11.8 eV can be attributed to a reaction between the $(C_2H_6)^*$ species and NO or H_2S:

$$(C_2H_6)^* + NO(H_2S) \rightarrow \text{Products other than ethane} \qquad (30)$$

but that no such reaction occurs with HI, and the $(C_2H_6)^*$ is stabilized to give C_2H_6. (The only alternate explanation for this discrepancy between the H_2S and NO-additive results and the HI results at 11.6–11.8 eV, might be that the same loss of $(C_2H_6)^*$ does occur in the presence of HI, but that some reaction of the $C_3H_8^+$ ion with HI results in the formation of ethane. (The ionization potential of propane is 11.1 eV, and at this energy, parent propane ions are formed with a quantum yield of 0.25.)

The results plotted in Fig. 1 can be interpreted in terms of the rate of decomposition of the n-$C_4H_{10}^*$ species formed in the insertion of CH_2 into propane (*i.e.* the reaction analogous to reaction 11). Assuming that the yield of stabilized C_4H_{10} can be explained in terms of the mechanism (11)–(15), we obtain by the usual kinetic treatment:

$$(C_4H_{10})_{max}/(C_4H_{10}) = 1 + k_D/k_S P$$

where k_D is the unimolecular rate constant for dissociation of $C_4H_{10}^*$, k_S is the rate constant for stabilization, $(C_4H_{10})_{max}$ is the maximum yield of C_4H_{10} obtained at high pressures, and P is the number density of molecules in the system. This equation predicts that a plot such as that given in Fig. 1 should be linear with an intercept equal to $(C_2H_6)/(C_4H_{10})_{max}$. The results obtained in the 8.4 and 10.0 eV photolysis coincide, as mentioned above, and give a plot which is linear at pressures below about 10 Torr, but shows curvature at higher pressures, indicating that no unique lifetime can be ascribed to the excited butane formed by methylene insertion into propane. It is of interest, however, that at 11.6–11.8 eV, the curvature is much less pronounced than at the lower energies, and that furthermore, the value one derives for k_D is lower over the entire pressure range. Derived values for k_D (assuming that k_S is equal to the collision rate) are given in Table 6. Both observations are consistent with the suggestion made above that at 11.6–11.8 eV, electronic excitation of the ethane formed in process (7) may occur; that is, one might expect that the $CH_2(CD_2)$ formed in such a reaction would, on the average, carry away less energy when energy goes into electronic excitation of the ethane. In addition, as discussed above, it is possible at 11.6–11.8 eV that methyl radicals are produced with enough energy to dissociate and give CH_2. However, if the CH_2 thus formed is in the triplet state it would escape detection by our method. The fact that k_D at 11.6–11.8 eV is still a factor of two higher than the lowest value reported in the literature (Table 6) indicates that the singlet CH_2 produced from propane does carry over some excess energy into the insertion product.

TABLE 6

RATE CONSTANTS FOR UNIMOLECULAR DISSOCIATION OF n-BUTANE FORMED BY METHYLENE INSERTION INTO PROPANE

Source of $^1CH_2$	Photon energy	k_D (s^{-1})	P (Torr)	Ref.
Photolysis of C_3H_8	8.4 eV, 10.0 eV	$1.9 \pm 0.5 \times 10^7$	(<10)	This work
		$3.9 \pm 0.5 \times 10^7$	(>10)	This work
	10.0 eV	6.6×10^7	(>10)	2f
	11.6–11.8 eV	$1.5 \pm 0.2 \times 10^7$	(<10)	This work
		$1.6 \pm 0.2 \times 10^7$	(>10)	This work
Photolysis of C_3D_8	11.6–11.8 eV	$3.5 \pm 0.2 \times 10^6$	0.2–20	This work
Photolysis of CH_2N_2	3.4 eV	$2.3 \pm 0.2 \times 10^7$		21
	2.8 eV	$7.3 \pm 0.6 \times 10^6$		21

Incidentally, the rate constant of decomposition of n-butane given in Table 6 for the deuterated system at 11.6–11.8 eV is considerably lower than that measured in the perprotonated system. Also, within experimental error, no curvature could be detected.

It should specifically be pointed out that these results demonstrate that the CH_2 species which insert to form n-butane have the same energy distribution in the 8.4 eV and the 10.0 eV photolysis. This implies that even though the energy taken up by the CD_2 in process (7) must be greater in the 10.0 eV than in the 8.4 eV experiments, this is not reflected in a difference in the rate of decomposition of the insertion product at these two energies. This observation is in agreement with the recent study[20] on the reactions of CH_2, in which it was shown that the fraction of excess photon energy carried into an insertion product rapidly decreases as the photon energy increases. (That is, it was shown that when the energy of the photon producing CH_2 was increased by 1.3 eV, the internal energy of the resulting insertion product was only 0.14 eV greater.)

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