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THE RADIOLYSIS OF LIQUID ISOBUTANE WITH PULSED ELECTRONS

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Abstract

Isobutane has been irradiated in the liquid state with 4.2 Mev
electrons from a microwave electron accelerator. Products through the
octanes have been identified. The heavier products are consistent with
combinations of methyl, isopropyl, isobutyl and tert-butyl radicals.
Methyl cyclopropane, n-butane and butene-2 were formed in low yields. It
is suggested that these are formed via a cyclic intermediate state.

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Introduction

Of the saturated hydrocarbons, isobutane represents the simplest case
where specificity in radiolytic behavior owing to structural configuration
should be apparent. The hydrogen bonded to the tertiary carbon atom should,
on the basis of bond strengths alone, be expected to be more reactive than
other hydrogen atoms in the molecule. In order to investigate such specificity,
liquid isobutane has been irradiated at 20° and an attempt made to identify and
measure all products through the C_8 hydrocarbons.

Isobutane has been irradiated in the liquid phase at -30° by Keenan,
Lincoln, Rogers and Burwasser[2] who reported compounds through C_8 hydrocarbons.
Recently Kivel and Voigt[3] irradiated liquid and gaseous isobutane containing
C^{14} and discussed the formation of products through the pentanes.

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2) V. J. Keenan, R. M. Lincoln, R. L. Rogers, and H. Burwasser, J. Amer. Chem.
   Soc. 79, 5125 (1957).

3) J. Kivel and A. F. Voigt, Intern. J. App. Radiation and Isotopes, 10, 181
   (1961).

Experimental

Phillips Research Grade isobutane of stated purity 100.00% was used without further purification other than degassing the condensed liquid in a cold trap. In all cases the isobutane was removed from the cylinder as the liquid. Gas chromatographic checks of the isobutane showed the presence of only traces (< 0.01%) of C_2 and C_3 hydrocarbons. A second tank similarly labeled showed traces of propane, n-butane, isobutane and butene-1 as impurities. The amounts found were subtracted from the radiolysis yields of these products.

The irradiation cell was a stainless steel cylinder, 35 mm ID and 76 mm high. This had a 0.05 mm thick stainless steel beam window welded into a 25 mm diameter port on the side. The top was held in place with a flange and Neoprene gasket. A valve, a cooling coil, and a thermocouple well were attached to the top. The cooling coil and thermocouple well were immersed in the liquid when the target was assembled. These were arranged to be beyond the range of the electrons in the liquid isobutane so no electron energy was dissipated directly in these units. Water cooling was used to maintain the isobutane at $20 \pm 5^\circ$ during the irradiation.

Irradiations were performed with the Lawrence Radiation Laboratory electron linear accelerator. The irradiation conditions were 15 or 30 pulses/sec., 50 ma/pulse, a pulse duration of 6 μsec., and a mean electron energy of 4.2 Mev. The samples were irradiated to a total dose of 5.4×10^{21} ev/gm. This dose resulted in approximately 2.5% decomposition of the isobutane.

After irradiation the gaseous products were removed by refluxing under vacuum[4] using a methyl cyclopentane slush bath ($\sim -140^\circ$) as a coolant.

4) A. S. Newton, Anal. Chem. 28, 1214 (1956).

Fractions volatile at -196^C and -140° were collected. These were analyzed with
the aid of a mass spectrometer, CEC Model 21-103. Blank experiments with
added propane and propene showed >95% recovery of the propane and propene
using this technique, but in actual runs on irradiated isobutane, small amounts
of propane and propene were left in the residual liquid as shown by gas chroma-
tographic analysis. These were added to the amounts found in the gas fractions.

The liquid products were concentrated by distilling the residual isobutane
through a Podbielniak Series 3300 semi-micro distillation column, using cold
acetone (-70°) as a coolant in the condenser. The isobutane was removed at a
reflux ratio of 20:1. In this way the higher boiling products were concentrated
by about a factor of 10. Neopentane, isobutene, n-butane, and methyl cyclo-
propane were found to be divided between distillate and residue in this opera-
tion. In some of the final runs, isopentane was added as a chaser for the low
boiling components in the distillation, and known amounts of ethyl chloride
and n-octane were added as internal standards for the intermediate and high
boiling products respectively. The low boiling fraction (isobutane to
isopentane) was then concentrated in a preparatory gas chromatography column,
by collecting all peaks after the isobutane was eluted. This collected material
was then run on an analytical column and the yields calculated by relating the
products to the ethyl chloride internal standard.

The products in the resulting high boiling concentrate were measured
and isolated by gas chromatography. A 4 meter glass column, 5 mm ID, packed
with 0.35 gms, dinonyl phthalate per gm of 40-60 mesh C-22 firebrick was used
for the separation. The temperature of the column was regulated in the range
$25-110^O$ depending on the boiling range of the compounds of interest in the run.
A composite chromatogram of some 22 peaks resulted. Several of these peaks
were mixtures of compounds. The identity of each peak was established by

collecting the eluted material and running the collected fraction on the mass spectrometer. Where possible, authentic samples were run in both instruments to check the authenticity of the identification as well as the sensitivity of the chromatograph.

The products found and the yields at this level of irradiation are given in Table I. For comparison, the yields of gaseous products in the Co^{60} γ-ray irradiation of liquid isobutane at 25° are included. These latter measurements were made in glass cells 25 mm OD and 75 mm high containing 15 ml of liquid isobutane. The largest differences in yields between the γ-rays and pulsed electron bombardments were in the hydrogen and methane yields. The γ-ray values of H_2 and CH_4 yields are in substantial agreement with those found by Kivel and Voigt[3], but the propane yield is much lower than found by those authors.

Discussion

The present data are not sufficient to justify proposing any complete kinetic mechanism for the radiolysis of isobutane, but certain regularities can be pointed out which are indicative of a free radical mechanism for the formation of the higher products. First, the pentanes, heptanes and octanes in highest yield are those formed by methyl, isopropyl, isobutyl and tertiary butyl radicals. Isomerization of these groups, if it occurs, must be less than a tenth of the total yield of these radicals.

If one assumes that the products, ethane, isopentane, neopentane, 2,3-dimethyl butane, 2,4-dimethyl pentane, 2,2,3-trimethyl butane, 2,2,4-tri-methyl pentane, 2,5-dimethyl hexane, and 2,2,3,3-tetramethyl butane are formed by combination of methyl, isopropyl, isobutyl and tertbutyl radicals, then from the yields of radical dimers one can calculate

Table I.

Products from the Radiolysis of Isobutane with Pulsed Electrons[a]

Product	G Electrons	G Co⁶⁰ γ-rays	Product	G Electrons
H_2	2.9	4.4	2-Methyl pentene-1[b]	0.0005
CH_4	1.4	2.2	4-Methyl pentene-1[b]	0.0025
C_2H_2	0.04	0.04	4-Methyl pentene-2[b]	0.0003
C_2H_4	0.07	0.08	2,3,-Dimethyl butene-1[b]	0.0005
C_2H_6	0.22	0.2	3,3-Dimethyl butene-1[b]	0.0003
C_3H_4	0.02	-	Hexadienes (or Isomers)[b]	0.0002
C_3H_6	1.1	0.6	2,2,3-Trimethyl butane	0.10
C_3H_8	0.5	0.3	2,4-Dimethyl pentane	0.12
$n\text{-}C_4H_{10}$	0.10		2,2-Dimethyl pentane[b]	0.098
$i\text{-}C_4H_8$	1.1		2-Methyl hexane[b]	0.014
Butene-1	0.01		4,4-Dimethyl pentene-1[b]	0.002
Butene-2 (cis + Trans)	0.05		Heptadienes (or Isomers)[b]	0.0008
Methyl cyclopropane	0.04		2,5-Dimethyl hexane	0.13
C_4H_6	≥0.0005		2,2,4-Trimethyl pentane	0.19
Neopentane	0.16		2,2,3,3-Tetramethyl butane	0.08
Isopentane	≥0.20			
n-Pentane	0.002			
2-Methyl butene-1	0.008			
2-Methyl butene-2	0.002			
n-Hexane	0.0009			
2-Methyl Pentane	0.008			
2,2-Dimethyl butane	0.004			
2,3-Dimethyl butane	0.030			

a) Probable errors in the yields are one unit in the last figure given or 10% whichever is larger.

b) Authentic sample not available for direct comparison.

the expected yield of mixed radical products assuming combination occurs according to the binomial expansion for any two types of radicals. This assumes no activation energy or steric effects in the combination. The results of such a calculation are shown in Table II.

Table II.

Calculated and Observed Yields of Mixed Products from Radicals

R_1	R_2	Mixed Product	$G_{R_1R_2}$ Observed	$G_{R_1R_2}$ [a] Calculated
CH_3	$(CH_3)_2CHCH_2$	isopentane	≥ 0.20	0.34
CH_3	$(CH_3)_3C$	neopentane	0.16	0.26
$(CH_2)_2CH$	$(CH_3)_2CHCH_2$	2,4-dimethyl pentane	0.12	0.118
$(CH_3)_2CH$	$(CH_3)_3C$	2,2,3-trimethyl butane	0.10	0.098
$(CH_3)_2CHCH_2$	$(CH_3)_3C$	2,2,4-trimethyl pentane	0.19	0.194

a) Calculated by the equation:

$$G_{R_1R_2} = 2G_{R_1R_1}^{\frac{1}{2}} \cdot G_{R_2R_2}^{\frac{1}{2}}$$

The agreement between calculated and observed yields in the heptanes and octanes is satisfactory. The lack of agreement in neopentane and isopentane may indicate that some of the ethane is formed by non-radical processes. A similar suggestion has been made by Taylor, Mori and Burton in the radiolysis of neopentane[5].
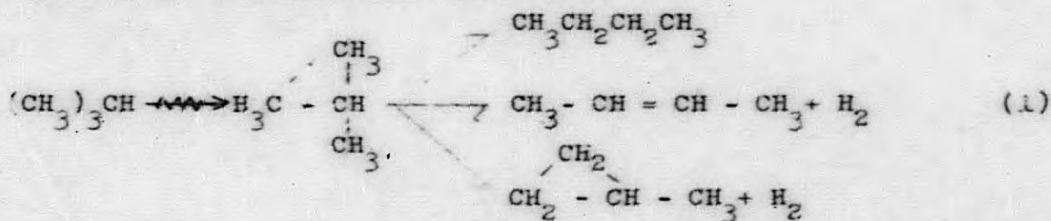
The distribution of heptanes and octanes is consistent with a ratio of isobutyl to tertiary butyl radicals of about 1.25:1. This distribution implies tertiary bonded H atoms are at least 7 times as reactive as primary H atoms in isobutane. It is a higher difference in reactivity than would be calculated

5) W. H. Taylor, S. Mori and M. Burton, J. Amer. Chem. Soc. 82, 5817 (1960).

from the results of Keenan, et al.,[2] but lower than that which would be calcu-
lated from the results of Kivel and Voigt[3] who found 2.5 to 3.6 times as much
neopentane as isopentane to be formed in the γ-radiolysis of isobutane,
suggesting a reactivity difference of a factor of 22 to 32.

An unexpected observation was the occurrence of methyl cyclopropane
among the radiolysis products. It appears that about 3% of the C_4H_8 yield is
formed as methyl cyclopropane. This is the first time a high energy isomer
has been observed to be formed in a radiolysis process. The identity of the
methyl cyclopropane was established by comparison of both its mass spectrometer
ionization pattern and gas chromatograph elution time with the mass spectrometer
pattern and elution time of an authentic synthetic sample of methyl cyclopropane.
Methyl cyclopropane may be formed via a cyclic intermediate in an highly excited
state of isobutane. The existence of such a state could also be used to explain
the formation of n-butane and the linear butenes in the radiolysis. It may
also explain the temperature sensitivity of the n-butane yield found by Kivel
and Voigt[3]. The competitive modes of decay of such a state as shown in
reaction (1) should be temperature sensitive.

$$(CH_3)_3CH \rightsquigarrow H_3C - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH}} \begin{cases} \longrightarrow CH_3CH_2CH_2CH_3 \\ \longrightarrow CH_3 - CH = CH - CH_3 + H_2 \\ \longrightarrow \underset{CH_2 - CH - CH_3}{\overset{CH_2}{\diagup \diagdown}} + H_2 \end{cases} \qquad (1)$$

Unfortunately the yields are low and the experimental difficulties inherent in
a meaningful investigation of the effect of temperature on this system, preclude
further work on this system at the present time.

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END