Studies in Vacuum-ultraviolet Photochemistry. Part II.† 2,2,4-Trimethylpentane

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2,2,4-Trimethylpentane has been photolysed at 123·6 and 147 nm at substrate pressures of 1—55 Torr, and conversions of 0·02—0·4%. Use of radical scavenging techniques show the existence of three molecular primary

$$C_8H_{18} \longrightarrow i\text{-}C_4H_8 + i\text{-}C_4H_{10} \quad \text{(i)}$$
$$\longrightarrow CH_4 + C_7H_{14} \quad \text{(ii)}$$
$$\longrightarrow C_3H_6 + neo\text{-}C_5H_{12} \quad \text{(iii)}$$
$$C_8H_{18} \longrightarrow Me + C_7H_{15} \quad \text{(iv)}$$
$$\longrightarrow Bu^t + Bu^i \quad \text{(v)}$$
$$\longrightarrow Pr^i + neo\text{-}C_5H_{11} \quad \text{(vi)}$$

processes (i)—(iii). In addition to processes (i)—(iii), radical processes (iv)—(vi) also occur. Deactivation of the excited molecular and radical primary products is incomplete, and secondary fragmentation reactions occur.

THE vacuum-ultraviolet photochemistry of lower alkanes has been investigated extensively.[1-6] Both molecular and free-radical primary processes occur, the latter increasing in proportion as the energy of the incident radiation increases. As part of an investigation of the photolysis of gaseous branched higher alkanes, 2,2,4-trimethylpentane has been photolysed at 147 and 123·6 nm. The effect of the addition of radical scavengers and inert gases upon the product distribution has been determined. A number of molecular and free-radical primary processes occur. Deactivation of the excited molecular and radical products is incomplete, and further secondary fragmentation reactions occur.

EXPERIMENTAL

The apparatus and experimental procedure has been described.[7] 2,2,4-Trimethylpentane was purified by preparative g.l.c. Nitric oxide, hydrogen sulphide, and argon were supplied by the Matheson Company. Xenon and krypton used in the manufacture of the rare-gas resonance lamps were British Oxygen Company Ltd. ' grade X ' gases, and were used as supplied.

RESULTS

Under all experimental conditions isobutene was the major product. Relative molar yields with respect to isobutene (100) are shown in Table 1 for the other major products isolated. The effect of the radical scavengers nitric oxide, oxygen, iodine, and hydrogen sulphide, and of 750 Torr (1 Torr = 133·32 N m^{-2}) of argon, on the product ratios is shown in Tables 2 and 3. Results obtained by Holroyd[8] for the liquid-phase photolysis of 2,2,4-trimethylpentane are included for comparison. The data in the Tables were obtained from photolyses taken to

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† Part I, ref 7.

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[6] P. Ausloos and A. A. Scala, *J. Chem. Phys.*, 1966, **45**, 847.

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conversions of less than 0·1%, with input powers to the lamps of 25—40 W.

Some other products, in addition to those in the Tables, were detected. At 123·6 nm and 13 Torr these included ethylene (4), 2-methylbut-2-ene (1·0), 2,2-dimethylbutane (2·0), 2,3-dimethylbutane (2·0), and four C_6 olefins and two C_7 alkanes (all $<1·0\%$). 2,3- and 2,2-Dimethylbutane were reduced to zero yield when radical scavengers were added. The C_7 alkanes were eliminated in the presence of nitric oxide, oxygen, and iodine, but were unchanged when hydrogen sulphide was added. The yields of the alkenes were unchanged in the presence of all four scavengers. G.l.c. traces showed no evidence for products with more than seven carbon atoms. At very low pressures (<1 Torr), allene was detected as a minor product, and extensive fragmentation of the major products was evident. Not all the higher products were positively identified. The C_7 alkenes (2,4- and 4,4-dimethylpent-2-ene) are present in the ratio of *ca.* 3 : 2, and the C_7 alkanes are probably 2,2- and 2,4-dimethylpentane.

TABLE 1

Yields of major products in the photolysis of 2,2,4-trimethylpentane

Pressure/Torr	1·6	13	53	1·6	13	Liquid[a]
Wavelength/nm	123·6	123·6	123·6	147	147	147
Methane	28	25	23	30	27	40
Ethane	46	32	28	33	27	
Propane		8	7		4	
Propene	66	48	42	55	42	13
Isobutane	60	64	69	62	73	110
Isobutene	100	100	100	100	100	100
Neopentane	15	11	11	22	17	18
Isopentane	11	12	10	7	11	2·5
C_7 alkenes		25			27	

[a] Ref. 8.

TABLE 2

Effect of radical scavengers on product distribution at 123·6 nm

Scavenger	None	O_2 (8%)	NO (5%)	I_2 (2%)	H_2S (7%)
Methane	25	10		9	79
Ethane	32	<1	<1	0·2	8
Propane	8	<1			22
Propene	48	62	63	65	40
Isobutane	64	41	40	35	83
Isobutene	100	100	100	100	100
Neopentane	11	7	6	6	12
Isopentane	12	0·3	0·4	0·5	0·5
C_7 alkenes	25	25	23	25	23

Pressure of 2,2,4-trimethylpentane = 13 Torr.

TABLE 3

Photolysis of 2,2,4-trimethylpentane at 147 nm

Pressure/Torr	13	13	13	Liquid[a]	Liquid[a]
Scavenger	None	O_2 1 Torr	O_2 1 Torr	None	I_2 1·2 mmol
Argon	None	None	750 Torr	None	None
Methane	27	18	20	40	
Ethane	27	0	0		
Propene	42	36	32	13	13
Isobutane	73	56	77	110	97
Isobutene	100	100	100	100	100
Neopentane	17	10	11	18	16
Isopentane	11	0	0	2·5	0·5
C_7 alkenes	27	25	27		

[a] Ref. 8.

DISCUSSION

The photolyses of hydrocarbons at wavelengths of less than 150 nm are known to involve both molecular and free-radical processes. To differentiate between the two processes recourse is made to the use of radical scavenging techniques. In the presence of nitric oxide, oxygen, or iodine, products arising from radical combination, disproportionation, and abstraction reactions are eliminated. Thus alkane products formed in the presence of these scavengers can be attributed solely to molecular processes, provided the radical scavenging reactions do not themselves lead directly, or indirectly, to alkane products. Alkenes produced under these conditions arise through molecular or very fast radical decomposition reactions. Table 2 shows that the product distribution obtained with each of these scavengers is similar. In the presence of hydrogen sulphide, radical-abstraction reactions are predominant, while combination and disproportionation reactions are eliminated.

Table 2 shows that the olefins produced in the presence of the scavengers are propene, isobutene, and the C_7 alkenes, while methane, isobutane, and neopentane are the major alkanes produced. Thus the primary processes (1)—(3) can be written.

$$C_8H_{18}^* \longrightarrow \text{iso-}C_4H_8 + \text{iso-}C_4H_{10} \qquad (1)$$

$$\longrightarrow CH_4 + C_7H_{14} \qquad (2)$$

$$\longrightarrow C_3H_6 + \text{neo-}C_5H_{12} \qquad (3)$$

There is always an excess of alkene over alkane. Thus either secondary fragmentation of the alkanes occurs, or there are other primary processes in which an alkene and two radicals are produced. Experiments in which argon (750 Torr) is added to the radical-scavenged photolysis show that only isobutane is increased, more so at 147 nm than at 123·6 nm. Even at high pressure there is an excess of isobutene. From the high pressure results, the relative importance of (1) : (2) : (3) is *ca.* 8 : 2 : 1 at 147 nm and 7 : 1·5 : 1 at 123·6 nm. Thus the split into fragments of near-equal size is preferred at both wavelengths. These figures are to be compared with those of Holroyd[8] of 7 : 3 : 1 at 147 nm in the liquid phase. The large difference in concentration in the two systems being considered, agreement is good.

To account for the excess of alkene over alkane other primary processes (4)—(6) must be operative, in which rapid fragmentation of initially produced internally excited radicals occurs. The fragments produced in

$$C_8H_{18}^* \longrightarrow \text{Me} + C_7H_{15} \qquad (4)$$

$$\longrightarrow \text{Bu}^t + \text{Bu}^i \qquad (5)$$

$$\longrightarrow \text{Pr}^i + \text{neo-}C_5H_{11} \qquad (6)$$

(4)—(6) are carrying *ca.* 460 kJ mol^{-1} at 147 nm and *ca.* 600 kJ mol^{-1} at 123·6 nm. Thus further fragmentation is likely, the processes being (7)—(14).

$$C_7H_{15} \longrightarrow H + C_7H_{14} \quad (7)$$

$$\longrightarrow Pr^i + iso\text{-}C_4H_8 \quad (8)$$

$$\longrightarrow C_3H_6 + Bu^t \quad (9)$$

$$Bu \longrightarrow H + iso\text{-}C_4H_8 \quad (10)$$

$$\longrightarrow Me + C_3H_6 \quad (11)$$

$$Pr \longrightarrow H + C_3H_6 \quad (12)$$

$$\longrightarrow Me + C_2H_4 \quad (13)$$

$$neo\text{-}C_5H_{11} \longrightarrow Me + iso\text{-}C_4H_8 \quad (14)$$

The overall effect of reactions (4)—(14) would be to increase the ratio of olefin to corresponding alkane in reactions (1)—(3). All these reactions occur, as Me, Pr, Bu, neo-C_5H_{11}, and C_7H_{15} radicals are all produced, in the approximate ratio 80 : 20 : 40 : 5 : 1 at 123·6 nm. The large inequality in yield of Me and C_7H_{15} implies extensive fragmentation of the larger radicals. Intercomparison of the data in the Tables emphasizes the overall importance of radical processes in the mechanism. The products isolated and the behaviour of the product distribution when radical scavengers are added are consistent with the known reactions of the radicals formed in the sequence (4)—(14).

Yields of hydrogen are very small, and are consistent with the reaction of hydrogen atoms produced in (10) and (12). As no C_8 alkene could be detected, we assume that molecular elimination of hydrogen in a primary process is unimportant.

It is of interest to compare the behaviour of the products isopentane and neopentane when radical scavengers are added. The data show that the ' free radical ' neopentane arises largely through an abstraction reaction (15), while isopentane, which is wholely free-radical in origin, arises in the combination reaction (16).

$$neo\text{-}C_5H_{11} + RH \longrightarrow neo\text{-}C_5H_{12} + R \quad (15)$$

$$Me + Bu^i \longrightarrow iso\text{-}C_5H_{12} \quad (16)$$

The presence of the neo-C_5H_{11} radical is further implied by the production of small amounts of 2,2-dimethylbutane. We assume this arises *via* (17). These observations imply that the Bu radicals are predominantly

$$neo\text{-}C_5H_{11} + Me \longrightarrow Bu^tEt \quad (17)$$

isobutyl radicals. We estimate a ratio of Bu^i : Bu^t of *ca.* 3 at 123·6 nm. Holroyd [8] in his liquid-phase experiments observed a 1·5 : 1 inequality in the yields of iso- and t-butyl radicals, and attributed this to isomerization of the latter to the former. If isomerization of t-butyl to isobutyl occurs, this is in marked contrast to the behaviour of t-butyl radicals produced in the vacuum-ultraviolet photolysis of tetramethylbutane,[7] in which no isomerization was observed. The other possibility is that in our gas-phase system the isobutyl radicals have a greater stability towards decomposition than the t-butyl radicals.

The results obtained in the gas-phase photolysis of 2,2,4-trimethylpentane support the nature of the primary molecular processes suggested by Holroyd [8] for the liquid-phase photolysis. In the gas phase the formation of products from radical precursors is greatly enhanced. In line with other hydrocarbons, radical participation is more important at 123·6 nm than at 147 nm. Addition of argon or of nitrogen (1 atm) has the same small effect on the product distribution. The data indicate that *ca.* 20% of the isobutane from process (1) decomposes in the absence of these additives, with less decomposition of the methane and neopentane from (2) and (3). As a comparison, addition of nitrogen or argon (900 Torr) in the photolysis of tetramethylbutane [7] gave a very similar increase in the yield of isobutane. This value is much less than would be required to account for the much greater participation of radical processes in the gas phase. Unless Holroyd [8] has underestimated the extent of radical processes, possibly owing to the occurrence of geminate radical reactions too rapid to be intercepted by the scavenger, then our results show that pressures of inert gas of the order of 1 atm are almost completely ineffective in deactivating excited primary molecular products.

We thank the Royal Society and Nuffield Foundation for the award of a Commonwealth Bursary (to E. S.)

[2/676 *Received, 22nd March,* 1972]