Supporting Information

Bromine kinetic isotope effect: insight into Grignard reagent formation

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1. Procedure for Grignard reagent formation

The desired amount of magnesium powder and 20 ml of anhydrous diethyl ether were added to the dry 100-ml round bottomed flask through the septum port under constant slow flow of N_2 gas. 30 mg of iodine crystals were previously added to the flask to activate the magnesium powder. The mixture was stirred at approximately 500 rpm and heated to reflux. The desired alkyl bromide/aryl bromides (10 mmol) was added through the septum using a 5ml disposable syringe. After the required period of time (30-60min), the N_2 flow was stopped and 5 ml of H_2O were carefully added to the reaction mixture. The mixture was acidified by adding 0.5 ml of HCl solution of pH 1.18 (prepared from 0.1 of 33 N hydrochloric acid and 49.9 ml of H_2O). The organic phase and aqueous phases were separated. The aqueous phase was extracted three times with 10 ml diethyl ether and extracts were combined with the organic phase. The volume of the combined organic phase was reduced to 1 ml by solvent evaporation. The remained organic solution was dried with anhydrous magnesium sulfate and analyzed by GC-MS. The desired reaction conversions

were achieved using magnesium as a limiting agent. For every substrate reaction with conversion of 60, 70, 80 and 90% was performed twice.

2. Bromine isotope ratio analysis

Bromine isotope analysis of the brominated organic compounds was based on the previously described GC-MC-ICPMS method. Briefly, the analyte solution in acetone was injected into a GC (HP 6890) interfaced to the MC/ICPMS (NU Instrument). Strontium external spike solution (SRM 987—National Institute of Standards and Technology), was continuously injected into the system by an Aridus desolvation nebulizer. Fine-tuning of the MC/ICPMS instrument was performed according to the maximum signal of Sr. Signals of ^{86}Sr, ^{84}Sr, ^{81}Br, ^{79}Br and ^{83}Kr were simultaneously collected by Faraday cups. Operating parameters for the GC-MC/ICPMS system are listed in Table S1. SRM 987 strontium reference material solution at a concentration of 1 mg l^{-1} was used as an external spike. The continuous signal obtained for ^{86}Sr was about 3 V. All samples were analyzed at least three times.

Table S1. Instrumental parameters for the GC-MC/ICPMS measurement.

GC parameters	
Injector conditions	300 °C, splitless injection
Column	HP-5 25 m (0.25 mm, 0.25 µm)
Oven temperature	60 °C, 10 °C min^{-1} to 250 °C
He carrier flow	3 ml min^{-1}
Transfer line temperature	240 °C
MC/ICPMS parameters	
RF power	1200 W
Coolant flow	12 l min^{-1}
Auxiliary flow	1.25 l min^{-1}
Nebulizer gas flow	0.69 l min^{-1}
Interface cones	Nickel
Instrument resolution	300 m/Δm
Nebulizer	PFA 50 µl min^{-1}
Spray chamber temp.	75 °C
Desolvator temp.	160 °C
Sweep gas (argon)	3.45 l min^{-1}
Integration time	0.5 s

3. KIE calculation

Bromine KIE values were calculated from the measured isotopic enrichment of the substrate during the reaction process using the equation (1):

$$KIE = k_{79}/k_{81} = 1/\alpha \quad (1)$$

Where α - isotope fractionation factor

In this work, we derive values of α from the experimental results by using the exponential function

$$Ln\ R/R_0 = (\alpha\text{-}1)\ Ln\ F \qquad (2)$$

where R and R_0 are the isotope ratios ($^{81}Br/^{79}Br$) of the residual and the initial, unreacted organobromide, respectively, and F is the fraction of organobromide remaining. Values of isotope fractionation factor α were calculated from the linear least-squared best fit to the eq. (2) (Fig. S1), refraining from forcing regressions through the origin as was suggested by Scott et al.[1]

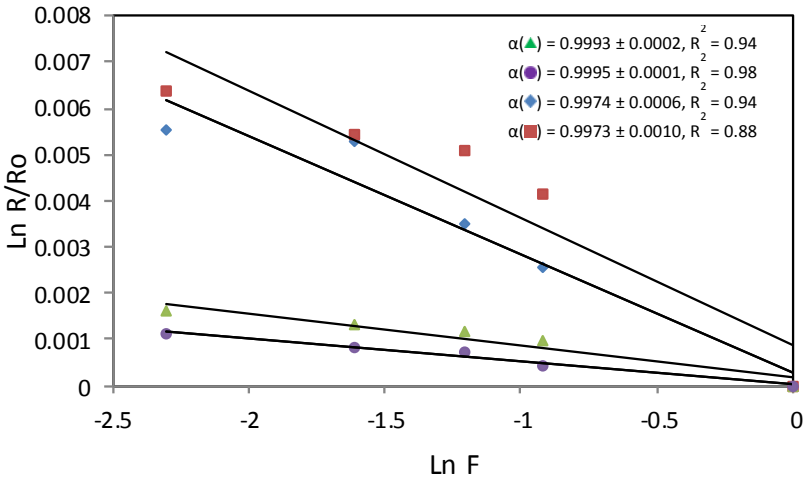

Fig. S1. Ln R/R_0 vs Ln F diagram showing change in bromine isotope ratios in 1-bromodecane (triangles); 1-bromohexane (circles); 1-bromonaphthalene (rhombs) and bromobenzene (squares) as a function of fraction remaining (F). For all the studied compounds initial point (0,0) was used.

4. Computational methods

All molecular geometries have been fully optimized using Gaussian09 package[1] at the M06-2X/6-31+G(d,p) level of theory[2] with the SMD[3] representation of solvent (diethyl ether). The natures of all stationary points have been confirmed by vibrational analysis and all transition state structures additionally by IRC calculations[4]. Bromine and carbon kinetic isotope effects (Br- and C-KIEs) have been calculated using the complete Bigeleisen equation[5] at 300 K as implemented in the ISOEFF program.[6]

a) radical pathway

In order to explore single electron transfer mechanism within outer-sphere pathway we used neutral and 1e reduced forms of PhBr and EtBr. The optimized neutral and radical anion species of PhBr where C-Br bond remained intact upon one electron reduction were used to estimate possible bromine fractionation using slightly modified method by Kavner et al. [7] Driving forces were computed for redox potentials of -2.5.[8] We spanned the typical range of reorganizational energies of 25-100 kcal/mol and did not observe any difference in predicted Br-KIE which for

this entire range was equal to unity. The radical anion species of PhBr was used as a starting structure for pulling off halide ion from the organic molecule. For EtBr species since in the radical anion species C-Br bond was already broken we decided to employ the approach presented by Costentin et al.[9] We modeled a Morse curve (Fig. S2) and based on the estimated bond dissociation energy (D), we subsequently calculated so called intrinsic barrier, $\Delta G_0^{\neq} = \frac{D+\lambda_0}{4}$, where λ_0 is the solvent reorganization free energy. Having calculated $\Delta G_0^{\neq}$ we could estimate free energy of activation according to the equation:

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta G^0}{4\Delta G_0^{\ddagger}}\right) \quad (3)$$

where ΔG^0 is a driving force and a experimentally determined redox potential for EtBr of -2.16 V. [10] In the case of solvent reorganization energy we explored the most typical value range from 25 to 100 kcal/mol with a step of 5 kcal/mol and the predicted Br-KIE did not differ more than 0.3‰ and did not exhibit any meaningful deviation from unity therefore led to the conclusion that DET in the case of alkyl halide is not accompanied by bromine fractionation.

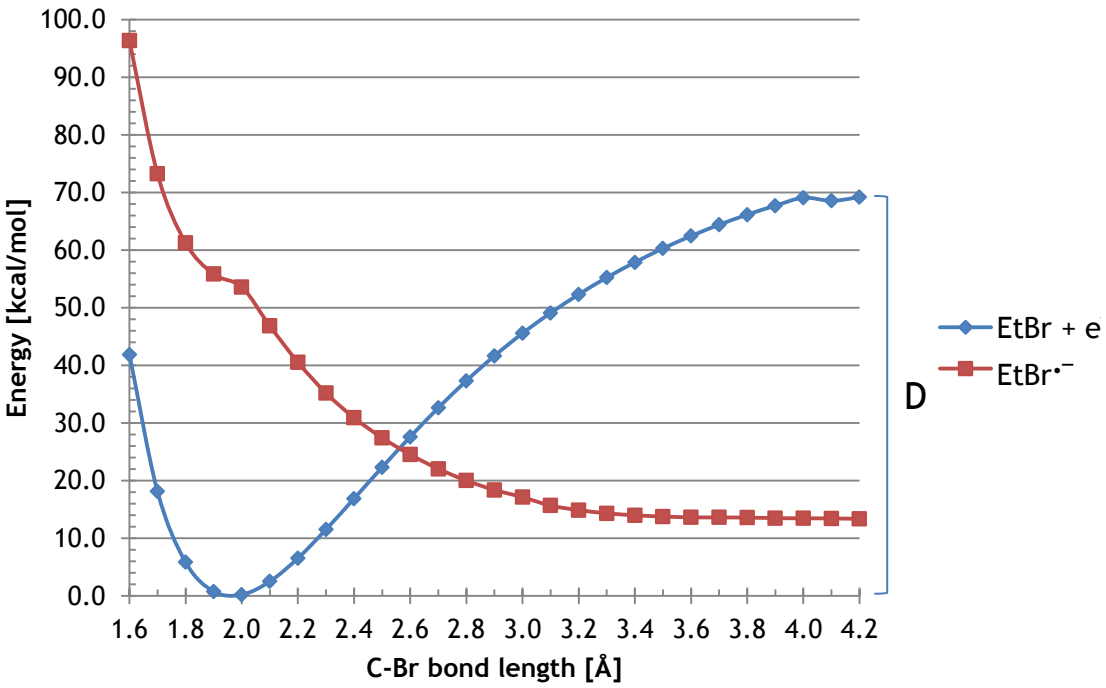

Fig. S2. Morse curve for C-Br bond breaking during DET in EtBr; D – bond dissociation energy.

b) non-radical pathway

Initial geometries of all considered models were fully optimized at the SMD/M06-2X/6-31+G(d,p) level of theory using default convergence and optimization criteria along with an

ultrafine grid for the integration (Fig. S3). They were subsequently used for locating respective transition states by decreasing the distance between magnesium atom and carbon atom substituted with bromine atom. The natures of all stationary points were confirmed by performing vibrational analysis (3N-6 real vibrations in the case of reactants and one imaginary frequency corresponding to the desired reaction coordinate in the case of transition state structure). The optimized products complexes are shown in Fig. S4.

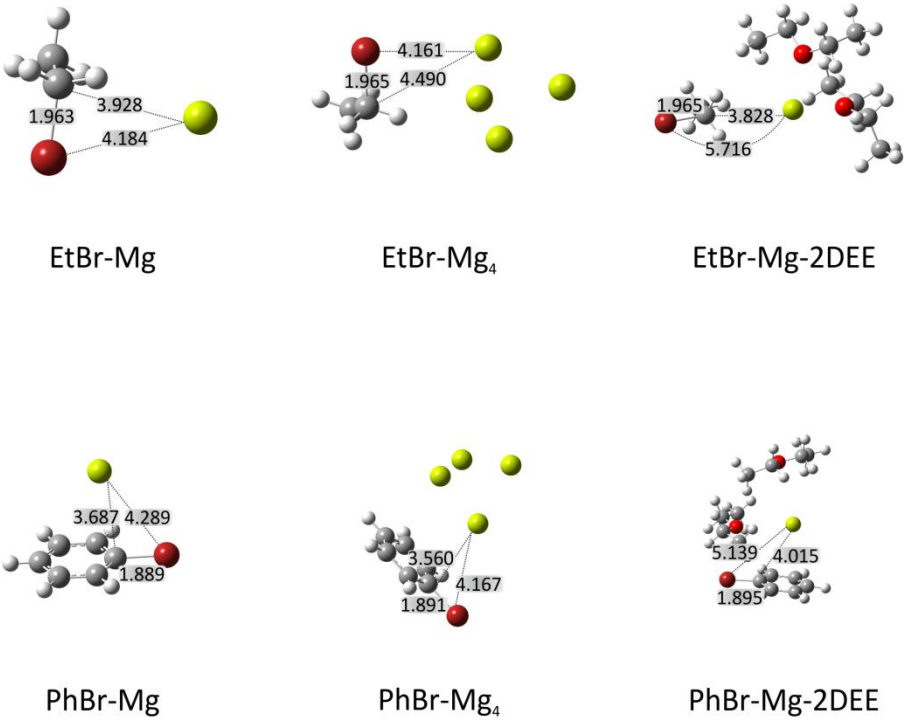

Fig. S3. Reacting complexes with the key distances obtained for different models of the non-radical pathway.

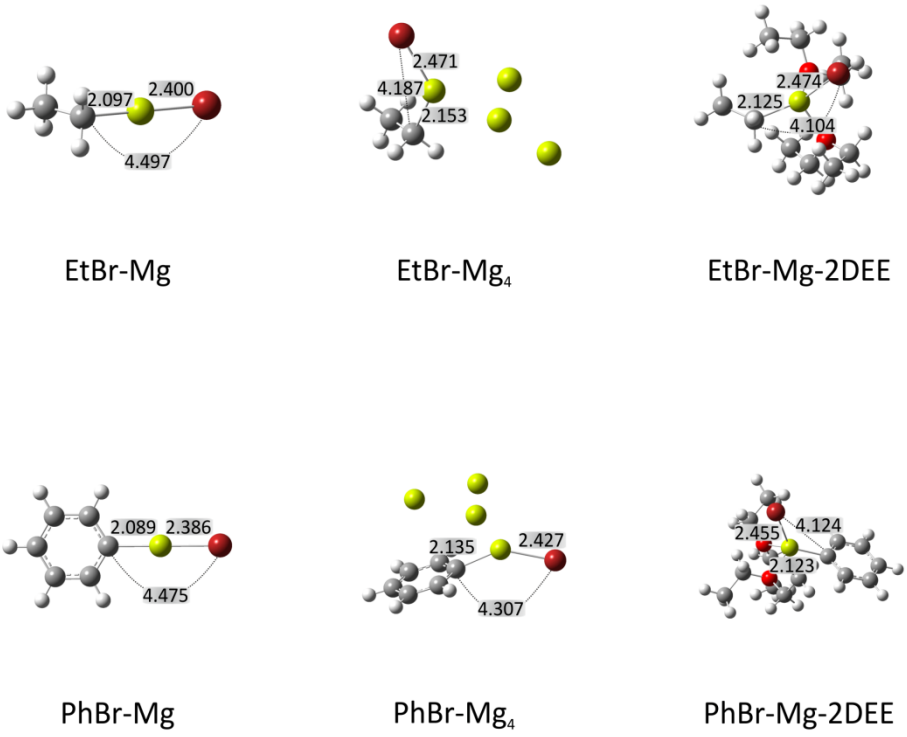

Fig. S4. Products complexes with the key distances obtained for different models of the non-radical pathway.

5. Optimized coordinates

6. Optimized coordinates

a) radical pathway

EtBr

Neutral

Electronic energy (E) = -2650.9833343 au

Gibbs Free Energy (G) = -2650.944207 au

C	1.02114500	0.68591600	0.00000000
H	1.07164600	1.31243400	-0.88957500
H	1.07164600	1.31243300	0.88957600
C	2.07303800	-0.40012600	0.00000000
H	3.06256900	0.06992300	-0.00000600
H	1.99302800	-1.03186600	0.88794000
H	1.99302000	-1.03187400	-0.88793400
Br	-0.79305700	-0.06702300	0.00000000

Radical anion

Electronic energy (E) = -2651.052866 au

Gibbs Free Energy (G) = -2651.024593 au

C	-2.44152200	0.80016800	-0.00613000

H	-1.47573800	1.29111700	0.02472100
H	-3.34616800	1.39998400	0.00604700
C	-2.50393900	-0.68567800	-0.00045800
H	-3.10220100	-1.07975100	-0.83482800
H	-1.48974600	-1.08858600	-0.06854700
H	-2.96860100	-1.07730500	0.91792400
Br	1.20157800	-0.00378300	-0.00016500

PhBr

Neutral

Electronic energy (E) = -2803.3652141 au

Gibbs Free Energy (G) = -2803.304264 au

C	2.16752800	-1.20474800	0.00021500
C	0.77351900	-1.21378200	0.00009000
H	3.95401000	0.00000000	0.00035700
C	2.86869400	0.00000000	0.00025700
C	0.09357000	0.00000000	0.00000700
C	0.77351900	1.21378200	0.00004100
C	2.16752800	1.20474800	0.00017100
H	0.22724600	2.15088800	-0.00002600
H	2.70324200	2.14907500	0.00020300
H	0.22724600	-2.15088800	0.00006100
H	2.70324200	-2.14907500	0.00028400
Br	-1.79660400	0.00000000	-0.00015900

Radical anion

Electronic energy (E) = -2803.3869005 au

Gibbs Free Energy (G) = -2803.335936 au

C	-2.20407100	-1.20807200	-0.04203200
C	-0.76249700	-1.24460200	0.07259400
H	-3.97181700	-0.01533200	-0.09600400
C	-2.88388500	-0.00801900	-0.03288400
C	-0.11204700	0.00885900	0.02538500
C	-0.75759700	1.21839300	-0.00902600
C	-2.20124200	1.23493900	0.05547300
H	-0.19096600	2.14159300	-0.08559600
H	-2.73820200	2.17746600	0.06770600
H	-0.20806900	-2.17048600	0.15930400
H	-2.75454400	-2.14305100	-0.12582000
Br	1.81118900	0.00002400	-0.00961900

TS of dehalogenation

product of C-Br cleavage

b) non-radical pathway

EtBr

- Mg model

Reacting complex

Electronic energy (E) = -2851.0312139 au

Gibbs Free Energy (G) = -2850.997207 au

Mg	3.19610000	-0.42595200	-0.01175100
Br	-0.98128500	-0.65356200	-0.06515900
C	-0.37383300	1.05268000	0.69164700
H	-1.15525900	1.35248200	1.38902900
H	0.53919700	0.82296600	1.24345500
C	-0.14834300	2.07698100	-0.39565400
H	0.61847500	1.74215000	-1.10016200
H	-1.06855500	2.27802500	-0.94955200
H	0.19097600	3.01250100	0.06285000

Transition state

Electronic energy (E) = -2850.9731666 au

Gibbs Free Energy (G) = -2850.940557 au

Mg	0.01456300	2.02134700	-0.03114600
Br	0.95595700	-0.47172000	-0.04490300
C	-1.47677100	-0.36582400	0.72982400
H	-1.18202300	-1.28347700	1.22472100
H	-1.65651000	0.45500500	1.41742300
C	-2.35581700	-0.50488800	-0.46471400
H	-2.71744100	0.45885200	-0.82796600
H	-1.86275600	-1.02649400	-1.28782300
H	-3.21898300	-1.12558700	-0.17167000

Product complex

Electronic energy (E) = -2851.1072407 au

Gibbs Free Energy (G) = -2851.073675 au

Mg	-0.60418100	-0.29008900	-0.00056600
Br	1.76679000	0.08090400	0.00009400
C	-2.67549900	-0.61452400	0.00038400
H	-2.91387000	-1.23523000	-0.87390600
H	-2.91403700	-1.23472000	0.87508500

C	-3.55588800	0.64360300	0.00001800
H	-3.37153900	1.27034700	0.87988800
H	-3.37125100	1.27012900	-0.87992100
H	-4.62846000	0.40444100	-0.00007400

- Mg4 model

Reacting complex

Electronic energy (E) = -3451.1920254 au

Gibbs Free Energy (G) = -3451.165410 au

Mg	-2.58868600	1.24389500	-1.35436200
Mg	-1.26321600	-1.39041300	-0.33780800
Mg	-4.30522600	-0.98506800	-0.02908800
Mg	-2.35883900	0.66808900	1.69119200
Br	2.79227500	-0.59215700	-0.07512900
C	1.85472500	0.94790600	0.70637800
H	0.94189200	0.54169600	1.14656100
H	2.51109700	1.31614500	1.49412300
C	1.56940600	1.99246000	-0.34639100
H	1.03108200	2.82597400	0.11968400
H	2.49270800	2.37713500	-0.78701400
H	0.94042000	1.58430600	-1.14297700

Transition state

Electronic energy (E) = -3451.1511968 au

Gibbs Free Energy (G) = -3451.127294 au

Mg	-0.16421100	1.76518900	-0.67994200
Mg	-2.90266200	0.35866800	-1.41655000
Mg	-2.20928000	1.18265200	1.67869800
Mg	-1.65114800	-1.69325200	0.57233700
Br	0.86580200	-0.93784900	-0.10570500
C	2.83532800	0.49371000	-0.59141800
H	3.37593400	-0.37222200	-0.96261700
H	2.62219400	1.22055700	-1.37179700
C	3.27121900	1.02561800	0.74029600
H	2.64188000	1.85641100	1.07296600
H	3.23427700	0.25403000	1.51522500
H	4.31099200	1.39087700	0.69812000

Product complex

Electronic energy (E) = -3451.2662786 au

Gibbs Free Energy (G) = -3451.242183 au

Mg	1.73135700	-0.27375500	1.95496900

Mg	-0.33569400	0.17202300	-0.35900000
Mg	1.74646700	-1.91891700	-1.09716700
Mg	4.25775000	-0.20134500	-0.12101100
Br	-2.62735900	-0.55941000	0.09619800
C	0.44178700	2.06661900	-0.93682400
H	1.54313600	2.07089800	-0.93575200
H	0.14612300	2.27943900	-1.97489000
C	-0.08210700	3.17922100	-0.01517200
H	0.26484800	4.18611400	-0.29292800
H	-1.17877700	3.21380000	-0.01185700
H	0.22560300	3.01801000	1.02700400

- Mg-2DEE

Reacting complex

Electronic energy (E) = -3318.1624066 au

Gibbs Free Energy (G) = -3317.873957 au

Mg	-0.63150000	-0.83322400	-0.16350800
Br	5.06949700	-0.46795400	-0.35784600
O	-1.45043400	1.41409300	-0.58853600
C	-1.12604100	2.68490500	-0.03469600
H	-0.89908700	3.38237100	-0.85360300
H	-1.98786800	3.08255300	0.51857200
C	-2.38510900	1.45966600	-1.66307400
H	-2.38938000	0.44820600	-2.08552600
H	-2.00373300	2.13986000	-2.43785300
C	0.06729200	2.53418300	0.88556400
H	0.93280000	2.14723100	0.33940200
H	0.32906200	3.50820800	1.31009900
H	-0.15769900	1.84968400	1.71017200
C	-3.78479900	1.86068500	-1.23178500
H	-4.46915100	1.76327000	-2.08053600
H	-4.13693000	1.20997800	-0.42594300
H	-3.82739800	2.89890400	-0.88969600
O	-2.96880400	-1.05648800	0.16651600
C	-3.65538500	-1.80837500	-0.83296500
H	-4.53970500	-1.23930700	-1.15653600
H	-2.95771000	-1.86481100	-1.67623700
C	-3.73144500	-0.80278600	1.34478400
H	-4.72929500	-0.44362200	1.05052700
C	-4.03701700	-3.20900200	-0.38618900

H	-4.80506700	-3.20146100	0.39199000
H	-4.43427000	-3.76362100	-1.24178900
H	-3.15688200	-3.73970300	-0.00976400
H	-3.86096300	-1.73378900	1.91006900
C	-3.01248800	0.23083300	2.18759500
H	-2.86045700	1.15506500	1.62280700
H	-3.60721200	0.45491800	3.07827500
H	-2.03760600	-0.14415800	2.51522700
C	3.16110500	-0.39034400	0.10251600
H	2.70598100	0.25976900	-0.64392500
H	2.78302200	-1.40231000	-0.03341100
C	2.97876500	0.11391300	1.51690400
H	3.48769900	-0.53502200	2.23436000
H	3.36366100	1.13088600	1.63149300
H	1.90845100	0.11108100	1.75276200

Transition state

Electronic energy (E) = -3318.1450092 au

Gibbs Free Energy (G) = -3317.853910 au

Mg	0.42175900	0.22398400	-0.66323200
Br	-4.69846300	0.28800400	-0.28640100
O	1.81590800	-1.51527400	-0.64270200
C	1.67242700	-2.83255800	-0.10259400
H	1.68565700	-3.55186700	-0.93175300
H	2.52474400	-3.04875500	0.55328300
C	2.98391600	-1.33439200	-1.45132400
H	2.81622100	-0.40372300	-2.00609100
H	3.03219600	-2.14968000	-2.18476100
C	0.37497800	-2.92267600	0.67189500
H	-0.48689800	-2.72460100	0.02779800
H	0.27120600	-3.92963400	1.08690700
H	0.36546700	-2.21224800	1.50458900
C	4.26087800	-1.24561600	-0.63640500
H	5.09976700	-1.01589400	-1.30076000
H	4.18381400	-0.45095900	0.11161600
H	4.49002200	-2.18601700	-0.12752600
O	2.21870200	1.27048600	0.13330000
C	2.86910900	2.20959800	-0.73126300
H	3.94715900	1.99630300	-0.72528700
H	2.48153100	1.99105900	-1.73270400
C	2.62637800	1.33855500	1.50345000

H	3.72484700	1.35809300	1.53839600
C	2.58639200	3.65629300	-0.37168900
H	3.04310600	3.94464800	0.57855700
H	2.99953700	4.30445200	-1.15039300
H	1.50730900	3.83078600	-0.31525300
H	2.25139400	2.26601100	1.95071200
C	2.08001700	0.13524400	2.24322300
H	2.45538900	-0.79619300	1.81012700
H	2.38350900	0.18332300	3.29291000
H	0.98422300	0.12470800	2.21265100
C	-2.39658500	0.13326500	-0.10315600
H	-2.29171600	-0.54406400	-0.93754400
H	-2.23065300	1.17721100	-0.31917800
C	-2.27856600	-0.37826300	1.31953100
H	-2.74376400	0.33529000	2.00528100
H	-2.80994400	-1.32937600	1.41590100
H	-1.24956900	-0.53520100	1.65056200

Product complex

Electronic energy (E) = -3318.3089124 au

Gibbs Free Energy (G) = -3318.013946 au

Mg	0.18578000	0.00592800	0.58024700
Br	-0.23109800	2.35362000	-0.07876800
O	-1.52517100	-0.69582500	-0.39323300
C	-2.76985000	-0.21580400	0.15417600
H	-2.97179600	0.77255500	-0.27723900
H	-3.56477500	-0.90743600	-0.14037800
C	-1.48708700	-0.61428900	-1.83359500
H	-0.45256800	-0.82509700	-2.10896000
H	-1.71274900	0.42016700	-2.12092300
C	-2.66686100	-0.14291100	1.66050900
H	-1.93321300	0.60430800	1.98378800
H	-3.63620900	0.15779200	2.06832600
H	-2.40190100	-1.11651700	2.08250700
C	-2.43166700	-1.59856900	-2.49641100
H	-2.24278300	-1.59684500	-3.57409100
H	-2.26362700	-2.61255900	-2.12005400
H	-3.48195200	-1.33754800	-2.34471300
O	1.52993000	-0.61904300	-0.88492100
C	2.45214500	0.37472700	-1.37997500
H	2.99360500	-0.06662700	-2.22463200

H	1.82795300	1.19011600	-1.74989200
C	2.10943500	-1.92790800	-0.73131600
H	2.62815100	-2.17134800	-1.66588900
C	3.39968900	0.85842800	-0.29909200
H	4.04929200	0.05735400	0.06444900
H	4.03456700	1.65167000	-0.70531000
H	2.84391000	1.27465900	0.54828700
H	2.84219400	-1.90990900	0.08308400
C	1.00930900	-2.92804300	-0.44894000
H	0.26629000	-2.93332600	-1.25179400
H	1.44477700	-3.92859200	-0.37651300
H	0.50740200	-2.71716000	0.50134000
C	0.96243900	-0.65371800	2.44540700
H	1.33168200	0.24926400	2.96014200
H	1.87689100	-1.22567700	2.20663000
C	0.12044100	-1.46783900	3.43970200
H	0.67461400	-1.78691700	4.33568400
H	-0.74242300	-0.89345000	3.79884100
H	-0.28430300	-2.38219600	2.98367400

PhBr

- Mg model

Reacting complex

Electronic energy (E) = -3003.4130418 au

Gibbs Free Energy (G) = -3003.357505 au

C	-2.02127900	-0.78031900	1.20533400
C	-0.63872600	-0.59987600	1.21326800
H	-3.79336400	-1.00155500	0.00003600
C	-2.71678100	-0.86449700	0.00003300
C	0.03497700	-0.50590600	0.00002400
C	-0.63869500	-0.60017000	-1.21321400
C	-2.02124900	-0.78060800	-1.20527000
H	-0.09699900	-0.52829100	-2.15032700
H	-2.55239000	-0.85076100	-2.14955900
Mg	-0.79910400	3.08592600	-0.00014800
Br	1.90548600	-0.24240700	0.00001600
H	-0.09705500	-0.52776400	2.15037800
H	-2.55244400	-0.85024300	2.14962600

Transition state

Electronic energy (E) = -3003.3626292 au

Gibbs Free Energy (G) = -3003.306892 au

C	-2.40580600	-0.14477500	1.20503400
C	-1.02892600	0.05868300	1.21647700
H	-4.18065200	-0.39901800	0.00000400
C	-3.10793000	-0.23623700	0.00000200
C	-0.35112000	0.23873200	-0.00000400
C	-1.02891400	0.05857000	-1.21647600
C	-2.40579200	-0.14489200	-1.20503000
H	-0.49783700	0.13190000	-2.15969400
H	-2.93159100	-0.23804800	-2.15143200
Mg	1.17128400	2.11730900	-0.00007600
Br	1.68443100	-0.67935100	0.00002500
H	-0.49786200	0.13210100	2.15969600
H	-2.93161500	-0.23783700	2.15143800

Product complex

Electronic energy (E) = -3003.4946425 au

Gibbs Free Energy (G) = -3003.437440 au

C	-3.50877300	1.20355900	-0.00026900
C	-2.11142100	1.19522000	0.00058800
H	-5.29964900	0.00020500	-0.00170700
C	-4.21317200	0.00011900	-0.00090800
C	-1.36580500	-0.00011800	0.00064700
C	-2.11161600	-1.19532700	0.00058700
C	-3.50896700	-1.20343500	-0.00026900
H	-1.60187400	-2.15782700	0.00117800
H	-4.04711500	-2.14798600	-0.00050400
Mg	0.72346000	-0.00005800	0.00061200
Br	3.10954100	0.00001000	-0.00026400
H	-1.60152600	2.15763900	0.00117800
H	-4.04676900	2.14819700	-0.00050500

- Mg4 model

Reacting complex

Electronic energy (E) = -3603.5730307 au

Gibbs Free Energy (G) = -3603.524061 au

C	-0.83405100	2.13669100	1.22200400
C	-1.52608800	0.92634100	1.22212800
H	0.01553500	3.71444300	0.02640400
C	-0.53302500	2.77793800	0.02122900
C	-1.90710600	0.36799100	0.00665100

C	-1.63587100	1.00366000	-1.20056000
C	-0.94200500	2.21293900	-1.18603400
H	-1.94737200	0.55777500	-2.13929400
H	-0.71565200	2.70683600	-2.12598700
Mg	1.32894400	-1.10818600	-0.14086800
Br	-2.83172300	-1.28159100	-0.00240800
H	-1.75092800	0.41927000	2.15453400
H	-0.52235500	2.57019100	2.16729200
Mg	3.28669900	0.48901300	1.63320000
Mg	3.44006400	0.74483700	-1.45146400
Mg	4.30262300	-1.93118100	-0.08346700

Transition state

Electronic energy (E) = -3603.5312522 au

Gibbs Free Energy (G) = -3603.483243 au

C	-2.07586500	2.04371200	1.20522600
C	-1.52117400	0.76859600	1.19982200
H	-2.81017300	3.69667800	0.02054900
C	-2.37878300	2.70126800	0.00848500
C	-1.19122300	0.16162300	-0.02604200
C	-1.59817000	0.76441000	-1.23113900
C	-2.15117700	2.03988600	-1.20350800
H	-1.41605200	0.27079300	-2.18041500
H	-2.40521100	2.52399300	-2.14287800
Mg	1.06999600	-0.68145200	-0.06847400
Br	-1.47653000	-2.01571800	0.00874400
H	-1.28428500	0.27442400	2.13666000
H	-2.27558900	2.52667800	2.15816000
Mg	2.88533900	0.87703900	1.80130400
Mg	2.61307800	1.71630700	-1.23194000
Mg	4.04560300	-1.04684500	-0.50215600

Product complex

Electronic energy (E) = -3603.6587942 au

Gibbs Free Energy (G) = -3603.609946 au

C	-3.02610600	-1.60048700	1.20081400
C	-1.69328400	-1.17617200	1.20987000
H	-4.71264900	-2.15142200	-0.02872100
C	-3.67533800	-1.82878200	-0.01220100
C	-0.94690500	-0.96979500	0.03054800
C	-1.64241400	-1.21675600	-1.17154500
C	-2.97606700	-1.63808500	-1.20462100

H	-1.13630800	-1.07114900	-2.12682700
H	-3.46974400	-1.81291000	-2.15747200
Mg	0.99607600	-0.08555600	0.05427200
Br	3.34978100	-0.67474000	-0.00110800
H	-1.22813300	-1.00180700	2.18113800
H	-3.55827100	-1.74827500	2.13750500
Mg	-0.01779400	2.33274800	1.71368900
Mg	-2.66529200	2.32973400	-0.07890400
Mg	0.07229700	2.25490000	-1.71272500

- Mg-2DEE

Reacting complex

Electronic energy (E) = -3470.5530191 au

Gibbs Free Energy (G) = -3470.244658 au

C	2.25604700	2.96094400	-0.67055100
C	2.42733900	1.62623800	-1.03691200
H	2.22929500	4.38533900	0.94502300
C	2.36205800	3.34503600	0.66553200
C	2.69455800	0.68471900	-0.04828200
C	2.81135500	1.05037200	1.28895900
C	2.63681700	2.38821100	1.64163500
H	3.04384200	0.30728400	2.04447500
H	2.72248100	2.67831100	2.68435300
Mg	-1.12986300	1.56951300	0.79579100
Br	3.04452200	-1.10834200	-0.55018800
H	2.36236300	1.32763200	-2.07797900
H	2.04381800	3.69932700	-1.43759600
O	-4.41248900	0.13694300	-0.22346300
C	-4.39623600	-0.61153300	0.97577600
H	-3.96130600	-0.00097700	1.78486100
H	-5.42614000	-0.86975700	1.27044300
C	-5.04047300	1.39438200	-0.07430300
H	-4.55269700	1.95548200	0.74001700
H	-6.09770400	1.25562100	0.20360300
C	-3.56214800	-1.85591300	0.75408500
H	-3.51608100	-2.44913400	1.67314200
H	-3.99663500	-2.47599400	-0.03629500
H	-2.54415200	-1.57411000	0.46360600
C	-4.92170400	2.15014900	-1.38053500
H	-5.40017400	1.59476300	-2.19236200

H	-5.40260000	3.12935300	-1.29838600
H	-3.86765400	2.30121500	-1.63526900
O	-0.22610600	-1.52898200	-0.04066700
C	-0.00616800	-2.54991800	0.91007900
H	0.89374400	-3.12381000	0.63575300
H	-0.85732700	-3.25133300	0.90715900
C	-0.40334900	-2.03894600	-1.34658100
H	-1.27692600	-2.71129600	-1.36646400
H	0.47921700	-2.63376000	-1.63253300
C	0.16203900	-1.90969600	2.27056200
H	0.40087500	-2.66687300	3.02339600
H	0.97416500	-1.17605400	2.23878200
H	-0.75451200	-1.39215900	2.57283600
C	-0.59664500	-0.87769900	-2.29670800
H	-0.66972800	-1.23779200	-3.32745600
H	-1.51043400	-0.32559400	-2.05500200
H	0.25218900	-0.18963100	-2.22451500

Transition state

Electronic energy (E) = -3470.5204893 au

Gibbs Free Energy (G) = -3470.205588 au

C	1.92756500	-1.28713400	2.06369300
C	1.78695100	-0.07508300	1.39541100
H	2.40767600	-3.39252500	1.91096100
C	2.28948300	-2.45185900	1.38340400
C	1.90522200	-0.01352900	-0.01984500
C	2.44072900	-1.16246100	-0.67418000
C	2.57772100	-2.35590300	0.00669500
H	2.65906800	-1.11134000	-1.73598800
H	2.92218800	-3.23197600	-0.53751600
Mg	-0.52832400	0.32113600	-1.04138500
Br	2.57191100	1.74526900	-0.67023500
H	1.54401400	0.82264600	1.95564000
H	1.77198200	-1.31128700	3.14000600
O	-2.20640800	1.45345500	-0.21148100
C	-2.20251700	2.40142600	0.85865300
H	-2.88364700	3.22207300	0.59994900
H	-2.57236300	1.92073900	1.77304600
C	-3.47642300	1.23153100	-0.83489900
H	-3.25454000	0.65213200	-1.73950800
H	-3.87655600	2.20302000	-1.15201100

C	-0.79103000	2.91613900	1.04679900
H	-0.44268200	3.43986900	0.15252200
H	-0.76153500	3.60740300	1.89448300
H	-0.09356400	2.09700900	1.25430800
C	-4.46257800	0.49008500	0.04598000
H	-5.40870000	0.37786000	-0.49306900
H	-4.08338300	-0.50509400	0.29226200
H	-4.67091000	1.03508000	0.97216700
O	-1.70499400	-1.41868100	-0.33198100
C	-1.93640700	-2.40819300	-1.34438300
H	-2.78210000	-3.03121900	-1.02572100
H	-2.24192500	-1.84307800	-2.23117900
C	-1.43069100	-1.96249400	0.96673300
H	-2.13819400	-2.78177300	1.15110300
C	-0.70919800	-3.24802800	-1.65189200
H	-0.41098800	-3.86902600	-0.80222300
H	-0.92926600	-3.90970900	-2.49566400
H	0.13287300	-2.60364400	-1.92744100
H	-0.41250400	-2.36998400	0.98473400
C	-1.58694100	-0.87623200	2.00988700
H	-2.61145200	-0.49671400	2.04016100
H	-1.33463000	-1.28592100	2.99280400
H	-0.90596400	-0.04036800	1.81639800

Product complex

Electronic energy (E) = -3470.6996298 au

Gibbs Free Energy (G) = -3470.383766 au

C	2.25604700	2.96094400	-0.67055100
C	2.42733900	1.62623800	-1.03691200
H	2.22929500	4.38533900	0.94502300
C	2.36205800	3.34503600	0.66553200
C	2.69455800	0.68471900	-0.04828200
C	2.81135500	1.05037200	1.28895900
C	2.63681700	2.38821100	1.64163500
H	3.04384200	0.30728400	2.04447500
H	2.72248100	2.67831100	2.68435300
Mg	-1.12986300	1.56951300	0.79579100
Br	3.04452200	-1.10834200	-0.55018800
H	2.36236300	1.32763200	-2.07797900
H	2.04381800	3.69932700	-1.43759600
O	-4.41248900	0.13694300	-0.22346300

C	-4.39623600	-0.61153300	0.97577600
H	-3.96130600	-0.00097700	1.78486100
H	-5.42614000	-0.86975700	1.27044300
C	-5.04047300	1.39438200	-0.07430300
H	-4.55269700	1.95548200	0.74001700
H	-6.09770400	1.25562100	0.20360300
C	-3.56214800	-1.85591300	0.75408500
H	-3.51608100	-2.44913400	1.67314200
H	-3.99663500	-2.47599400	-0.03629500
H	-2.54415200	-1.57411000	0.46360600
C	-4.92170400	2.15014900	-1.38053500
H	-5.40017400	1.59476300	-2.19236200
H	-5.40260000	3.12935300	-1.29838600
H	-3.86765400	2.30121500	-1.63526900
O	-0.22610600	-1.52898200	-0.04066700
C	-0.00616800	-2.54991800	0.91007900
H	0.89374400	-3.12381000	0.63575300
H	-0.85732700	-3.25133300	0.90715900
C	-0.40334900	-2.03894600	-1.34658100
H	-1.27692600	-2.71129600	-1.36646400
H	0.47921700	-2.63376000	-1.63253300
C	0.16203900	-1.90969600	2.27056200
H	0.40087500	-2.66687300	3.02339600
H	0.97416500	-1.17605400	2.23878200
H	-0.75451200	-1.39215900	2.57283600
C	-0.59664500	-0.87769900	-2.29670800
H	-0.66972800	-1.23779200	-3.32745600
H	-1.51043400	-0.32559400	-2.05500200
H	0.25218900	-0.18963100	-2.22451500

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