THE PHOTOLYSIS OF NEOPENTANE AND ISOBUTANE WITH 7.6, 8.4, AND 10.0 eV PHOTONS

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Summary

The photolysis of neopentane has been studied using photons of energies 7.6, 8.4, and 10.0 eV, at pressures in the range 1 - 760 Torr and in the liquid phase. Quantum yields of all molecular and radical products smaller than C_5 have been determined in the gas phase experiments, and have been estimated in the liquid phase. In contrast to results obtained with other alkanes studied to date, hydrogen elimination is found to be an unimportant process in the photolysis of neopentane. The two predominant primary processes are elimination of methane (neo-C_5H_{12} → CH_4 + iso-C_4H_8) and direct C–C bond cleavage (neo-C_5H_{12} → CH_3 + t-C_4H_9). A fraction of the t-C_4H_9 radicals dissociate further unless collisionally stabilized, either by loss of a H atom or by loss of a methyl radical (presumably preceded by an initial rearrangement to the isobutyl structure). With an increase in photon energy, the importance of direct bond cleavage increases at the expense of the methane elimination process. In the liquid phase, secondary decomposition processes are quenched, and the estimated quantum yields of primary processes are similar, at all energies, to those found in the 7.6 eV gas phase photolysis at high pressures.

Quantum yields of molecular and radical products formed in the 7.6 and 8.4 eV photolysis of isobutane are also reported and are discussed briefly, with particular emphasis on the effect of energy on the mechanisms of the molecular elimination processes: (iso-C_4H_{10} → CH_4 + C_3H_6) and (iso-C_4H_{10} → iso-C_4H_8 + H_2). For both of these primary processes, the lower energy pathway, in which the olefin is formed directly, predominates at 7.6 eV, but diminishes in importance relative to the higher energy channel (presumably involving carbene formation) when the photon energy is increased.

Introduction

Several studies from this and other laboratories have examined the relative importances of primary processes occurring in the photolysis of

alkanes as a function of photon energy [1]. Most of this work has been concerned with the lower linear alkanes, ethane, propane, and butane, for which it was demonstrated that as the photon energy is increased, the probability for the occurrence of H_2 elimination processes diminishes drastically at the expense of competing alkane elimination or C–C and C–H bond cleavage processes.

The results reported here involve an examination of the modes of dissociation of the branched alkanes, isobutane and neopentane, as a function of photon energy. The onset of absorption of these two compounds is, respectively, 7.4 and 7.2 eV [2]. Therefore, it was considered of interest to include some experiments using 7.6 eV photons in order to determine whether a single primary process (possibly associated with a given transition) predominates at the onset, as H_2 elimination predominates near the onset in linear alkanes, and whether the importance of alkane elimination, C–H and C–C bond cleavage processes will vary as a function of energy. The elimination of a molecule of hydrogen has been shown to be less important in branched alkanes; this process essentially does not occur in neopentane.

The most recent studies of the photolysis of neopentane [3] and isobutane [4] were carried out in this laboratory several years ago. The current effort, in addition to supplying information about processes occurring at the absorption onset, also provides quantum yield determinations, which were not made in the earlier studies, and information about the photolysis of neopentane in the liquid phase.

Experimental

The gas phase photolysis procedure and the xenon and krypton lamps have been described in previous studies from this laboratory [5]. The bromine lamp used in this study was similar in design to that described by Loucks and Cvetanović [6]. The 163.3 nm line was the major resonance line (78.5%) transmitted through a 0.1 cm thick quartz window. The quantum yields were based on the production of C_2H_2 in the photolysis of ethylene ($\Phi(C_2H_2) = 0.7 \pm 0.05$ at 163 nm and $\Phi(C_2H_2) = 0.95 \pm 0.05$ at 147 nm [8] and at 123.6 nm [7]). These last two have been checked against the production of ^{13}CO (taking $\Phi(^{13}CO = 1)$ in the photolysis of $^{13}CO_2$ [7].

Liquid phase experiments were carried out using reaction vessels of two different designs. For the experiments with the bromine lamp a high quality flat quartz cell was used which consisted of two circular quartz plates (diameter 1.5 cm) separated by a distance of 0.05 cm. Only small quantities of high purity (99.97%) neopentane had to be used in each experiment with this cell of small volume. The cell was placed in a fixed position with regard to the bromine lamp, and both were contained in a chamber which was evacuated prior to irradiation. In some experiments, an interference filter which peaks at 165 nm and has a pass band of half width of 22.5 nm and transmission of 20%, was placed between the lamp window and the

reaction vessel to further reduce the absorption of light from the longer wavelength region. The liquid phase photolysis experiments with 8.4 and 10.0 eV photons were carried out using, respectively, xenon and krypton lamps provided with LiF windows (diameter 1 cm) attached to Pyrex tubing by means of an AgCl–Ag seal [1a]. The lamp was mounted vertically with the window immersed in the hydrocarbon liquid, which was contained in a cylindrical capsule only slightly wider than the window. The distance between the window and the bottom of the cylindrical container was 0.1 cm. After irradiation, the liquid and accumulated bulk products were expanded into a 1 liter bulb and analyzed by gas chromatography and mass spectrometry.

At present, quantum yield determinations in the liquid phase are only approximate. Cyclobutane, which dissociates uniquely into two ethylene molecules at 147 and 163.3 nm was taken as an actinometer under the assumption that $\Phi(C_2H_4) = 2$. Several other branched hydrocarbons, including 2,2,4-trimethylpentane, to which Holroyd [9] ascribed a quantum yield of unity for total decomposition, were photolyzed with the bromine lamp in order to assess if the quantum yields of decomposition based on the cyclobutane actinometry were in reasonable agreement with quantum yields estimated earlier [9]. For all compounds, the quantum yields of decomposition assessed from the alkane and H_2 products were 1.0 ± 0.4.

Discussion

Neopentane

When neopentane is photolyzed in the presence of NO or O_2 as a radical scavenger, more than 99% of the observed products smaller than C_5 consist of methane, propylene, isobutene, and hydrogen. On the basis of this observation, it has been proposed in an earlier study [3] that excited neopentane dissociates in the following overall modes:

$$neo\text{-}C_5H_{12}{}^* \rightarrow CH_4 + iso\text{-}C_4H_8 \tag{1}$$

$$neo\text{-}C_5H_{12}{}^* \rightarrow CH_3 + CH_3 + CH_3CHCH_2 \tag{2}$$

Because the yield of isobutene was greater than that of methane, the following overall mode of dissociation was proposed:

$$neo\text{-}C_5H_{12}{}^\bullet \rightarrow H + CH_3 + iso\text{-}C_4H_8 \tag{3}$$
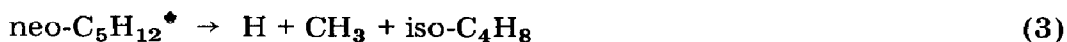
It was suggested [3] that this process proceeds either through a loss of a methyl radical from the parent molecule:

$$neo\text{-}C_5H_{12}{}^* \rightarrow CH_3 + t\text{-}C_4H_9 \tag{4}$$

and the subsequent loss of a H atom from the excited t-butyl radical, and/or through the initial loss of a H atom from the excited neopentane molecule:

$$neo\text{-}C_5H_{12}{}^* \rightarrow H + (CH_3)_3CCH_2 \tag{5}$$

and the subsequent loss of a methyl radical from the neopentyl radical.

It was not possible in the earlier study to establish the occurrence of primary processes (4) and/or (5). The radicals were determined using H_2S as a scavenger:

$$R^{\cdot} + H_2S \rightarrow RH + HS \tag{6}$$

and no t-butyl radicals were intercepted (*i.e.* there was no isobutane formed in experiments with added H_2S). Actually, H_2S is a very inefficient scavenger of tertiary radicals. In the present study, the yields of radicals are determined by using HI as a scavenger [10]:

$$R^{\cdot} + HI \rightarrow RH + I \tag{7}$$

Isobutane is a product of all experiments carried out using an HI additive, so primary process (4) definitely does occur (Figs. 1, 2 and 3).

It is more difficult to say anything about the occurrence of primary process (5). Neopentyl radicals, if intercepted by HI would give neopentane as a product, and thus would not be detected. Since quantum yields of the products are determined in this study, it will be possible at the end of the discussion section to make a rough estimate of the relative importance of process (5) on the basis of the H atom yield and material balance considerations.

Finally, as mentioned above, an important primary process in the photolysis of most linear alkanes is the elimination of a molecule of hydrogen. The yield of molecular hydrogen in neopentane was determined by photolyzing neo-C_5D_{12} in the presence of HI. Hydrogen eliminated from neopentane as a molecule will, in this mixture, be D_2, while D atoms are intercepted by HI to form HD. Since some molecular hydrogen could originate from further dissociation of excited fragment species, the observed yields of D_2 in these experiments, given in Table 1, are the maximum possible yields which can be attributed to the primary process:

$$\text{neo-}C_5D_{12}^{\star} \rightarrow D_2 + C_5D_{10} \tag{8}$$

The quantum yields of the molecular hydrocarbon products as well as the radicals formed in the photolysis of neopentane with 7.6, 8.4, and 10.0 eV photons are shown in Figs. 1, 2 and 3, respectively. The yields of molecular products are simply the yields of these respective compounds formed in the photolysis in the presence of NO, which effectively scavenges the free radicals to form non-hydrocarbon products which are not analyzed in our experiments. The radical yields are obtained by subtracting the yields of the corresponding molecular products from the total yield of a given hydrocarbon product formed in the presence of HI, which scavenges free radicals according to reaction (7). Results which have already been interpreted in terms of processes (1) and (3) are also given. That is, since each methane molecule formed in process (1) is accompanied by the formation of one isobutene molecule, the isobutene originating in process (1) has been subtracted from the total yield of isobutene and the difference has been attributed to process (3), as shown by the indicated lines. (There
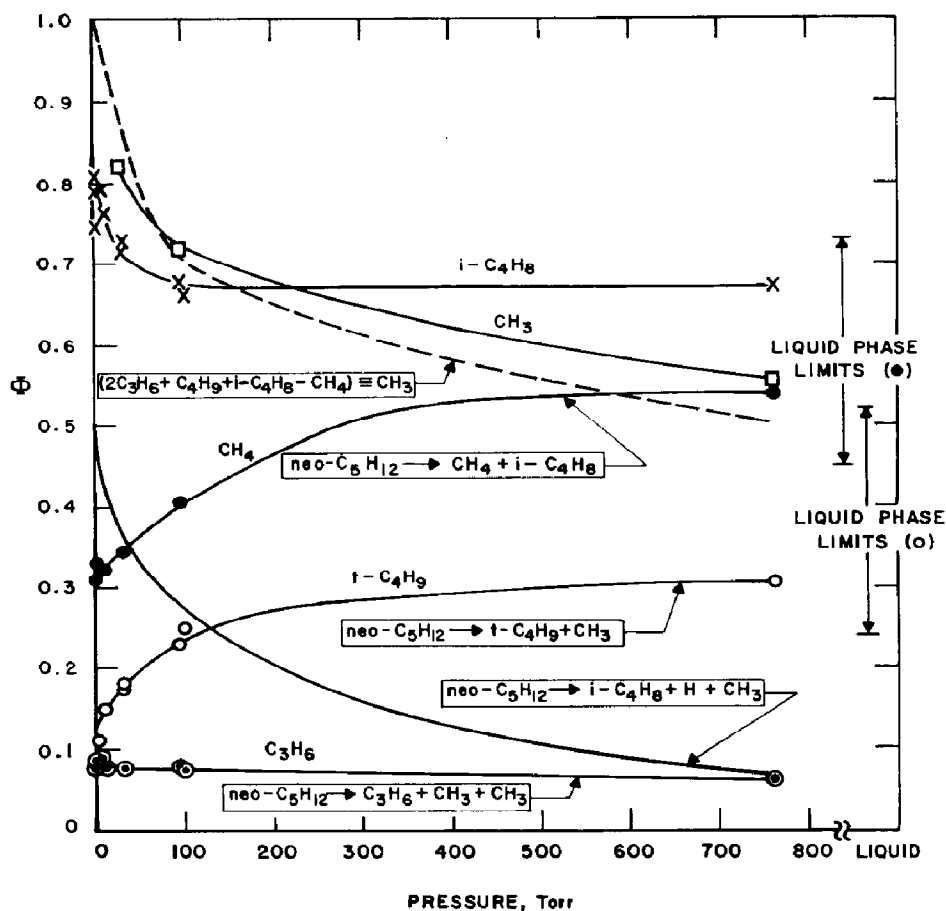
Fig. 1. Quantum yields of molecular and radical fragments formed in the 7.6 eV photolysis of neopentane at pressures in the range 1 - 760 Torr, and in the liquid phase. Also shown are the quantum yields which can be attributed to processes (1) - (4). For the sake of comparison with the measured methyl radical yield, the yields of methyl radicals which would be predicted from material balance considerations are given by the broken line.

is no evidence that the isobutene formed in process (1) undergoes any further dissociations, except possibly to a slight extent in the 10.0 eV photolysis, where C_4H_7 and C_3H_5 are formed with quantum yields of 0.07 and 0.03 respectively.) We shall now discuss the results given in Table 1 and Figs. 1, 2 and 3 in terms of process (1) - (5) and (8).

$$neo\text{-}C_5H_{12} \rightarrow H_2 + C_5H_{10}$$
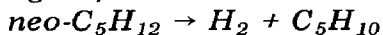
The yields of molecular D_2 formed in the photolysis of neo-C_5D_{12} listed in Table 1, can be assumed to be at least approximately the same as those which would be observed in undeuterated neopentane. These yields are the maximum yields which can be assigned to hydrogen elimination process (8), since some molecular hydrogen could originate from secondary decomposition of excited fragment species. Such secondary decompositions leading to the formation of molecular $H_2(D_2)$ are, however, not very important since the quantum yield of this product does not change substantially with increasing density. Accepting that the yields of molecular
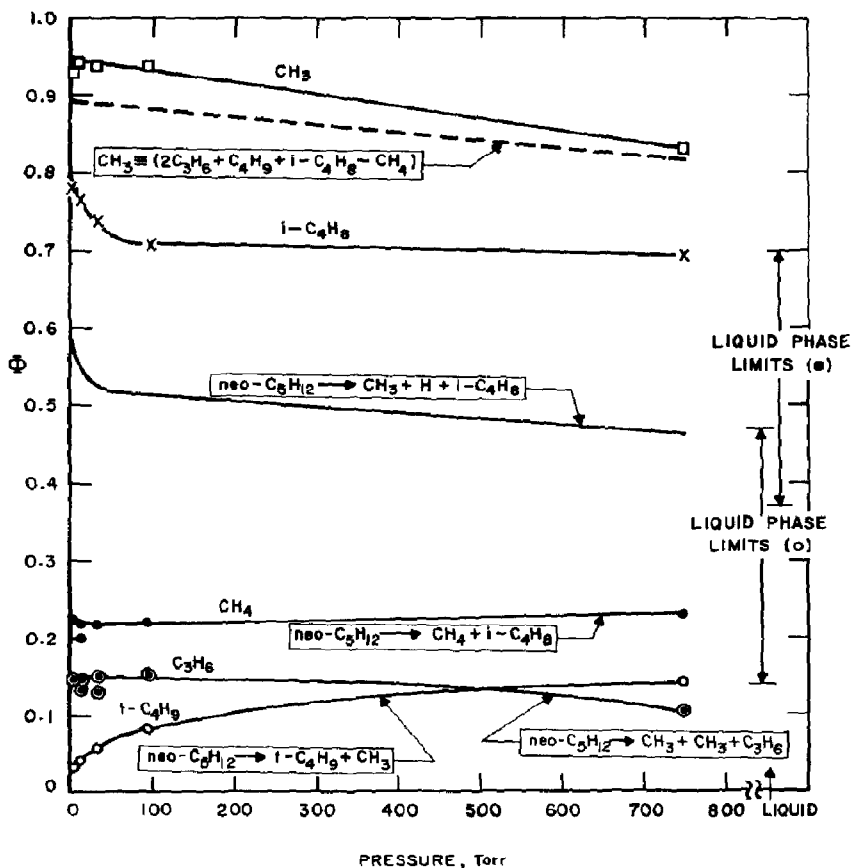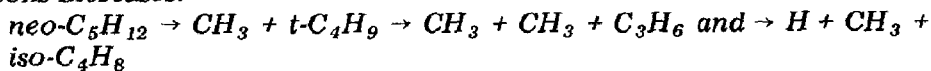
Fig. 2. Quantum yields of molecular and radical fragments formed in the 8.4 eV photolysis of neopentane at pressures in the range 1 - 760 Torr, and in the liquid phase. Also shown are the quantum yields which can be attributed to processes (1) - (4). For the sake of comparison with the measured methyl radical yield, the yields of methyl radicals which would be predicted from material balance considerations are given by the broken line.

D_2 correspond approximately to the quantum yields which can be attributed to process (8), the results show that in contrast to the trends observed for linear alkanes, the probability of elimination of a molecule of hydrogen from excited neopentane, apparently increases as the energy of the absorbed photons increases.

$neo\text{-}C_5H_{12} \rightarrow CH_3 + t\text{-}C_4H_9 \rightarrow CH_3 + CH_3 + C_3H_6$ and $\rightarrow H + CH_3 + iso\text{-}C_4H_8$

The yields of stable t-butyl radicals intercepted by HI are plotted as a function of pressure in Figs. 1, 2 and 3. The yield of stabilized radicals increases as a function of pressure, indicating that excited t-butyl radicals formed in primary process (4) undergo further dissociation unless they are collisionally stabilized.

It has been reported [11] that the most probable mode of dissociation of a vibrationally excited t-butyl radical is the loss of a H atom to form isobutene:
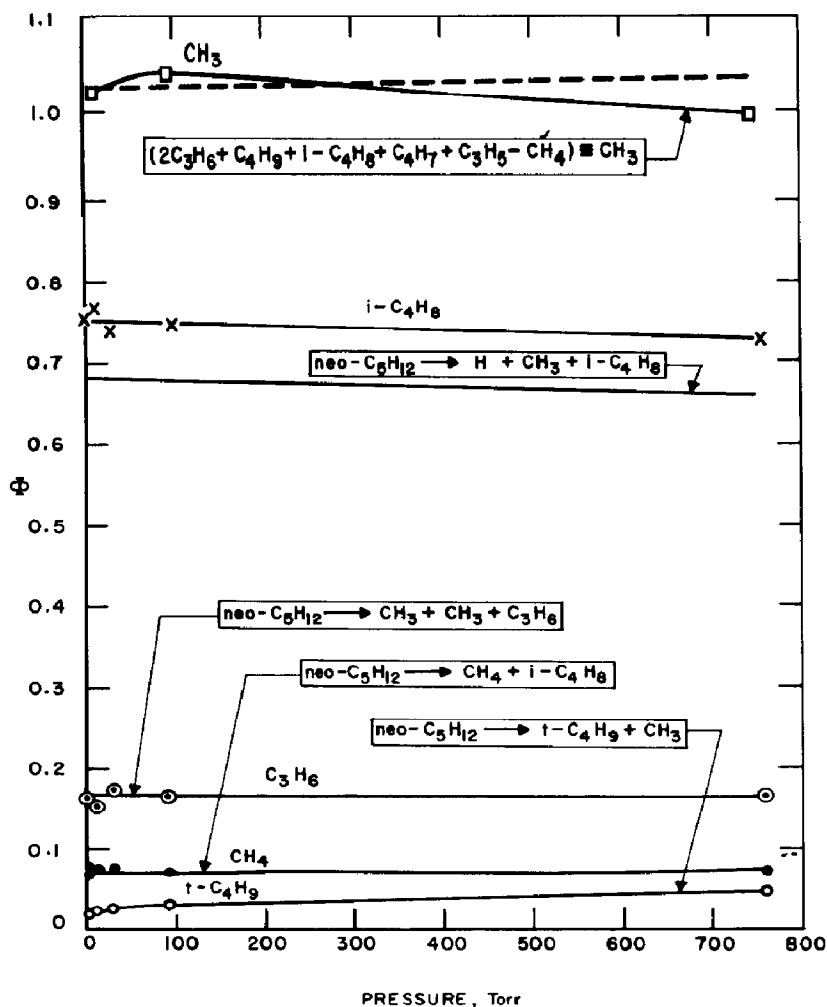
Fig. 3. Quantum yields of molecular and radical fragments formed in the 10.0 eV photolysis of neopentane at pressures in the range 1 - 760 Torr. Also shown are the quantum yields which can be attributed to processes (1) - (4). For the sake of comparison with the measured methyl radical yield, the yields of methyl radicals which would be predicted from material balance considerations are given by the broken line.

TABLE 1

Quantum yields of D_2 and HD formed in the photolysis of neo-C_5D_{12} + HI (1:0.02)

Photon energy (eV)	Pressure (Torr)	Φ	
		D_2	HD
7.6	10.6	0.0099	0.349
	101.0	0.0081	0.166
	729.0	0.010	0.109
	Liquid	⩽0.03	
8.4	10.6	0.020	0.519
10.0	10.4	0.061	0.580

$$t\text{-}C_4H_9 \rightarrow H + iso\text{-}C_4H_8 \tag{9}$$

Process (4) followed by reaction (9) is, of course, the overall process (3), which is indeed observed in these experiments. The results given in Figs. 1, 2 and 3 show that the yield which can be attributed to overall process (3) does diminish as the yield of C_4H_9 increases and by an amount, in the 8.4 and 10.0 eV photolysis which approximately compensates the corresponding increase in the yield of the C_4H_9 radical. (In the 7.6 eV photolysis, the decrease in the yield of process (3) is much greater than that required to balance the increase in the yield of C_4H_9 radical, which we will consider below.) This result suggests that those t-butyl radicals which are collisionally stabilized would have dissociated mainly through process (9). This does not necessarily mean, however, that process (3) occurs exclusively through the pathway [process (4) followed by process (9)]. We cannot entirely exclude the possibility that process (3) to some extent involves dissociation of the methane formed in process (1) or dissociation of the neopentyl radicals formed in process (5).

The propylene formed in process (6) can only originate through the loss of a methyl radical from a butyl radical. Since dissociation of a t-butyl radical cannot directly lead to propylene formation, the propylene must result either from rearrangement of a CH_3CCH_3 diradical, or from an initial rearrangement of the t-butyl radical to an isobutyl structure, followed by dissociation:

$$neo\text{-}C_5H_{12} \rightarrow (CH_3)_3C + CH_3 \rightarrow (CH_3)_2CHCH_2 + CH_3 \rightarrow CH_3CHCH_2 + {} + 2CH_3 \tag{10}$$
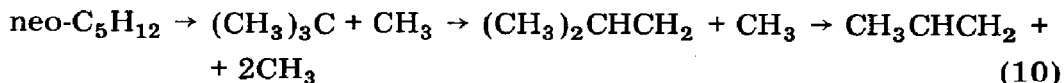
Although radical rearrangement processes are believed not to occur in pyrolysis, such isomerizations have been observed [9] in liquid phase photolysis experiments. Specifically, rearrangement of t-butyl radicals to the isobutyl structure has been observed in the liquid phase photolysis of 2,2-dimethylbutane. In our experiments, the t-butyl radicals will come into being with, respectively, as much as 4.2, 5.0 or 6.6 eV excess energy. The isomerization from a t-butyl to an isobutyl structure is about 0.35 eV endothermic.

It is striking that the propylene product shows only a very slight diminution in yield with increasing pressure in the photolysis at all three energies. As mentioned above, those t-butyl radicals which are collisionally stabilized in this pressure range apparently dissociate mainly through process (9). The process which leads to the formation of propylene therefore must occur at a time shorter than 10^{-9} s (the approximate collision interval at a pressure of about 1 atm). As the results given in Table 2 (which will be discussed later) show, the formation of propylene in process (2) is strongly quenched in the liquid phase photolysis. In the liquid phase photolysis at 7.6 eV there is no propylene, and at 8.4 and 10.0 eV, the quantum yield of propylene is less than 0.04 or 0.02, respectively.

$$neo\text{-}C_5H_{12} \rightarrow CH_4 + iso\text{-}C_4H_8$$
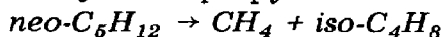
The yields of molecular methane formed in the photolysis of neo-

pentane with 7.6, 8.4, and 10.0 eV photons are shown as a function of pressure in Figs. 1, 2 and 3, respectively. In the 10.0 eV photolyses, there is no discernible effect of pressure on the yield of methane in this pressure range, while in the 8.4 eV photolysis there may be a slight increase in the yield of methane with increasing pressure, but this increase is so slight as to be within experimental error. However, in the 7.6 eV photolysis, the observed yield of methane shows a pronounced increase with increasing pressure. This result suggests, at first glance, that excited methane molecules formed in primary process (1) undergo further dissociation:

$$CH_4^\star \rightarrow CH_3 + H \tag{11}$$

and can be collisionally stabilized in the 7.6 eV photolysis. As the yield of methane increases with pressure, the yield which can be attributed to overall process (3) [which would correspond to primary process (1) followed by dissociation reaction (11)] decreases. As mentioned earlier, a part of this decrease must be because of the collisional stabilization of excited t-butyl radicals which in the absence of stabilization dissociate through loss of a H atom. The total decrease in the yield which can be attributed to process (3) (—0.43) is just balanced by the increases in the yields of methane (+0.23) and t-butyl radicals (+0.20).

Methane formation in neopentane can only come about through a process in which an olefin product, iso-C_4H_8, is formed directly. Such a 1,3-elimination is apparently a lower energy process than 1,2-methane elimination processes, which must involve carbene formation or the formation of a high energy transition state. Therefore, the methane product of a 1,3-elimination might be expected to carry away more excess energy than that formed in a 1,2-elimination. In the photolysis of n-butane it has been shown that the ethane formed in a 1,3-elimination process dissociates further while that formed in a 1,2-elimination is stable [5].

However, an alternate interpretation must be considered — that the increase in the yield of methane with increasing pressure in the 7.6 eV photolysis comes about because the excited parent molecule itself is collisionally deactivated to a lower vibrational level of the upper electronic state, so that the relative probabilities of the various primary processes change with pressure. This is a fairly startling interpretation in that evidence for such an effect has never been observed in the gas phase photolysis of alkanes. It is true that fluorescence ($\Phi \sim 10^{-4}$ - 10^{-3}) has been observed [12] in linear alkanes having five or more carbon atoms, and that the lifetimes of the fluorescing states have been shown to be in the range 10^{-9} s. Excited states with lifetimes as long as this could be collisionally deactivated in the pressure range 1 - 700 Torr. No fluorescence is observed in neopentane, but this does not necessarily mean that the dissociative lifetime of neopentane is short.

Actually, no final conclusion can be drawn from our results about the reason for the pressure dependence of the methane yield at 7.6 eV.

$$neo\text{-}C_5H_{12} \rightarrow H + C_5H_{11}$$
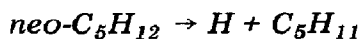
One possible pathway for the occurrence of overall process (3) is the initial loss of a hydrogen atom, and the subsequent loss of a methyl radical from the resulting neopentyl radical. Since neopentyl radicals could not be determined in our experiments, any information about the occurrence of process (5) must be derived from material balance considerations. Since the quantum yields which can be attributed to processes (1) - (4) add up approximately to unity, and because the D atom yields determined in neo-C_5D_{12} (Table 1) are not greater than the yields of process (3), we can conclude that the yield of stable C_5H_{11} radicals formed in process (5) is very small at all energies. We cannot exclude the possibility that some of the yield which we have attributed to process (3), originates through dissociation of neopentyl radicals formed in process (5) in the 8.4 and 10.0 eV photolysis. However, at 7.6 eV, this cannot be very important because at high pressures where secondary dissociations have nearly been quenched (the yield of process (3) is only 0.06 at 760 Torr), there still is apparently little excess H atom yield.

Photolysis of neopentane in the liquid phase

Table 2 shows the product distributions and approximate quantum yields of the products formed in the liquid phase photolysis of neopentane. In the presence of dissolved oxygen, which scavenges radicals, essentially the only products are methane and isobutene which are formed in approximately equal yields with a quantum yield of about ~ 0.8. These products are formed in process (1), as well as through a geminate disproportionation reaction between the methyl and t-butyl radical products formed in process (4):

$$[CH_3 + t\text{-}C_4H_9] \rightarrow CH_4 + iso\text{-}C_4H_8 \qquad (12)$$

However, if gas phase disproportionation/recombination ratios prevail in the liquid phase, about 56% of the methyl and t-butyl radicals interacting in a cage would be expected to undergo recombination to regenerate neopentane [13]:

$$[CH_3 + t\text{-}C_4H_9] \rightarrow neo\text{-}C_5H_{12} \qquad (13)$$

Since the estimated quantum yield of decomposition is at least as high as 0.8 the quantum yield which can be attributed to reaction (13) is 0.2 or less, which means that the maximum possible quantum yield which could be attributed to cage reactions (12) and (13) is 0.36 in both the 7.6 and 8.4 eV photolysis.

When HI is dissolved in the liquid neopentane, isobutane becomes an important product:

$$t\text{-}C_4H_9 + HI \rightarrow iso\text{-}C_4H_{10} + I \qquad (14)$$
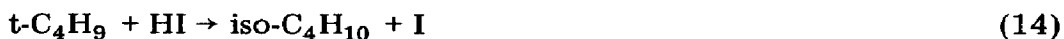
demonstrating that process (4) does indeed occur in the liquid phase, with a quantum yield of at least 0.16 - 0.24 at 7.6 eV and 0.11 - 0.14 at 8.4 eV.

TABLE 2

Yields of products formed in the liquid phase photolysis of neopentane

Photon energy (eV)	Additive	Φ					
		CH_4	iso-C_4H_8	iso-C_4H_{10}	C_3H_6	C_2H_6	H_2
7.6	None	1.00	0.99	0.026	0.000	0.018	0.03
	O_2	1.00	0.97	0.012	0.000	0.000	
	0.3% HI	1.00*	0.72	0.24	0.000	0.000	
8.4	None	1.00	1.03	0.045	0.011	0.048	0.16
	0.2% HI	1.00*	0.80	0.14	0.040	0.004	
10.0	None	1.00	0.88	0.049	0.020	0.087	0.28
	0.2% HI	1.00	n.d.	$\leqslant 0.18$	0.018	0.020	

*$\Phi \approx 1 \pm 0.2$.

Taking into account the maximum possible occurrence of cage reactions (12) and (13), we can say that the maximum quantum yield for process (4) is about 0.5 at both 7.6 and 8.4 eV. The maximum and minimum limits, we have estimated for the quantum yield of process (4) at these energies are shown in Figs. 1 and 2.

As mentioned above, secondary decompositions such as process (11), leading to the formation of propylene, are substantially quenched at the high densities of the liquid phase.

Unfortunately, isotopic experiments were not performed in the liquid phase, so it is impossible to say just how much of the observed hydrogen is formed in a molecular elimination process and how much results from H atom reactions. Since it would be expected that at the high densities of the liquid phase, secondary decompositions would not contribute significantly to the formation of H atoms or H_2 (i.e., process (3) is of negligible importance in the liquid phase as evidenced by the equivalence in the yields of i-C_4H_8 and CH_4), the observed hydrogen must result from H_2 elimination or from reactions of H atoms formed in process (5).

In the liquid phase, there is a sharp increase in the yield of hydrogen when the photon energy is increased. In the 10.0 eV photolysis, however, it is possible that ionic processes also contribute to hydrogen formation. (The gas phase ionization potential of neopentane is 10.55 eV, but it is thought that ionization potentials are lowered in the liquid phase.)

Since process (1) is the only other decomposition mode available to the excited neopentane molecules in addition to the hydrogen-forming process(es) and process (4), we can make a rough estimate of the maximum and minimum quantum yields which can be attributed to process (1) since the total quantum yield of decomposition is 0.8 - 1.0. These are shown in Figs. 1 and 2.

If we compare, in Figs. 1 and 2, the estimated limits of the yields of processes (1) and (4) with the observed quantum yields of the processes

occurring in the gas phase at pressures of about 760 Torr, we see that in the 7.6 eV photolysis (Fig. 1) the yields at high pressures in the gas phase fall well within the estimated limits for these processes in the liquid phase. (In making this comparison, we make the simplifying assumption that in the gas phase, decomposition processes (2) and (3) mainly involve a $C_4H_9{}^*$ intermediate, so the yields of these processes should be attributed to primary process (4).) In other words, although there are strong pressure effects in the photolysis at 7.6 eV from 1 to 760 Torr, there is apparently little further change in the relative importances of primary processes in going to liquid phase densities. In the 8.4 eV photolysis, on the other hand, there is no apparent correlation at all between the yields of the various processes observed at a high pressure in the gas phase and the estimated yields for processes (1) and (4) in the liquid phase. In fact, if we compare the liquid phase yield estimates from the 7.6 and 8.4 eV experiments, we see that in the liquid phase, there is actually very little difference between the results obtained at the two energies. No quantum yield determinations were made at 10.0 eV, but the product distributions measured in the 10.0 eV experiments are very similar to those obtained at the lower energies. Apparently, in the liquid phase excited molecules formed upon photon absorption are deactivated to lower vibrational levels of the upper electronic state before dissociation occurs, and it is also from these levels that dissociation occurs in the 7.6 eV photolysis, at least at a pressure of 760 Torr. It is clear, however, that more quantitative gas and liquid phase work is needed on the photolysis of other alkanes close to the absorption threshold in order to understand the effect of density on photochemical decomposition processes.

Photolysis of isobutane

Table 3 gives the quantum yields of products formed in the 7.6 and 8.4 eV photolysis of $(CH_3)_3CD$ in the presence of NO as a radical scavenger as well as the yields of radicals scavenged by HI (reaction 7). The latter yields were determined in $(CD_3)_3CD/HI$ mixtures, and isotopic analyses were carried out to determine the relative yields of fully deuterated products and the monoprotonated analogues formed in reaction (7).

The molecular hydrogen formed in the 7.6 eV photolysis of $(CH_3)_3CD$ consists predominantly (85 - 90%) of HD, indicating that the major hydrogen elimination process is that giving an isobutene product directly:

$$(CH_3)_3CD \rightarrow (CH_3)_2C\!\!=\!\!CH_2 + HD \qquad (15)$$

A small amount of H_2 is observed in this experiment, indicating that the process:

$$(CH_3)_3CD \rightarrow H_2 + C_4H_7D \qquad (16)$$

may also occur at this energy. When a 1:1 mixture of iso-C_4H_{10} and iso-C_4D_{10} are photolyzed with 7.6 eV photons in the presence of NO as a radical scavenger, about 12% of the hydrogen fraction consists of HD, so there is

TABLE 3

Quantum yields of products formed in the photolysis of $(CH_3)_3CD/NO$ (1:0.05) mixtures and $(CD_3)_3CD/HI$ (1:0.03) mixtures

Photon energy	Pressure (Torr)	$(CH_3)_3CD/NO$					$(CD_3)_3CD/HI$		
		HD	H_2	CH_3D	CH_4	Propylene	D atoms	Methyl radicals	Propyl radicals
7.6	5*	0.28	0.043	0.0055	0.033	n.d.	0.67	0.32	0.037
	51*	0.38	0.050	0.0055	0.041	0.21	0.64	0.38	0.040
	326	0.34	0.042	0.0055	0.047	0.19	0.46	0.43	0.11
8.4	31	0.088	0.052	0.096	0.056	0.44	n.d.	n.d.	n.d.

n.d. = not determined.
*Quantum yield determinations not made. Relative yields are given and are normalized to the higher pressure experiment on the assumption that the quantum yield of CH_3D will show little or no pressure effect.

some contribution of H atoms to the so-called molecular hydrogen determined in the presence of NO. For this reason, it isn't really possible to determine exactly what the relative importances of processes (15) and (16) are in the 7.6 eV photolysis, but we can say that process (15) is at least 7 times more important than process (16). From results reported in earlier studies [14], we have estimates that the ratio of process (15) to process (16) in the 8.4 eV photolysis is 1.7, and in the 10.0 eV photolysis, is about 0.5. Process (15), in which an olefin is formed directly, would be expected to be a lower energy process than reaction (16), which must involve either carbene formation or a high energy transition state. The overall quantum yield of hydrogen elimination processes diminishes as a function of energy; the same trend is observed in the photolysis of linear alkanes.

Similarly, we can examine the two modes of formation of methane, the 1,2-elimination involving the transfer of the tertiary H(D) to the departing methyl group:

$$(CH_3)_3CD \rightarrow CH_3D + C_3H_6 \qquad (17)$$

or the 1,3-elimination, in which the departing methyl takes a hydrogen atom from another methyl group:

$$(CH_3)_3CD \rightarrow CH_4 + CH_3CDCH_2 \qquad (18)$$

Again, the 1,3-elimination involves the direct formation of an olefin, and presumably is a lower energy process than process (17) in which a carbene or a high energy transition state must be formed. As in the case of hydrogen formation, the lower energy elimination (process 18) predominates strongly in the 7.6 eV photolysis, and diminishes in importance relative to the competing higher energy elimination (process 17) when the photon energy is increased. The ratio of 1,3-elimination (18) to 1,2-elimination (17) is about 6 - 8 at 7.6 eV, $\sim$ 0.7 at 8.4 eV, and $\sim$ 0.6 at 10.0 eV. It is probably

significant that in the 7.6 eV photolysis, the ratio of the 1,3-elimination (18) to the 1,2-elimination (17) increases as a function of pressure. Unfortunately, quantum yield determinations could not be made in the lower pressure experiments at 7.6 eV because of incomplete light absorption, and therefore we cannot say definitely whether the changing ratio represents a change in the relative probabilities of competing primary processes (17) and (18), or rather, if a fraction of the methane formed in the lower energy process (18) carries off enough excess energy that it dissociates unless it is collisionally stabilized. It is difficult to decide between these two interpretations. The fragments formed in the methane elimination process (18) share 6.8 eV excess energy in the 7.6 eV photolysis; this is coincidentally the same amount of excess energy as that shared by the products of methane elimination process (1) in neopentane, where a much stronger dependence on pressure was observed for the methane yield. The accompanying fragment in the neopentane dissociation, C_4H_8, has more degrees of freedom than the C_3H_6 fragment in process (18), and so the methane formed in isobutane probably carries away more energy on the average than that formed in neopentane, and would be expected to show a smaller pressure effect.

Other primary processes which could occur in isobutane are cleavage of a C—H bond:

$$(CH_3)_3CH \rightarrow H + C_4H_9 \tag{19}$$

cleavage of a C—C bond:

$$(CH_3)_3CH \rightarrow (CH_3)_2CH + CH_3 \tag{20}$$

and methylene elimination:

$$(CH_3)_3CH \rightarrow C_3H_8 + CH_2 \tag{21}$$

Process (21) has been shown [4] to occur in the 8.4 and 10.0 eV photolysis, where it is a very minor process (Φ at 8.4 eV $\sim$ 0.008). No molecular propane is observed in the 7.6 eV photolysis, so process (21) apparently does not occur at this energy.

As the results given in Table 3 show, isopropyl radicals are intercepted by HI in the photolysis of isobutane, demonstrating the occurrence of process (20). At low pressures a fraction of the isopropyl radicals would be expected to dissociate further, either by loss of a H atom to give the overall process:

$$(CH_3)_3CH \rightarrow CH_3CHCH_2 + H + CH_3 \tag{22}$$
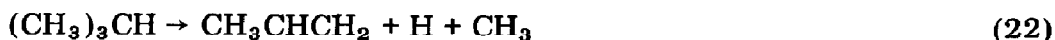
or by loss of a methyl radical to give the overall process:

$$(CH_3)_3CH \rightarrow CH_3 + CH_3 + C_2H_4 \tag{23}$$

The increase in the yield of propyl radicals with pressure confirms the fact that such secondary dissociation processes do occur at 7.6 eV. Process (22) would also result if the C_4H_9 radical formed in process (19) dissociated
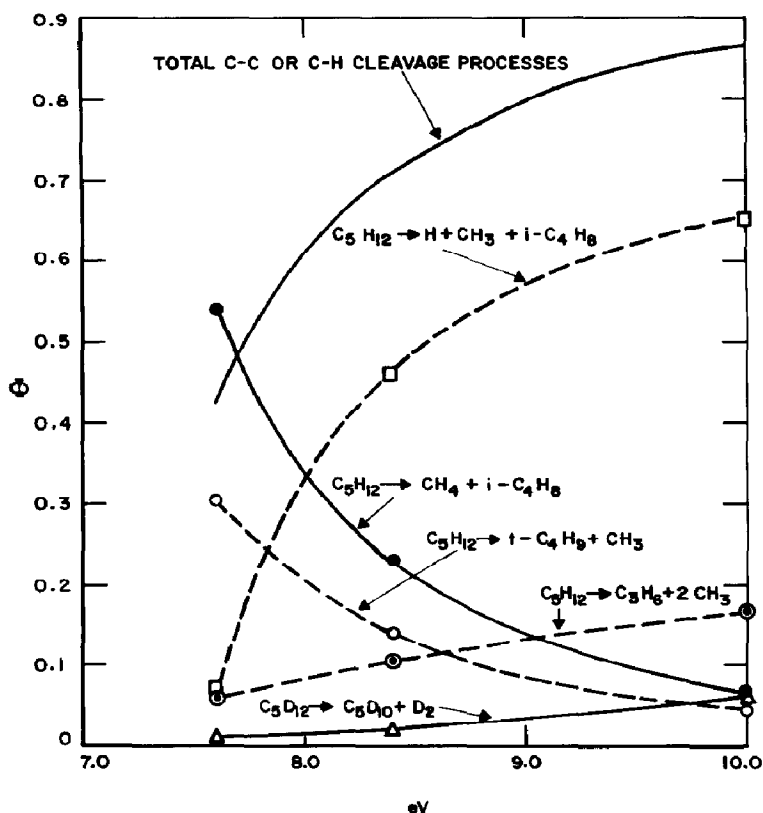
Fig. 4. Quantum yields of processes (1) - (4) and (8) measured at a pressure of 760 Torr in the photolysis with 7.6, 8.4, and 10.0 eV photons. Also shown is the total quantum yield of processes (2) - (4), which can be assumed to be approximately equal to the initial quantum yield of primary process (4) (plus possibly a small contribution from process (5) at the higher energies) since under these conditions processes (2) and (3) mainly represent secondary decompositions of the C_4H_9 product of process (4).

further by losing a methyl radical as it does in the photolysis of neopentane (reaction 11).

Conclusions

Quantum yields of primary processes in neopentane as a function of energy

Figure 4 shows the quantum yields which were attributed to processes (1) - (4) and (8) in the photolysis of neopentane at a pressure of about 760 Torr, as a function of the photon energy. Dissociation of the methane product of process (1), if it occurs at all, should be minimal at this pressure, and we can assume that the yields attributed to this process do represent the initial quantum yields of the primary process (1). The Figure also shows the total quantum yield which can be attributed to primary processes involving direct C—C or C—H cleavage [processes (4) and (5)]. The Figure shows that the quantum yield of methane elimination process (1) diminishes drastically with energy, while there is an increase in the yields of the direct

C—C or C—H bond cleavage processes. This is reasonable, since as one goes to higher energies one would expect the excited molecule to have a shorter dissociative lifetime, and hence to undergo processes requiring rearrangement (such as 1) with a lower probability. The same general trend — a diminution of the quantum yields of molecular elimination processes and an increase in the yields of faster direct bond cleavage processes as a function of increasing energy — has been reported before in the photolysis of ethane [15]. As mentioned above, the minor hydrogen elimination process in neopentane appears to increase in importance with increasing energy, in contradiction to the trend usually observed.

Effects of molecular structure on the importances of primary processes

Recent theoretical and experimental work has shed some light on the nature of the excitation process and the lifetimes of excited states in alkanes. For instance, it has been predicted [16] that the first singlet—singlet transitions in methane, ethane, and propane involve the departure of an electron from a molecular orbital mainly populated in the C—H bonds, while for n-butane and the higher linear homologues, the orbital of departure is mainly of C—C character. For the branched alkanes, the orbital of departure is said to be of mixed C—C and C—H character. In recent studies of fluorescence in alkanes [17], it has been shown that the C_1—C_3 linear alkanes, and the branched isomers do not fluoresce, and this has been interpreted to mean that the excitation process results in distortion of the molecule. It is tempting to try to correlate all this information with what we know about the primary photochemical processes in alkanes. Such an attempt meets with only limited success. For instance, the character of the orbital of departure for the lowest singlet—singlet transition does not seem to be the determining factor in deciding the nature of the primary photo-chemical decomposition process which will predominate at energies near the absorption onset. All linear alkanes studied thus far [1] eliminate H_2 with a high probability at low energies, no matter whether the orbital of departure for the lowest singlet–singlet transition is of C—C or C—H character.

On the other hand, in the photolysis of neopentane at 7.6 eV, 90% or more of the primary photochemical decompositions are accounted for by methane elimination or direct C—C bond cleavage. This is consistent with the picture of an excited state in which the C—C bonds of the molecule are distorted, *i.e.* in which the excitation energy is localized in the carbon skeleton. Among the alkane molecules whose photolysis has been studied to date, neopentane is unique in that the elimination of a molecule of hydrogen is unimportant at all energies, and apparently actually decreases in importance as the energy approaches the absorption threshold.

In the photolysis of isobutane on the other hand, hydrogen elimination is of major importance near the absorption threshold and decreases in importance with increasing photon energy, just as it does in the photolysis of the normal alkanes. However, in isobutane the mechanism of the

hydrogen elimination process is not the same as that which predominates in the lower alkanes. In the photolysis of partly labelled ethane and propane, it has been shown that the predominant process leading to the split out of a hydrogen molecule involves the departure of two H(D) atoms from a single carbon atom. The results given in Table 3 on the photolysis of $(CH_3)_3CD$ show that the mechanism for the hydrogen elimination process in this branched compound mainly involves loss of the tertiary H(D) species and a hydrogen from one of the methyl groups. A cursory examination of the results of this and other studies seems to indicate that the strengths of the individual C—H (or C—D) bonds have a large part in determining which H(D) atoms preferentially participate in the hydrogen elimination process. The most obvious example is isobutane, where the single weakly bonded tertiary hydrogen is included in the eliminated hydrogen molecule in 89% of the cases at 7.6 eV. In the dissociation of excited propane [18] the major hydrogen elimination process involves loss of the two secondary hydrogens; furthermore, the process shows a hydrogen isotope effect, being more important in $CD_3CH_2CD_3$ than in $CH_3CD_2CH_3$.

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