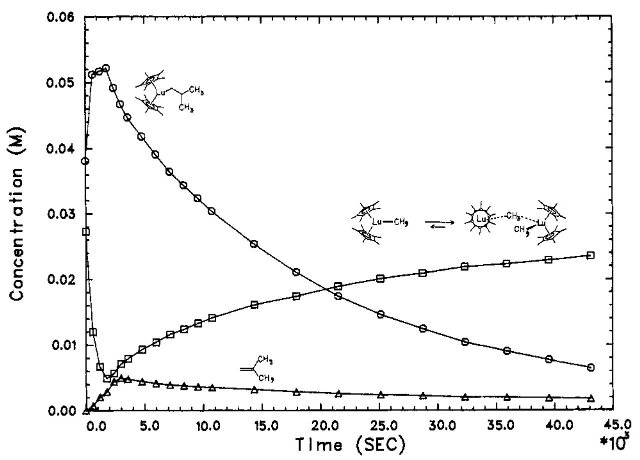

Figure 1. Lutetium–isobutyl rearrangement and decomposition: Time-dependent concentration of three species observed during decay of **1** at 22 °C in C_6D_{12}. In situ preparation of **1** was from **3** and propene in equimolar amounts. Lines drawn merely connect experimental points and are not calculated profiles. All species were monitored by 360-MHz ^{1}H NMR over a 12-h period.

rapidly with propene to give C_3 and C_6 lutetium–alkyl species. Isobutylene is observable since it is too sterically hindered to undergo insertion reactions into the lutetium–carbon bonds of **3** or **1**.

To account for the final allyl products **5** and **6**, we postulate the intermediacy[17] of $\overline{\mathrm{Lu}(\eta^5\text{-}C_5Me_5)\eta^5\text{-}C_5Me_4CH_2}$ (**4**), which reacts with olefins generated by β-alkyl and β-hydrogen elimination. Alternative pathways, such as direct reaction of **1** via vinylic C–H bond activation (eq 11) or reaction of **1** and olefin

$$\mathbf{1} + CH_2{=}CH(CH_3) \rightarrow \mathbf{5} + C_4H_{10} \qquad (11)$$

$$\mathbf{2} + CH_2{=}CH(CH_3) \rightleftharpoons \mathbf{5} + H_2 \qquad (12)$$

$$\mathbf{1} + H_2 \rightarrow \mathbf{2} + C_4H_{10} \qquad (13)$$

via the hydride (eq 12–13)[18] are vitiated as major pathways by isotopic analysis of isobutane formed from $Lu(\eta^5\text{-}C_5Me_5)_2CD_2CD(CD_3)(CH_3)$ in cyclohexane-d_{12}. Primarily $C_4D_6H_4$ was produced, indicating that neither vinylic C–H bonds nor solvent were the major direct source of reducing hydrogen. Further clarification of this process is necessary.

β-Alkyl transfer is evidenced by the formation of **3** during decomposition of all three β-methyl complexes, **1**, **7**, and **8**. Additionaly, the complex $Lu(\eta^5\text{-}C_5Me_5)_2CD_2CD(CD_3)(CH_3)$ produced both $LuCD_3$ and $LuCH_3$ species as shown by hydrolysis, which gave the methanes CD_3H and CH_4 (approximately equal amounts). We propose a concerted four-center transition state for the β-alkyl transfer reaction. Radical processes are not considered reasonable since the microscopic reverse, olefin insertion into the Lu–C bond, is a concerted addition.[19]

Data for the changes in concentration of three principal solution species are illustrated in Figure 1.[15] The rate constants k_{-1}, k_{-2}, and k_{-7} (see scheme) were determined independently[16] while the others have been estimated to provide a consistent fit with observed data. Although further refinement is necessary, it is clear that β-hydrogen and β-alkyl elimination reactions have rate constants of $\sim 5 \times 10^{-5}$ and $\sim 1.5 \times 10^{-4}$ s^{-1}. The equilibrium constant for eq 1 is thus $\approx 10^{-3}$ and for eq 2 is $\approx 10^{-5}$. Work is in progress to provide independent experimental evdience for rate constants k_1 and k_2.

In conclusion, we have detailed a number of important reactions and products observed during decomposition of lutetium–alkyl species. We expect such chemistry to show generality for the lanthanide elements and early transition metals. A critical and interesting feature of the lutetium–isobutyl decomposition is that although β-hydrogen and β-alkyl elimination are energetically accessible reactions, they are readily observable only when coupled to processes that remove olefin from the system. We are currently investigating the generality of the intriguing β-alkyl transfer reaction.

Acknowledgment. The excellent technical assistance of R. Swiatek is gratefully acknowledged. Comments from Drs. F. N. Tebbe and J. E. Bercaw are also most appreciated.

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[17] We have no direct evidence for this structure at the present time. The structure suggested is akin to bercaw's zirconium "tuck-in" intermediates: Bercaw, J. E. *Adv. Chem. Ser.* **1978**, *No. 167*, 136–148.

[18] It should be noted that reactions analogous to eq 12 and 13, but with propene replaced by aromatics such as benzene or toluene, are rapid at 22 °C. Thus, $Lu(\eta^5\text{-}C_5Me_5)_2H$ is a true catalyst for the conversion of $Lu(\eta^5\text{-}C_5Me_5)_2R$ (R = alkyl) to $Lu(\eta^5\text{-}C_5Me_5)_2C_6H_5$ in benzene solution, via the hydrogenolysis mechanism: Watson, P. L., these results will be published in detail later.

[19] Addition of 1,2-*cis*-propene-d_2 to **1** initially gives only one diastereomer of labeled **7**. These results will be reported fully elsewhere.

Limits on the Activation Parameters for Automerization of Cyclobutadiene-*1,2*-d_2

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Received August 26, 1982

In this communication we report temperature and concentration dependence studies on the trapping of vicinally dideuterated cyclobutadiene in dichloromethane solution. The results allow limits to be placed on the activation parameters for automerization of cyclobutadiene.

The source of cyclobutadiene-d_2 was the azo compound **1**, whose preparation we have described previously.[1]

If one assumes that decomposition of **1** produces only one isomer of the labeled cyclobutadiene (depicted to be cyclobutadiene-*1,4*-d_2 in Figure 1, although we have no evidence on this point) then the ratio of S:U products should be given by

$$[S]/[U] = 1 + k_2[A]/k_1$$

where the products that are symmetrically labeled with respect to the bicyclo[2.2.0]hexene skeleton are designated S and those that are unsymmetrically labeled are designated U (see Figure 1). A is the alkene trapping reagent (methyl (*Z*)-3-cyanoacrylate).

To test this hypothesis, we investigated the concentration dependence of the S:U ratio at −9 °C. The products were converted to iodolactones and analyzed by ^{1}H NMR as described previously.[1] Figure 2 shows the graph of ([S]/[U]) − 1 vs. [A]. We take the linearity of this plot ($r^2 = 0.9987$) to be good support for the hypothesis.[2]

The next step of the investigation was to determine how the ratio k_2/k_1 varied with temperature. This was achieved by nonlinear least-squares[3] optimization of the parameters $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ in the equation

$$[S]/[U] = 1 + [A]\exp(\Delta\Delta H^{\ddagger}/RT - \Delta\Delta S^{\ddagger}/R)$$

$\Delta\Delta H^{\ddagger}$ is defined as $\Delta H^{\ddagger}{}_1 - \Delta H^{\ddagger}{}_2$ (i.e., $\Delta H^{\ddagger}$(automerization) − $\Delta H^{\ddagger}$(trapping)). $\Delta\Delta S^{\ddagger}$ is defined similarly. For display purposes only, Figure 3 shows a plot of ln (k_2/k_1), vs. $10^3/T$, which should be linear.

Measurements were made at −9 °C (four concentrations), −17 °C (three concentrations), −40 °C (one concentration), and −50

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[1] Whitman, D. W.; Carpenter, B. K. *J. Am. Chem. Soc.* **1980**, *102*, 4272–4274.

[2] The gradient of this line gives k_2/k_1. The result (0.35 ± 0.01 L/mol) is smaller than that estimated from our previous work.[1] This presumably is caused by the change in solvent from Me_2SO to dichloromethane.

[3] Wentworth, W. E. *J. Chem. Educ.* **1965**, *42*, 96–103.

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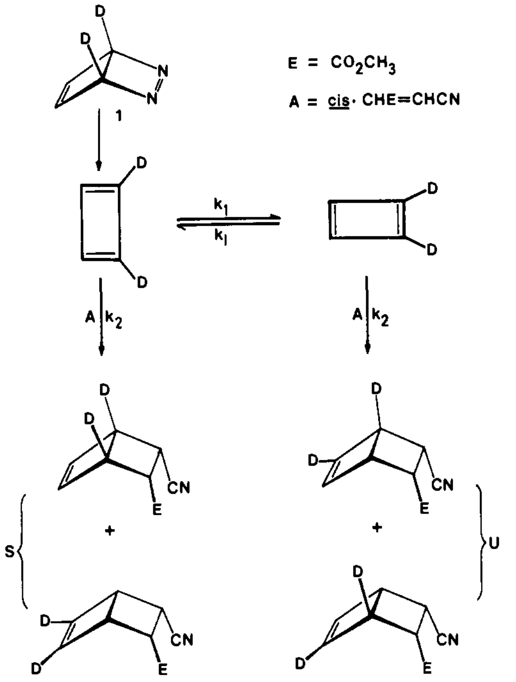

Figure 1. Generation and trapping of cyclobutadiene-*1,2*-d_2 and -*1,4*-d_2.

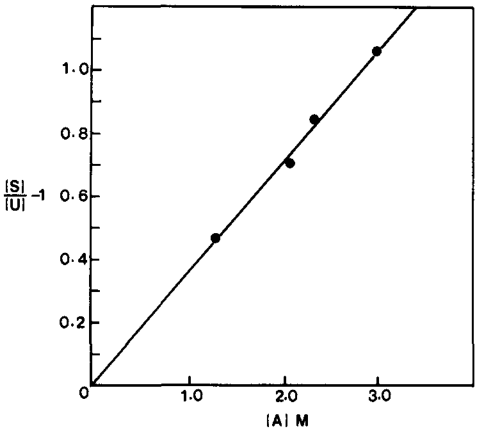

Figure 2. Dependence of the ratio [S]/[U] on the concentration of methyl (*Z*)-3-cyanoacrylate (A).

°C (three concentrations). As can be seen from the graph, the −40 °C point ($10^3/T = 4.29$) does not fit very well. If it is included in the nonlinear least-squares optimization, the results are

$$\Delta\Delta H^{\ddagger} = 1.41 \pm 0.68 \text{ kcal/mol}$$

$$\Delta\Delta S^{\ddagger} = 7.5 \pm 2.8 \text{ cal/(mol K)}$$

If it is excluded, the results are

$$\Delta\Delta H^{\ddagger} = 1.61 \pm 0.07 \text{ kcal/mol}$$

$$\Delta\Delta S^{\ddagger} = 8.2 \pm 0.3 \text{ cal/(mol K)}$$

The reduction in standard deviations by a factor of ≈10 upon exclusion of the −40 °C point leads us to prefer the second set of results, although the differences in value for the parameters are not large. The entropy differences are defined with respect to a standard state of 1 M.

Since the lower limit for $\Delta H^{\ddagger}_2$ is presumably 0, *the lower limit for* $\Delta H^{\ddagger}_1$ *is 1.6 kcal/mol.* A plausible, but less rigorous, upper limit of 10 kcal/mol for $\Delta H^{\ddagger}_1$ can be deduced if one assumes that the enthalpy of activation for the trapping reaction is less than that for the Diels–Alder reaction of cyclopentadiene with benzoquinone ($\Delta H^{\ddagger} = 8.3$ kcal/mol in CCl_4).[4] The most recent calculations[5] estimate the potential energy difference between square and rectangular structures of singlet cyclobutadiene to be between 8.3 and 14.0 kcal/mol.

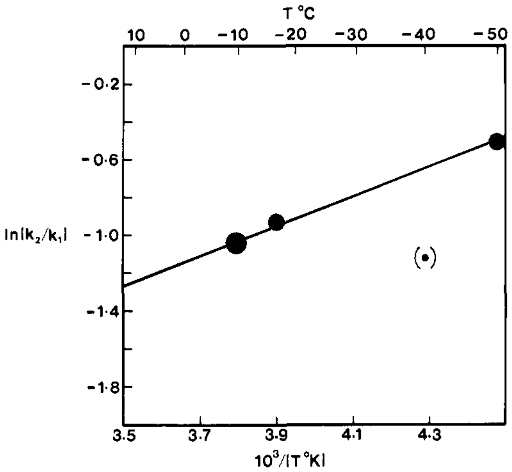

Figure 3. Temperature dependence of k_2/k_1. The diameters of the points are proportional to their statistical weights, i.e., the number of concentrations at which k_2/k_1 was determined.

By far the most surprising outcome of the present study is the small value of $\Delta\Delta S^{\ddagger}$. With respect to a standard state of 1 M, entropies of activation in the range −25 to −40 cal/(mol K) are observed for most Diels–Alder reactions.[4] If the trapping reaction in the present study had a similar entropy of activation the range for $\Delta S^{\ddagger}_1$ would be −17 to −32 cal/(mol K)! One might wonder whether the present trapping reaction could be especially exothermic, leading to a loose transition state with low-frequency vibrational modes that might make the entropy of activation less negative than normal. A simple calculation suggests that this hypothesis cannot account for the results. The statistical mechanical formula for vibrational contributions to entropy[6] shows that in order to take the entropy of activation for the trapping reaction from a typical value of −30 to a value of −8 cal/(mol K) (the latter required if one wishes $\Delta S^{\ddagger}_1 \approx 0$), the forming carbon–carbon bonds would have to have vibrational frequencies of ≈2 cm^{-1}. It is inconceivable that the transition state could be this loose while exhibiting the almost complete endo stereospecificity that we and others[7] have observed.

We have also considered the possibility that solvent ordering could lead to an apparent negative entropy of activation for the isomerization of cyclobutadiene. Again we find this explanation unpalatable. Dichloromethane is known to show only weak solvation of free carbonium ions[8] and so it is difficult to believe that a profound solvation effect of the magnitude required here could occur with a neutral hydrocarbon solute. Accordingly, we are forced to conclude that *the entropy of activation for automerization of cyclobutadiene is probably negative and possibly substantially so.* We are presently attempting to determine possible reasons for this phenomenon.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank the NSF for a fellowship to D.W.W. and for a grant (CHE-7904825) to support the 300-MHz NMR used in this work. Finally, we thank Professors B. Widom and C. F. Wilcox, Jr., for helpful discussions.

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[5] (a) Kollmar, H.; Staemmler, V. *J. Am. Chem. Soc.* **1977**, *99*, 3583–3587. (b) Borden, W. T.; Davidson, E. R.; Hart, P. *Ibid.* **1978**, *100*, 388–392. (c) Jafri, J. A.; Newton, M. D. *Ibid.* **1978**, *100*, 5012–5017. For a more complete list of theoretical results see ref 1.

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[7] Watts, L.; Fitzpatrick, J. D.; Pettit R. *J. Am. Chem. Soc.* **1966**, *88*, 623–624.

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