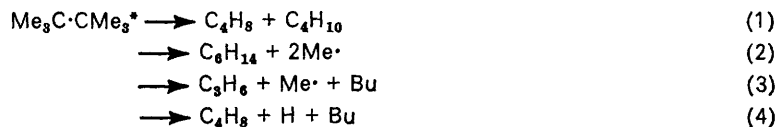# Studies in Vacuum Ultraviolet Photochemistry. Part I. 2,2,3,3-Tetramethylbutane

By **B. G. Gowenlock** and **C. A. F. Johnson**,* Department of Chemistry, Heriot–Watt University, Edinburgh EH1 1HX

2,2,3,3-Tetramethylbutane has been photolysed at 123·6 and 147 nm at substrate pressures of 1—25 Torr, and conversions of 0·03—0·3%. The primary processes are both molecular and free-radical in nature. The use of the free-radical scavengers oxygen, nitric oxide, and hydrogen sulphide show the existence of four important primary processes (1)—(4). At 147 nm, a further primary process producing molecular methane also occurs. The

$$Me_3C \cdot CMe_3{}^* \longrightarrow C_4H_8 + C_4H_{10} \qquad (1)$$
$$\longrightarrow C_6H_{14} + 2Me \cdot \qquad (2)$$
$$\longrightarrow C_3H_6 + Me \cdot + Bu \qquad (3)$$
$$\longrightarrow C_4H_8 + H + Bu \qquad (4)$$

photolysis mechanism involves extensive free-radical participation, and in this respect behaves in a manner similar to that of neopentane.

A NUMBER of investigations into the vacuum-u.v. photochemistry of alkanes have been carried out, although interest has been restricted mainly to those containing five or fewer carbon atoms.[1-4] Results have shown that both molecular and free-radical primary processes occur. Neopentane [5] differs from other alkanes studied in that free-radical processes play the more important role, especially at short wavelengths. The next higher hydrocarbon with a similarly highly branched symmetric structure is 2,2,3,3-tetramethylbutane, which, by analogy with neopentane, should undergo extensive free-radical fragmentation. 2,2,3,3-Tetramethylbutane has been photolysed at 123·6 and 147 nm, both in the presence and absence of inert gases and free-radical scavengers. The results obtained show that the photolysis follows a path similar to that of neopentane.

EXPERIMENTAL

A mercury-free, oil-diffusion pumped high-vacuum system of conventional design was used. The krypton (123·6 nm)

and xenon (147 nm) air-cooled electrodeless resonance lamps were modified versions of the type described by McNesby and Okabe.[6] The discharge was produced by an Electromedical Supplies Microtron 200 microwave generator operating at 2450 MHz, with an output power variable from 5 to 200 W. Accurate tuning of the microwave cavity was aided by an EMS reflected power meter. The lithium fluoride window was sealed to the lamp with ' Torr-seal' epoxy cement, and one end of the lamp was maintained at 77 or 112 K to condense any water vapour liberated from the walls. The rare-gas pressure was about 0·5 Torr (1 Torr = 133·32 N m⁻²). The lamp was attached to the 300 cm³ photolysis cell by means of a B45 ground joint.

Product analysis was by g.l.c. Small gaseous samples (ca. 1 cm³) could be removed from the photolysis cell and injected directly into a Perkin-Elmer model F11 gas chromatograph, fitted with a flame ionisation detector. Most analyses were carried out on a 2 m squalane column. In some cases various lengths (30—200 cm) of 2,2'-oxydipropiononitrile columns were used in series with the

1 A. A. Scala and P. Ausloos, *J. Chem. Phys.*, 1968, **49**, 2282.
2 S. G. Lias and P. Ausloos, *J. Chem. Phys.*, 1968, **48**, 392.
3 R. Gordon and P. Ausloos, *J. Chem. Phys.*, 1967, **46**, 4823.

4 A. A. Scala and P. Ausloos, *J. Chem. Phys.*, 1966, **45**, 847.
5 S. G. Lias and P. Ausloos, *J. Chem. Phys.*, 1965, **43**, 2748.
6 J. R. McNesby and H. Okabe, *Adv. Photochem.*, 1964, **3**, 157.

squalane column. 2 m Columns of silicone oil or di-iso-decyl phthalate were also used.

To analyse for hydrogen the contents of the photolysis cell were expanded into an evacuated bulb. The bulb was attached to a Töpler pump, and the gases non-condensible at 77 K were transferred to and sealed off in a small glass tube.[7] This was crushed in the inlet of an F and M model 720 gas chromatograph fitted with a ' hot-wire ' detector. The column used was a 120 cm molecular sieve type 5A.

2,2,3,3-Tetramethylbutane was obtained from the Aldrich Chemical Company, and subjected to several sublimations *in vacuo* before use. It was then pure by g.l.c. Argon, nitric oxide, and hydrogen sulphide were supplied by the Matheson Company. Nitrogen (oxygen free) was supplied by B.O.C. Ltd. The xenon and krypton used for filling the resonance lamps were B.O.C. ' grade X ' special gases.

RESULTS

Under all photolytic conditions the major product was isobutene. The Tables show the yields of the other major products relative to isobutene, which was taken as being equal to 100. The results were obtained by use of input powers to the lamps of 25—50 W, and conversions of 0 03—0·3%.

Photolysis at 123·6 *nm.*—Table 1 shows the effect of

TABLE 1

Effect of pressure of 2,2,3,3-tetramethylbutane upon the product distribution at 123·6 nm

Pressure/Torr	1·0	4·0	8·0	15·0	20·0
Methane	24	25	22	23	22
Ethane	40	30	30	26	24
Propene	38	31	28	29	27
Isobutane	58	55	47	47	48
Isobutene	100	100	100	100	100
Neopentane	24	19	14	12	13
2,3-Dimethylbut-2-ene	21	25	25	27	27
2,2,3-Trimethylbutane	7	9	6	5	6

pressure upon the product distribution at a wavelength of 123·6 nm. At low pressures fragmentation is extensive, but at pressures greater than 10 Torr the product distribution remains essentially constant. In addition to the products listed in Table 1, some other products were detected. Typical yields (relative to isobutene = 100) at 123·6 nm and 15 Torr are: ethylene, 0·5; propane, 2·0; allene, 0·5; 2,3-dimethylbutane, 0·5; 2,3-dimethylbut-1-ene, 0·2; 3,3-dimethylbut-1-ene, 0·1; 2,2-dimethylbutane, 0·4; and 2-methylbut-1-ene, 0·5. The identities of three other products, in yields of less than 0·1, were not pursued. No evidence could be obtained for the presence of C_8 alkenes, or for products with more than eight carbon atoms.

The effect of various additives upon the distribution of the major products is shown in Table 2. Of the minor products, ethylene and allene were unaffected by radical scavengers. Propane was decreased in the presence of oxygen and nitric oxide, but increased in the presence of hydrogen sulphide. 2,3-Dimethylbutane was eliminated in the presence of all the radical scavengers. In the presence of both oxygen and nitric oxide a number of new products were produced. In the case of nitric oxide, one of the new products has been shown to be 2-methyl-2-nitrosopropane, while one of the other products, not yet identified, is also produced in the

[7] A. U. Chaudhry and B. G. Gowenlock, *J. Organometallic Chem.*, 1969, **16**, 221.

vacuum-u.v. photolysis of 2-methyl-2-nitrosopropane.[8] If it is assumed that the relative molar response of 2-methyl-2-nitrosopropane in the flame ionisation detector is the same

TABLE 2

Effect of added gases upon photolysis [a] at 123·6 nm

Additive	None	O_2	O_2 +N_2	N_2 [b]	H_2S	NO
Pressure/Torr		15	15 +900	900	6·5	1·5
		15				
Methane	23	1·4	1·6	18	61	1·0
Ethane	26	0·3	0·2	14	9	0·2
Propene	29	30	29	31	28	28
Isobutane	47	33	35	43	71	22
Isobutene	100	100	100	100	100	100
Neopentane	12	0·0	0·0	0·5	0·3	0·0
2,3-Dimethylbut-2-ene	27	26	24	24	27	26
2,2,3-Trimethylbutane	5	0·0	0·0	0·2	5	0·0

[a] Pressure of 2,2,3,3-tetramethylbutane, 15 Torr. [b] Pressure of oxygen, ca. 2 × 10⁻³ Torr.

as that of C_4 hydrocarbons, then the yield of 2-methyl-2-nitrosopropane relative to isobutene (100) is ca. 23. The oxygenated products in oxygen-scavenged systems were not identified.

Addition of 900 Torr of nitrogen or of argon to a mixture of 15 Torr of 2,2,3,3-tetramethylbutane and 15 Torr of oxygen had no significant effect upon the product distribution, although nitrogen reduced the overall yield by a factor of ca. 2, and argon by a factor of ca. 4.

Owing to variations in the output from the lamps (as detected by changes in the visible discharge) and to deposition of polymer upon the window during a photolysis, no absolute quantum yield measurements were undertaken. With a constant input power of 30 W to the lamps and a photolysis time of 10 min, g.l.c. showed the yield of iso-butene to be constant to within ±10% with substrate pressures of 4—25 Torr, and in the presence of oxygen, nitric oxide, and hydrogen sulphide. The addition of high pressures of inert gas, however, caused reductions in the yield of isobutene.

TABLE 3

Photolysis of 2,2,3,3-tetramethylbutane at 147 nm

Me₃C·CMe₃/Torr	15	15	15	15
Scavenger	None	Oxygen	$O_2 + N_2$	H_2S
Methane	50	18	20	100
Ethane	31	0·0	0·0	3·0
Propene	42	40	38	39
Isobutane	80	62	77	115
Isobutene	100	100	100	100
Neopentane	25	0·0	0·0	0·0
2,3-Dimethylbut-2-ene	14	15	16	18
2,2,3-Trimethylbutane	5	0·0	0·0	6

Photolysis at 147 *nm.*—The results obtained in the photolysis of 2,2,3,3-tetramethylbutane at a wavelength of 147 nm are summarised in Table 3. The products produced are the same as at 123·6 nm although the distribution is changed. In addition to the products listed in Table 3, other products included propane (7·0), allene (1·0), and ethylene (0·2). The yield of propane was reduced in the presence of oxygen, and increased in the presence of hydrogen sulphide. Yields of other minor products were, within experimental error, little different from those produced at 123·6 nm.

[8] P. J. Carmichael, B. G. Gowenlock, and C. A. F. Johnson, unpublished results.

DISCUSSION

In the photolysis of hydrocarbons at wavelengths of less than 150 nm, it is well established that both free-radical and molecular processes occur. To differentiate between the two types of fragmentation it is common practice to add to the reactant free-radical scavengers. These are of two types. Oxygen and nitric oxide are assumed to react with free radicals to produce products which contain heteroatoms, in processes of the form (1) and (2). Hydrogen sulphide is used to trap radicals
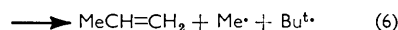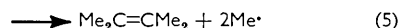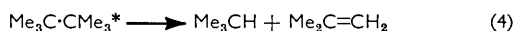
$$R\cdot + O_2 \longrightarrow RO_2\cdot \longrightarrow products \quad (1)$$

$$R\cdot + NO \longrightarrow RNO \longrightarrow products \quad (2)$$
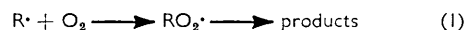
through a hydrogen-abstraction reaction [9] (3). The HS· radical is assumed to disappear in radical-recombination reactions.

$$R\cdot + H_2S \longrightarrow RH + HS\cdot \quad (3)$$
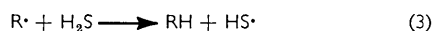
On the basis of these arguments the following conclusions are drawn. Alkane products that are formed in the presence of oxygen and nitric oxide have their origin in a molecular process, while a reduction in their yield indicates that a radical precursor is involved. An increase in yield of an alkane in the presence of hydrogen sulphide again indicates free-radical participation. Products arising from the combination of two radicals are reduced in the presence of oxygen, nitric oxide, and hydrogen sulphide.

Alkene products that are unchanged in the presence of any of the radical scavengers may arise either through a direct molecular process, or from the decomposition of a primary product (molecule or radical) still excited from the primary photochemical process.

In the photolysis of 2,2,3,3-tetramethylbutane, the major alkene products are isobutene, propene, and 2,3-dimethylbut-2-ene. The major alkane in the oxygen- and nitric oxide-scavenged systems is isobutane. Thus the primary processes (4)—(6) can be written. Reaction (5)

$$Me_3C\cdot CMe_3^* \longrightarrow Me_3CH + Me_2C=CH_2 \quad (4)$$

$$\longrightarrow Me_2C=CMe_2 + 2Me\cdot \quad (5)$$

$$\longrightarrow MeCH=CH_2 + Me\cdot + Bu^t\cdot \quad (6)$$

is assumed to produce two methyl radicals, rather than a molecule of ethane, as the ethane yield is reduced to zero in the presence of sufficient radical scavenger. By the same argument, reaction (6) also produces two radical fragments, as the only C_5H_{12} product, neopentane, is entirely free-radical in origin. It is to be noted that reactions (5) and (6) are overall processes. It is possible that they occur as written, or by a process involving rapid fragmentation of an initially internally excited radical, e.g., reaction (5) could be the sum of (5a) and (5b). Similar overall primary processes are found in the photolysis of neopentane [5] and isopentane.[10]

$$C_8H_{18}^* \longrightarrow Me\cdot + C_7H_{15}^* \quad (5a)$$

$$C_7H_{15}^* \longrightarrow Me\cdot + C_6H_{12} \quad (5b)$$
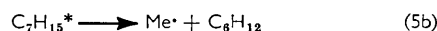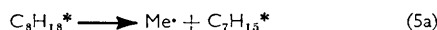
If we assume that in the presence of oxygen and high pressures of nitrogen the yields of isobutane, 2,3-di-

methylbut-2-ene, and propene are direct measures of the occurrence of the primary processes (4), (5), and (6), then the following values are obtained. At 123·6 nm: (4) = 100; (5) = 71; (6) = 83, and at 147 nm: (4) = 100; (5) = 21; (6) = 49. Thus it can be seen that the entirely molecular process (4) is of greater importance at the lower energy (147 nm) of radiation. This behaviour is found in other hydrocarbon photolyses.[5]

There is always an excess of isobutene over isobutane, and the yield of isobutene is unchanged in the presence of radical scavengers. Thus (4) is not the sole source of isobutene. If the t-butyl radical produced in reaction (6) contains excess of energy carried over from the primary act, then further decomposition of this radical is possible [reactions (7a) and (7b)]. At 123·6 nm, the

$$Bu^{t*} \longrightarrow H\cdot + C_4H_8 \quad (7a)$$

$$\longrightarrow Me\cdot + C_3H_6 \quad (7b)$$
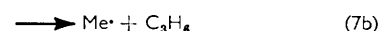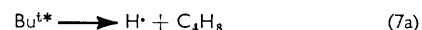
excess of isobutene over isobutane is much greater than could be accounted for by (6) followed by (7a). Thus a further primary process (8) is required. As the excess of isobutene is much less at 147 nm, then (8) shows a

$$Me_3C\cdot CMe_3^* \longrightarrow Me_2C=CH_2 + H\cdot + Bu \quad (8)$$
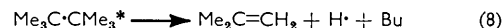
similar wavelength-dependence to (5) and (6).

A possible source of isobutene is that due to decomposition [(9a), (9b)] of the C_8 radical formed by abstraction of a hydrogen atom from the substrate.

$$R\cdot + C_8H_{18} \longrightarrow RH + C_8H_{17} \quad (9a)$$

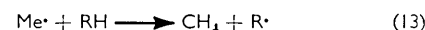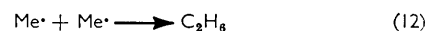$$C_8H_{17} \longrightarrow i-C_4H_8 + Bu^t\cdot \quad (9b)$$
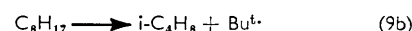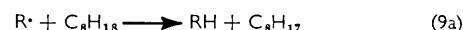
In the presence of oxygen, nitric oxide, and hydrogen sulphide, however, there is little change in the yield of isobutene, while if (9) was an important source of isobutene, then the presence of the radical scavenger would be expected to reduce the yield of isobutene.

The greatest wavelength-dependence is shown in the yield of ' molecular ' methane, which at 123·6 nm has an upper limit of less than 2 (isobutene = 100). At 147 nm however the yield is some ten times higher. If the source of this ' molecular ' methane is the primary process (10), then the C_7 alkene must undergo further reaction, as trace amounts only of alkene could be detected.

$$Me_3C\cdot CMe_3^* \longrightarrow CH_4 + Me_3C\cdot CMe=CH_2 \quad (10)$$
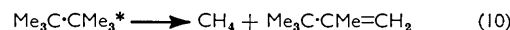
Products that are predominantly free-radical in nature are neopentane, ethane, methane (at 123·6 nm), and 2,2,3-trimethylbutane. The first three arise through reactions (11)—(13). The effect of hydrogen sulphide
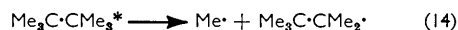
$$Me\cdot + Me_3C\cdot \longrightarrow Me_4C \quad (11)$$

$$Me\cdot + Me\cdot \longrightarrow C_2H_6 \quad (12)$$

$$Me\cdot + RH \longrightarrow CH_4 + R\cdot \quad (13)$$

upon the formation of these products is consistent with (11)—(13), i.e., neopentane and ethane are greatly reduced, while methane is increased.

[9] P. Ausloos and S. G. Lias, J. Chem. Phys., 1966, 44, 521.

[10] A. A. Scala and P. Ausloos, J. Chem. Phys., 1967, 47, 5129.

2,2,3-Trimethylbutane is not reduced in the presence of hydrogen sulphide, and the most likely mechanism for its formation involves a further primary process (14), followed by (15).

$$Me_3C \cdot CMe_3{}^* \longrightarrow Me \cdot + Me_3C \cdot CMe_2 \cdot \quad (14)$$

$$Me_3C \cdot CMe_2 \cdot + RH \longrightarrow Me_3C \cdot CHMe_2 + R \cdot \quad (15)$$

The formation of neopentane (11), together with the increase in isobutane in the presence of hydrogen sulphide, and decrease in the presence of oxygen and nitric oxide, implies the production of t-butyl radicals, (6) and (8). In addition to reactions (7) and (11), the t-butyl radicals may undergo disproportionation or hydrogen abstraction reactions. Further support for the presence of t-butyl radicals is to be found in the nitric oxide-inhibited photolysis, where one of the new products produced was shown to be 2-methyl-2-nitrosopropane, the yield relative to isobutene being ca. 23.

It has often been assumed that nitric oxide acts as an inhibitor in the vacuum-u.v. photolyses of hydrocarbons. This observation constitutes the first direct proof of the inhibition step (16) in such systems. We have em-

$$Me_3C \cdot + NO \longrightarrow Me_3CNO \quad (16)$$
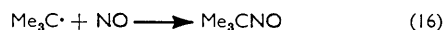
phasised [11] that it is necessary to establish that the nitroso-compound does not itself undergo other free-radical reactions or subsequent substantial photolysis that will markedly affect the total system. Only traces of specific products of the photolysis of 2-methyl-2-nitrosopropane are observed, and we therefore conclude that our assumptions are substantially correct. We expect that nitric oxide will similarly remove primary and secondary alkyl radicals from the system, but in these cases the isomeric oxime will presumably result. Such products are unlikely to appear in the analytical system.

The presence of small amounts of propane, together with 2,3-dimethylbutane, implies the presence of isopropyl radicals. Propane is increased in the presence of hydrogen sulphide, whereas the dimethylbutane is eliminated. Thus the reactions producing these products are (17) and (18). We suggest that the isopropyl

$$Me_2CH \cdot + RH \longrightarrow C_3H_8 + R \cdot \quad (17)$$

$$2Me_2CH \cdot \longrightarrow Me_2CH \cdot CHMe_2] \quad (18)$$
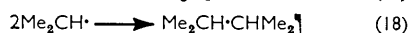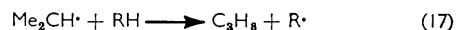
radicals arise from the decomposition of isobutane, produced in the molecular fragmentation (4) and carrying excess of energy. Fragmentation (4) is 75 kJ mol^{-1}

$$Me_3CH{}^* \longrightarrow Me_2CH \cdot + Me \cdot \quad (19)$$
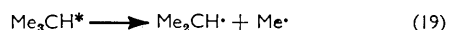
endothermic, thus the products are carrying 890 kJ mol^{-1} excess of energy at 123·6 nm and 740 kJ mol^{-1} at 147 nm.

Decomposition (20) of isobutene still excited from reaction (4) could lead to the small amounts of allene found among the products.

$$Me_2C=CH_2{}^* \longrightarrow CH_2=C=CH_2 + CH_4 \text{ (or Me + H)} \quad (20)$$

Addition of a large excess (900 Torr) of nitrogen or of

argon had little effect upon the product distribution in the oxygen-inhibited photolyses at 123·6 nm. At 147 nm the yield of isobutane was increased, probably owing to the collisional stabilisation of internally excited isobutane from reaction (4).

The absolute yields of products in the presence of excess of inert gas decreased by a factor of two for nitrogen, and a factor of four for argon. The decrease in yield of all the products to the same extent indicates that a common excited-state precursor is being deactivated. This type of behaviour has been observed [12] in other systems. Some photolyses were carried out in the presence of added nitrogen alone. The yields of the olefins were the same as in the nitrogen–oxygen mixtures. However the relative yields of the saturated products which have a free-radical origin were less than in the photolysis of 2,2,3,3-tetramethylbutane alone. We assume that the residual oxygen content of the nitrogen (ca. 2 p.p.m.; 2 × 10^{-3} Torr at 900 Torr) was sufficient to interfere to some extent with free-radical reactions.[13]

In some photolyses analysis of hydrogen was attempted. Yields of the permanent gases were small owing to the low conversions employed, requiring the katharometer detector to be operated very close to its detection limit. At 123·6 nm and pressures of 8—20 Torr, the yield of hydrogen was of the order of 50% of the yield of methane. Analysis of hydrogen from photolyses in the presence of inert gas or radical scavenger was not attempted. As no C$_8$ olefins could be detected in our analyses, most of the hydrogen production must occur via reactions (7) and (8), followed by an abstraction reaction.

The overall photolysis mechanism is complex, and, without an extensive series of experiments using deuterium-labelled 2,2,3,3-tetramethylbutane substrate a completely unambiguous interpretation is not possible. It is, however, possible to draw a number of general conclusions. The photolysis involves both molecular and free-radical processes, the contribution of the molecular process being more important at 147 nm than at 123·6 nm. This effect is observed in the photolysis of other hydrocarbons. The extent of free-radical participation in the photolysis of 2,2,3,3-tetramethylbutane is much greater than for a number of smaller hydrocarbons, and may be compared with that of neopentane,[5] which also involves considerable free-radical participation, especially at 123·6 nm. Thus in highly branched hydrocarbons containing only primary C–H bonds, C–C bond fission is preferred to molecular elimination of hydrogen.

It is of interest to note that stable t-butyl radicals are produced in a primary process in the photolysis of 2,2,3,3-tetramethylbutane, whereas in the photolysis of neopentane [5] all the butyl radicals arise in the secondary process H + C$_4$H$_8$ → C$_4$H$_9$ and formation of isobutane does not occur in the presence of hydrogen sulphide.

[11] B. G. Gowenlock, Progr. Reaction Kinetics, 1965, 3, 171.
[12] P. Borrell and A. E. Platt, Trans. Faraday Soc., 1970, 66, 2279, 2286.
[13] J. G. Calvert and J. N. Pitts, 'Photochemistry,' Wiley, New York, 1966, p. 599.