

Mechanistic investigations of the ethylene tetramerisation reaction

Supporting information

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Full analysis of ethylene tetramerisation product mixture

Table 1. Identified peaks of the light fraction of a standard ethylene tetramerisation sample as obtained using GC/MS.

Peak number	Identified peaks
1	Methyl propane
2	1-Butene
3	n-Butane
4	Acetone (syringe solvent)
5	1,5-Hexadiene
6	1-Hexene
7	n-Hexane
8	2-Hexene
9	Internal hexene
10	Methyl cyclopentane
11	Methylene cyclopentane
16	Methyl cyclohexane (reaction solvent)
18	1-Octene
19	4-Octene
20	Octane
21	2-Octene
22	2-Octene
23	Propenyl cyclopentane (3-cyclopentyl-1-propene)
25	Propyl cyclopentane

The numbered chromatogram that corresponds to Table 1 is shown in Figure 1.

Figure 1. Numbered chromatogram (see Table1) of light fraction of tetramerisation sample

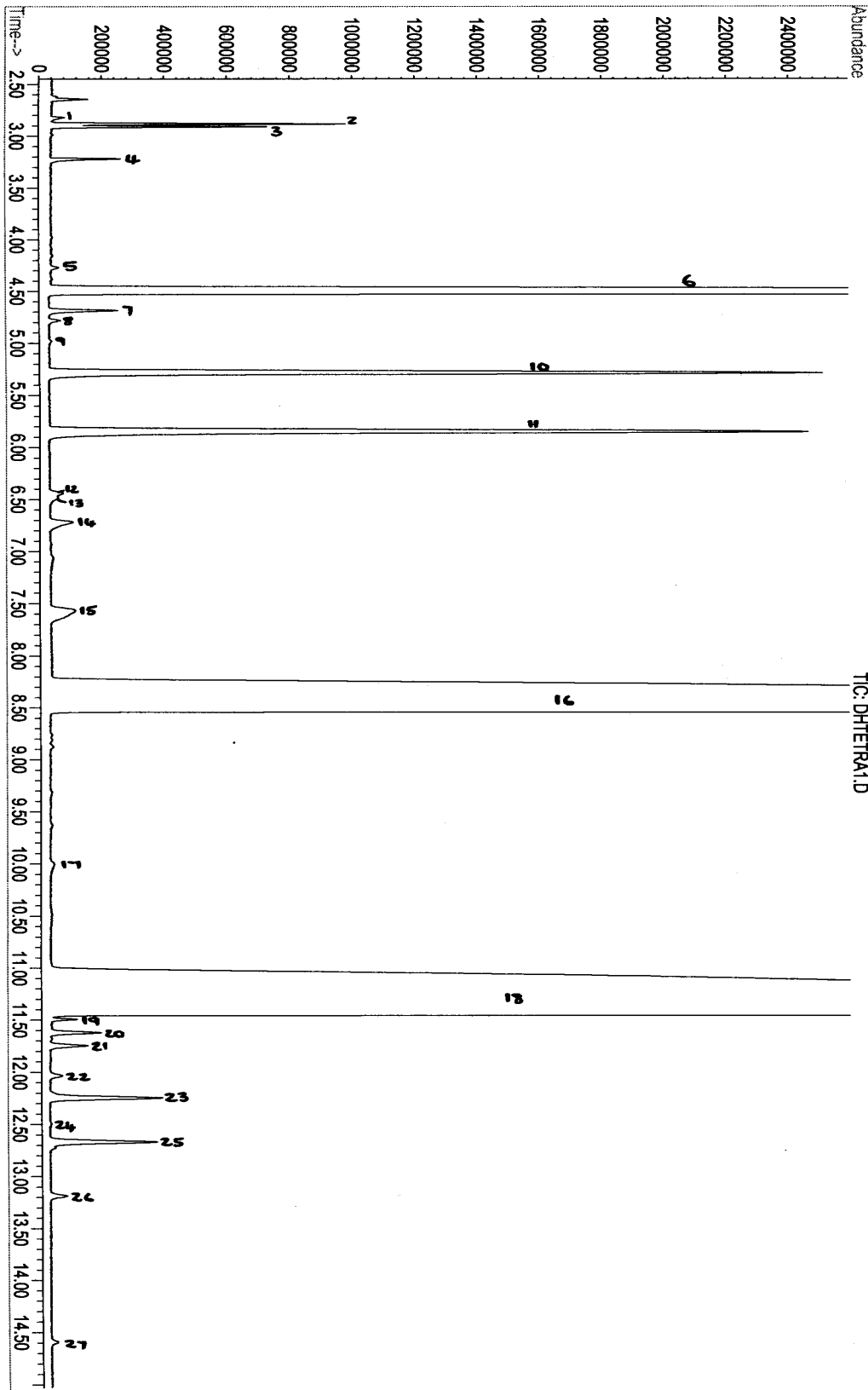


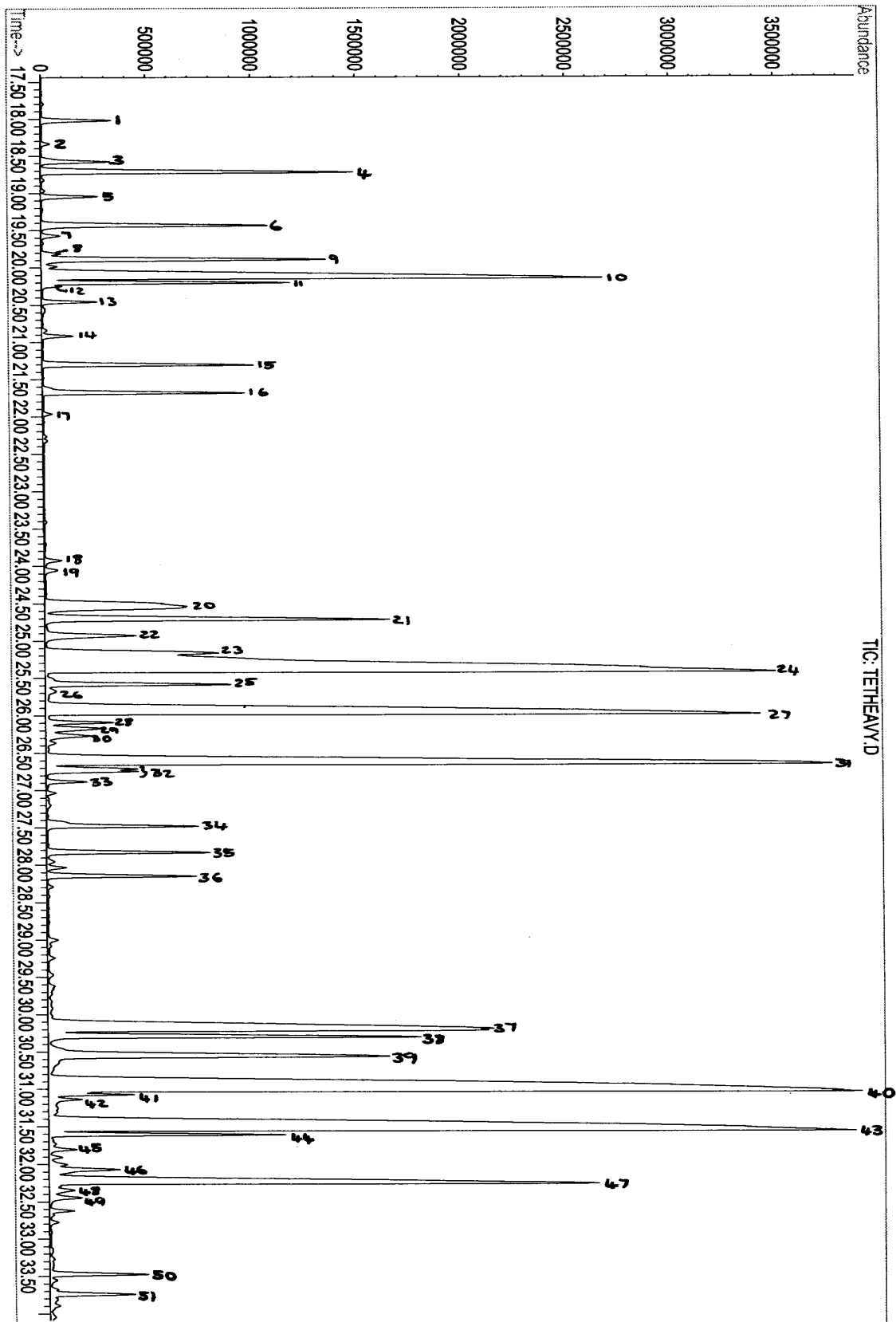
Table 2. Identified peaks of the heavy fraction of a standard tetramerisation sample as obtained using GC/MS (Identified secondary products in bold)

Peak number	Identified Peaks
3	(4-Ethyl-1-octene)
4	(5-Methyl-1-nonene)
6	5-Methylene nonane
9	(3-Propyl-1-heptene)
10	1-Decene
11	Internal decene
12	Internal decene
13	n-Decane
15	(Pentenyl cyclopentane)
16	Pentyl cyclopentane
24	(5-Methyl-1-undecene)
27	5-Methylene undecane
31	1-Dodecene (c.a. 40%) + co-eluent
33	Dodecane
35	Heptenyl cyclopentane
36	Heptyl cyclopentane
40	(7-Methyl-1-tridecene)
43	7-Methylene tridecane
47	1-Tetradecene
49	Tetradecane
50	(Nonenyl cyclopentane)
51	(Nonyl cyclopentane)
52	1-Hexadecene
53	(Undecenyl cyclopentane)
54	(Undecyl cyclopentane)
55	1-Octadecene
56	C20 1-alkene
57	C22 1-alkene
58	C24 1-alkene
59	C26 1-alkene
60	C28 1-alkene

Products in brackets were not unambiguously identified but may be deduced with a high degree of probability from first principles and comparative mass spectra of related compounds in the Wiley275 library.

The numbered chromatogram that corresponds to Table 2 is shown in Figure 2.

Figure 2. Numbered chromatogram (see Table2) of heavy fraction of tetramerisation sample



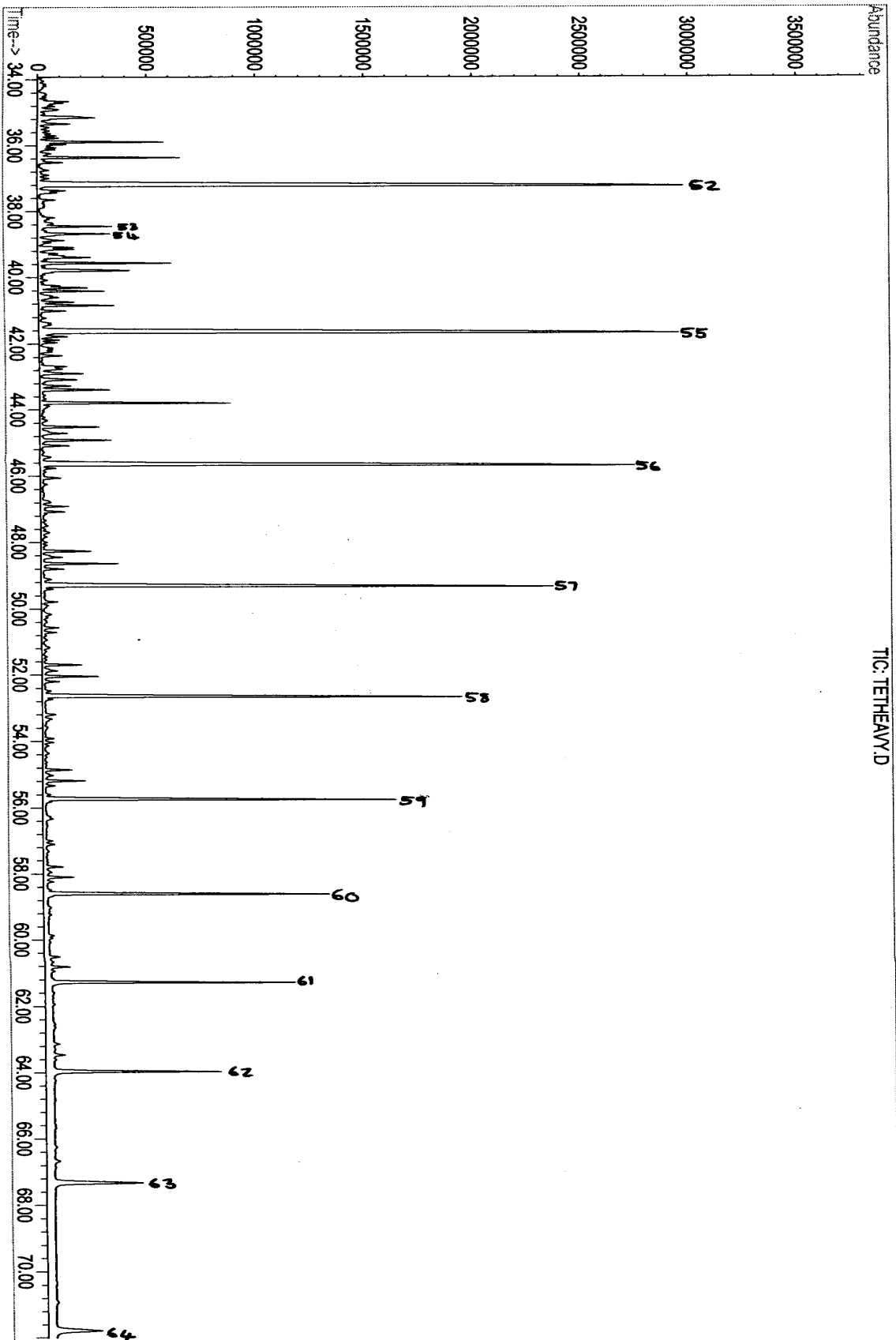


Figure 3. GC-FID chromatogram of the C14 region: unhydrogenated and hydrogenated (no correspondence of elution times as different columns were used)

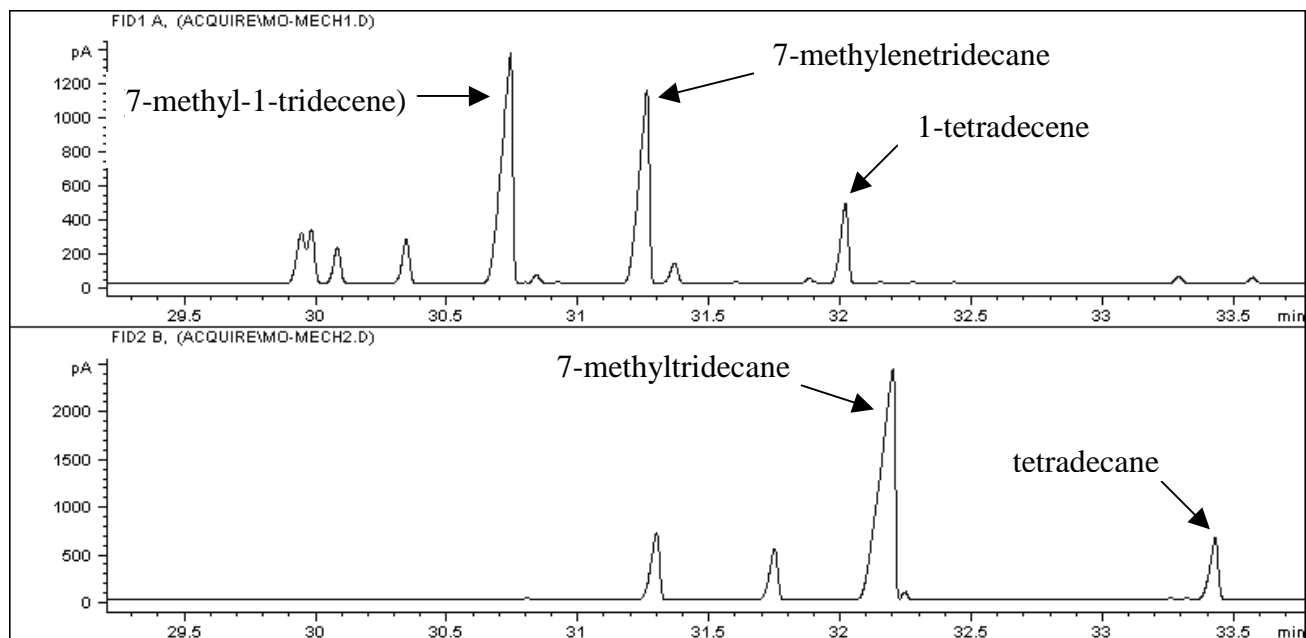


Figure 4. Postulated origin of 7-methylenetridecane and 7-methyl-1-tridecene *via* alternative tetramerisation mechanism (β -hydride transfer to alkene) and other secondary products expected in this case

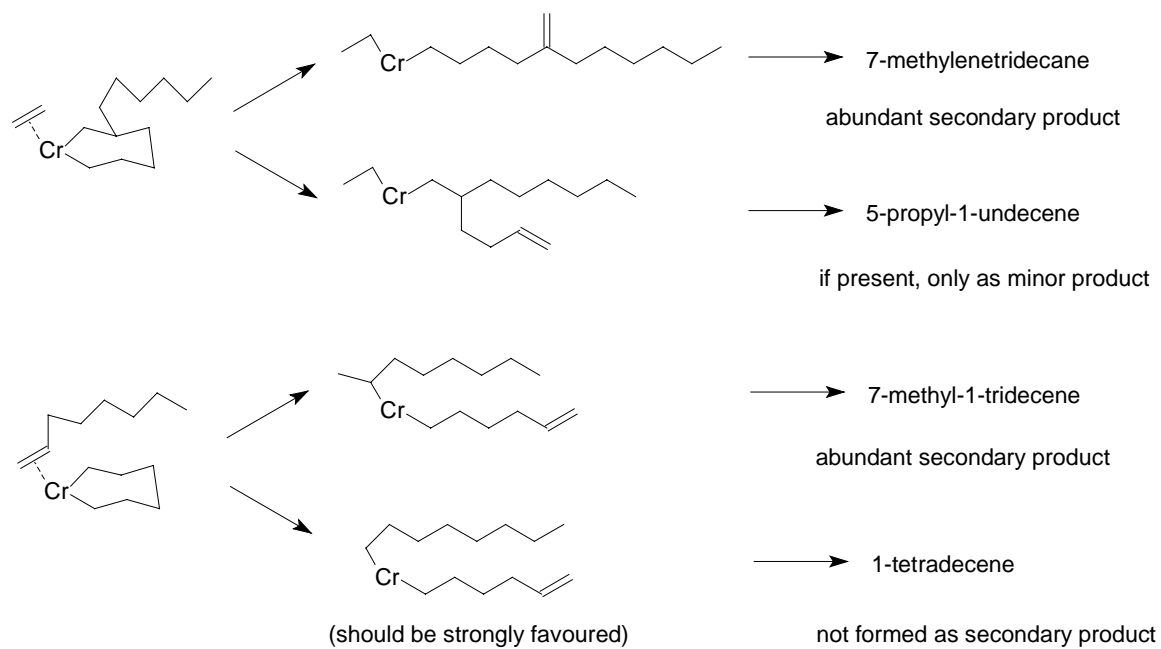
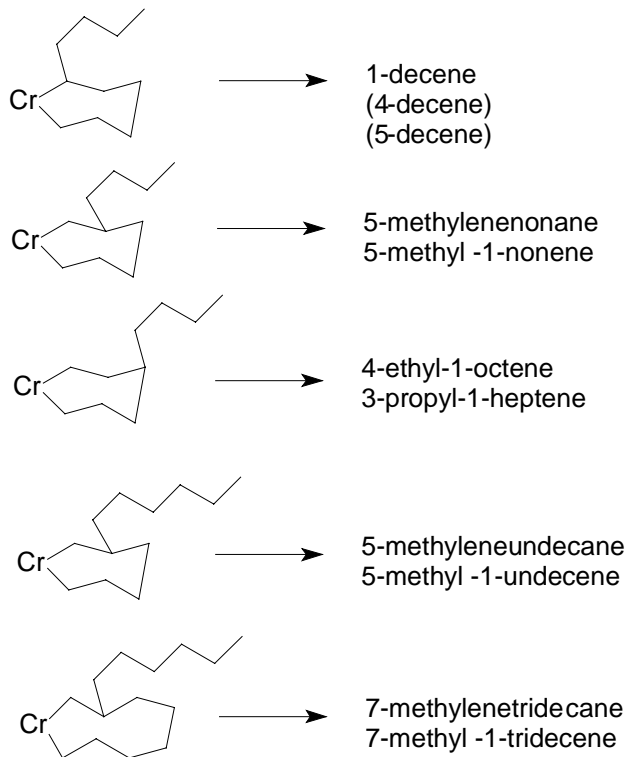


Figure 5. Metallacyclic origin of secondary products that could be identified



Mathematical analysis for deuterium labeling studies

Metallacyclic:

If the ratio of $C_2H_4:C_2D_4$ is defined as x (x may easily be calculated from the observed isotopomer distribution; this is independent of mechanism), then the isotopomer distribution will follow the generalized Pascal's triangle distribution:

	C₂H₄		C₂D₄									
C2	x		1									
	C₄H₈		C₄H₄D₄		C₄D₈							
C4	x^2		2x		1							
	C₆H₁₂		C₆H₈D₄		C₆H₄D₈		C₆D₁₂					
C6	x^3		$3x^2$		3x		1					
	C₈H₁₆		C₈H₁₂D₄		C₈H₈D₈		C₈H₈D₁₂		C₈D₁₆			
C8	x^4		$4x^3$		$6x^2$		4x		1			
	C₁₀H₂₀		C₁₀H₁₆D₄		C₁₀H₁₂D₈		C₁₀H₈D₁₂		C₁₀H₄D₁₆		C₁₀D₂₀	
C10	x^5		$5x^4$		$10x^3$		$10x^2$		5x		1	

It is possible to calculate a first order correction for the natural abundance of deuterium in normal ethylene (0.79%) and the residual abundance of hydrogen in the deuterated ethylene (0.5% from manufacturer's analysis). This correction is demonstrated for 1-hexene below.

Isotopomer	Idealised metallacyclic mechanism	Correction for imperfect C ₂ H ₄ and C ₂ D ₄
C ₆ H ₁₂	x ³	x ³ (1-0.0079*12)
C ₆ H ₁₁ D ₁		x ³ (0.0079*12)
C ₆ H ₁₀ D ₂		0
C ₆ H ₉ D ₃		3x ² (0.005*4)
C ₆ H ₈ D ₄	3x ²	3x ² (1 – 0.005*4 – 0.0079*8)
C ₆ H ₇ D ₅		3x ² (0.0079*8)
C ₆ H ₆ D ₆		0
C ₆ H ₅ D ₇		3x(0.005*8)
C ₆ H ₄ D ₈	3x	3x(1 – 0.005*8 – 0.0079*4)
C ₆ H ₃ D ₉		3x(0.0079*4)
C ₆ H ₂ D ₁₀		0
C ₆ H ₁ D ₁₁		1(0.005*12)
C ₆ D ₁₂	1	1(1-0.005*12)

Cossee mechanism:

In the Cossee linear chain growth mechanism, H/D scrambling occurs, and isotopomers with odd numbers of H or D are predicted. The isotopomers are of the form (C₂H₄)_m(C₂D₄)_m – (H or D) + (H or D).

The following assumptions or approximations are made:

- 1) The probability of H v/s D lost (β -H/D elimination) is determined by the H:D ratio in the isotopomer
- 2) The probability of the H v/s D gained (insertion into Cr-H/D) is determined by the value of x (the ratio of C₂H₄:C₂D₄)
- 3) Kinetic isotope effects may be discounted

As an example, the calculation of relative amounts for 1-hexene is shown below:

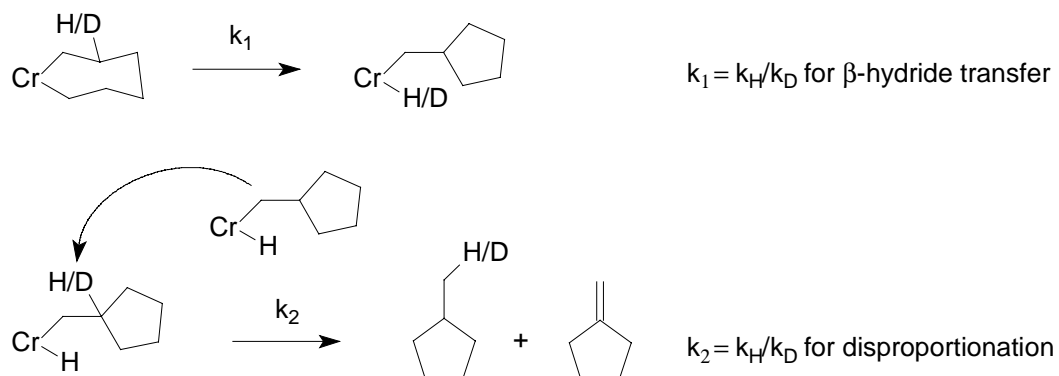
$(C_2H_4)_m(C_2D_4)_n$		$(C_2H_4)_m(C_2D_4)_n$ - (H or D) (Red: loss of H Blue: loss of D)		$(C_2H_4)_m(C_2D_4)_n$ - (H or D) + (H or D) (Red: gain of H Blue: gain of D)	
C_6H_{12}	x^3	C_6H_{11}	x^3	C_6H_{12}	x^4
				$C_6H_{11}D_1$	x^3
				$C_6H_{10}D_2$	
				$C_6H_9D_3$	x^3
$C_6H_8D_4$	$3x^2$	$C_6H_8D_3$ $C_6H_7D_4$	x^2 $2x^2$	$C_6H_8D_4$	$x^2 + 2x^3$
				$C_6H_7D_5$	$2x^2$
				$C_6H_6D_6$	
				$C_6H_5D_7$	$2x^2$
$C_6H_4D_8$	$3x$	$C_6H_4D_7$ $C_6H_3D_8$	$2x$ x	$C_6H_4D_8$	$2x + x^2$
				$C_6H_3D_9$	x
				$C_6H_2D_{10}$	
C_6D_{12}	1	C_6D_{11}	1	$C_6H_1D_{11}$	x
				C_6D_{12}	1

The distribution can now be corrected for the natural abundance of deuterium in the normal ethylene and the imperfectly labeled deuterated ethylene. The first order correction is made as for the metallacyclic mechanism.

Disproportionation mechanism for the formation of C6 cyclics:

The prediction of an isotopomer distribution must take account of two different kinetic isotope effects in operation (Scheme 1), relating to: i) β -H/D elimination to the metal from the metallacycloheptane (k_1), and ii) H/D transfer in the disproportionation step (k_2)

Scheme 1. Kinetic isotope effects for the disproportionation mechanism of cyclic formation



The following assumptions/approximations are made:

- 1) For a given metallacycloheptane isotopomer, the normal and deuterated ethylenes are statistically distributed in the metallacycle (no secondary isotope effects)
- 2) The ratio of β -H : β -D elimination from a given metallacycloheptane isotopomer = $k_1 * (\text{number of H's in isotopomer}) : (\text{number of D's in isotopomer})$
- 3) All steps are irreversible

The calculation of relative amounts is shown below:

Metalla-cyclopentane	Corrected for imperfect C ₂ H ₄ and C ₂ D ₄)	After β-H/β-D transfer	red: loss of β-H; blue: loss of β-D	Methyl-cyclopentane	(*) red: gain of H; blue: gain of D
MC ₆ H ₁₂	$x^3(1-0.0079*12)$	= a		C ₆ H ₁₂	ZA
MC ₆ H ₁₁ D ₁	$x^3(0.0079*12)$	= b	a + b/(1+11k₁)	C ₆ H ₁₁ D ₁	A + ZB
MC ₆ H ₁₀ D ₂			11bk₁/(1+11k₁)	C ₆ H ₁₀ D ₂	B + ZC
MC ₆ H ₉ D ₃	$3x^2(0.005*4)$	= c	3c/(3+9k₁)	C ₆ H ₉ D ₃	C + ZD
MC ₆ H ₈ D ₄	$3x^2(1 - 0.005*4 - 0.0079*8)$	= d	9ck₁/(3+9k₁) + 4d/(4+8k₁)	C ₆ H ₈ D ₄	D + ZE
MC ₆ H ₇ D ₅	$3x^2(0.0079*8)$	= e	8dk₁/(4+8k₁) + 5e/(5+7k₁)	C ₆ H ₇ D ₅	E + ZF
MC ₆ H ₆ D ₆			7ek₁/(5+7k₁)	C ₆ H ₆ D ₆	F + ZG
MC ₆ H ₅ D ₇	$3x(0.005*8)$	= f	7f/(7+5k₁)	C ₆ H ₅ D ₇	G + ZH
MC ₆ H ₄ D ₈	$3x(1 - 0.005*8 - 0.0079*4)$	= g	5fk₁/(7+5k₁) + 8g/(8+4k₁)	C ₆ H ₄ D ₈	H + ZI
MC ₆ H ₃ D ₉	$3x(0.0079*4)$	= h	4gk₁/(8+4k₁) + 9h/(9+3k₁)	C ₆ H ₃ D ₉	I + ZJ
MC ₆ H ₂ D ₁₀			3hk₁/(9+3k₁)	C ₆ H ₂ D ₁₀	J + ZK
MC ₆ H ₁ D ₁₁	$1(0.005*12)$	= i	11i/(11+k₁)	C ₆ H ₁ D ₁₁	K + ZL
MC ₆ D ₁₂	$1(1-0.005*12)$	= j	ik₁/(11+k₁) + j	C ₆ D ₁₂	L

(*) **Z = ratio of H v/s D transfer for the disproportionation step.** This is dependent on the **ratio of H v/s D available (Y)** and on the **intrinsic kinetic isotope effect (k₂)** for the disproportionation. Y and Z may be calculated as follows:

Calculation of Y:

Y = ratio of H : D available for disproportionation transfer = ratio of β -H : β -D transfer from metallacycloheptane

(The cyclisation is such that the H or D available for disproportionation transfer comes from the same ethylene as the H or D lost in the β -hydride transfer.) Thus,

$$Y = [a + 11bk_1/(1+11k_1) + 9ck_1/(3+9k_1) + 8dk_1/(4+8k_1) + 7ek_1/(5+7k_1) + 5fk_1/(7+5k_1) + 4gk_1/(8+4k_1) + 3hk_1/(9+3k_1) + ik_1/(11+k_1)]$$

$$[b/(1+11k_1) + 3c/(3+9k_1) + 4d/(4+8k_1) + 5e/(5+7k_1) + 7f/(7+5k_1) + 8g/(8+4k_1) + 9h/(9+3k_1) + 11i/(11+k_1) + j]$$

Calculation of Z:

Cyclopentylmethyl moieties either have H or D available for disproportionation transfer, ratio H:D = Y.

For disproportionation, there are three possible combinations of these moieties:

Combinations	Relative probability of this combination	Probability of transfer	H	Probability of transfer	D
(H, H)	Y^2	Y^2		0	
(H, D)	$2Y$	$2Yk_2/(1+k_2)$		$2Y/(1+k_2)$	
(D, D)	1	0		1	

Thus,

$$Z = \frac{Y^2 + 2Yk_2/(1+k_2)}{2Y/(1+k_2) + 1}$$

Isotopomer distributions generated with these calculations (scaled such that peaks of maximum intensity are equal) relative to the observed isotopomer distributions (determined by using the integrated molecular ions extracted from the GC-MS total ion chromatogram)

1-hexene (x = 2.5)

Isotopomer	84	85	86	87	88	89	90	91	92	93	94	95	96
Observed	12092470	1297630	196723	336576	14959001	1251702	150142	414176	5772063	376641	30561	90243	637202
Metalla-cyclic	12337364	1292070	0	326331	14959001	1031205	0	260446	6044940	205752	0	51966	814127
Cossee	14847168	7482190	665497	6281930	14959001	5783978	418549	4917720	4603297	1116625	81847	999476	398325

Methylcyclopentane (x = 2.4)

Isotopomer	84	85	86	87	88	89	90	91	92	93	94	95	96
Observed	894771	146407	27324	234792	1042386	154453	17370	198143	337695	43319	0	45525	14707
Reductive elimination	813008	85145	0	22740	1042386	71857	0	19191	445422	15161	0	4049	63435
Disproportionation	923205	167000	10016	191920	1042386	147419	12139	217035	328374	33336	4284	73080	5791

For disproportionation mechanism:

$$k_1 = 3.0$$

$$k_2 = 4.9$$

1-octene (x = 1.9)

Isotopomer	112	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127	128
Observed	4178721	452068	33265	86503	8457943	838165	79955	140662	6887445	599749	44599	120252	2504991	186275	0	30090	347479
Metalla-cyclic	3906359	565206	0	191097	8457943	905799	0	306252	6866162	483878	0	163600	2476898	86162	0	29132	335014
Cossee	4241184	2878013	345171	2463985	8457943	4546197	505105	3958246	6095272	2393264	244150	2119551	1857448	419872	38903	378322	196825

Figure 6. GC-FID chromatogram for 1-hexene produced from a mixture of C_2H_4 and C_2D_4

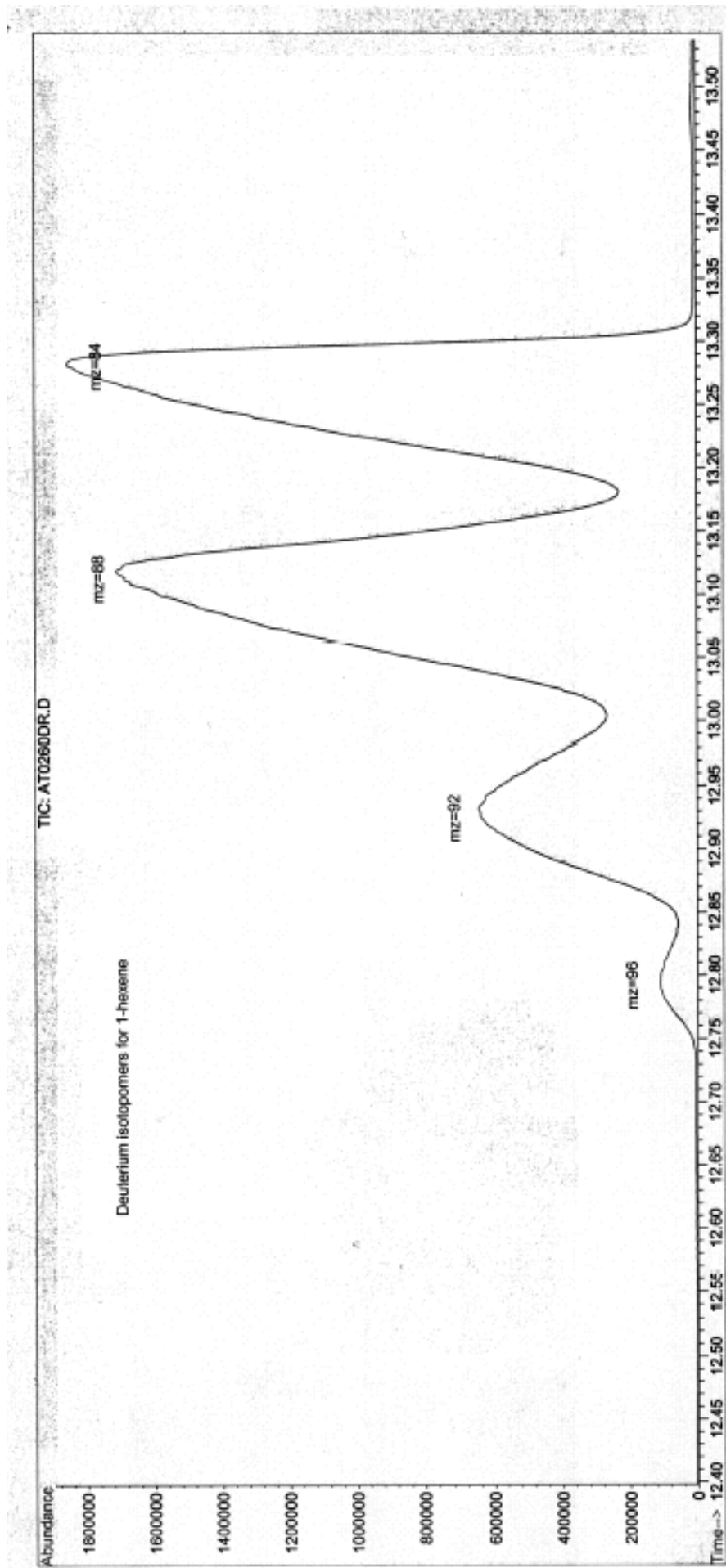


Figure 7. GC-FID chromatogram for methylcyclopentane produced from a mixture of C_2H_4 and C_2D_4

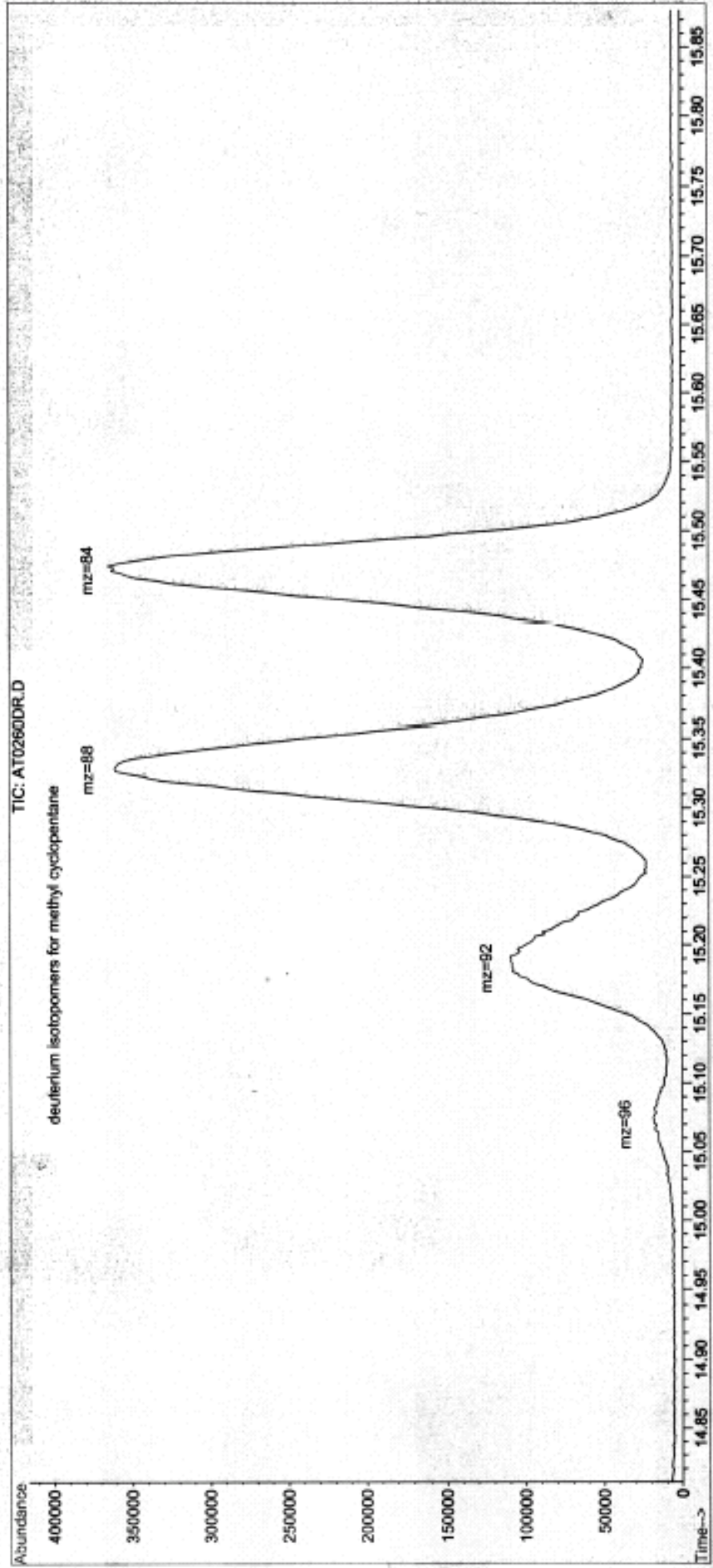


Figure 8. GC-FID chromatogram for 1-octene produced from a mixture of C_2H_4 and C_2D_4

