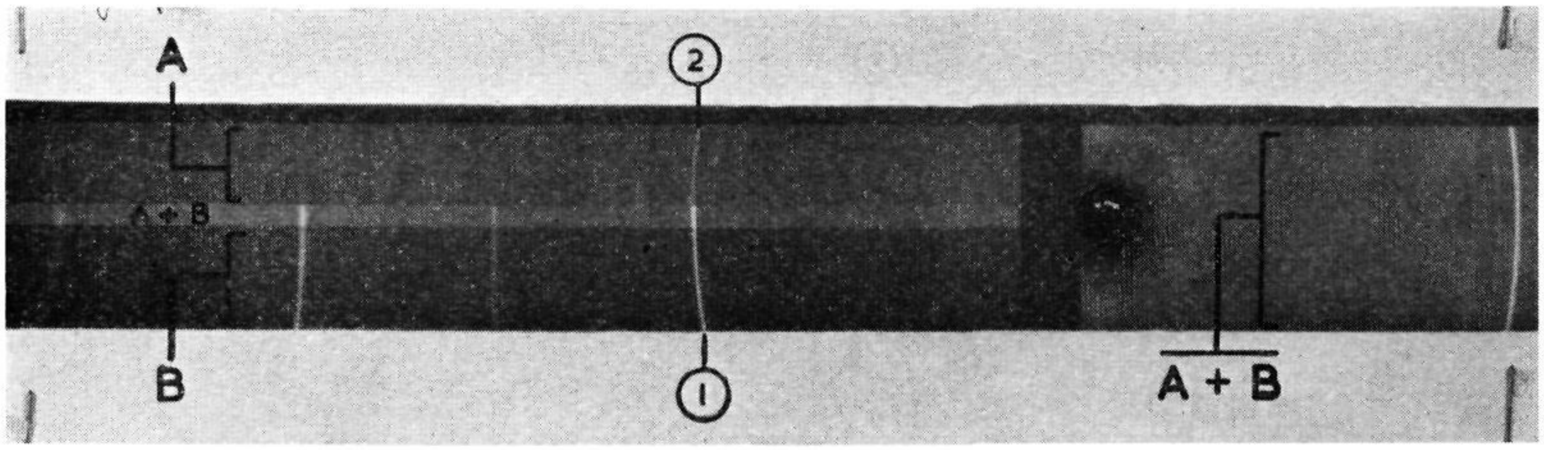

Fig. 2.—A, X-ray interference diagram of almost pure FeC (contaminated by Fe_3O_4); B, X-ray interference diagram of α-Fe; (1) most intense line at $d = 2.05$ kX. units; (2) most intense line at $d = 2.004$ kX. units.

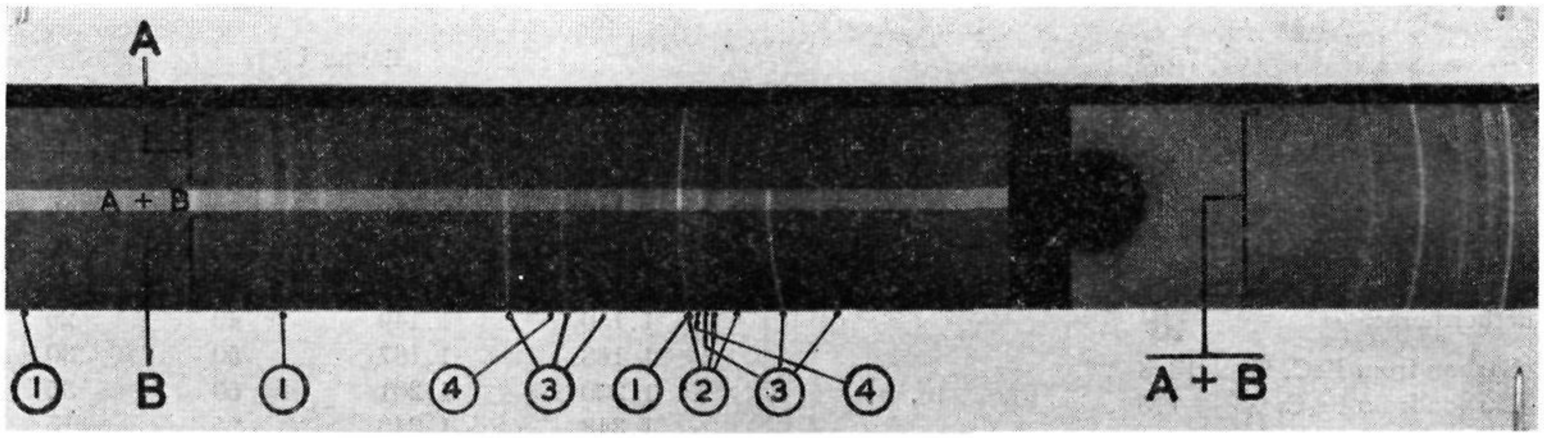

Fig. 3.—A, X-ray interference diagram of almost pure FeC (contaminated by Fe_3O_4); B, X-ray interference diagram of catalyst sample containing Fe_2C, Fe_3O_4, Fe and FeC, where $Fe_2C:Fe_3O_4:Fe$ is approximately 25:25:1 and the relative amount of FeC has not been established: (1) α-Fe; (2) FeC; (3) Fe_3O_4; (4) Fe_2C (Hägg). The cluster of lines due to 1, 2 and 4 which are grouped around the most intense line of FeC ($d = 2.004$ kX. units) is clearly shown.

In all three figures Fe_3O_4 is present as a contaminant in the X-ray diagrams of FeC.

Further work, studying the catalytic behavior, the physical and chemical properties and the mode of formation of this carbide is being continued.

SASOLBURG, UNION OF SOUTH AFRICA

[CONTRIBUTION FROM THE MICHELSON LAB., U. S. NAVAL ORDNANCE TEST STATION]

Reactions of CD_3 Radicals with the Butenes

BY JAMES R. MCNESBY AND ALVIN S. GORDON

RECEIVED MAY 22, 1957

The photolysis of acetone-d_6 in the presence of each of the four butenes has been carried out. The product analysis is interpreted in terms of two mechanisms, (1) addition of CD_3 to each carbon atom comprising the double bond, and (2) the abstraction by CD_3 of the α-hydrogen atoms of the butene. A striking feature of the methane analyses is that large amounts of CH_4 and CH_3D are produced. This has been interpreted as evidence for addition of CD_3 at a particular position in the double bond in a butene, followed by the loss of a CH_3 radical. Using this interpretation, rate constants for addition of CD_3 to these positions are obtained relative to the rate constant for abstraction of D from acetone-d_6 by the CD_3 radical. For butene-1, addition of CD_3 to the non-terminal carbon atom end of the double bond results in the formation of propylene-d_3. This can be used as a measure of the rate of addition of methyl radicals to the non-terminal carbon atom of the double bond.

The addition of methyl radicals to olefins in the gas phase has been the subject of only a few investigations. Rust and his co-workers[1] examined the products of the reaction of methyl radicals with various olefins in a flow system at 235° and found evidence for non-terminal as well as terminal addition. Raal and Danby[2] indicate that the abstraction of H from acetaldehyde by CH_3 is about three times as fast as addition of CH_3 to the various butenes at 300°.

There is no detailed account in the literature of the mechanism of the reaction of methyl radicals with butene-1.[3] The present work is a report on the reactions of methyl radicals with the four butenes in the temperature range 350–500°.

Experimental

Techniques of photolysis,[4] mass spectrometry,[4] and gas chromatography[5] have been described elsewhere. The 50-cc. cylindrical reaction vessel with plane windows was fabri-

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(1) F. F. Rust, F. H. Seubold and W. E. Vaughan, THIS JOURNAL, **70**, 95 (1948).

(2) F. A. Raal and C. J. Danby, *J. Chem. Soc.*, 2222 (1949).

(3) In the reaction of $CD_3CH_2CH{=}CH_2$ and light methyl radicals, propylene-d_3 has been observed in the products (private communication, Paul Kebarle and W. A. Bryce).

(4) J. R. McNesby and A. S. Gordon, THIS JOURNAL, **76**, 4196 (1954).

(5) C. M. Drew, J. R. McNesby, S. R. Smith and A. S. Gordon, *Anal. Chem.*, **28**, 979 (1956).

cated from quartz. The reaction mixture was between 30 and 100 mm. of a 1:1 acetone–butene blend. The butenes were Phillips Research Grade compounds. The areas under each peak in a gas chromatogram were measured and compared with the areas obtained using a synthetic blend of the compounds in question. It was found that the area under a peak was approximately proportional to the amount of the compound. Using this information, the product analyses reported in Table III were obtained. The light source was a Hanovia medium pressure mercury arc. Reactions were permitted to proceed less than 10% toward completion. Under our own reaction conditions, this corresponds to five minutes irradiation with full intensity of the mercury arc. A 12 ft. 1.5% squalane on carbon black (Pelletex) column was used for the chromatographic analyses.

Results and Discussion

The *a priori* formulation of the mechanism of the reaction of CD_3 radicals with butene-1 should predict all of the products of the reaction. To simplify the presentation of the possible reactions, the butene molecule is labeled as

$$\underset{(1)}{CH_2}{=}\underset{(2)}{CH}{-}\underset{(3)}{CH_2}{-}\underset{(4)}{CH_3}$$

The abstraction of H from position 3 should be favored since a resonance stabilized radical results. Abstraction of H from position 1 would result in a $CH{=}CHCH_2CH_3$ radical which could pyrolyze to acetylene and an ethyl radical. No acetylene is observed in the products of reaction at temperatures up to 500°. Attack on position 2 would result in the $CH_2{=}C{-}CH_2CH_3$ radical which should pyrolyze to allene and a methyl radical. No allene is noted in the products. Position 4 is an unlikely point of attack, since it is a primary H and is more resistant to attack than position 1.

The methyl radical attack on position 3 results

$$CD_3 + CH_2{=}CHCH_2CH_3 \longrightarrow CD_3H + CH_2{=}CHCHCH_3 \quad (1)$$

in the $CH_2{=}CHCHCH_3$ radical. This radical can undergo the reactions

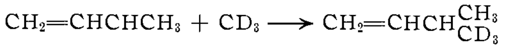
$$CH_2{=}CHCHCH_3 \longleftrightarrow CH_2CH{=}CHCH_3 \quad (2)$$

$$CH_2{=}CHCHCH_3 + HR \longrightarrow CH_2{=}CHCH_2CH_3 + R \quad (3)$$

$$CH_2CH{=}CHCH_3 + HR \longrightarrow CH_3CH{=}CHCH_3 + R \quad (3')$$

$$CH_2{=}CHCHCH_3 + Ad_6 \longrightarrow CH_2{=}CH{-}CHDCH_3 + CD_2COCD_3 \quad (4)$$

$$CH_2CH{=}CHCH_3 + Ad_6 \longrightarrow CH_2DCH{=}CHCH_3 + CD_2COCD_3 \quad (4')$$



$$CH_2{=}CHCHCH_3 + CD_3 \longrightarrow CH_2{=}CHCH\substack{CH_3\\CD_3} \quad (5)$$

$$CH_2CH{=}CHCH_3 + CD_3 \longrightarrow CD_3CH_2CH{=}CHCH_3 \quad (5')$$

$$2CH_2CH{=}CHCH_3 \longrightarrow CH_3CH{=}CHCH_2CH_2CH{=}CHCH_3 \quad (6)$$

Reaction

$$CH_2{=}CHCHCH_3 \longrightarrow CH_2{=}CHCH{=}CH_2 + H \quad (7)$$

is eliminated since no H_2 or HD is found in the products.

Besides the attack of CD_3 on position 3 to give CD_3H, one other methane is generated by CD_3 attack.

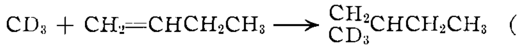
$$CD_3 + CD_3COCD_3 \longrightarrow CD_4 + CD_2COCD_3 \quad (8)$$

Similar arguments for hydrogen abstraction apply to other butenes. Only the α-hydrogens are abstracted with facility in our temperature range. It follows that

$$\frac{CD_3H}{CD_4} = \frac{k_1(B)}{k_8(Ad_6)} \quad (1)$$

Similar relations hold for the other butenes and the CD_3H/CD_4 ratios are given in Table I for each of the four butenes studied. The table also shows that large amounts of CH_4 and CH_3D are formed, increasing with temperature. These light methanes result from the addition of CD_3 to the double bond of the butenes followed by elimination of CH_3 from the pentyl radical. The reaction sequence is shown for the case of butene-1.

$$CD_3 + CH_2{=}CHCH_2CH_3 \longrightarrow CD_3CH_2CHCH_2CH_3 \quad (9)$$

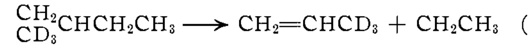


$$CD_3 + CH_2{=}CHCH_2CH_3 \longrightarrow \substack{CH_2\\CD_3}CHCH_2CH_3 \quad (10)$$

The most likely fates of the pentyl radical formed in (9) are to decompose to the original olefin (reverse of 9) or to form butene-1-d_3.

$$CD_3CH_2CHCH_2CH_3 \longrightarrow CD_3CH_2CH{=}CH_2 + CH_3 \quad (11)$$

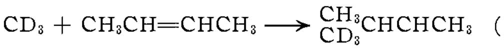
with about equal probability. The CH_3 radical will stabilize itself as CH_4 and CH_3D. Table IV shows that the parent butene-1 is, as required by (11), clearly marked with butene-1-d_3 at 375°. The radical formed in reaction 10 should produce propylene and an ethyl radical.



$$\substack{CH_2\\CD_3}CHCH_2CH_3 \longrightarrow CH_2{=}CHCD_3 + CH_2CH_3 \quad (12)$$

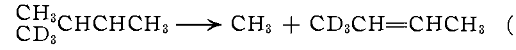
The propylene fraction should consist of propylene and propylene-d_3. Experiment 65C (Table V) in which CD_3 radicals were generated by photolysis and pyrolysis in the system, shows that CD_3 radicals add efficiently to butene-1 in the non-terminal position and produce propylene-d_3 even at 500°.

The addition of CD_3 to butene-2 proceeds as



$$CD_3 + CH_3CH{=}CHCH_3 \longrightarrow \substack{CH_3\\CD_3}CHCHCH_3 \quad (13)$$

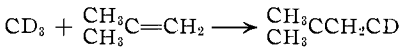
The most likely fates of the pentyl radical formed in (13) are either the reverse of (13) or the formation of butene-2-d_3



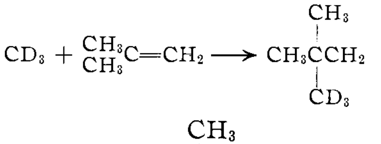
$$\substack{CH_3\\CD_3}CHCHCH_3 \longrightarrow CH_3 + CD_3CH{=}CHCH_3 \quad (14)$$

with about equal probability.

The CD_3 radical adds to isobutene in two positions



$$CD_3 + \substack{CH_3\\CH_3}C{=}CH_2 \longrightarrow \substack{CH_3\\CH_3}CCH_2CD_3 \quad (15)$$



$$CD_3 + \substack{CH_3\\CH_3}C{=}CH_2 \longrightarrow CH_3\underset{CD_3}{\overset{CH_3}{C}}CH_2 \quad (16)$$

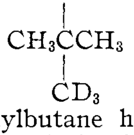
A small amount of  $CH_3\underset{CD_3}{\overset{CH_3}{C}}CH_3$ and a tenfold larger amount of 2-methylbutane have been definitely identified in the photolysis of acetone in the presence of isobutene at 373°. Their origins are undoubtedly (15) and (16) followed by abstraction of

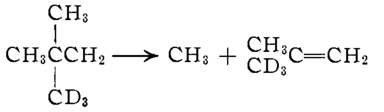
TABLE I

METHANE ANALYSES IN REACTION OF CD_3 WITH THE BUTENES

Expt.	Butene	CD_4	CD_3H	CH_2D_2[a]	CH_3D	CH_4	CH_4/CD_3H	CD_3H/CD_4	CH_4/CH_3D	*T*, °C.	*A/B*
57A	1	24.5	306.8	6.03	3.3	23.7	0.077	12.52	..	252	0.95
57B	1	59.9	375.4	11.8	48.4	302.3	.81	6.27	6.25	400	.95
57C	1	3.0	14.8	4.4	64.3	315.3	21.3	4.9	4.90	500	.95
58A	2-*trans*	35.8	321.7	4.7	2.4	26.6	0.083	8.99	..	253	1.00
58B	2-*trans*	72.6	390.4	7.5	36.2	212.9	.54	5.38	5.88	400	1.00
58C	2-*trans*	1.8	8.0	0.8	15.1	67.1	8.4	4.4	4.4	502	1.00
60A	2-*cis*	44.6	474.6	7.7	2.6	29.5	0.062	10.64	..	252	0.97
41B	2-*cis*	13.8	86.6	1.8	4.8	34.6	.40	6.28	7.2	375	.93
60B	2-*cis*	91.7	560.2	10.3	32.6	212.2	.38	6.11	6.51	400	.97
59A	Iso	17.4	187.3	3.4	0	5.6	.030	10.76	..	252	.83
59B	Iso	99.4	590.1	11.8	8.6	75.5	.13	5.94	8.8	400	.83
59C	Iso	2.8	13.5	1.8	10.7	49.5	3.66	4.80	4.63	502.5	.83

[a] This methane occurs in small percentage due to the 5% acetone-d_5 impurity in the acetone-d_6.

H by the pentyl radical. Reaction 16 may be followed by



$$CH_3\underset{\underset{CD_3}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_2 \longrightarrow CH_3 + \overset{CH_3}{\underset{CD_3}{}}C{=}CH_2 \qquad (17)$$

and the reverse of (16). The pentyl radical formed in (15) can also abstract a hydrogen atom, or expel an H atom to form a pentene. As previously discussed, the last possibility is quite unlikely.

In order to estimate the rates of addition of CD_3 radicals to the butenes in the various positions, it is necessary to examine the methane formed in the reactions. At 400° it is a good approximation that every pentyl radical formed in (9), (13) and (16) decomposes into the original reactants or *via* reactions (11), (14) and (17), respectively. Reactions 11 and 14 should have *a priori* probabilities equal to the reverse of reactions 10 and 13, respectively, while the probability of reaction 17 should have an *a priori* probability of only half the reverse of (16). The addition of ethyl radicals to the olefin to produce CH_3 radicals and a pentane is not important; examination of the amount of CH_4 and CH_3D produced relative to the pentenes supports this assumption. In the case of butene-1, terminal addition of CH_3 produces another CH_3 by reactions similar to (9) and (11) so that CH_3 is not removed by terminal addition. Non-terminal addition removes CH_3 and produces propylene by a reaction like (12). Examination of the data shows that this non-terminal addition accounts for the removal of only a small number of CH_3 radicals.

Reaction (8) represents the rate at which D is abstracted from acetone-d_6 by CD_3; $d(CH_4 + CH_3D)/dt$ is half the rate at which CD_3 is added to the terminal carbon atom of butene-1. Thus in the early stages of reaction, one CH_3 is expelled for every two CD_3 radicals added.

$$\frac{k_9(CD_3)(B)}{k_8(CD_3)(Ad_6)} = \frac{2[(CH_4) + (CH_3D)]}{(CD_4)} \qquad (2)$$

$$k_9/k_8 = 2(Ad_6)/(B)\left[\left(\frac{CH_4}{CD_4}\right) + \left(\frac{CH_3D}{CD_4}\right)\right] \qquad (3)$$

In the case of butene-2 a similar situation exists.

$$k_{13}/k_8 = 2(Ad_6)/(B)\left[\left(\frac{CH_4}{CD_4}\right) + \left(\frac{CH_3D}{CD_4}\right)\right] \qquad (4)$$

With non-terminal addition in isobutene, each CD_3 added results in the expulsion of $^2/_3$ of a CH_3 radical on the average.

$$k_{16}/k_8 = \frac{3}{2}[(Ad_6)/(B)]\left[\left(\frac{CH_4}{CD_4}\right) + \left(\frac{CH_3D}{CD_4}\right)\right] \qquad (5)$$

For non-terminal addition of CD_3 to butene-1 the assumption is made that the decomposition of the pentyl radical to original reactants proceeds just as fast as reaction 12, and the rate of production of $CH_2{=}CHCD_3$ is then a measure of the rate of addition of CD_3 to the non-terminal carbon atoms, and eq. *6* holds.

$$\frac{k_{10}(CD_3)(B)}{k_8(CD_3)(Ad_6)} = \frac{2(CD_3CH{=}CH_2)}{(CD_4)} \qquad (6)$$

In Table II the relative rates obtained by substituting the experimental data in eq. *6* are shown.

TABLE II

RATES OF ADDITION OF CD_3 TO BUTENES RELATIVE TO ABSTRACTION OF D FROM ACETONE-d_6 AT 400°

	Terminal carbon	Non-terminal carbon
Butene-1	11.0	1.5
cis-Butene-2	No terminal C atom	5.2
trans-Butene-2	No terminal C atom	6.8
Isobutene	....	1.4

It is noteworthy that in the reaction of CH_3 with propylene[1] the *n*-butane/isobutane ratio is about 6 at 235°. This ratio is an estimate of the ratio of the rates of terminal to non-terminal addition. The value obtained from Table II for the same addition ratio for butene-1 at 400° is about 7.

The data also indicate the mechanism of isomerization of butene-1. At 375° very little isomerization to butene-2 occurs, but at 503° a very rapid isomerization takes place, giving butene-2 containing 9% d_1 and 89% d_0. The butenyl radical which is resonance stabilized, is reluctant to abstract hydrogen at 375°, but does so readily at 500°, exhibiting the same behavior as the resonance stabilized allyl radical.[6]

$$CH_3CHCH{=}CH_2 \longleftrightarrow CH_3CH{=}CHCH_2 \qquad (18)$$

$$CH_3CH{=}CHCH_2 + HR \longrightarrow CH_3CH{=}CHCH_3 \qquad (3')$$

$$CH_3CH{=}CHCH_2 + Ad_6 \longrightarrow CH_3CH{=}CHCH_2D \qquad (4')$$

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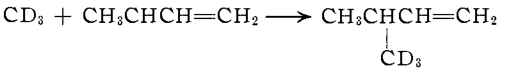
(6) J. R. McNesby and A. S. Gordon, THIS JOURNAL, submitted for publication.

These results show that $k_3'/k_4' = 10$ at 498°. Two pentenes appear in the products, but their identities have not been established. It seems reasonable that they are produced by reactions 19 and 20 since they contain large percentages of pentene-d_3 as well as pentene. It should be noted that these are minor products of the reaction.

$$CD_3 + CH_3CH{=}CHCH_2 \longrightarrow CH_3CH{=}CHCH_2CD_3 \quad (19)$$



$$CD_3 + CH_3CHCH{=}CH_2 \longrightarrow CH_3\underset{\displaystyle CD_3}{\underset{|}{C}H}CH{=}CH_2 \quad (20)$$

In the results presented in Table III it may be noted that in the reaction between CD_3 and butene-1 the methane/propylene ratio decreases with increasing temperature, while the ethane/ethylene ratio is nearly unity from 220–504°. The propylene in the products increases very rapidly with temperature. At 220° there is no propylene since reaction 12 does not take place at this temperature. Reaction 12 is the source for propylene at 400°. At 500° there is an additional source of propane and methane. In the pyrolysis of butene-1 at 500°, one of the main reaction paths results in a split to a methyl and an allyl radical. The methyl forms methane and the allyl forms propylene, butene-1 and diallyl. The rough correspondence of ethylene and ethane over the temperature range may be only a coincidence. At temperatures where butene-1 does not pyrolyze, we should expect one ethyl radical formed for each propylene formed. At 400° there is twice as much propylene as ethane, showing that about half of the ethyl radicals do not abstract hydrogen at this temperature, but add to the butene-1.

TABLE III

PER CENT. COMPOSITION OF PRODUCTS OF THE PHOTOCHEMICAL AND THE THERMAL REACTION OF ACETONE-d_6 AND BUTENE-1

Expt. no.	65D	68A	57E[a]
T, °C.	220	400	504
CO	61.5	29.0	2.7
Methane	31.0	49.7	32.1
Ethylene	1.7	4.9	11.5
Ethane	1.7	3.3	9.1
Propylene	0.0	7.7	20.1
Propane	0.3	0.9	0.8
Butene-2	0.0	2.2	21.8
3-Me-Butene-1	1.0	1.2	0.4
Pentene	0.4	1.0	1.4
Hexane	2.5	0	0
% Reacted	3	5	10

[a] Some of the higher molecular weight products were not identified. The percentages have a precision of about 5%.

TABLE IV

ISOTOPIC COMPOSITION OF PARENT BUTENES AND ISOMERS FORMED IN REACTION

	Butene	T, °C.	P, mm.	t, min.	A/B	Parent butene % d_0	% d_1	% d_3	Butene isomer % d_0	% d_1	% d_3
65B	1	375	124	30	0.90	82.5	..	17.5	..	..	..
57D	1	379	30	40	.95	75	..	25	..	..	..
65A	1	503[a]	110	15	.90	99	..	1	..	..	..
65C	1	498[b]	100	10	.90	94	1	5	89	9	2
58D	*trans*-2	379	30	40	1.00	92	1	7	..	..	..
60D	*cis*-2	378	88	35	.97	99	..	1.2	90	8	2
59D	Iso	381	70	28	.83	92	7	1	..	..	..

[a] Thermal reaction. [b] Thermal reaction plus photochemical reaction.

TABLE V

ISOTOPIC PERCENTAGE COMPOSITION OF C_2 AND C_3 HYDROCARBON PRODUCTS IN ACETONE-d_6–BUTENE-1 SYSTEM

	Butene	T, °C.	C_2H_4	C_2H_3D	$C_2H_2D_2$	C_2H_6	C_2H_5D	C_3H_6	$C_3H_3D_3$	$C_3H_5D_3$	$C_3H_4D_4$
65B	1	375	>90	<5	<5	95	5	61	39	86	14
65A	1	503[a]	>92	<4	<4	81	19	>99	<1	..	..
65C	1	498[b]	79	16	5	82	18	89	11	..	..
51D	1	379	..	..	..	..	..	..	..	85	14

[a] Thermal reaction. [b] Thermal reaction plus photochemical reaction.

Table IV shows that in the photolysis of butene-1 acetone-d_6 mixtures, butene-1 becomes severely marked with butene-d_3 at lower temperatures. Even at 500°, terminal addition of CD_3 to butene-1 is still a very efficient reaction.

A small amount of propane is formed. At 375° the propane is mostly propane-d_3 with about 15% propane-d_4, as noted in Table V.

***trans*-Butene-2.**—At 379° no ethane, propylene or propane and only a trace of ethylene are observed in the products of the photolysis of acetone-d_6–*trans*-butene-2 mixtures. A single pentene is observed which contains a maximum of 3 D atoms; a second pentene may be concealed by the acetone. The parent butene-2 after reaction is 7% butene-2-d_1. Isomerization to butene-1 occurs *via* the mechanism

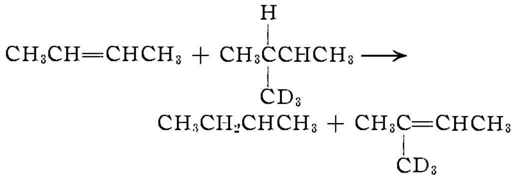
$$CD_3 + CH_3CH{=}CHCH_3 \longrightarrow CD_3H + CH_2CH{=}CHCH_3 \quad (21)$$

$$CH_2CH{=}CHCH_3 \longleftrightarrow CH_2{=}CHCHCH_3 \quad (2)$$

$$CH_2{=}CHCHCH_3 + HR \longrightarrow CH_2{=}CHCH_2CH_3 + R \quad (22)$$

$$CH_2{=}CHCHCH_3 + Ad_6 \longrightarrow CH_2{=}CHCHDCH_3 + Ad_5 \quad (23)$$

Contrary to the butene-1 case, the propylene is much larger in the thermal reaction at 500° than the sum of ethylene and ethane. Therefore, propylene, ethane and ethylene do not arise from the butene-1 formed by isomerization of butene-2. A possible source of propylene is



$$CH_3CH{=}CHCH_3 + CH_3\overset{H}{\underset{CD_3}{C}}CHCH_3 \longrightarrow CH_3CH_2CHCH_3 + CH_3\underset{CD_3}{C}{=}CHCH_3 \qquad (24)$$

$$CH_3CH_2CHCH_3 \longrightarrow CH_3 + CH_2{=}CH{-}CH_3 \qquad (25)$$

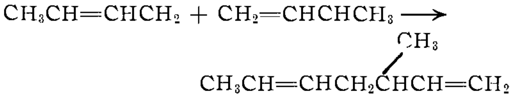
Butene-1 is formed rapidly in this reaction and could be the source of ethylene and ethane.

cis-**Butene-2.**—The photolysis of acetone in the presence of *cis*-butene-2 at 374° was carried out to identify the products. The products were CO, CH_4, and small amounts of ethane, propylene, propane, butene-1, pentane and approximately equal amounts of three isomers of octadiene. The butenyl radical may be represented by two equivalent formulas.

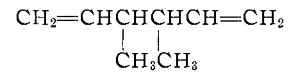
$$CH_2CH{=}CHCH_3 \longleftrightarrow CH_2{=}CH{-}CHCH_3 \qquad (2)$$

There are three combinations of these radicals to give three octadienes.

$$2CH_3CH{=}CHCH_2 \longrightarrow CH_3CH{=}CHCH_2CH_2CH{=}CHCH_3 \qquad (26)$$



$$CH_3CH{=}CHCH_2 + CH_2{=}CHCHCH_3 \longrightarrow CH_3CH{=}CHCH_2\overset{CH_3}{C}HCH{=}CH_2 \qquad (27)$$

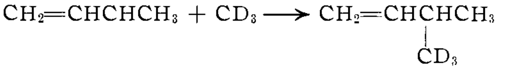


$$2CH_2{=}CH{-}CHCH_3 \longrightarrow CH_2{=}CH\underset{CH_3}{C}H\underset{CH_3}{C}HCH{=}CH_2 \qquad (28)$$

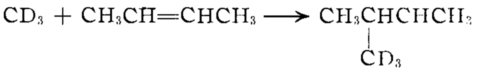
An experiment on the addition of CD_3 to *cis*-butene-2 was performed. Slight isomerization to butene-1 is again observed at 370°, with about 10% of the butene-1 having one D atom. Two pentenes and a pentane containing three D's each were recovered.

$$R + CH_3CH{=}CHCH_3 \longrightarrow CH_2CH{=}CHCH_3 + RH \qquad (29)$$

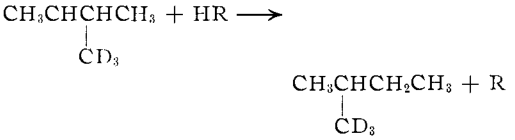
$$CH_2CH{=}CHCH_3 + CD_3 \longrightarrow CD_3CH_2CH{=}CHCH_3 \qquad (30)$$



$$CH_2{=}CHCHCH_3 + CD_3 \longrightarrow CH_2{=}CH\underset{CD_3}{C}HCH_3 \qquad (31)$$



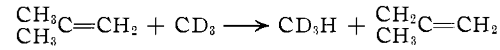
$$CD_3 + CH_3CH{=}CHCH_3 \longrightarrow CH_3\underset{CD_3}{C}HCHCH_3 \qquad (32)$$



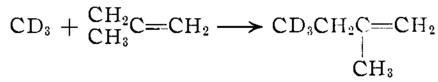
$$CH_3\underset{CD_3}{C}HCHCH_3 + HR \longrightarrow CH_3\underset{CD_3}{C}HCH_2CH_3 + R \qquad (33)$$

No ethylene, ethane, propylene or propane appears in the products.

Isobutene–Acetone-d_6 Photolysis.—At 381° a single pentene-d_3 peak and two pentane-d_3 peaks are observed.



$$\substack{CH_3\\CH_3}C{=}CH_2 + CD_3 \longrightarrow CD_3H + \substack{CH_2\\CH_3}C{=}CH_2 \qquad (34)$$



$$CD_3 + \substack{CH_2\\CH_3}C{=}CH_2 \longrightarrow CD_3CH_2\underset{CH_3}{C}{=}CH_2 \qquad (35)$$

Only one pentene can be formed from this butene.

The pentanes are formed by the terminal and non-terminal addition of CD_3 to the double bond, followed by the pentyl radicals abstracting H.

CHINA LAKE, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KENTUCKY]

Solvents Having High Dielectric Constants. VIII. The Conductimetric Behavior of Several Salts in Formamide at 25°[1]

BY LYLE R. DAWSON, EUGENE D. WILHOIT AND PAUL G. SEARS

RECEIVED MAY 18, 1957

The conductivities of eight electrolytes in formamide at 25° have been measured at several concentrations within the range 3–100 × 10^{-3} *N*. The limiting equivalent conductance in each case has been determined by a mathematical extrapolation of a Shedlovsky plot of Λ'_0 *versus C*. The results illustrate the additivity of limiting ionic conductances in formamide. In most cases, the slopes of the plots of Λ *versus* $\sqrt{C}$ (for the above concentration range) are 10–30% numerically less than those calculated by the Onsager equation. Limiting ionic equivalent conductances based upon the approximation method using trimethylphenylammonium benzenesulfonate as the reference electrolyte agree within 3% with those which have been determined by the Hittorf method.

The first unit in this series[2] describes the conductances of hydrogen and potassium chlorides in formamide at 3, 20 and 40°. Anabatic phoreograms[3] characterize the conductimetric behavior of these electrolytes in formamide. The magnitude of Λ_0 for HCl also indicates the absence of any unique mechanism for the conductance of the solvated proton in this medium.

Despite the numerous inherent difficulties associated with the purification and preservation of formamide of desirable quality, there is need for additional information concerning the properties of solutions of electrolytes in un-N-substituted amide solutions. The melting points of acetamide and propionamide being above 80° presents concomitant experimental difficulties which eliminate any advantages in selecting these solvents preferentially with respect to formamide.

The objectives of the present study were to extend generally the previous studies using form-

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[1] This research was supported in part by a contract with the Office of Ordance Research.

[2] L. R. Dawson, T. M. Newell and W. J. McCreary, THIS JOURNAL, **76**, 6024 (1954).

[3] R. M. Fuoss, *J. Chem. Educ.*, **32**, 527 (1955).