and Scheme I).

$$[W(\eta\text{-}C_5H_5)_2(CH_2PMe_2Ph)CH_3]PF_6 \xrightarrow[75\ °C]{12\ days} \underset{6}{[W(\eta\text{-}C_5H_5)_2(PMe_2Ph)(C_2H_5)]PF_6} \quad (4)$$

Evidence in support of the intramolecular nature of the reaction converting **1** into **2** was obtained from isotopic labeling studies. A 1:1 mixture of **1** and $[W(\eta\text{-}C_5H_5)_2(CD_3)_2]PF_6$ (**1**-d_6) was treated with 1 mol equiv of the trityl radical dimer in THF to give an 85% yield of the crude ethylene hydride cation. A 1:3 mixture of Ph_3CD and Ph_3CH, as determined by mass spectroscopy, was also recovered from the reaction mixture; the isolated alkane corresponded to an 83% recovery of the starting trityl dimer, and it is presumed that the excess $Ph_3C\cdot$ abstracts hydrogen atoms from the solvent or the walls of the vessel. The isotopic composition of the ethylene ligand was determined by deprotonation of the product in acetone with aqueous KOH and examination of the mass spectrum of the mixture of **3**-d_n complexes obtained. This indicated that the product was mainly **3**-d_0 (46%) and **3**-d_4 (42%), together with small quantities of **3**-d_1 (4%) and **3**-d_3 (8%). Since the isotopic envelope of the $[W(\eta\text{-}C_5H_5)_2]^+$ fragmentation peak indicates that no deuterium has been incorporated into the cyclopentadienyl ligands, we can assume that these figures give the isotopic composition of the ethylene ligand directly.

The observation that **3**-d_1 and **3**-d_3 were formed led us initially to question the significance of this labeling experiment, but we have been able to demonstrate that scrambling occurs after the formation of **2**. When a 1:1 mixture of **2**-d_0 and **2**-d_5 (prepared from **4**-d_6) was stirred in THF for 24 h and the cation subsequently deprotonated under the same conditions as in the labeling study, the recovered **3** was demonstrated by mass spectroscopy to contain an identical mixture of **3**-d_n species to that obtained in the labeling study. Scrambling does not occur during the deprotonation as demonstrated by deprotonation of a 1:1 mixture of **2**-d_0 and **2**-d_5 to give a 1:1 mixture of **3**-d_0 and **3**-d_4. A reasonable interpretation of these experiments involves a facile exchange of the metal-bound hydride and deuteride between **2**-d_0 and **2**-d_5 (eq 5), followed by

$$[W(\eta\text{-}C_5H_5)_2(CH_2CH_2)H]^+ + [W(\eta\text{-}C_5H_5)_2(CD_2CD_2)D]^+ \rightleftarrows [W(\eta\text{-}C_5H_5)_2(CH_2CH_2)D]^+ + [W(\eta\text{-}C_5H_5)_2(CD_2CD_2)H]^+ \quad (5)$$

an ethylene insertion/elimination sequence, probably solvent promoted, which exchanges H and D within **2**-d_1 and **2**-d_4[14] (e.g., eq 6).

$$[W(\eta\text{-}C_5H_5)_2(CD_2CD_2)H]^+ \xrightarrow{S} [W(\eta\text{-}C_5H_5)_2(S)CD_2CD_2H]^+ \xrightarrow{-S} [W(\eta\text{-}C_5H_5)_2(CD_2CDH)D]^+ \quad (6)$$

It is now clear that the particular mixture of **3**-d_n complexes obtained in the labeling experiment must imply that **2** was originally formed as a 1:1 mixture of **2**-d_0 and **2**-d_5, and we can conclude that the formation of **2** must involve an intramolecular carbon–carbon bond forming step such as the migratory insertion shown in Scheme I.

The facile intramolecular methylidene insertion in A stands in marked contrast to the intermolecular thermal decomposition of $[Ta(\eta\text{-}C_5H_5)_2(CH_2)CH_3]$ (**7**),[15] isoelectronic with A, to give $[Ta(\eta\text{-}C_5H_5)_2(C_2H_4)CH_3]$, and we suggest that this difference can be attributed to electronic differences at the unsaturated carbon center. The methylidene ligand in A is electrophilic while that in **7** is known to be nucleophilic, and the electrophilicity of the unsaturated carbon in A presumably facilitates migration of the methyl group with its bonding pair.[3] This is consistent with the recent observation of alkyl migrations in niobium–carbene complexes, closely related to **7**, in which zirconoxy substituents render the unsaturated carbons electrophilic.[16]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Exxon Educational Foundation, and the National Science Foundation (Grant CHE80-16162) for their support of this research.

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[13] ^{1}H NMR (acetone-d_6) δ 7.89–7.39 (m, 5 H, C_6H_5), 5.18 (d, J_{H-P} = 2.2 Hz, 10 H, $2C_5H_5$), 2.07 (d, J_{H-P} = 9.6 Hz, 6 H, $P(CH_3)_2$), 1.37 (t of d, J = 5.8 Hz, J_{H-P} = 1 Hz, 3 H, CH_3CH_2), 1.11 (q of d, J = 5.8 Hz, J_{H-P} = 1.5 Hz, 2 H, CH_3CH_2). Anal. Calcd for $C_{20}H_{26}P_2F_6W$: C, 38.36; H, 4.18. Found: C, 38.38; H, 4.21.

[14] This mechanism explains why 50% of the **3** formed is **3**-d_0 + **3**-d_1 and 50% is **3**-d_3 + **3**-d_4. The formation of twice as much **3**-d_3 as **3**-d_1 implies a kinetic isotope effect in the ethylene insertion reaction.

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Role of Solvent in the Mechanism of Amine Oxide Thermolysis Elucidated by the Temperature Dependence of a Kinetic Isotope Effect

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Received February 23, 1981

Thermolysis of normal sulfoxides, e.g., $C_6H_{11}CHDCH_2X$ (**1**, X = SOC_6H_5), forms terminal olefins via a cis elimination[1-3] characterized by a temperature dependence of k_H/k_D over a (at least) 100 °C temperature range.[4] In keeping with a cyclic transition state, $[\Delta E_a]_D{}^H$ was equal to the zero-point energy difference $[\Delta E_0]_D{}^H$ = 1.15 kcal/mol and A_H/A_D = 0.76, the latter value being within the range 0.75–1.2[5] established for linear H transfer. On the other hand, under nearly identical experimental conditions [diglyme solvent, a temperature range of 120 °C, and a substrate structure of **1** (X = $ONMe_2$)], isotope effect;[4] $k_H/k_D = A_H/A_D = 2.209 \pm 0.007$. These results, and a number of others previously reported,[7] comprise the supporting evidence for the postulate that in a reaction process with a single rate-determining step,[8] a bent (transition state) TS‡ involving nonlinear H transfer is characterized by a temperature independent isotope effect; i.e., $[\Delta E_a]_D^H$ approaches zero and k_H/k_D approaches A_H/A_D. In this report we wish to rationalize the temperature dependence of k_H/k_D as a criterion for identifying a bent TS‡ of H transfer and demonstrate the sensitivity of this criterion for distinguishing the changes in TS‡ structure which can attend any alteration in reaction conditions, for example, a change in the nature of the solvent.

Virtual Temperature Independence of k_H/k_D and the Unusual Magnitudes of A_H/A_D of the Bent TS‡. The representation in Figure 1 is intended to show that for linear transfer between the

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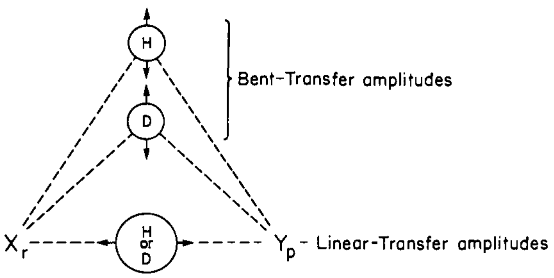


Figure 1. Comparison of critical bond vibration amplitudes in linear and bent TS‡ of H and D transfers.

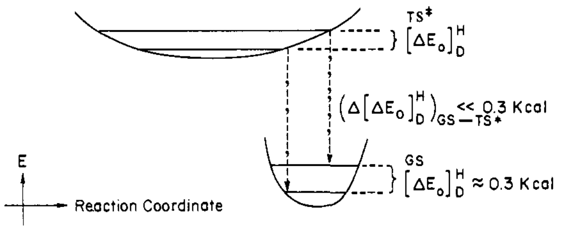


Figure 2. Illustrated overlap of the potential functions of ground and bent TS‡ of H and D transfer reactions.

reactant center X_r and the product center Y_p there is no significant difference in the corresponding amplitudes of H and D vibration, assuming that the centers X_r and Y_p are fixed by the barrier dimensions at the TS‡ and only the hydrogen or deuterium experience (stretching) vibrational motion. But, in the bent TS‡, though the potential functions for H and D motion are the same in accordance with the Born–Oppenheimer approximation,[9] there is greater amplitude of the hydrogen than the deuterium motion. The effect of this on the temperature dependence of k_H/k_D can be seen when we draw the common potential-energy diagram (as in Figure 2). The weaker restoring forces associated with the TS‡ vibrations result in an even greater amplitude for the hydrogen motion than the deuterium. For a bending motion of (say) a C–H bond, the ground-state zero-point energy difference, $([\Delta E_0]^H_D)_{gs}$, is usually less than 0.3 kcal/mol. The value of $([\Delta E_0]^H_D)_{TS^‡}$ will, of course, be diminished from the zero-point energy difference in the ground state, consistent with the reductions in the corresponding force constants as depicted by the shallow well of the TS‡, but this difference will *not* be significantly less. That is to say, therefore, that $([\Delta E_0]^H_D)_{gs} - ([\Delta E_0]^H_D)_{TS^‡}$ *will be* considerably less than 0.3 kcal. This conclusion is well correlated with a number of experimental observations that in reactions with a bent TS‡, $[\Delta E_a]^H_D$ is less than 0.1 kcal, i.e., is virtually temperature independent.

The second point this analysis must explain is why the magnitude of A_H/A_D in the bent TS‡ is greater than the $A_H/A_D \leq 1.2$ established for the linear TS‡. The increased amplitude of the H vs. the D motion in the bent TS‡, but not in the linear H transfer, implies a more spread-out *wave function*. This, in turn, should have a significantly larger degree of overlap with the ground-state function than does the corresponding deuterium. The vertical dotted lines in Figure 2 are intended to convey this distinction in the degree of overlap of the respective wave functions resulting from differences in vibrational amplitude in the TS‡ of nonlinear transfer. Even though the difference in the internal energy change for corresponding H and D bonds on going to a nonlinear transfer TS‡ approaches zero, the larger extent of overlap (of the H wave functions) between the ground and transition state implies a faster rate for the H-transfer than for the D-transfer process. This rate difference must have its origin in the entropy component of the activation energy, i.e., in the A_H/A_D term as found experimentally.

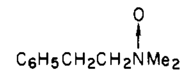
Table I. Temperature Dependence of the Kinetic Deuterium Isotope Effect in Thermolysis[a] of 1 (X = $ONMe_2$) in Dimethyl Sulfoxide (Me_2SO) Solution

temp, °C	k_H/k_D[b]	temp, °C	k_H/k_D[b]
170.0 ± 0.1	2.517	130.0 ± 0.1	2.720
160.0 ± 0.1	2.561	120.0 ± 0.1	2.778
139.9 ± 0.1	2.665	100.0 ± 0.1	2.919

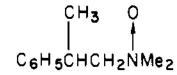
calcd quantities: $[E_a]^H_D = 0.695$ kcal/mol, $A_H/A_D = 1.14$, correlation coeff = 0.9999

[a] In a typical run 150 mL of dry Me_2SO was brought to the stipulated reaction temperature in a Pyrex pressure vessel secured in an inert atmosphere by means of an inert, elastomer stopple. After temperature control had been established, a sample of ~100 mg of substrate was rapidly injected through the stopple and beneath the surface of the swirling, thermostatted Me_2SO. This procedure was devised to assure against any but a negligible temperature change on introduction of the reactant as well as the absence of a heating-up period during which reaction could take place at lower than the stipulated temperature. After a predetermined period of reaction required to effect almost complete conversion to product, the Me_2SO solution was cooled, a large excess of water was added along with a small amount of pentane, and the olefin products recovered by (steam) distillation of a few milliliters of the mixture. The product was freed of the pentane residue by passage through a GLC column and trapping in a capillary at −78 °C. The efficiency of recovery of reaction product in this way was >95%. Capillaries containing the product were adapted for application in the mass spectroscopic analysis method[17] used. [b] Measured from samples composed of the reaction product proportions of $C_6H_{11}CH{=}CH_2$ and $C_6H_{11}CD{=}CH_2$, analyzed by the high precision mass spectroscopic technique previously developed and applied in these laboratories.[17]

This model rationalization has proven to be a valuable guide in our studies of various thermolysis reactions. Almost simultaneously with our earlier report[4] on amine oxide thermolysis in diglyme, Chaio and Saunders,[10] studying k_H/k_D of the amine oxides **2** and **3**, reached the same conclusion regarding the bent


$C_6H_5CH_2CH_2\overset{O}{\overset{\uparrow}{N}}Me_2$

2


$C_6H_5\overset{CH_3}{\overset{|}{C}}HCH_2\overset{O}{\overset{\uparrow}{N}}Me_2$

3

structures of the TS‡ in amine oxide thermolysis but based their conclusion on the size of the isotope effect ($k_H/k_D \simeq 2$–3) in a solution of Me_2SO (and water or butanol as cosolvent) rather than on the temperature dependent characteristic[11] of k_H/k_D. In fact, these authors reported[8] isotope effect parameters of $[\Delta\Delta H^‡]_D{}^H \simeq 0.3$–1.6 kcal/mol and $[\Delta\Delta S^‡]_D{}^H$ ranging from nearly 0 to 3 eu, with an error probability of up to 5 eu. On the assumption that the differences in our results was somehow due to the change of solvent to Me_2SO, which is known[12] to accelerate the amine oxide (and sulfoxide) thermolysis, it was considered to be possible that complexing of the substrate by the Me_2SO had altered the geometry of H transfer. We therefore undertook to repeat our studies of the amine oxide **1** (X = $ONMe_2$) by using the "faster" Me_2SO solvent composition, having in mind that a high precision determination of k_H/k_D could be a sensitive indicator of such a change of mechanism induced by the use of high dielectric, aprotic solvents.

It is recognized[13] that maximum accuracy is associated with competition methods of k_H/k_D determination in preference to the direct rate measurement approach used by Chiao and Saunders,[10] particularly over a wide range of reaction rates and temperatures, as demonstrated previously.[4] The α-deuterated amine oxide (**1**

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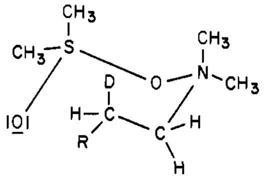
(13) For a full discussion of these methods and other aspects of the temperature dependence of the isotope effect, see: Melander, L.; Saunders, W. H., Jr. "Reaction Rates of Isotopic Molecules"; Wiley: New York, 1980.

X = $ONMe_2$), containing approximately 1.6 mol of H_2O per mole of **1**, was run in dilute Me_2SO solution at each of six temperatures over a 70 °C temperature interval. The data gathered in Table I clearly show a regular variation of k_H/k_D with temperature, in distinction to the temperature invariant values realized in the earlier studies[5] in diglyme solvent. The activation parameters calculated[11a,14] from these data, $[\Delta E_a]_D{}^H = 0.695$ kcal/mol and $A_H/A_D = 1.14$, reflect the fact that the change to the coordinating solvent Me_2SO has indeed effected a change in the transition-state structure. Under these altered circumstances, the H transfer takes place linearly between carbon and oxyanion centers of the solvent-coordinated substrate. An attractive representation of this, shown in **4**, would suggest that 1 mol of Me_2SO has coordinated the oxyanion center of the original amine oxide **1** (X = $ONMe_2$) and thereby created a seven-membered cyclic arrangement which makes possible the geometry required for linear H transfer. One possible $TS^{\ddagger}$ conformation is the chair shown as **4a**, wherein the greater length of the S–O bonds has served to accommodate the reaction barrier width, i.e., the distance of separation of the centers between which H transfer must occur in the $TS^{\ddagger}$, which permits linear H transfer without tunneling.



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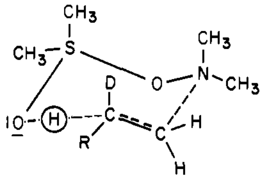

4a

The fact that $[\Delta E_a]_D{}^H$ is little more than half as great as the zero-point energy difference, $[\Delta E_0]_D{}^H$, is in keeping with the premise that the Me_2SO-coordinated reaction is not a pericyclic process[14] as was identified for the thermolysis of sulfoxides;[5] nor is it a pseudopericyclic reaction[15] similar to that proposed for the uncoordinated amine oxide in diglyme solvent. We have here, instead, an example of an unsymmetrical $TS^{\ddagger}$, i.e., a product-like or reactant-like $TS^{\ddagger}$ of linear H transfer,[16] probably the former in view of the extraordinary capability of Me_2SO for stabilization of the anionic character developing in accompaniment to the proton transfer.

Finally, these results make it clear that the lower activation energy observed for sulfoxide and amine oxide thermolysis in Me_2SO compared to inert, noncoordinating solvents is due to a change in mechanism, rather than to the mere sequestering of water as has been alleged.[6]

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(16) For a full discussion, see: (a) Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265. (b) Bigeleisen, J. *Pure Appl. Chem.* **1964**, *8*, 217.

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Additions and Corrections

Isolation and Characterization of the First Host Recognition Substance for Parasitic Angiosperms [*J. Am. Chem. Soc.* **1981**, *103*, 1868–1870]. DAVID G. LYNN,* JOHN C. STEFFENS, VINAYAK S. KAMAT, DAVID W. GRADEN, JEFFREY SHABANOWITZ, and JAMES L. RIOPEL,* Departments of Chemistry and Biology, University of Virginia, Charlottesville, Virginia 22901.

The third author's name should read Vinayak S. Kamat (not Kamut).

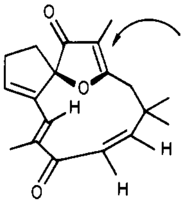
Competitive Condensation and Proton-Transfer Processes in the Reaction of *t*-$C_4H_9{}^+$ Ions with Ammonia in Gaseous Systems at Atmospheric Pressure [*J. Am. Chem. Soc.* **1980**, *102*, 6896–6898]. M. ATTINÀ, FULVIO CACACE,* P. GIACOMELLO, and M. SPERANZA, University of Rome, 00100 Rome, Italy, and Istituto di Chimica Nucleare del C.N.R., 00016 Monterotondo Stazione, Rome, Italy

Page 6897, lines 18 and 31, right column: In both lines 2-butene should be isobutene.

A Strategy for the Total Synthesis of Jatrophone: Synthesis of Normethyljatrophone [*J. Am. Chem. Soc.*, **1981**, *103*, 219]. A. B. SMITH, III,* M. A. GUACIARO, S. R. SCHOW, P. M. WOVKULICH, B. H. TODER, and T. W. HALL, The Department of Chemistry, The Laboratory for Research on the Structure of Matter and the Monell Chemical Senses Center, The University of Pennsylvania, Philadelphia, Pennsylvania 19104

In the note added in proof the minus sign was inadvertently deleted by the production editor from both jatrophone and epijatrophone. It should read: Since acceptance of the manuscript, we have successfully completed the first stereocontrolled total synthesis of both (±)-jatrophone (**1**) and that of its epimer (±)-epijatrophone, exploiting the synthetic strategy outlined above; **5a** its epimer served, respectively, as starting materials. A complete account of this effort will be forthcoming in the near future.

In ref 15 the 3(2*H*)-furanone ring of structure **15** should contain a double bond as indicated below.



15

Interaction of Pyruvate–Thiamin Diphosphate Adducts with Pyruvate Decarboxylase. Catalysis through "Closed" Transition States [*J. Am. Chem. Soc.* **1981**, *103*, 1214–1216]. RONALD KLUGER* and TIMOTHY SMYTH, Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1

The Michaelis–Menten expression on p 1216 should read: $1/v = (K_m/V_{max})(1/s) + 1/V_{max}$. K_m is $[k_3(k_{-1} + k_2)]/k_1k_2$. If $k_2 \gg k_{-1}$, $K_m = k_3/k_1$.

The discussion and analysis that follow were based on the *correct* equations (K_m inversely proportional to k_1).