Reactions 5 as well as 7 may be important, however, and may compete with reactions 1 and 2. The data at −70° shown in Table V suggest this to

$$H + R \longrightarrow RH \qquad (7)$$

be the case. The yield of $C_2{}^{14}H_5$'s is calculated indirectly from the measured value of $G_{C_2H_5}$ for each hydrocarbon and the ratio $(C_2{}^{14}H_5)/(C_2H_5)$. The value of $G_{C_2{}^{14}H_5}$ is much larger than at 10° and for *n*-hexane increases from 0.2 to 1.4 in the concentration region where the yield of secondary hexyl radicals is observed to be constant. Since reaction 2 is unimportant here, some reaction such as 7 must be competing with 1 for hydrogen atoms.

The limiting value of $G_{C_2{}^{14}H_5}$ at high ethylene concentration should be G_H. The highest values observed so far are 1.4 and 1.8. Therefore G_H must be equal to or greater than these values. Reported values of G_H vary from 2.0[13] to 3.16[23] for *n*-hexane; Meshitsuka and Burton[24] measured G_{HI} from *n*-hexane as a function of irradiation time with iodine present and by extrapolation found the initial value of G_{HI} to be 2.5. Values of 4.25 and 3.70 have been reported for G_H for *n*-pentane and *n*-heptane.[23]

Thus the use of this ethylene-C^{14} scavenging method not only provides a measure of the radical yields but also of the yield of scavenged hydrogen atoms in $G_{C_2{}^{14}H_5}$. A great deal of information may be obtained in experiments employing ethylene-C^{14} scavenging. Comparison of the results obtained with other results using various scavengers further justifies the assertion that relative radical yields are determined.

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[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C.]

Vacuum Ultraviolet Photochemistry. V. Photolysis of Isobutane

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The photolysis of isobutane was carried out at room temperature at 1470 Å. and 1236 Å. Certain specifically labeled deuterium compounds were used to gain information on the mechanisms of product formation. From isotopic analysis of products, hydrogen, methane and ethane, in the photolysis of an equimolar mixture of isobutane + isobutane-d_{10} the following conclusions were drawn: (1) Hydrogen is formed both from atomic and molecular processes. The atomic process becomes more important at the shorter wave length (1236 Å.). From scavenger experiments, it was found that approximately half the hydrogen is formed by the atomic process at 1470 Å. (2) Methane is predominantly formed by a molecular process at 1470 Å. and 1236 Å. (3) Ethane is formed primarily by the combination of methyl radicals. From the photolysis of isobutane-2-*d*, it was concluded that (a) there is no apparent preference of the position (primary or tertiary) for the expulsion of atomic hydrogen at 1470 Å. However there is some discrimination with regard to position for the hydrogen produced by molecular elimination. (b) The primary and tertiary hydrogen participate almost equally in the intramolecular production of methane. Reactions responsible for the formation of other products, ethylene, propane, propylene, isobutene, neopentane and isopentane, are discussed.

Introduction

The photolyses of some alkanes, such as methane,[1] ethane,[2] propane[3] and butane,[4] have been carried out recently in the vacuum ultraviolet region.

From isotopic analysis of the products of certain specifically deuterium labeled hydrocarbons it has been established that molecular detachment processes play a major role in the formation of hydrogen[1-4] and methane.[3] The relative importance of the molecular *vs.* free radical process depends on wave length.[3] Molecular detachment processes also have been observed in the radiolysis of gaseous hydrocarbons.[5]

Since isobutane contains a tertiary CH bond whose energy is lower than that of the primary CH bond by almost 10 kcal./mole,[6] it is of interest to know whether the tertiary hydrogen preferentially participates in the formation of products.

The mercury sensitized photolysis of isobutane has been studied[7] and it was found that the primary process is the split of a C–H bond.

$$i\text{-}C_4H_{10} + Hg(6\ {}^3P_1) \longrightarrow C_4H_9 + H + Hg(6\ {}^1S_0)$$

The radiolysis of isobutane has been studied over the temperature range from −20 to 50°.[8] The dependence of the yield of products on temperature suggests that hydrogen was formed primarily by an atomic process while methane was formed partly by a molecular process.

Experimental

Light Source.—A water-cooled rare gas resonance lamp with a LiF window was used as the light source. Tantalum electrodes were employed. Detailed descriptions of the construction and operation of this lamp have been reported.[2-4] The lamp produced radiation mainly at 1470 Å. (Xe) or 1236 Å. (Kr).

In the later part of this work an air-cooled electrodeless discharge lamp operated with a Raytheon 2450-MC unit (125 w.) was used to excite the resonance lines. Approximately 500 μ of pure rare gas was used. It was found that the microwave discharge powered lamp has several advantages: (1) it is free from impurities originating in the electrodes, (2) the LiF window can be replaced easily, (3) it has more intensity than the a.c. operated lamp.

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A reaction vessel, 120 cc. in volume, was used in connection with a Hoke brass bellows valve. The system was free of mercury.

Materials. Isobutane.—Phillips Research Grade material was used. It contained 0.1% ethane, 0.2% propane and less than 0.1% isobutene. It was purified by a chromatographic technique using a 2-meter column of silica gel and was purged of water and carbon dioxide by passing through P_2O_5 and Ascarite.

Isobutane-2-*d*, obtained from Merck and Co., Montreal, Canada, contained less than 0.1% ethane and less than 2% isobutene. It was purified by a chromatographic technique and was purged of water and carbon dioxide. The isotopic purity was verified[9] by pyrolysis and subsequent examination of the methane fraction. The absence of CH_2D_2 ruled out the presence of isobutane-1-*d*. Mass spectrometric analysis showed that the amount of isobutane-d_2 was less than 0.1%.

Isobutane-d_{10}, obtained from Merck and Co., contained less than 0.1% ethane as an impurity. A mass spectrometric analysis showed that it contained 5.5% isobutane-d_9. It was used without further purification.

Ethylene.—Phillips research grade ethylene was used without further purification. Its stated purity was better than 99.9 mole %.

Ethylene-d_4, obtained from Merck and Co., contained 1% propylene. The amount of ethylene-d_3 was 4%. This was also used without further purification.

Analysis.—The analysis of C_2–C_5 products was made by means of a Perkin–Elmer model 154 C fractometer using either a 2-meter column H (diethylene glycol and silver nitrate) in series with column D (tetraisobutene) or a 5-meter column of di-*n*-butyl maleate on Chromosorb P and a 2-meter column of H in series at room temperature.

Quantitative analysis of the products was made by first introducing known amounts of pure samples and comparing their peak areas with those of products under the same flow rate and temperature conditions.

Hydrogen and methane were separated from condensable gases by means of a liquid nitrogen trap, were collected by means of a Toepler pump, and their total volume was measured. The amounts of hydrogen and methane were subsequently obtained by measuring their ratio on a CEC model 21–620 mass spectrometer.

The isotopic ethane in the photolyzed samples was separated chromatographically by means of a 2-meter silica gel column and was trapped at liquid nitrogen temperature after emerging from the detector. Isotopic analyses of hydrogen, methane and ethane were made mass spectrometrically. The standard cracking patterns of isotopic methane and ethane were obtained from pure samples supplied by Merck and Co.

Absorption.—The absorption coefficients of ethylene and isobutane at 1470 Å. were measured with a 50-cm. Seya–Namioka monochromator in conjunction with a sodium salicylate-coated photomultiplier. An absorption cell, 41 mm. in length, fitted with two 2-mm. LiF windows, was attached behind an exit slit of the monochromator. A hydrogen discharge lamp was used as a light source.

Results

Absorption Coefficient.—The absorption coefficients were measured in order to understand the isotope effect. The absorption of isobutane starts in the neighborhood of 1700 Å. The coefficients *k* at 1470 Å. defined by $I = I_0\, e^{-\mathrm{kpx}}$ where p, the pressure in atmospheres at 25°, and x, the path length in cm., were

$$k_{(C_2H_4)} = 435 \pm 10 \qquad k_{(C_2D_4)} = 438 \pm 13$$
$$k_{(i\text{-}C_4H_{10})} = 510 \pm 20 \qquad k_{(i C_4D_{10})} = 425 \pm 15$$

In agreement with the results of Sauer and Dorfman,[4] there was no difference in *k* for ethylene and ethylene-d_4. However, *k* for isobutane-d_{10} is smaller than that for isobutane. Similar results were obtained for ethane and propane,[3] where deuterated alkanes have a smaller absorption coefficient.

Photolysis.—The products of the photolysis were found to be hydrogen, methane, ethane, propane, propylene, isobutene, neopentane, isopentane and small amounts of ethylene, butene-1, *n*-butane and *cis*-butene-2. Table I shows the relative amounts of these products at the Xe and Kr resonance lines. The extent of decomposition was approximately 2%. There is no significant dependence of the distribution of products on wave lengths. Table II shows the isotopic distribution of hydrogen, methane and ethane in the photolysis of mixtures of isobutane and isobutane-d_{10}. Table III (A) shows the analysis of isotopic hydrogen and methane at the Xe and Kr resonance lines in the photolysis of isobutane-2-*d* and (B) shows the isotopic distribution of hydrogen in the presence of ethylene-d_4.

TABLE I

PHOTOLYSIS OF ISOBUTANE AT ROOM TEMPERATURE. THE RELATIVE AMOUNTS OF PRODUCTS[a]

Products[b] (hydrogen = 1.00)	Exciting lines	
	Xe	Kr
Hydrogen	1.00	1.00
Methane	0.49	0.55 ± 0.05
Ethane	.35	.32 ± .02
Ethylene	.03	.02
Propane	.13	.13 ± .01
Propylene	.74	.71 ± .03
Butane	.01	.01
Isobutene	.28	.20 ± .01
Butene-1	.04	.05
cis-Butene-2	.01	n.d.
Isopentane	.09	0.09 ± .01
Neopentane	.18	0.13 ± .02

[a] Initial pressure of isobutane = 23.0 mm. [b] Amounts of hydrogen produced; 2.3 μmoles for Xe, 1.6 and 2.4 μmoles for Kr.

In order to assess the contribution of the molecular process in the production of hydrogen, the photolysis of isobutane-d_{10} at the Xe lines was carried out with and without added ethylene. Since ethylene scavenges atomic hydrogen and produces H_2 only upon photolysis, the relative quantum yield of D_2 production with and without ethylene added represents the fraction of the deuterium produced in a molecular elimination process. The percentage of absorption by isobutane-d_{10} was obtained from the measured absorption coefficients of isobutane-d_{10} and ethylene at 1470 Å. and their relative pressures. The result shows that approximately half the hydrogen is produced by a molecular process at the Xe lines.

Discussion

Formation of Hydrogen.—Isotopic analysis of hydrogen formed in the photolysis of a 50:50 mixture of i-C_4H_{10}–i-C_4D_{10} (Table II(A)) shows that of the total hydrogen, HD is 27% at the Xe lines and 40% at the Kr lines. This indicates that considerable hydrogen is produced by an atomic process, which becomes more important at shorter wave length. Table IV further shows that of the total hydrogen less than 5% HD is produced in the photolysis of the mixture i-C_4D_{10}–C_2H_4, indicating that hydrogen is primarily formed molecularly and that approximately 56% of the hydrogen in the photolysis of isobutane is produced by the molecular

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TABLE II

PHOTOLYSIS OF MIXTURES OF ISOBUTANE–ISOBUTANE-d_{10}. ISOTOPIC ANALYSIS OF PRODUCTS[a]

(A) Hydrogen and methane

Isobutane (mm.) i-C_4H_{10}	Isobutane (mm.) i-C_4D_{10}	Exciting lines	Hydrogen, % H_2	Hydrogen, % HD	Hydrogen, % D_2	Methane, % CH_4	Methane, % CH_3D	Methane, % CH_2D_2	Methane, % CD_3H	Methane, % CD_4
0	10.3	Xe	..	5.7	94.3	..	..	..	4.3	95.7
10.8	10.8	Xe	55.5	29.3	15.2	48.1	3.0	3.1	13.3	32.5
10.9	10.9	Xe	56.2	26.7	17.1	48.8	3.1	2.5	12.1	33.5
	Average[b]	Xe	56.0	27.3	16.7	48.8	3.1	3.0	11.4	33.7
0	12.0	Kr	..	4.6	95.4	..	..	..	4.6	95.4
10.8	10.8	Kr	50.7	39.3	10.0	43.5	2.5	3.7	17.7	32.6
10.9	10.9	Kr	49.1	41.2	9.7	43.8	2.0	5.2	17.5	31.5
	Average[b]	Kr	50.2	39.9	9.9	44.3	2.2	4.4	16.5	32.6

(B) Ethane, %

i-C_4H_{10}	i-C_4D_{10}	Exciting lines	C_2H_6	C_2H_5D	$C_2H_4D_2$	$C_2H_3D_3$	$C_2D_4H_2$	C_2D_5H	C_2D_6
10	10	Xe	39	..	6	41	..	1	13
10	10	Xe	39	..	..	40	..	5	16

[a] Amounts of hydrogen produced: 0.4~1.5 μmoles; exposure time, 15 ~ 60 min. [b] The results of 50:50 mixtures of i-C_4H_{10}–i-C_4D_{10} averaged and corrected for HD and CD_3H from the i-C_4D_{10}.

process at the Xe lines. Since a self-scavenging effect by the products (mainly propylene) is expected, the correct percentage of hydrogen formed by molecular elimination would be somewhat lower.

Table III(A) represents the distribution of isotopic hydrogen produced by the molecular as well as the atomic process in the photolysis of isobutane-2-d, while Table III(B) shows the distribution by the molecular process (scavenger present). Since nearly 50% of the hydrogen is produced by the molecular process at the Xe lines, it is possible to calculate the distribution of the hydrogen produced by the atomic process

$$[H_2]:[HD]:[D_2] = 20:26:3$$

using the following ratio for the molecular process

$$[H_2]:[HD] = 19:31, ([H_2] + [HD] = 50)$$

TABLE III

(A) Photolysis of isobutane-2-d. Isotopic analysis of hydrogen and methane

Isobutane-2-d, mm.)	Exciting line	Hydrogen, % H_2	Hydrogen, % HD	Hydrogen, % D_2	Methane, % CH_4	Methane, % CH_3D	Methane, % CH_2D_2	Methane, % CD_3H	Methane, % CD_4
20.2	Xe	39.5	57.8	2.7	55.6	44.4	....	....	....
19.4	Xe	41.6	55.5	2.9	54.4	45.6	....	....	....
20.3	Kr	64.7	32.1	3.2	56.5	43.5	....	....	....
19.4	Kr	62.5	34.2	3.2	55.2	44.8	....	....	....

(B) Photolysis of 50:50 mixtures of isobutane-2-d and ethylene-d_4. Isotopic analysis of hydrogen

i-C_4H_9D, mm.	C_2D_4, mm.	Exciting lines	Hydrogen, % H_2	Hydrogen, % HD	Hydrogen, % D_2
9.9	9.9	Xe	12.3	20.9	66.8
9.9	9.9	Kr	28.2	14.7	57.1
0	11.2	Xe	..	1.8	98.2

It is apparent that both H and D atoms are produced in the photolysis. For an estimate of their relative concentrations, information on the relative rates of hydrogen production by H and D atoms is required, assuming that hydrogen is produced primarily by the abstraction of hydrogen from isobutane.

$$H + i\text{-}C_4H_9D \longrightarrow HD + i\text{-}C_4H_9 \quad (1a)$$

$$H + i\text{-}C_4H_9D \longrightarrow H_2 + i\text{-}C_4H_8D \quad (1b)$$

$$D + i\text{-}C_4H_9D \longrightarrow D_2 + i\text{-}C_4H_9 \quad (2a)$$

$$D + i\text{-}C_4H_9D \longrightarrow HD + i\text{-}C_4H_8D \quad (2b)$$

Such information on abstraction by H and D atoms is not available.

Recent results[9] of hydrogen abstraction by the methyl radical from isobutane-2-d shows that the relative ratio k_{3a}/k_{3b} is equal to 4.7 at room temperature

$$CD_3 + i\text{-}C_4H_9D \longrightarrow CD_4 + i\text{-}C_4H_9 \quad (3a)$$

$$CD_3 + i\text{-}C_4H_9D \longrightarrow CD_3H + i\text{-}C_4H_8D \quad (3b)$$

It is to be expected, on this basis, that the reactions 1a and 2a would be faster than 1b and 2b, respectively. From the observed distribution of hydrogen formed by the atomic process, these ratios are obtained.

$$k_{1a}/k_{1b} = k_{2a}/k_{2b} = 1.2, \text{ and } k_{1a}[H]/k_{2a}[D] = 8$$

If it is now assumed that $k_{1a} \approx k_{2a}$, the result indicates that H and D atoms are produced in almost the statistical ratio at the Xe lines.

The molecular elimination of hydrogen from the primary and the tertiary positions is favored at the Xe lines over that from two primary positions, but the reverse is true at the Kr lines (Table III(B)).

Formation of Methane.—Table II(A) shows that CH_4 and CD_4 are predominant methanes in the photolysis of an equimolar mixture of i-C_4H_{10}–i-C_4D_{10}, indicating that methane is formed primarily by a molecular process. The isotopic ratio CH_4/CD_4 of 1.4 agrees fairly well with the ratio $k(i\text{-}C_4H_{10})/(i\text{-}C_4D_{10})$ of 1.2 at 1470 Å. No significant dependence on wave length is observed. Table III(A) further shows that $[CH_4]:[CH_3D]$ = 55:45, indicating that methane is formed in two ways with almost equal probability

$$i\text{-}C_4H_9D \xrightarrow{h\nu} CH_4 + CH_3CD{=}CH_2 \quad (4a)$$

$$i\text{-}C_4H_9D \xrightarrow{h\nu} CH_3D + CH_3CCH_3 \quad (4b)$$

Again no significant trend with wave length is observed for this ratio.

Formation of Ethane.—The isotopic ethanes produced in the photolysis of an equimolar mixture of isobutane–isobutane-d_{10} (Table III(B)), are mainly C_2H_6, CH_3CD_3 and C_2D_6. This indicates that ethane is formed primarily by association of methyl radicals. The value $(CH_3CD_3)/(C_2H_6)^{1/2}(C_2D_6)^{1/2}$

TABLE IV

PHOTOLYSIS OF ISOBUTANE-d_{10} IN THE PRESENCE OF ETHYLENE

i-C_4D_{10}, mm.	C_2H_4, mm.	Exciting lines	Exposure time t, min.	Relative amounts of hydrogen produced H_2	HD	D_2	Percentage absorption (α) by i-C_4D_{10}	$D_2/t\alpha$[a] (arbitrary units)
10.3	0	Xe	30	10	18	305	100	1.00
10.0	10.0	Xe	60	646	36	170	49.5	0.56
10.1	0	Xe	30	2	18	295	100	0.97

[a] The quantity D_2/t_α represents the relative quantum yield of deuterium production.

is equal to 1.7 ± 0.1, which agrees reasonably well with the value 1.9 measured by Wijnen.[10]

Other Processes.—Two main processes can be considered for the formation of propylene

$$i\text{-}C_4H_{10} \xrightarrow{h\nu} CH_4 + C_3H_6 \qquad (4)$$

$$2i\text{-}C_3H_7 \longrightarrow C_3H_8 + C_3H_6 \qquad (5)$$

Equal amounts of methane and propylene, and of propane and propylene, should be produced from the reactions 4 and 5, respectively. Therefore, the yield of ($CH_4 + C_3H_8$) must be equal to the yield of C_3H_6. From Table I, the yield ($CH_4 + C_3H_8$) = 0.61 is found in reasonable agreement with the yield of C_3H_6 = 0.71.

Isobutene is formed by the reactions

$$i\text{-}C_4H_{10} \xrightarrow{h\nu} i\text{-}C_4H_8 + H_2 \qquad (6)$$

$$2C_4H_9 \longrightarrow i\text{-}C_4H_8 + i\text{-}C_4H_{10} \qquad (7)$$

Neopentane and isopentane probably are produced from the reactions 8 and 9

$$CH_3 + t\text{-}C_4H_9 \longrightarrow \text{neo-}C_5H_{12} \qquad (8)$$

$$CH_3 + i\text{-}C_4H_9 \longrightarrow i\text{-}C_5H_{12} \qquad (9)$$

Ethylene probably is formed by the expulsion of two methyl radicals from isobutane

$$i\text{-}C_4H_{10} \xrightarrow{h\nu} 2CH_3 + C_2H_4 \qquad (10)$$

No reliable isotopic analysis of ethylene could be made since the amount was small, but it is certain that [C_2H_3D] is small in comparison with [C_2D_4] in the photolysis of the 50:50 mixture of i-C_4H_{10}–i-C_4D_{10}. The result supports reaction 10.

The formulas obtained from the products analysis (Table I) are $C_4H_{10.9}$ and $C_4H_{11.2}$ at the Xe and Kr lines, respectively. They are in good agreement with that for isobutane, indicating that amounts of unobservable alkenes and higher alkanes are small.

Other products, isobutene, *cis*-butene-2 and *n*-butane, amount to less than 5% of the total hydrogen. It is difficult to explain their formation unless extensive rearrangement of excited species occurs. These products may be coming from secondary reactions.

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[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, CELANESE CHEMICAL CO., A DIVISION OF CELANESE CORPORATION OF AMERICA, CLARKWOOD, TEX.]

Photolysis of Alkyl Nitrites. I. *tert*-Butyl Nitrite

BY G. R. MCMILLAN[1]

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Quantum yields have been measured in the vapor phase photolysis of mixtures of *tert*-butyl nitrite and nitric oxide. An excited radical mechanism is proposed. At 99° with incident light of 2537 Å., the quantum yield of excited *tert*-butoxy radical formation is unity. The excited radicals decompose to acetone and methyl with an activation energy of a few kcal. Collisional deactivation can be observed at quite low pressures. The range of deactivation efficiencies of various gases is suggestive of the relative efficiencies reported for deactivation of molecules in very high states of vibrational excitation. No evidence for abstraction of hydrogen by the excited radicals could be obtained. The importance of excited radical decomposition increases with temperature due to two influences: an increase in rate of radical decomposition at higher temperatures and an increase in the fraction of excited radicals produced in the primary process.

Introduction

Alkyl nitrites have been the subject of many photochemical studies, but few quantitative investigations and no detailed quantum yield measurements have been reported. Recent interest in these compounds, has been mostly in the fields of air pollution[2] and organic preparations.[3]

tert-Butyl nitrite seemed the simplest nitrite to study because: (1) something is known of the reactions of the *tert*-butoxy radical, an expected product of the primary process; (2) a disproportionation step between the *tert*-butoxy radical and nitric oxide does not occur[4,5]; and (3) unlike the primary and secondary nitrites, *tert*-butyl nitrite at room temperature is almost a single species, that is, almost entirely the *trans* isomer.[6]

tert-Butyl nitrite exhibits two regions of absorption[7] in the near ultraviolet: a banded region extending from 4100 to 3200 Å. and a supposedly

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