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A Quantum-Chemical Approach to Understanding Reversible Addition Fragmentation Chain-Transfer Polymerization

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Accessory Materials

Tables S1–S2 (3 pages)

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Table S1. B3-LYP/6-31G(d) Optimised Geometries

CH_2=CHCOOCH$_3$


```
1\1\GINC-SC160\FOpt\RB3LYP\6-31G(d)\C4H6O2\MLC501\29-Jul-2003\0\\# B3L
 YP/6-31G* OPT=TIGHT FREQ MAXDISK=65536000\\MA monomer (EA conf)\\0,1\C
 ,-2.1851672447,-1.1974051869,0.\C,-0.8505755331,-1.195445029,0.\C,-0.0
 942225207,0.0824973952,0.\O,-0.5786799699,1.1964333627,0.\H,-2.7552323
 954,-2.1214903814,0.\H,-2.7357023382,-0.2608659481,0.\H,-0.2670857787,
 -2.1113552261,0.\O,1.2396703808,-0.1538078991,0.\C,2.0675325938,1.0186
 116574,0.\H,3.0947993306,0.6527922553,0.\H,1.8749470608,1.6251812858,-
 0.8891958892\H,1.8749470608,1.6251812858,0.8891958892\\Version=DEC-AXP
 -OSF/1-G98RevA.11.3\State=1-A'\HF=-306.467753\RMSD=9.326e-09\RMSF=5.35
 8e-06\Dipole=0.3096799,-0.5008947,0.\PG=CS [SG(C4H4O2),X(H2)]\\@
```


CH_3–C•HCOOCH$_3$


```
1\1\GINC-SC160\FOpt\UB3LYP\6-31G(d)\C4H7O2(2)\MLC501\30-Jul-2003\0\\#
 B3LYP/6-31G* OPT=TIGHT FREQ MAXDISK=39321600 GEOM=CHECK GUESS=READ\\MA
 _rad-csc-6dub3 (EA conf)\\0,2\C,2.4427069032,-0.6700725424,0.\C,0.9884
 454995,-0.9680099437,0.\C,0.0000531191,0.0925714969,0.\O,0.2492141423,
 1.2915528696,0.\O,-1.2690884584,-0.4038514401,0.\C,-2.3055213085,0.584
 7337423,0.\H,-3.2434106254,0.0277541879,0.\H,2.6133119038,0.4089560571
 ,0.\H,0.6334677625,-1.9941959598,0.\H,2.9379202621,-1.1090091687,0.878
 9917495\H,2.9379202621,-1.1090091687,-0.8789917495\H,-2.2371601584,1.2
 192780488,0.8886413064\H,-2.2371601584,1.2192780488,-0.8886413064\\Ver
 sion=DEC-AXP-OSF/1-G03RevB.03\State=2-A"\HF=-307.0484404\S2=0.756686\S
 2-1=0.\S2A=0.750029\RMSD=9.256e-09\RMSF=1.294e-06\Dipole=-0.0936169,-0
 .6405142,0.\PG=CS [SG(C4H3O2),X(H4)]\\@
```


TS: CH_3–C•HCOOCH$_3$ + CH_2=CHCOOCH$_3$


```
1\1\GINC-SC160\FTS\UB3LYP\6-31G(d)\C8H13O4(2)\MLC501\31-Jul-2003\0\\#
 B3LYP/6-31G* OPT=(TS,CALCFC,NOEIGENTEST) FREQ MAXDISK=134217728 INT(GR
 ID=ULTRAFINE)\\MA_propTS-b-6dub3 (EA conf)\\0,2\C,-0.9813750009,-1.232
 2262491,-1.300964857\C,0.3844757328,-1.2431407547,-1.3043386414\C,1.14
 41812253,0.0168170693,-1.2979516715\O,0.6606998123,1.1361880372,-1.343
 8668141\O,2.4767079905,-0.2175750981,-1.2448861554\C,3.3017959903,0.95
 48057044,-1.2019085821\H,4.3290120035,0.5897339653,-1.1731889693\H,-1.
 5045236156,-0.2994496587,-1.4859710568\H,-1.5353170939,-2.1537777172,-
 1.4489092512\H,0.9521042659,-2.1664800549,-1.2480698643\H,3.1385795745
 ,1.5750838608,-2.087701944\H,3.0792574506,1.5452611773,-0.3088165668\C
 ,-1.7037619869,-1.2020409431,0.8810149717\H,-2.7463670801,-1.177926695
 ,0.5752210304\C,-1.1622866968,-2.4526496564,1.493753803\C,-1.113095440
 6,0.0848934472,1.2668581834\O,-0.0394959007,0.2124468348,1.8333605005\
 O,-1.892016993,1.1249366201,0.8817831925\C,-1.3197132202,2.4269193598,
 1.0899203021\H,-2.0803767761,3.1345163063,0.7573504133\H,-0.0767473249
 ,-2.3892365229,1.6034215722\H,-1.4213233694,-3.3388306391,0.9044355926
 \H,-1.5838441167,-2.5984920349,2.5005005544\H,-0.4098159218,2.53017541
 7,0.4947105718\H,-1.0891208861,2.5811835799,2.1475910811\\Version=DEC-
 AXP-OSF/1-G03RevB.03\State=2-A\HF=-613.5105425\S2=0.777872\S2-1=0.\S2A
 =0.75023\RMSD=5.735e-09\RMSF=7.363e-07\Dipole=-0.2501824,-0.4985734,-0
 .240662\PG=C01 [X(C8H13O4)]\\@
```

Table S2. Total Energies,[a] Thermal Corrections,[b] and Entropies[c]

Species	E_0 hartrees	$\Delta\Delta H_{298}$ kJ mol^{-1}	S_{298} J mol^{-1} K^{-1}
CH_2=CHCOOCH$_3$	-306.02164	19.9	333.9
CH_3C•HCOOCH$_3$	-306.58567	21.8	354.9
TS: CH_2=CHCOOCH$_3$ + CH_3C•HCOOCH$_3$	-612.60547	40.1	510.5

[a]Total energy (E_0, 0 K) calculated at the G3(MP2)-RAD level of theory and includes scaled B3-LYP/6-31G(d) zero-point energy correction. [b]Thermal correction to the enthalpy at 298 K ($\Delta\Delta H_{298}$) calculated using B3-LYP/6-31G(d) geometries and frequencies, using standard formulae for the statistical thermodynamics of an ideal gas in conjunction with the harmonic oscillator approximation. [b]Entropy at 298 K (S_{298}) calculated using B3-LYP/6-31G(d) geometries and frequencies, using standard formulae for the statistical thermodynamics of an ideal gas in conjunction with the harmonic oscillator approximation.