

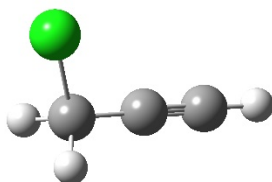
Imaging the Infrared Multiphoton Excitation and Dissociation of Propargyl Chloride

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Nureshan Dias and Arthur G. Suits

We found two dissociation pathways for propargyl chloride through which it is dissociated to linear C_3H_2 and HCl. Our calculations show a third reaction pathway with higher barrier energy in which cyclic C_3H_2 is produced. The geometry of structures at ground electronic state were optimized using DFT-WB97xD/cc-pvDz and also CBS-QB3. The structures of transition states were confirmed by Intrinsic Reaction coordinate (IRC) calculations. The optimized geometry of reactant, transition states and products with these two levels of theory as well as IRC pathway of the roaming transition state are given below:

Pathway 1:



reactant

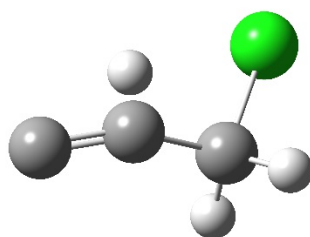
Z-matrix:

DFT-WB97xD/cc-pvDz

H	-1.10675600	0.69537000	0.00000100
H	2.30229500	3.06458200	-0.89525300
H	2.30244100	3.06453100	0.89483100
C	-0.15911100	1.19280200	-0.00006300
C	0.91105500	1.75360800	-0.00013500
C	2.19074300	2.44408100	-0.00022000
Cl	3.58198300	1.28361600	-0.00036600

CBS-QB3:

H	-3.26549500	-0.89171800	0.00024100
H	0.13799600	1.45170600	-0.88870800
H	0.13814100	1.45165500	0.88876800
C	-2.32341200	-0.40018300	0.00017800
C	-1.25506400	0.14685000	0.00010700
C	0.01710900	0.83366200	0.00002200
Cl	1.43279800	-0.32315400	-0.00012600



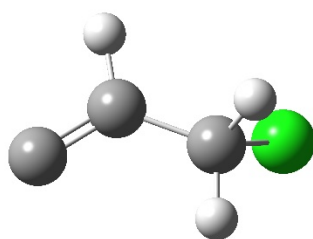
Transition state1

Z-matrix:

DFT-WB97xD/cc-pvDz

CBS-QB3:

H	-0.49341600	-0.35552000	-0.57299600	H	1.59833500	-0.50873800	1.09464500
H	1.32994300	1.50891500	-1.05681900	H	-0.09924200	1.49734100	0.80650900
H	1.42681300	1.81380800	0.70611000	H	0.04831000	1.33221500	-0.95893900
C	-1.16235100	0.25778300	0.78567300	C	2.43406700	-0.43654900	-0.21305300
C	-0.05785800	0.41954100	0.14549200	C	1.29942100	0.04041300	0.12709500
C	1.25985500	1.05621700	-0.06403500	C	0.04652700	0.79701000	-0.01250300
Cl	2.61060600	-0.13740000	0.05536900	Cl	-1.42514700	-0.27800400	-0.02067300



Product 1

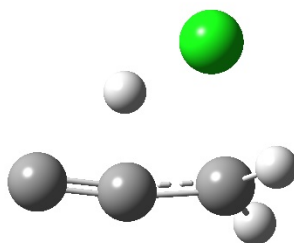
Z-matrix:

DFT-WB97xD/cc-pvDz

H	-1.47886600	0.89556200	0.01832900
H	0.90022800	1.70365100	0.70735900
H	0.49543800	1.36839100	2.41917200
C	-2.11657100	1.47172400	1.83716000
C	-1.14074500	1.13404300	1.03747300
C	0.31665200	1.07101600	1.38256000
Cl	0.95946400	-0.60666400	1.19376200

CBS-QB3:

H	1.35452200	-0.59775700	1.33066600
H	-0.04408600	1.50768300	0.76453500
H	0.23143900	1.20735500	-0.96770400
C	2.33843300	-0.33230200	-0.39873500
C	1.30174900	-0.10798100	0.35359400
C	0.11823600	0.74307900	0.00802900
Cl	-1.41719900	-0.23141500	-0.05322500



Transition state2

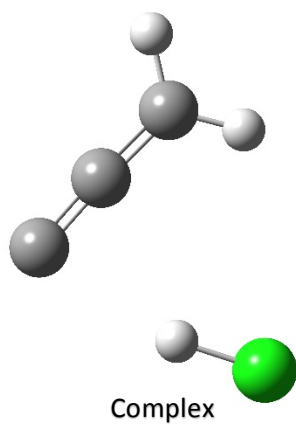
Z-matrix:

DFT-WB97xD/cc-pvDz

H	0.37675000	1.95772200	0.47580800
H	1.82832100	3.92831500	-0.47327700
H	1.78280200	3.97736400	1.38061700
C	-1.26715300	2.96945700	0.40378400
C	-0.08419500	3.42442200	0.42142500
C	1.29710600	3.67884900	0.44844200
Cl	1.81272700	1.52027300	0.52087000

CBS-QB3:

H	0.24622600	-0.72641700	0.45444700
H	0.03349400	1.60611300	0.66064200
H	1.28374600	1.89936200	-0.69242200
C	2.09524600	-1.02137300	-0.08217800
C	1.21217100	-0.08609200	0.11330700
C	0.79654300	1.22009600	0.00178900
Cl	-1.54042500	-0.20322600	-0.03648100



Z-matrix:

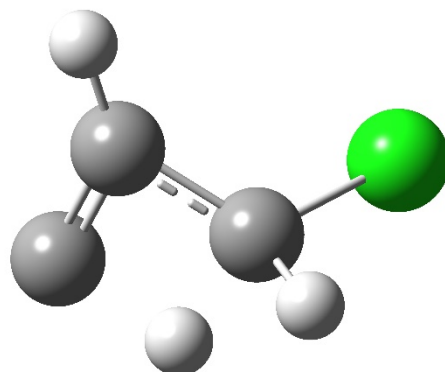
DFT-WB97xD/cc-pvDz

H	3.10388900	1.82355900	-0.14473200
H	1.82457000	3.15317800	0.18162300
C	0.27059000	0.19129000	0.18712800
C	1.12701700	1.15535600	0.12676500
C	2.06229300	2.09457700	0.05126700
H	2.17748600	-1.10667000	-0.23982900
Cl	3.39580400	-1.50792400	-0.48038500

CBS-QB3:

H	-0.91404800	1.52938600	-0.92541900
H	-0.91331600	1.52889300	0.92538400
C	-2.79045800	-1.03847400	0.00002100
C	-2.04769600	0.00844600	0.00002200
C	-1.25694700	1.07051000	-0.00000300
H	1.58630800	-1.26568700	-0.00055900
Cl	2.16539200	-0.11973400	0.00002100

Pathway 2:



Transition state 2

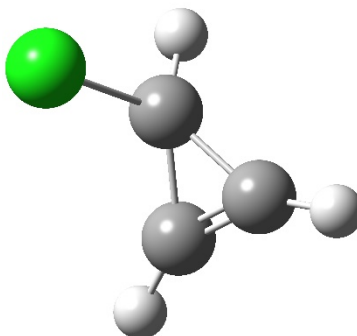
Z-matrix:

DFT-WB97xD/cc-pvDz

H	-4.27598500	0.84154600	-0.83078000
H	-2.24304300	2.70854200	0.38087300
H	-3.57298700	2.44849900	1.68777300
C	-4.61281700	1.97933700	1.09616200
C	-4.02201000	1.40736400	0.05294600
C	-2.83351300	1.86156100	0.73671200
Cl	-1.78946600	0.67933900	1.58049900

CBS-QB3:

H	-1.70010500	1.62735200	-0.22351700
H	-0.21015900	-0.14616900	1.65885400
H	-0.77771900	-1.23802300	0.24962400
C	-1.74437100	-0.61946400	-0.38130300
C	-1.38406400	0.61369000	-0.06448900
C	-0.28342600	-0.06785700	0.57846600
Cl	1.36230300	0.01168400	-0.14594100



Product 2

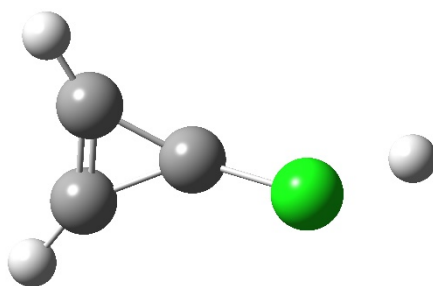
Z-matrix:

DFT-WB97xD/cc-pvDz

H	1.85869000	-1.59642600	-0.49060700
H	0.22925200	0.00000300	1.66331500
H	1.85874700	1.59639500	-0.49062300
C	1.43553500	0.65476700	-0.16066600
C	1.43554200	-0.65476500	-0.16066800
C	0.34002700	0.00000000	0.57768700
Cl	-1.36548900	0.00000100	-0.13060000

CBS-QB3:

H	1.85233900	-1.58675500	-0.48545400
H	0.23098700	0.00000700	1.65374500
H	1.85243000	1.58669400	-0.48551000
C	1.43266500	0.65027900	-0.16058300
C	1.43267500	-0.65028100	-0.16057700
C	0.34018400	0.00001100	0.57514700
Cl	-1.36287700	0.00000000	-0.12980600



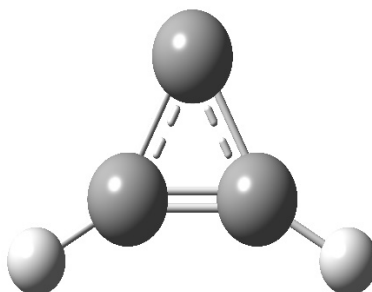
Transition state3

Z-matrix:

DFT-WB97xD/cc-pvDz

CBS-QB3:

H	-2.54715400	-0.86054800	0.33458300	H	2.08527400	-1.56847400	-0.17933600
H	1.92848700	-0.49885500	2.25159200	H	-2.34421800	0.00000000	1.24650000
H	-2.75611200	0.55901900	3.13212200	H	2.08527500	1.56847400	-0.17933500
C	-2.12702500	0.03604900	2.42112400	C	1.52945900	0.65811100	-0.02582400
C	-2.03908000	-0.56120500	1.24395900	C	1.52945900	-0.65811100	-0.02582400
C	-0.80518400	-0.45452500	2.02538300	C	0.28286800	0.00000000	0.36101400
Cl	0.45464400	-1.31978700	2.55834000	Cl	-1.28688500	0.00000000	-0.16141300



Cyclic C₃H₂

Z-matrix:

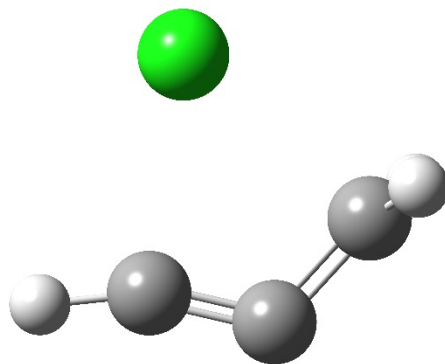
DFT-WB97xD/cc-pvDz

C	-0.66501000	-0.31962400	-0.00000100
C	0.66501000	-0.31962400	0.00000300
C	0.00000000	0.93885000	-0.00000400
H	-1.60452800	-0.86385300	-0.00000100
H	1.60452800	-0.86385300	0.00000800

CBS-QB3:

C	-0.66131300	-0.32400600	-0.00000100
C	0.66131300	-0.32400600	0.00000300
C	0.00000000	0.93579800	-0.00000400
H	-1.59649300	-0.86335700	-0.00000100
H	1.59649300	-0.86335700	0.00000800

Pathway 3:



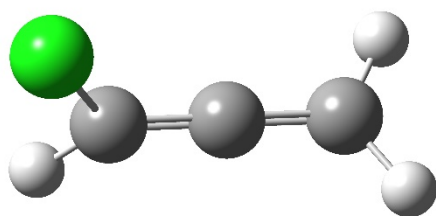
Transition state 1

Z-matrix:

DFT-WB97xD/cc-pvDz

CBS-QB3:

H	1.40735400	-0.02910800	-0.03186000	H	0.59972900	2.31456000	0.00000000
H	5.09517000	1.15161800	-0.99786100	H	1.02663200	-1.68737400	0.92923800
H	5.12151700	1.12259200	0.86542300	H	1.02663300	-1.68737400	-0.92923800
C	2.47811400	0.08424200	-0.04526400	C	0.87148000	1.28348500	0.00000000
C	3.70606300	-0.20038300	-0.06720500	C	1.43172000	0.18092400	0.00000000
C	4.63915800	0.81679200	-0.06457500	C	1.09649200	-1.13256500	0.00000000
Cl	2.81427700	2.41978600	-0.01380600	Cl	-1.35595000	-0.05475700	0.00000000



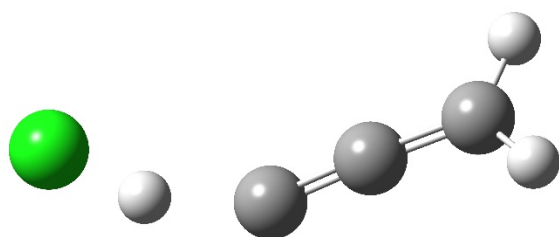
1-chloroallene

Z-matrix:

DFT-WB97xD/cc-pvDz

CBS-QB3:

H	-0.51881100	-0.98888200	-0.00099000	H	-0.25785000	1.78081200	0.00042000
H	3.33130500	-1.38711200	-0.99640200	H	2.85294000	-0.52831300	0.92747700
H	3.35726500	-1.41727400	0.87337800	H	2.85333100	-0.52733000	-0.92750600
C	0.35300400	-0.33839800	-0.00261000	C	-0.05647000	0.71864200	0.00000600
C	1.58534300	-0.76879400	-0.02683400	C	1.13303700	0.19814100	0.00000500
C	2.81545400	-1.21234800	-0.05110700	C	2.33243200	-0.30767800	-0.00000700
Cl	-0.03999600	1.37062900	0.03051000	Cl	-1.52367200	-0.25763500	-0.00002400



Transition state 2

Z-matrix:

DFT-WB97xD/cc-pvDz

H	-1.29895500	-3.04765600	-0.17010800
H	2.91524500	-1.51757300	-0.76720200
H	2.88257300	-1.85515700	1.07345100
C	0.14310100	-3.21138000	-0.17500300
C	1.22603300	-2.54833000	-0.03459100
C	2.40030100	-1.94403300	0.09701200
Cl	-2.44715400	-2.19938600	-0.03443000

CBS-QB3:

H	0.99611800	0.53172100	-0.00000200
H	-3.44069600	-0.59030200	-0.92835000
H	-3.44070400	-0.59027700	0.92835400
C	-0.58293300	0.76290800	-0.00000300
C	-1.71486400	0.18351700	-0.00000100
C	-2.92338500	-0.35778500	0.00000100
Cl	2.18896300	-0.16958700	0.00000100

IRC pathway (for Roaming transition state):

