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An EPR Study of the C−O Bond Activation of 1,2-Epoxybutane by Ground-State Al Atoms

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Group 13 metal atoms react with ethers under matrix isolation conditions to give a number of interesting products. This work has been extended to include the reaction of Al atoms with 1,2-epoxybutane ($CH_3CH_2CHOCH_2$) and its isotopomers, 1,2-epoxybutane-1,1-*d*$_2$ ($CH_3CH_2CHOCD_2$) and 1,2-epoxybutane-2-*d*$_1$ ($CH_3CH_2CDOCH_2$). The paramagnetic species generated in the reaction have been studied by electron paramagnetic resonance (EPR) spectroscopy. Two divalent Al insertion products were spontaneously formed. Species A, with the magnetic parameters $a_{Al} = 855$ MHz, $a_H(1) = 28.8$ MHz, $a_H(2) = 13.6$ MHz, and $g = 2.0014$, is the C_1-O insertion radical $CH_3CH_2CHCH_2AlO$. Species B, thought to result from the insertion of Al atoms into the C_2-O bond, $CH_3CH_2CHCH_2OAl$, has the magnetic parameters $g = 2.0003$, $a_{Al} = 739$ MHz, $a_H(1) = 15.1$ MHz, $a_H(2) = 18.5$ MHz, and $a_H(1) = 37.8$ MHz. Support for these assignments was obtained by comparing the experimental values of the Al and H hyperfine interaction (hfi) with those calculated using a DFT method. At temperatures < 150 K, there is evidence for the formation of the alkyl radical $CH_3CH_2CH(O^-)CH_2^{\bullet}$ due to ring opening at the C_1-O bond, while at higher temperatures a radical with magnetic parameters similar to those reported for 1-methallyl was detected.

Introduction

Our knowledge of Al atom chemistry has increased considerably over the years. One of the interesting features noted is the tendency for Al atoms to insert into many different types of bonds, such as O−H,[1] N−H,[2] S−H, Se−H,[3] P−H,[4] and C−H,[5] yielding novel divalent Al radicals.

Of particular importance to this study are the reports dealing with Al atom C−O insertion reactions.[6−8] In an EPR study[6] of the products generated in the reaction of Al atoms with dimethyl ether, Chenier et al. assigned the species with the Al hyperfine interaction (hfi) of 1002 MHz to the C−O insertion product, CH_3AlOCH_3. The large isotropic hfi indicates that the unpaired electron is found in an sp-hydridized orbital of the Al atom. However, the absence of additional coupling from neighboring hydrogen atoms made the assignment tentative. For the Al atom reactions involving diethyl ether, tetrahydrofuran, and 1,3,5-trioxane, sextets with large Al hfi between 977 and 1050 MHz were observed. These spectra were attributed to the respective Al atom C−O insertion products because the Al hfi values were similar to those determined for CH_3AlOCH_3.

More recently, Kasai[7] studied the reaction of Al atoms with dimethyl ether and trimethylene oxide in argon and neon matrixes. He also found that the Al atoms insert into the C−O bond of the ethers. Two isomers of CH_3AlOCH_3 were detected. The magnetic parameters reported for *trans*-CH_3OAlCH_3 are very close to those found for the species isolated in adamantane while the Al hfi for *cis*-CH_3OAlCH_3 is ca. 10% larger. The detection of the $Al{:}O(CH_3)_2$ complex as well as the results of a semiempirical self-consistent field molecular orbital study suggested that insertion occurs by a three-step process. The Al atom first approaches the ethereal O. Next, formation of an Al−O bond induces the rupture of the C−O bond. Finally interaction of the unpaired electron on the alkyl terminus and the lone pair of electrons on Al results in Al−C bond formation. Also of interest in this study was the suggestion that complexation of the insertion radicals by one or two ether molecules occurs, i.e., $CH_3AlOCH_3{:}O(CH_3)_2$ and $CH_3AlOCH_3{:}[O(CH_3)_2]_2$. Although this phenomenon had been suggested previously in a number of other systems including the reactions of Al atoms with NH_3,[2] H_2S[3] and alcohols,[8] respectively, Kasai[7] demonstrated the presence of $CH_3AlOCH_3{:}O(CH_3)_2$ and $CH_3AlOCH_3{:}[O(CH_3)_2]_2$ by performing concentration experiments. Complexation of one ether molecule causes the Al hfi of the insertion radical to decrease by 4% whereas an 8% decrease is observed when two ether molecules are complexed.

In the case of trimethylene oxide,[7] Al atoms insert spontaneously to give $CH_2CH_2CH_2OAl$ with an Al hfi of 941 MHz. Examination of the $M_I = 1/2$ line of the insertion product in second derivative form revealed a triplet with a spacing of ca. 10 MHz indicative of the interaction of the unpaired electron with two equivalent hydrogen atoms confirming the proposed structure.

In the present study, we have been able to characterize, by EPR spectroscopy, the two new aluminaoxetanes resulting from the insertion of Al atoms into the C_1-O and C_2-O bonds of 1,2-epoxybutane. Although transition metal metallaoxetanes[9] have been implicated as possible intermediates in oxygen transfer reactions, to our knowledge little is known about the nature of aluminaoxetanes. The divalent Al radicals were prepared by cocondensing Al atoms with 1,2-epoxybutane in an adamantane matrix at 77 K. The Al and H hfi of the aluminaoxetanes calculated using a DFT method are comparable to those obtained experimentally. Surprisingly, examination of the intensity of the spectral lines indicates that there is only a slight preference for insertion of Al atoms into the C_1-O bond. In addition, there is EPR evidence suggesting that the epoxide undergoes ring opening primarily at C_1-O to form $CH_3CH_2CH(O^-)CH_2^{\bullet}$ at temperatures below 150 K. The magnetic

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parameters of the organic radical remaining at higher temperatures (> 150 K) are very similar to those reported for 1-methallyl.

Experimental Section

The paramagnetic products formed in the reaction of Al atoms with 1,2-epoxybutane were prepared in a metal atom reactor known as a rotating cryostat described in detail elsewhere.[10] Aluminum atoms were produced by resistively heating wire (20 mg, Fisher) placed in a tungsten basket (No. 12070, Ernest F. Fullam, Schenectady, NY) suspended between the electrodes of a furnace. The reaction mixtures were produced by cocondensing Al atoms, 1,2-epoxybutane (or one of its isotopomers), and adamantane on the surface of the liquid nitrogen cooled drum housed in the center of a stainless steel reaction vessel maintained at $< 10^{-6}$ Torr. In general, the metal:1,2-epoxybutane:adamantane was 1:10:1000. The adamantane and 1,2-epoxybutane were purchased (Aldrich) and used without further purification. The syntheses of the isotopomers, 1,2-epoxybutane-1,1-d_2 and 1,2-epoxybutane-2-d_1, are described below. The reaction mixtures were transferred under vacuum at 77 K to a suprasil quartz tube. Once sealed, X-band EPR spectra of the reaction mixtures were recorded between 77 and 298 K on a Varian E109 spectrometer equipped with a Varian gaussmeter, Systron-Donner 6016 frequency counter, and a Lakeshore 330 temperature controller.

Data Analysis and Computer Simulation. The magnetic parameters for each mononuclear aluminum species formed in the reaction of Al atoms and 1,2-epoxybutane, i.e., the Al hfi and g values, were determined from the exact solution of the spin Hamiltonian using the computer program ESRLSQ.[11] The simulations of specific regions of the EPR spectra presented in the Results section were generated using the computer program ISOPLOT.[11]

Synthesis of 1,2-Epoxybutane-1,1-d_2. The synthesis of 1,2-epoxybutane-1,1-d_2 involved three steps. In the first step, 2-aminobutanoic acid was converted to 2-chlorobutanoic acid.[12] The 2-chlorobutanoic acid was next reacted with BD_3 in THF to form 2-chloro-1-butanol-1,1-d_2. Finally, the addition of a solution of KOH to 2-chloro-1-butanol-1,1-d_2 resulted in the formation of the desired epoxide.

Conversion of 2-Aminobutanoic Acid to 2-Chlorobutanoic Acid. A 6 M HCl solution (300 mL) was added to 25.8 g (0.25 mol) of 2-aminobutanoic acid in a 500 mL, three-neck, round-bottom flask equipped with a magnetic stirrer, reflux condenser, and thermometer. The reaction mixture was maintained at −9 °C with the aid of an ice−water bath. Sodium nitrite (27.0 g, 0.391 mol) was added over a 3 h period. The solution was stirred vigorously for an additional hour before placing the stoppered flask in a freezer (−5 °C to −15 °C) overnight. The product was extracted from the solution with four 120 mL portions of diethyl ether. The ether layers were combined, washed with two 125 mL portions of distilled water, and dried over magnesium sulfate. The ether was removed under reduced pressure with the aid of a rotary evaporator. Pure 2-chlorobutanoic acid (16.3 g, 53%) was collected between 97 and 103 °C at 6 Torr (bp 46−50 °C, 0.25 Torr).[12] ^{1}H NMR (200 MHz, $CDCl_3$) δ in ppm: 1.05 (t, 3H), 2.02 (m, 2H), 4.20 (dd, 1H) in agreement with lit.[12]

Conversion of 2-Chlorobutanoic Acid to 2-Chloro-1-butanol-1,1-d_2. A three neck, 500 mL, round-bottom flask was equipped with a thermometer, a reflux condenser, a dropping funnel, and a magnetic stirrer. The condenser was connected to a mineral oil bubbler to monitor the gas flow. The system was flushed with nitrogen for approximately 15 min before 11.0 g (0.090 mol) of 2-chlorobutanoic acid was added to the flask. The flask was placed in an ice bath to maintain the reaction temperature at approximately 0 °C. A dropping funnel was charged with 120 mL of BD_3 in THF (1 M, Aldrich), and the mixture was added dropwise to the flask. After the reaction mixture was stirred vigorously for an additional 20 min, the ice bath was replaced by a water bath adjusted to 25 °C, and the solution was stirred for approximately 40 min. The excess BD_3 was destroyed by adding 55 mL of a THF−water solution (50/50 v/v). Next, 15 g of K_2CO_3 as well as 35 mL of a saturated K_2CO_3 solution was added to the reaction mixture. The aqueous phase was washed with three 75 mL portions of ether. The organic phases were combined and dried with $MgSO_4$. THF and diethyl ether were removed under reduced pressure with the aid of a rotary evaporator. The yield of the crude 2-chloro-1-butanol-1,1-d_2 was 8.53 g (86%). ^{1}H NMR (200 MHz, $CDCl_3$) δ in ppm: 1.06 (t, 3H), 1.64−1.90 (m, 2H), 2.02 (s, 1H), 3.61−3.79 (m, 1H). The chemical shifts are consistent with those reported for the undeuterated analogue.[12]

Conversion of 2-Chloro-1-butanol-1,1-d_2 to 1,2-Epoxybutane-1,1-d_2. A KOH solution (16 mL, 8.9 M) was placed in a Claisen flask equipped with a magnetic stirrer, dropping funnel, thermometer and Liebig condenser. The crude 2-chloro-1-butanol-1,1-d_2 (8.53 g, 0.077 mol) was added dropwise from the dropping funnel over a period of 30 min. The 1,2-epoxybutane-1,1-d_2 (5.05 g, 88%) was distilled from the reaction mixture and collected between 58 and 60 °C (bp 59−61 °C).[12] ^{1}H NMR (200 MHz, $CDCl_3$) δ in ppm: 1.00 (t, 3H), 1.58 (m, 2H), 2.89 (t, 1H). The chemical shifts are consistent with those reported for the undeuterated analogue.[12]

Synthesis of 1,2-Epoxybutane-2-d_1. To synthesize 1,2-epoxybutane-2-d_1, 1-bromobutanone was first reduced to 1-bromo-2-butanol-2-d_1 using a solution of BD_3 in THF. Treating 1-bromo-2-butanol-2-d_1 with a solution of NaOH resulted in the formation of 1,2-epoxybutane-2-d_1.

Conversion of 1-Bromobutanone to 1-Bromo-2-butanol-2-d_1. A 250 mL, three-neck flask charged with 10 g (0.066 mol) of 1-bromobutanone was equipped with a magnetic stirrer, thermometer, dropping funnel, and a mineral oil bubbler. A solution of BD_3 in THF (80 mL, 1 M) was added dropwise over a period of 85 min. The reaction mixture was left to stir overnight. The excess BD_3 was destroyed with 36 mL of a THF-water solution (50/50 v/v). Next, 35 mL of a saturated K_2CO_3 solution was added to the reaction mixture. The aqueous phase was washed with three 75 mL aliquots of diethyl ether. The organic phases were combined and dried with the aid of $MgSO_4$. The THF and ether were removed under reduced pressure using a rotary evaporator. The synthesis yielded 8.42 g (83%) of the crude 1-bromo-2-butanol-2-d_1. ^{1}H NMR (200 MHz, $CDCl_3$) δ in ppm: 0.987 (t, 3H), 1.60 (q, 2H), 3.39 (dt, 1H), 3.56 (d, 1H). The chemical shifts are consistent with those reported for the undeuterated analogue.[13]

Conversion of 1-Bromo-2-butanol-2-d_1 to 1,2-Epoxybutane-2-d_1. A NaOH solution (8.5 mL, 9.5 M) was transferred to a pear shaped flask fitted with a short path distillation head, dropping funnel, receiver, and a mineral oil bubbler. After adding 8.42 g of 1-bromo-2-butanol-2-d_1 (0.055 mol) to the flask over a 30 min period, the tip of the receiver was immersed in a bath maintained at −80 °C and N_2 gas was passed through the system. The reaction mixture was next heated, and 3.06 g (76%) of the 1,2-epoxybutane-2-d_1 was collected at 55 °C (bp 59−61 °C).[12] ^{1}H NMR (200 MHz, $CDCl_3$) δ in ppm: 0.98

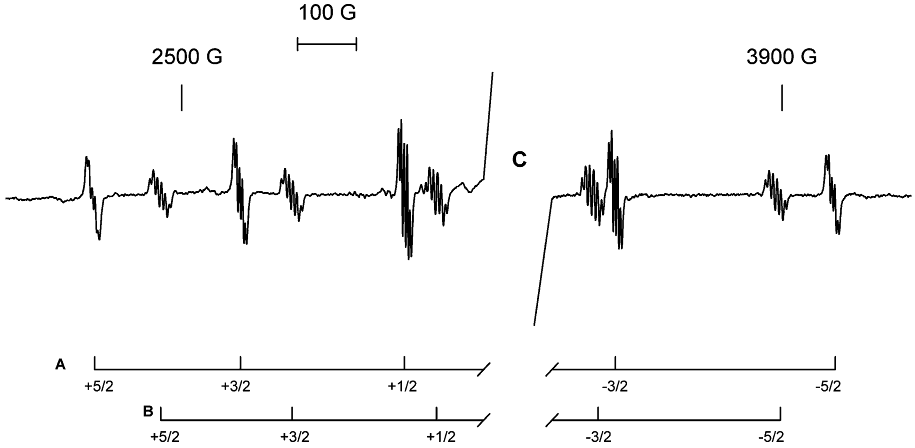


Figure 1. EPR spectrum recorded at 210 K ($\nu = 9117$ MHz, mp = 2 mW) of the paramagnetic products (A and B) formed in the reaction of Al atoms with 1,2-epoxybutane in adamantane at 77 K. C is the central feature and is off scale at the gain required to observe A and B.

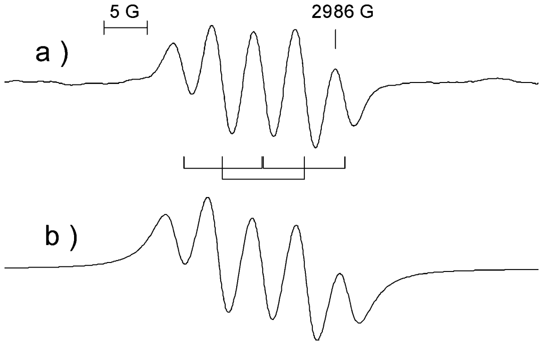


Figure 2. (a) The $M_I = 1/2$ line of Species A formed in the Al/1,2-epoxybutane reaction ($\nu = 9118$ MHz, mp = 2 mW, $T = 210$ K). (b) A simulation of the spectral line assuming the interaction of the unpaired electron of species A with three H nuclei; one with $a_H(1) = 28.8$ MHz and two with $a_H(2) = 13.6$ MHz.

(t, 3H), 1.54 (q, 2H), 2.46 (d, 1H), 2.72 (d, 1H). The chemical shifts are consistent with those reported for the undeuterated analogue.[13]

Results

Al/1,2-Epoxybutane/adamantane. The reaction of Al atoms with 1,2-epoxybutane in an adamantane matrix at 77 K produced a brown deposit. The EPR spectrum of the paramagnetic products was recorded at 10 K intervals from 77 to 300 K. The resolution of the spectral features of the paramagnetic species improved significantly upon annealing the sample to 210 K in the cavity of the EPR spectrometer, Figure 1. Aluminum ($I = 5/2$) containing radicals give rise to six EPR transitions. The detection of ten widely spaced transitions is strong evidence for the formation of two mononuclear aluminum radicals, A and B. The two missing transitions are obscured by the spectrum of an organic radical centered at $g \approx 2.00$.

The magnetic parameters, a_{Al} and g_{iso}, for species A, determined by solving the spin Hamiltonian using the computer program ESRLSQ,[11] are 855 ± 0.27 MHz and 2.0014 ± 0.0001, respectively. The Al $M_I = 1/2$ transition of species A, Figure 2a, consists of five equidistant lines, suggesting the unpaired electron interacts with at least three H ($I = 1/2$) nuclei. A simulation, Figure 2b, of the superhyperfine structure was obtained by assuming the interaction of the unpaired electron with three H nuclei; one with $a_H(1) = 28.8$ MHz and two with $a_H(2) = 13.6$ MHz.

The $M_I = 1/2$ transition for B, Figure 3a, also displays superhyperfine interaction. The six equivalently spaced lines were simulated by assuming the interaction of the unpaired electron with four H nuclei, i.e., one H with $a_H(1) = 37.8$ MHz, one H with $a_H(1) = 15.1$ MHz and two H with $a_H(2) = 18.5$ MHz. The a_{Al} and g_{iso} for B are $a_{Al} = 739 \pm 0.25$ MHz and 2.0003 ± 0.0001, respectively.

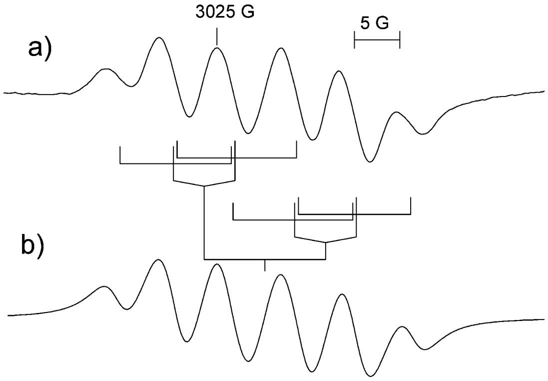


Figure 3. (a) The $M_I = 1/2$ line of Species B formed in the Al/1,2-epoxybutane reaction ($\nu = 9117$ MHz, mp = 2 mW, $T = 160$ K). (b) A simulation of the superhyperfine structure was generated by assuming the interaction of the unpaired electron of Species B with four H nuclei; one with $a_H(1) = 37.8$ MHz, two with $a_H(2) = 18.5$ MHz and one with $a_H(1) = 15.1$ MHz.

Al/1,2-Epoxybutane-1,1-d_2/adamantane. The experiment was repeated with 1,2-epoxybutane-1,1-d_2 with the intention of using isotopic substitution to help identify the products formed in the Al atom reaction. Upon annealing the sample to 210 K in the cavity of the EPR spectrometer, spectral lines corresponding to Al transitions ($I = 5/2$) of Species A and B were found in the same approximate magnetic field positions reported for undeuterated 1,2-epoxybutane, Figure 4. Although isotopic substitution does not significantly change the values for g_{iso} and a_{Al}, it does alter the splitting pattern of the individual Al transitions. The spectral lines for A are reduced to a doublet of quintets corresponding to the interaction of the unpaired electron with a H nucleus and two D nuclei, Figure 5 a. The best spectral simulation was obtained with $g = 2.0008 \pm 0.0004$, $a_{Al} = 866 \pm 1$ MHz, $a_H(1) = 28.5$ MHz and $a_D(2) = 2.10$ MHz, Figure 5 b.

Spectrum B, a sextet of doublets of doublets of quintets, was simulated using the magnetic parameters $g = 2.0013 \pm 0.0002$, $a_{Al} = 738 \pm 0.53$ MHz, a_H (1)= 39.0 MHz, a_H (1) = 15.1 MHz and $a_D(2) = 2.80$ MHz, Figure 6.

Al/1,2-Epoxybutane-2-d_1/adamantane. Similarly Al atoms react with 1,2-epoxybutane-2-d_1 to give two mononuclear Al

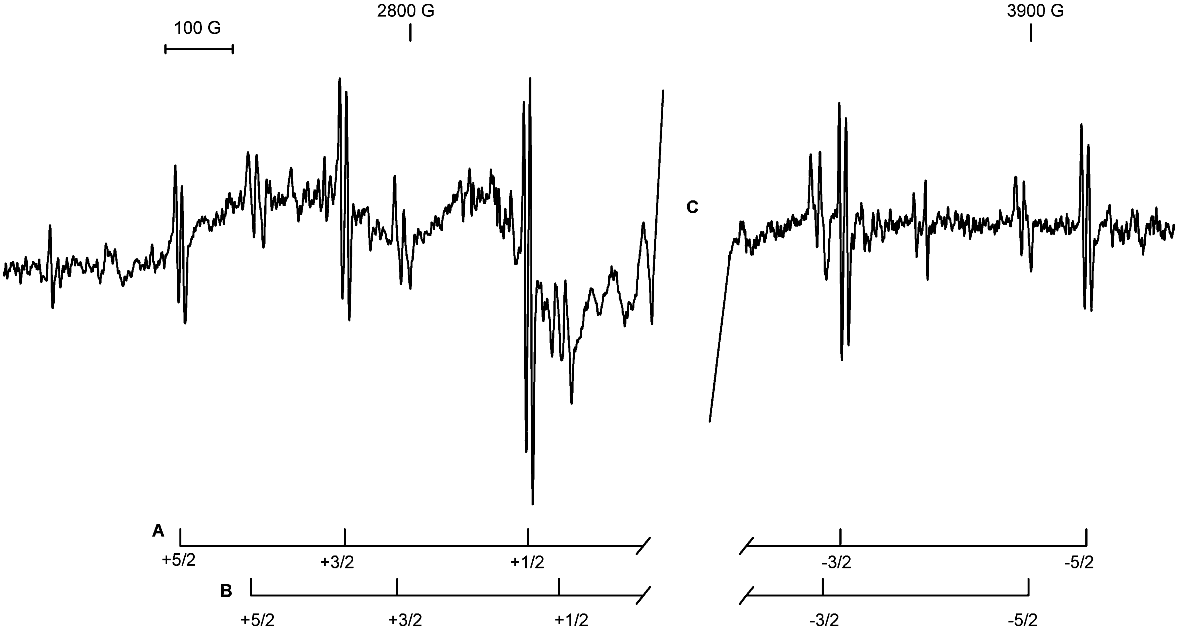


Figure 4. EPR spectrum recorded at 210 K ($\nu = 9117$ MHz, mp = 2 mW) of the paramagnetic products (A and B) formed in the reaction of Al atoms with 1,2-epoxybutane-1,1-d_2 in adamantane at 77 K. C is the central feature and is off scale at the gain required to observe A and B.

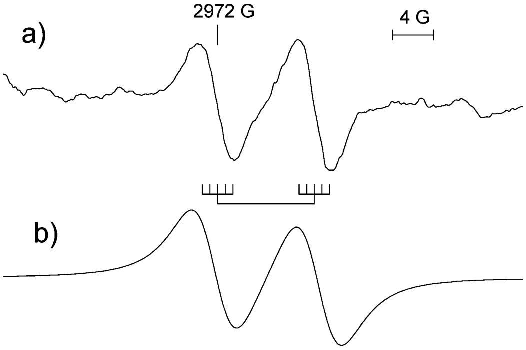


Figure 5. (a) The $M_I = 1/2$ line of Species A formed in the Al/1,2-epoxybutane-1,1-d_2 reaction ($\nu = 9113$ MHz, mp = 2 mW, $T = 210$ K). (b) A simulation of the spectral line assuming the interaction of the unpaired electron of species A with a H nucleus and two D nuclei with $a_H(1) = 28.5$ MHz and $a_D(2) = 2.10$ MHz.

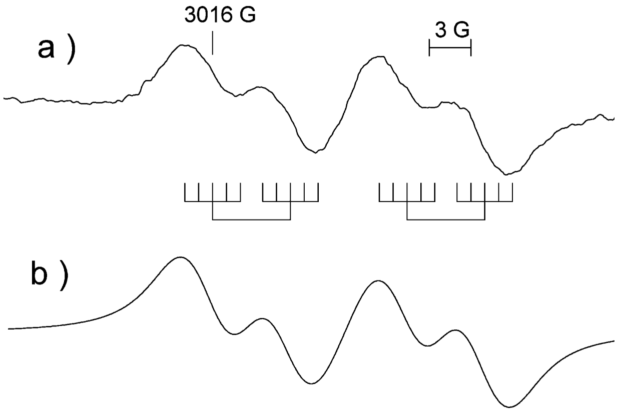


Figure 6. (a) The $M_I = 1/2$ line of Species B formed in the Al/1,2-epoxybutane-1,1-d_2 reaction (ν= 9115 MHz, mp = 2 mW, $T = 170$ K). (b) A simulation of the spectral line assuming the interaction of the unpaired electron of species B with two H nuclei and two D nuclei with $a_H(1) = 39$ MHz, $a_H(1) = 15.1$ MHz and $a_D(2) = 2.80$ MHz.

species with the same a_{Al} and g_{iso} values, within experimental error, as those determined for Species A and B formed in the Al/1,2-epoxybutane and Al/1,2-epoxybutane-1,1-d_2 reactions. The EPR spectrum of the Al/1,2-epoxybutane-2-d_1 reaction mixture recorded at 200 K is shown in Figure 7. The introduction of deuterium at C2 alters the splitting pattern for the Al transitions of Species A and B. For species A, the interaction of the unpaired electron with 2 H nuclei and 1 D nucleus results in a sextet of triplets of triplets, Figure 8, and a good simulation was obtained with $g = 2.0009 \pm 0.0003$, $a_{Al} = 863 \pm 0.81$ MHz, $a_H(2) = 15.9$ MHz, and $a_D(1) = 4.42$ MHz. Species B, gave a sextet of doublets of triplets of triplets, Figure 9, which was simulated using the magnetic parameters $g = 2.0013 \pm 0.0001$, $a_{Al} = 745 \pm 0.24$ MHz, $a_H(1) = 37.5$ MHz, $a_H(2) = 18.5$ MHz, and $a_D(1) = 2.32$ MHz.

Central Feature. In addition to the EPR transitions for the two mononuclear Al species, A and B, a number of strong features centered at $g \approx 2.00$ were detected. As the sample was annealed from 77 to 300 K in the cavity of the spectrometer, the appearance of the features changed considerably, Figure 10. To eliminate the possibility that the spectral changes were due to a conformational change, the sample was recooled to 100 K. The spectrum was identical to that observed at 300 K, suggesting that two different radicals were formed. The original low-temperature spectrum is characterized by four main features centered at $g = 2.0024$ and separated by ≈ 56 MHz; the outside features are very broad relative to the two inner lines. An increase in temperature causes the radical to decay. The spectrum recorded at higher temperatures, due to the second radical, consists of seven equally spaced doublets centered at $g = 2.0023$; the septet and doublet spacings are 41 and 11 MHz, respectively. At intermediate temperatures, the spectra of the two radicals are superimposed.

Deuteration at C1 and C2 of 1,2-epoxybutane changes the appearance of both the high (Figure 11) and low (Figure 12) temperature spectra indicating that the unpaired electron in the two radicals interacts with the C1 and C2 hydrogen nuclei. At low temperature, deuteration at C2 resulted in a triplet pattern with a spacing of ≈ 56 MHz suggesting that the unpaired electron interacts with the 2 H nuclei on C1. A poorly resolved superhyperfine interaction of ≈ 11 MHz was also visible, consistent with the interaction of the unpaired electron with D on C2. As the temperature is increased to 200 K, the spectrum

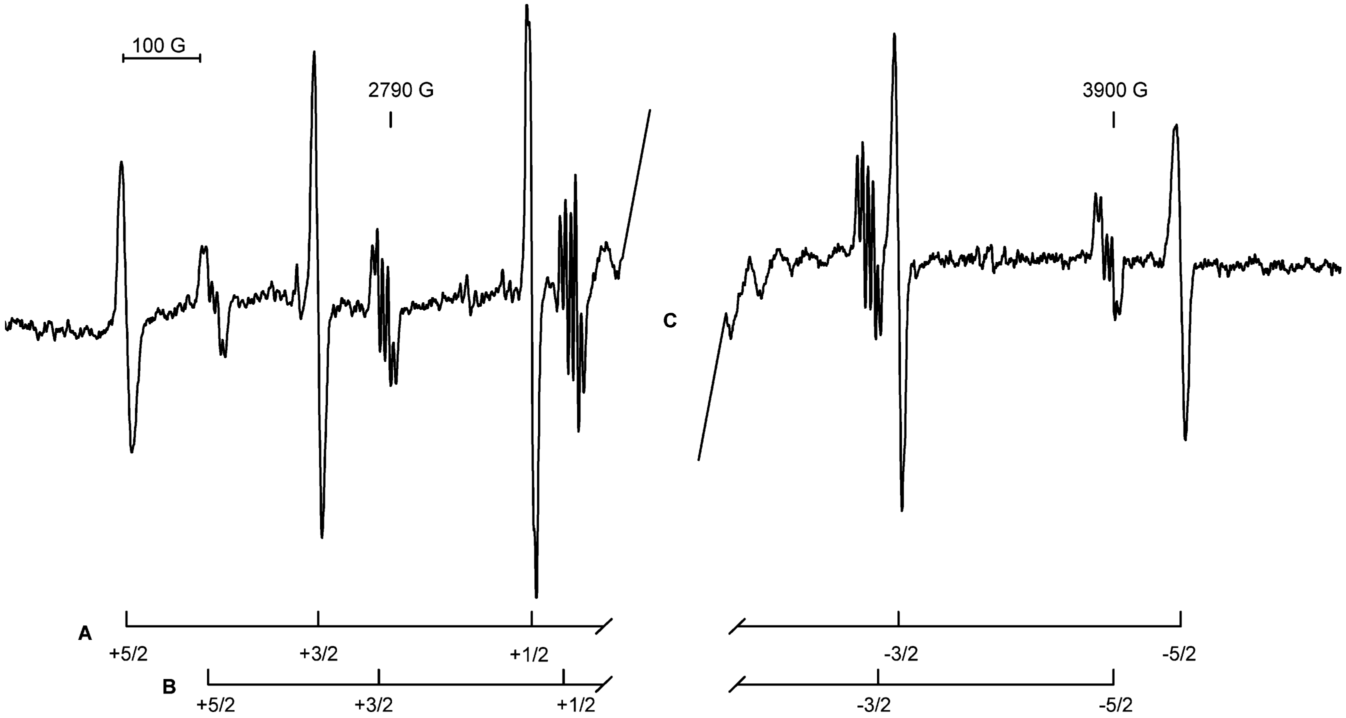


Figure 7. EPR spectrum recorded at 200 K ($\nu = 9113$ MHz, mp = 2 mW) of the paramagnetic products (A and B) formed in the reaction of Al atoms with 1,2-epoxybutane-2-d_1 in adamantane at 77 K. C is the central feature and is off scale at the gain required to observe A and B.

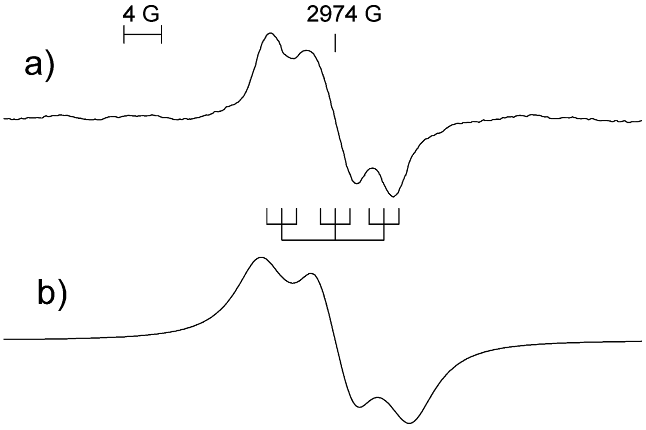


Figure 8. (a) The $M_I = 1/2$ line of Species A formed in the Al/1,2-epoxybutane-2-d_1 reaction ($\nu = 9115$ MHz, mp = 2 mW, $T = 200$ K). (b) A simulation of the spectral line assuming the interaction of the unpaired electron of species A with a D nucleus and two H nuclei with $a_D(1) = 4.42$ MHz and $a_H(2) = 15.9$ MHz.

is reduced to seven lines separated by 39 MHz. The loss of the doublet spacing indicates that the H hfi of the C_2−H is 11 MHz. To generate a seven line pattern one can assume that the unpaired electron interacts with six hydrogen nuclei with an $a_H(6) \approx 39$ MHz.

Deuteration at C1 results in complex spectra which are significantly different from those of the undeuterated and C2-deuterated substrates. At the lower temperatures, we are able to detect a doublet with a spacing of ≈ 56 MHz. Although there is evidence for additional coupling, the resolution is too poor for the coupling constants to be estimated. A multiple-lined spectrum with the general features of a quintet was obtained at higher temperatures, indicating the unpaired electron is interacting with four hydrogen nuclei with $a_H(4) = 39$ MHz. The superhyperfine interaction is estimated at ≈ 6 MHz. The best simulation of the EPR spectrum was obtained by assuming $a_H(4) = 39$ MHz, $a_H(1) = 11$ MHz, and $a_D(2) = 6$ MHz.

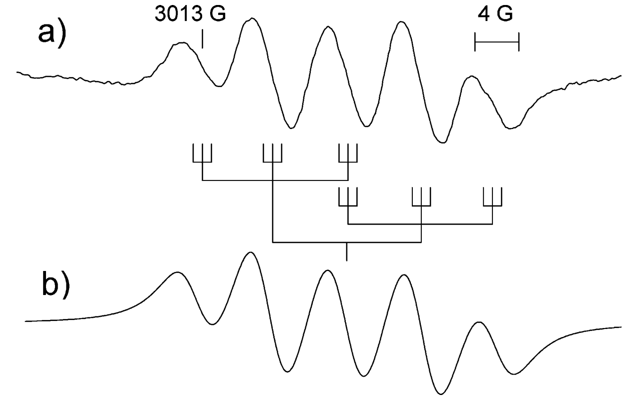
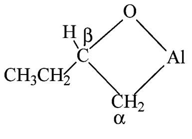


Figure 9. (a) The $M_I = 1/2$ line of Species B formed in the Al/1,2-epoxybutane-2-d_1 reaction ($\nu = 9115$ MHz, mp = 2 mW, $T = 160$ K). (b) A simulation of the spectral line assuming the interaction of the unpaired electron of species B with three H nuclei and one D nucleus with $a_H(1) = 37.5$ MHz, $a_H(2) = 18.5$ MHz and $a_D(1) = 2.32$ MHz.

Discussion

The EPR analysis of the light brown deposit resulting from reaction of ^{27}Al (I=5/2) atoms with 1,2-epoxybutane and its isotopomers (1,2-epoxybutane-1,1-d_2 and 1,2-epoxybutane-2-d_1) in adamantane at 77 K showed that two Al-centered radicals form, Species A and B, Table 1.

The change in the spectral patterns of the Al transitions of Species A and B upon isotopic substitution of C1 and C2 of 1,2-epoxybutane indicates that the Al atom is either bonded to or is in close proximity to C1 and C2. The three Al atom insertion products (I−III) shown below were considered as possible carriers of the EPR spectra assigned to Species A and B. The insertion of Al into the C_1−O or C_2−O bond of 1,2-epoxybutane yields the aluminaoxetanes, I and II, respectively, while III results from the oxidative addition of Al to the C_1−C_2 bond of the epoxide.



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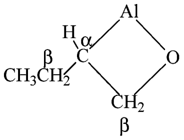
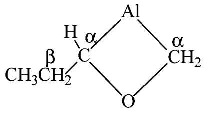


II



III

The H hfi and change in spectral pattern observed for Species A are most consistent with I where there are two α carbon hydrogens and only one β carbon hydrogen. The undeuterated analogue of I would be expected to give a sextet of doublets of triplets. From the experimental spectrum, the doublet and triplet spacings correspond to 28.8 and 13.6 MHz, respectively. Replacing the α hydrogens of I with deuterium would result in a sextet of doublets of quintets. The doublet splitting should remain unchanged while the approximate value of the quintet spacing can be estimated from $a_H(2) = 13.6$ MHz and the gyromagnetic ratios of H and D, i.e., $a_D = a_H\gamma_D/\gamma_H = 13.6/6.5$ or 2.10 MHz. In fact, this was the case as a good simulation of the spectral lines was obtained using $a_H(1) = 28.5$ MHz and $a_D(2) = 2.10$ MHz, respectively. Substitution of the β-hydrogen in I with deuterium is expected to yield a triplet of triplets due to the interaction of the unpaired electron with two α hydrogens ($I = 1/2$) and one β deuterium ($I = 1$). Based on the results obtained for the undeuterated epoxide, the hfi of the α hydrogens should be 13.6 MHz while $a_D \approx 28.8/6.5$ or 4.43 MHz. The best simulation was obtained assuming $a_H(2) = 15.9$ MHz and $a_D(1) = 4.42$ MHz.

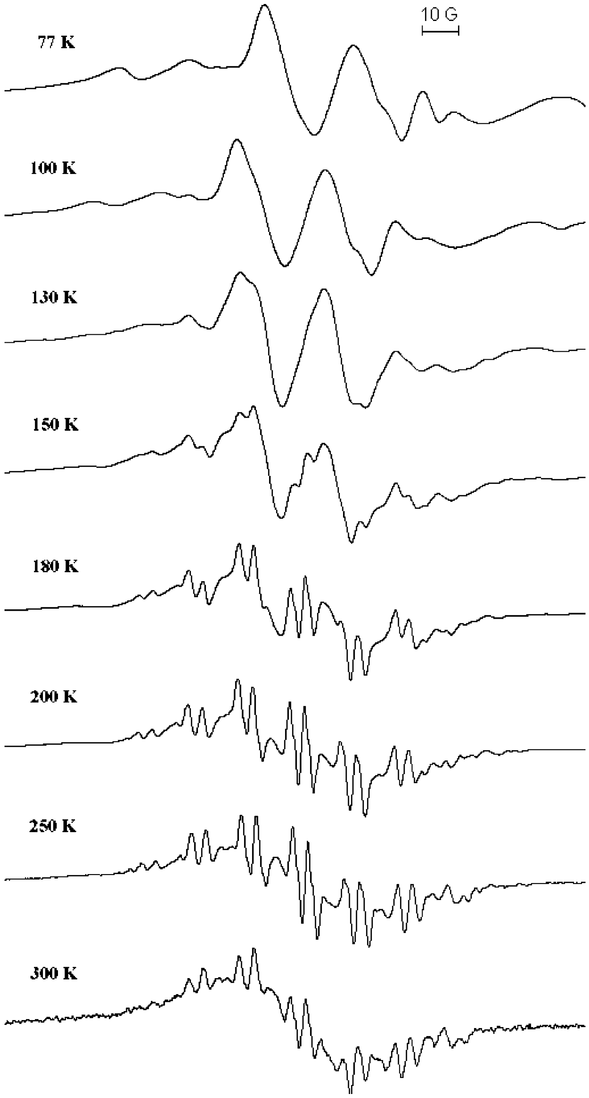


Figure 10. The central features ($g \approx 2.00$) of the EPR spectrum for the Al/1,2-epoxybutane reaction mixture recorded between 77 and 300 K (≈ 9114 MHz, mp = 2 mW).

TABLE 1: EPR Parameters of the Mononuclear Aluminum Products from the Reaction of Al Atoms with 1,2-Epoxybutane and Its Isotopomers in Adamantane at 77 K[a]

1,2-epoxybutane	a_{Al}	$a_H(1)$	$a_H(2)$	$a_H(1)$	g_{iso}
A	855 (0.27)[b]	28.8	13.6	-	2.0014 (1)
B	739 (0.25)	15.1	18.5	37.8	2.0003 (1)
1,2-epoxybutane-1,1-d_2	a_{Al}	$a_H(1)$	$a_D(2)$	$a_H(1)$	g_{iso}
A	866 (1.0)	28.5	2.10	-	2.0008 (4)
B	738 (0.53)	15.1	2.80	39.0	2.0013 (2)
1,2-epoxybutane-2-d_1	a_{Al}	$a_D(1)$	$a_H(2)$	$a_H(1)$	g_{iso}
A	863 (0.81)	4.42	15.9	-	2.0009 (3)
B	745 (0.24)	2.32	18.5	37.5	2.0013 (1)

[a] The hfi is in MHz. [b] The value in parentheses represents the error.

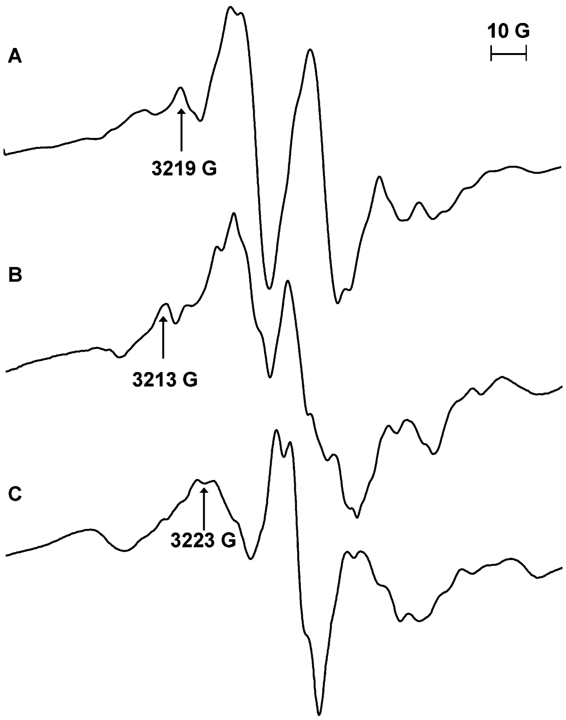


Figure 11. The central feature of the low-temperature EPR spectrum (mp = 2 mW) for the Al/1,2-epoxybutane reaction. (A) 1,2-epoxybutane, $T = 140$ K, $\nu = 9111$ MHz; (B) 1,2-epoxybutane-1,1-d_2, $T = 150$ K, $\nu = 9114$ MHz; (C) 1,2-epoxybutane-2-d_1, $T = 130$ K, $\nu = 9119$ MHz.

In studying the effect of isotopic substitution on the behavior of the spectral lines assigned to Species B it is clear there are more than the three ring hydrogens that interact with the unpaired electron. The Al $M_I = 1/2$ transition line of Species B was reduced from a equally spaced sextet to a doublet of doublets with $a_H(1) = 39.0$ MHz and $a_H(1) = 15.1$ MHz upon deuteration of C1. The large doublet spacing is generated by a proton on the alkyl chain. The change effected by deuteration suggested a deuterium hfi of approximately 2.8 MHz and allows one to estimate the hfi of the two C1 hydrogens at 6.5 × 2.8 or 18.2 MHz. The Al transition lines attributed to Species B in the EPR of the Al/1,2-epoxybutane-2-d_1 reaction mixture are quintets. This is consistent with the results discussed above for the 1,1-d_2 analogue of Species B assuming the quintet is

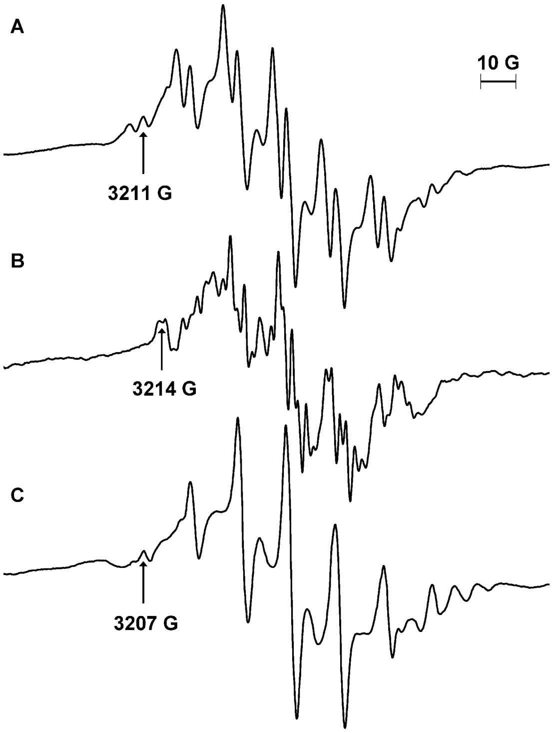


Figure 12. The central feature of the high-temperature EPR spectrum (mp = 2 mW) for the Al/1,2-epoxybutane reaction. (A) 1,2-epoxybutane, sample annealed to $T = 240$ K and spectrum recorded at 150 K, $\nu = 9114$ MHz; (B) 1,2-epoxybutane-1,1-d_2, $T = 210$ K, $\nu = 9116$ MHz; (C) 1,2-epoxybutane-2-d_1, $T = 200$ K, $\nu = 9115$ MHz.

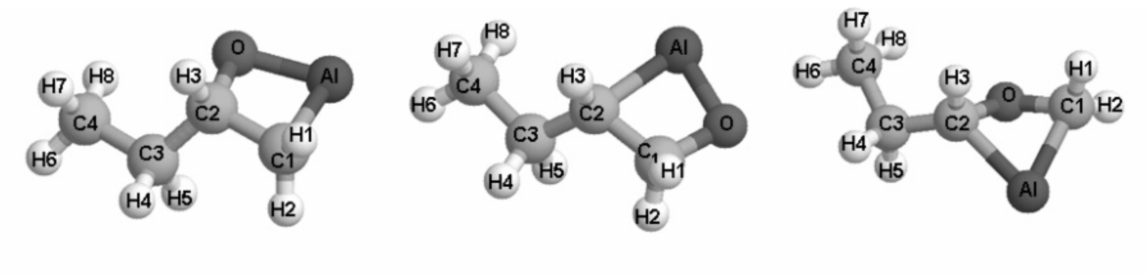
produced by a doublet ($a_H(1) = 37.5$ MHz) of triplets ($a_H(2) = 18.5$ MHz) of triplets ($a_D(1) = 15.1/6.5$ or 2.32 MHz). Finally, this information was used to obtain a simulation of the undeuterated Species B's Al $M_I = 1/2$ transition line assuming that the unpaired electron interacts with the C2 hydrogen ($a_H(1) = 15.1$ MHz), the two C1 hydrogens ($a_H(2) = 18.5$) and one of the C3 hydrogens ($a_H(1) = 37.8$ MHz).

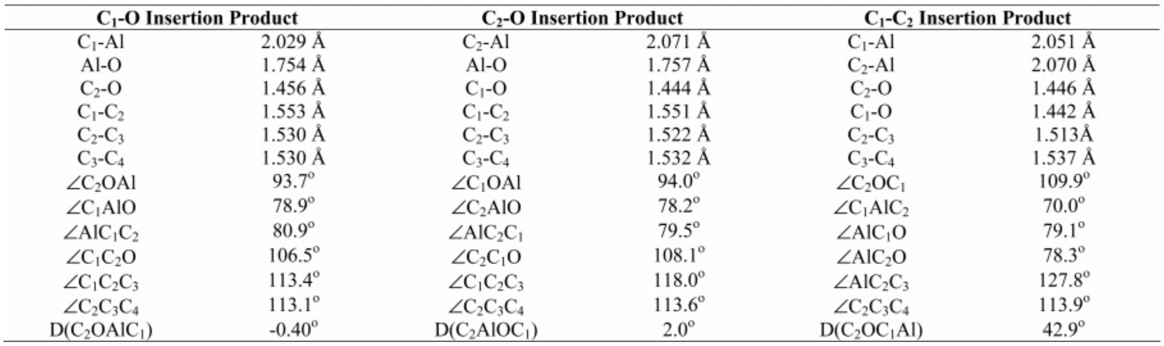
Both compounds II and III could produce the splitting pattern displayed by Species B. A DFT method[8] which proved effective at predicting the hfis of a number of divalent Al radicals was used to help distinguish between these two possibilities. This was carried out with the aid of Gaussian 98.[14] The geometry of I, II, and III was optimized using the B3LYP[15] functional and the split valence 6−31(d,p) basis set, Chart 1. These species were characterized as minimum energy conformers using frequency analysis. Single point calculations using the B3LYP,[15] BPW91,[15a,16] MPW1PW91,[17] and BP86[15a,18] model functionals and the split valence 6−311 + G(2df, p) basis set were used to determine the energies and the nuclear hfis of I, II, and III, Table 2. From the calculated potential energies it can be concluded that I is the most stable of the insertion products at all levels of theory. The potential energy for I and II differ by 4−4.7 kcal mol^{-1} while for I and III the energy difference is 43−47 kcal mol^{-1}.

As a test of the theoretical methods, we compared the calculated values of the Al and H hfis for compound I with those extracted from the EPR spectrum. As seen previously,[8] all the DFT methods underestimate the Al hfi for I with the smallest discrepancy (≈ 16%) occurring at the B3LYP and MPW1PW91 levels using a 6−311 + G(2df, p) basis set. The H hfis are also in good agreement with the values determined experimentally. These results can be compared to those of the cis and trans isomers of the C−O insertion product of dimethyl ether, CH_3AlOCH_3.[8] At the B3LYP level of theory the cis and trans isomers differed in energy by at least 1 kcal mol^{-1} with the trans isomer being more stable. The corresponding calculated Al hfi were strongly dependent on the structure and increased by 22% as the configuration changed from a trans to a cis arrangement. The trans and cis CH_3AlOCH_3 isomers isolated in Ar were found[3] to have an experimental Al hfi of 901 and 1046 MHz, respectively, differing by 16% and deviating from the calculated values by 11% and 7%, respectively.

The experimental Al hfi of Species B is closer (20% vs 61%) to the value calculated for II, the product resulting from insertion into the C_2−O bond. II as noted above is the second most stable of the insertion products. Species B is therefore assigned to II. It is interesting to note that (a) the H hfi calculated for one of the methylene hydrogens of the ethyl moiety is much greater than the other which supports the experimental results, and (b) the experimental Al hfi of the four-membered aluminaoxetanes

CHART 1





C_1-O Insertion Product		C_2-O Insertion Product		C_1-C_2 Insertion Product	
C_1-Al	2.029 Å	C_2-Al	2.071 Å	C_1-Al	2.051 Å
Al-O	1.754 Å	Al-O	1.757 Å	C_2-Al	2.070 Å
C_2-O	1.456 Å	C_1-O	1.444 Å	C_2-O	1.446 Å
C_1-C_2	1.553 Å	C_1-C_2	1.551 Å	C_1-O	1.442 Å
C_2-C_3	1.530 Å	C_2-C_3	1.522 Å	C_2-C_3	1.513Å
C_3-C_4	1.530 Å	C_3-C_4	1.532 Å	C_3-C_4	1.537 Å
$\angle C_2OAl$	93.7°	$\angle C_1OAl$	94.0°	$\angle C_2OC_1$	109.9°
$\angle C_1AlO$	78.9°	$\angle C_2AlO$	78.2°	$\angle C_1AlC_2$	70.0°
$\angle AlC_1C_2$	80.9°	$\angle AlC_2C_1$	79.5°	$\angle AlC_1O$	79.1°
$\angle C_1C_2O$	106.5°	$\angle C_2C_1O$	108.1°	$\angle AlC_2O$	78.3°
$\angle C_1C_2C_3$	113.4°	$\angle C_1C_2C_3$	118.0°	$\angle AlC_2C_3$	127.8°
$\angle C_2C_3C_4$	113.1°	$\angle C_2C_3C_4$	113.6°	$\angle C_2C_3C_4$	113.9°
$D(C_2OAlC_1)$	-0.40°	$D(C_2AlOC_1)$	2.0°	$D(C_2OC_1Al)$	42.9°

TABLE 2: Calculated Al hfi, H hfi, and Potential Energies (E) for $CH_3CH_2\overline{CHCH_2AlO}$ (I), $CH_3CH_2\overline{CHCH_2OAl}$ (II), and $CH_3CH_2\overline{CHAlCH_2O}$ (III)

		calcd hfi in MHz				
radical		B3LYP/ 6-31G(d, p)	B3LYP/ 6-311 + G(2df, p)	BPW91/ 6-311 +G(2df, p)	MPW1PW91/ 6-311+G(2df, p)	BP86/ 6-311 +G(2df, p)
$CH_3CH_2\overline{CHCH_2AlO}$	Al	560	720	693	721	695
	H1	−14	−12	−11	−13	−10
	H2	−15	−13	−11	−14	−11
	H3	21	20	19	18	20
	H4	−1.0	−0.95	−1.0	−1.0	−0.94
	H5	0.35	0.37	0.47	0.24	0.55
E (in hartrees)		−474.9003	−474.9914	−474.9351	−474.9113	−474.9840
$CH_3CH_2\overline{CHCH_2OAl}$	Al	457	592	575	591	576
	H1	29	28	27	25	27
	H2	11	11	9.1	9.7	9.4
	H3	−15	−13	−11	−14	−9.8
	H4	44	42	40	38	41
	H5	4.1	3.8	3.6	3.6	3.7
E (in hartrees)		−474.8929	−474.9843	−474.9287	−474.9038	−474.9773
$CH_3CH_2\overline{CHAlCH_2O}$	Al	213	287	271	281	277
	H1	29	27	30	24	30
	H2	−11	−10	−9.0	−11	−9.0
	H3	27	25	27	21	28
	H4	3.6	3.8	3.9	3.6	3.9
	H5	1.9	1.5	1.5	1.5	1.4
E (in hartrees)		−474.8301	−474.9188	−474.8664	−474.8371	−474.9154

TABLE 3: A Comparison of the Al hfi (in MHz) and Al 3s Unpaired Spin Density (ρ_{3s}) for a Number of Divalent Aluminum Radicals

radical	a_{Al}	ρ_{3s}	matrix	ref
cis-CH_3OAlCH_3	1046	0.27	Ar	7
trans-CH_3OAlCH_3	901	0.23	Ar	7
CH_3OAlCH_3	1002	0.26	adamantane	6
$CH_3CH_2OAlCH_2CH_3$	1027	0.26	adamantane	6
$\overline{CH_2CH_2CH_2OAl}$	951	0.24	Ar	7
$\overline{CH_2CH_2CH_2CH_2OAl}$	1050	0.27	adamantane	6
$CH_3CH_2\overline{CHCH_2AlO}$	855	0.22	adamantane	this work
$CH_3CH_2\overline{CHCH_2OAl}$	739	0.19	adamantane	this work

(I and II) differ by ≈ 14% while the calculated values differ by 18% at the B3LYP level.

The Al 3s unpaired spin density (ρ_{3s}) of the C−O insertion products, estimated by dividing the isotropic Al hfi by the one electron atomic parameter for the Al 3s orbital (3911 MHz)[19] is 0.22 and 0.19 for I and II, respectively. The Al hfi and ρ_{3s} values for a number of divalent aluminum radicals are summarized in Table 3. The large isotropic Al hfi observed for all the C−O insertion products indicates that the unpaired electron is found in an sp-hybridized orbital of the Al atom. It has been previously suggested that the Al hfi and thus the ρ_{3s} values are sensitive to the type of ligands attached to the Al atom. Electron-withdrawing (electronegative) groups increase the ionic character of the σ bonds. This means that the p-orbital involvement in the σ bond increases. Consequently, the s orbital contribution to the SOMO is increased and a larger Al hfi is observed. It has been clearly shown in the characterization of cis and trans CH_3AlOCH_3 that geometry significantly affects the magnitude of the Al hfi. More specifically, a 16% increase in Al hfi was observed between the trans and cis isomers. Despite the similarity in the electron-withdrawing capability of the ligands in the cyclic and acyclic C−O insertion products, there is a 30% variation in the Al hfi; cis-CH_3AlOCH_3 and $\overline{CH_2CH_2CH_2CH_2OAl}$ have the largest Al hfi while $CH_3CH_2\overline{CHCH_2OAl}$ has the smallest. Ring strain also appears to contribute to the magnitude of the Al hfi. This is evident from the observation that the Al hfi increases from 951 to 1050 in going from the five- to the six-membered aluminaoxetane.[6] This would therefore suggest that the relatively small values observed for the four-membered metallaoxetanes must be due in large part to the ring strain.

There have been no previous reports on four-membered aluminaoxetanes. However, four-membered transition metal metallaoxetanes have been implicated as intermediates in deoxygenation of epoxides as well as in many oxygen transfer reactions involving transition metal centers.[9] Although their existence has been inferred in large part from product studies, there are a few reports providing structural information. For example, ferraoxetane,[20] $\overline{CH_2CH_2OFe}$, prepared by the cocondensation of Fe atoms and ethylene oxide was characterized by IR spectroscopy. Two mechanisms have been proposed to explain the formation of transition metal metallaoxetanes. In the first mechanism, the metal, acting as a nucleophile, attacks one of the epoxide ring carbons leading to the homolytic cleavage of a C−O bond and the formation of a radical intermediate. The intermediate undergoes cyclization to produce the metallaoxetane in a subsequent step. Alternatively, the O atom of the epoxide could coordinate with the metal resulting in the cleavage of one of the C−O bonds and the oxidative addition to the metal center. In the present study, insertion into the C_1−O and C_2−O bond is fairly equally favored, i.e., the intensity of the spectral lines are approximately the same. For the two-step mechanism proposed above, one would have expected that the Al atom would have a preference for the less hindered carbon atom (C1) leading to a greater amount of the C_1−O insertion product. Activation of C−O ring rupture by the coordination of the Al atom is reminiscent of the acid-catalyzed ring opening of asymmetric epoxides where mixtures of reaction products are obtained.

Central Feature: The spectrum generated at low temperatures is typical of that expected for an alkyl radical containing α and β hydrogens. The broadening of the outer features is characteristic of radicals possessing exchanging α hydrogens. The rapid exchange of the α-hydrogens via rotation or tunneling causes their hfi to be equivalent. The H hfi of an alkyl radical's β hydrogens ($a_{\beta H}$) is isotropic and dependent upon the dihedral angle, θ, of the C_β−H bond relative to the p_π orbital, i.e.,

$$a_{\beta H} = B_o + B \cos^2 \theta$$

where the constants B_o and B have been found to be 4 and 50 G, respectively.[21] The spectral pattern observed at low temperatures can be interpreted as resulting from the interaction of the unpaired electron with two α (C_1−H) and one β (C_2−H) hydrogens where $a_{\alpha H}(2) \approx 62$ MHz and $a_{\beta H}(1) \approx 56$ MHz. An $a_{\beta H}$ of 20 G (56 MHz) suggests that θ is ≈ 56°. The spectrum is therefore attributed to $CH_3CH_2CH(O^-)CH_2^\bullet$, the radical resulting from ring opening of the epoxide at C_1−O. The reaction of Na atoms with 1,2-epoxybutane in Ar[21] also resulted in the formation of $CH_3CH_2CH(O^-)CH_2^\bullet$. It was proposed that a Na atom transfers an electron because of its low ionization potential (5.139 ev) to the epoxide which acts as the acceptor causing the ring to open at C_1−O in an 'S_N2'-like reaction. Whereas the matrix in the Na atom reaction needs to be irradiated at $\lambda > 580$ nm, $CH_3CH_2CH(O^-)CH_2^\bullet$ forms spontaneously in the Al atom/1,2-epoxybutane reaction.

As the sample is annealed in the cavity of the spectrometer, the EPR signal for $CH_3CH_2CH(O^-)CH_2^\bullet$ decays and the spectrum becomes a septet of doublets with spacings of 39 and 11 MHz, respectively. When C2 is deuterated the doublet spacing is lost and can therefore be assigned to a_H of C_2−H. A small a_H of 11 MHz is reminiscent of that found in allyl systems. The seven lines are therefore due to six nearly equivalent hydrogens on neighboring carbons, leading us to propose 1-methallyl as the carrier of the spectrum. The magnetic parameters reported[22] for *cis*-1-methallyl are $a_{CH3} = 39$ MHz, $a_{C1-H,exo} = 40$ MHz, $a_{C2-H} = 11$ MHz, $a_{C3-H,exo} = 42$ MHz and $a_{C3-H,endo} = 38$ MHz whereas those for *trans*-1-methallyl are $a_{CH3} = 46$ MHz, $a_{C1-H,endo} = a_{C3-H,endo} = 39$ MHz, $a_{C2-H} = 11$ MHz and $a_{C3-H,exo} = 41$ MHz. Simulation of the spectra showed that although the best fit was obtained using the magnetic parameters for *cis*-1-methallyl radical the possibility of a small contribution from *trans*-1-methallyl could not be ruled out. This observation suggests that Al is capable of deoxygenation of epoxides.

Conclusions

The reaction of Al atoms and 1,2-epoxybutane resulted in the formation of the two novel four-membered aluminaoxetanes, $CH_3CH_2\overline{CHCH_2AlO}$ and $CH_3CH_2\overline{CHCH_2OAl}$ from insertion of the Al atom in the C_1−O or C_2−O bond, respectively. The ratio of the aluminaoxetanes is approximately 1:1. The two mechanisms by which this could occur are (a) the Al attacks one of the epoxide ring carbons leading to the homolytic cleavage of a C−O bond and the formation of a radical intermediate. The intermediate undergoes cyclization to produce the aluminaoxetane in a subsequent step; or (b) the O atom of the epoxide coordinates Al resulting in the cleavage of one of the C−O bonds and oxidative addition to the metal center.

Confirmation of the identity of the aluminaoxetanes required the preparation and EPR characterization of the deuterated analogues, $CH_3CH_2\overline{CDCH_2AlO}$, $CH_3CH_2\overline{CHCD_2AlO}$, $CH_3CH_2\overline{CDCH_2OAl}$, and $CH_3CH_2\overline{CHCD_2OAl}$. The Al hfi values extracted from the EPR spectra of $CH_3CH_2\overline{CHCH_2AlO}$, and $CH_3CH_2\overline{CHCH_2OAl}$ are smaller than those determined for acyclic C−O insertion products. This suggests that ring strain has a large effect on the magnitude of the Al hfi.

Along with the aluminaoxetanes, there is EPR evidence that $CH_3CH_2CH(O^-)CH_2^\bullet$ forms spontaneously in the Al atom/1,2-epoxybutane reaction. As the sample is annealed in the cavity of the spectrometer, a radical with magnetic parameters similar to those of *cis*-methallyl appears indicating that Al atoms are capable of contributing to the deoxygentation of epoxides.

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