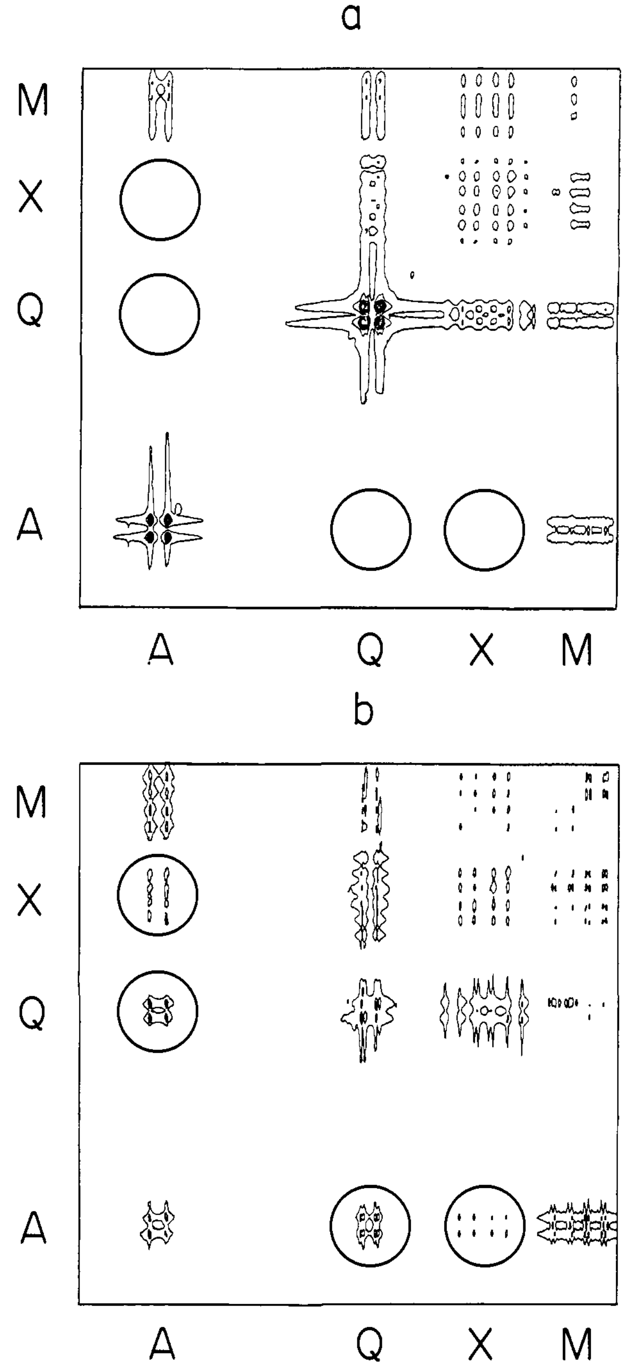

Figure 1. Two-dimensional proton spectra of crotonaldehyde (I) in the isotropic phase (50% acetone-d_6), obtained with a home-built 90-MHz spectrometer: (a) conventional 2-D correlation map, showing the absence of connectivity between the aldehyde proton, the methyl group, and the trans proton (empty circles); (b) relayed correlation map obtained with two consecutive magnetization transfer steps, showing that all resonances belong to the same coupling network. Resonances A and Q appear folded, as the spectral width has been set to 250 Hz in both dimensions. The delay τ equals 32 ms; free-induction decays were recorded for 256 t_1 values.

backbone of the molecule by assigning neighboring carbon sites.[12]

Acknowledgment. We are indebted to M. Linder for valuable assistance and to L. Braunschweiler and O. Sørensen for helpful discussions. This research has been supported in part by the Swiss National Science Foundation.

Registry No. (*E*)-I, 123-73-9.

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Potential-Energy Surface of the S_N2 Reaction in Hydrated Clusters

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Received February 16, 1982

The S_N2 nucleophilic substitution reaction is one of the most extensively studied chemical reactions in solution.[1] Recent studies have revealed that the reaction proceeds up to 20 orders of magnitude faster in the gas phase than in solution.[2] The gap between the gas phase and the solution rate has recently been filled somewhat by a study in hydrated cluster. Bohme and Mackay have found[3] that the rate constant of the reaction

$$OH^-(H_2O)_n + CH_3Br \rightarrow Br^-(H_2O)_n + CH_3OH \qquad (1)$$

decreases gradually from $n = 0$ to $n = 3$. This change has been interpreted in terms of the qualitative potential energy profile proposed by Brauman et al.;[2b,c] the reaction proceeds via a three-step mechanism: the formation of a stable complex $OH^-(H_2O)_n\cdots H_3CBr$ without an activation barrier, the subsquent isomerization of the complex to $HOCH_3\cdots Br^-(H_2O)_n$ with an activation barrier, and the final dissociation of the complex. As the nucleophile is hydrated more, the complex becomes less stable and the overall barrier higher.

In the present paper we present the results of ab initio SCF calculations of potential-energy surfaces for a similar S_N2 reaction:

$$Cl^-(H_2O)_n + CH_3Cl \rightarrow ClCH_3 + Cl^-(H_2O)_n \qquad (2)$$

for $n = 0$ (unhydrated), 1, and 2. Relevant equilibrium and transition-state geometries and energies have been determined with the energy gradient method[4] with the 3-21G basis set.[5] The potential-energy profiles and the geometries of some important species are shown in Figures 1 and 2, respectively. We find that for $n = 1$ the H_2O migration and CH_3 transfer-inversion occurs either sequentially or simultaneously. For $n = 2$, the initial sequential or simultaneous H_2O migration and CH_3 transfer-inversion followed by the migration of the other H_2O is the most favorable path of reaction.

In the reaction of an unhydrated chloride, Cl^- at first forms the complex **1** with CH_3Cl at the H_3 end and then climbs a barrier to reach the transition state **2** of the CH_3 transfer-inversion,[5a] consistent with previous ab initio calculations for various S_N2 reactions.[6]

In the reaction of the complex **4** of the hydrated Cl^- **3**, we find two reaction paths at a comparable energy, in one the H_2O migration and the CH_3 tranfer-inversion taking place sequentially and in the other simultaneously. The sequential path climbs over the transition state **5** of the CH_3 transfer to form a complex **6**,

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(1) (a) Ingold, C. K. "Structure and Mechanism in Organic Chemistry", 2nd ed.; Cornell University Press: Ithaca, NY, 1969. (b) Hartshorn, S. R. "Aliphalic Nucleophilic Substitution"; Cambridge University Press: London, 1973. (c) Parker, A. J. *Chem. Rev.* **1969**, *69*, 1.

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(4) (a) Komornicki, A.; Ishida, K.; Morokuma, K.; Ditchfield, R.; Conrad, M. *Chem. Phys. Lett.* **1977**, *45*, 595. (b) Morokuma, K.; Kato, S.; Kitaura, K.; Ohmine, I.; Sakai, S.; Obara, S. IMS Computer Center Library Program, No. 0372, 1980. (c) Pulay, P. In "Applications of Electronic Structure Theory"; Schaefer, H. F., Ed.; Plenum: New York, 1977; Chapter 7.

(5) (a) A diffuse *p* basis function, added to better describe an anion, decreases the complex stability but does not change the general features of potential surface profiles. (b) Complexes **6** and **12** are local minima. Because the potential surfaces are rather flat near **6** and **12**, the transition states, **7** and **11**, could not be precisely determined. Therefore, the paths connecting **6** to **4** and **12** to **10** are traced by fixing the ClCO angle at various values and optimizing all the other coordinates. Geometry **11′** of Figure 2 is one of such geometries.

(6) (a) Wolfe, S.; Mitchell, D. J.; Schlegel, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7692, 7694. (b) Talaty, E. R.; Woods, J. J.; Simons, G. *Aust. J. Chem.* **1979**, *32*, 2289. (c) Keil, F.; Ahlrichs, R. *J. Am. Chem. Soc.* **1976**, *98*, 4787. (d) Bader, R. F. W.; Duke, A. J.; Messer, R. R. *Ibid.* **1973**, *95*, 7715. (e) Dediu, A.; Veillard, A. *Ibid.* **1972**, *94*, 6730.

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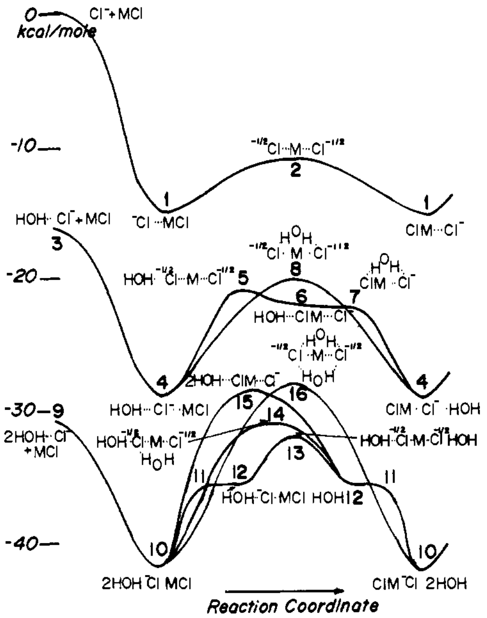

Figure 1. Profiles of the potential-energy surfaces. The energy is relative to isolated molecules and ions.

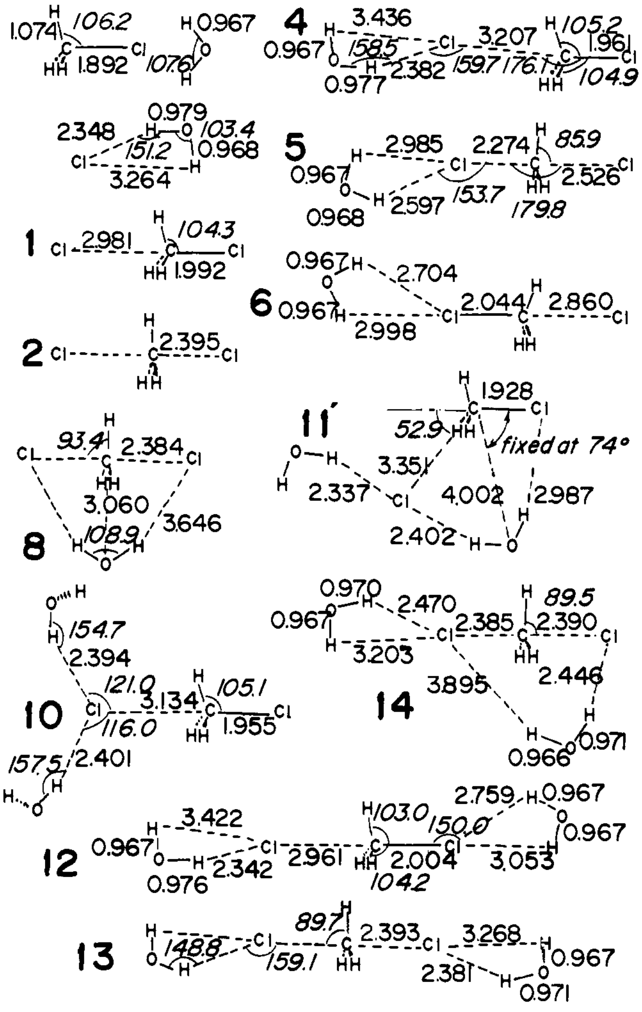

Figure 2. Optimized geometries of some important species.

from which H_2O migrates with little or no barrier 7^{5b} to give the product **4**. Because of the symmetry of the system, the reverse sequence, **4** → **7** → **6** → **5** → **4**, namely H_2O migration followed by the CH_3 transfer (not shown in Figure 1 for clarity) is of course equally feasible. The simultaneous path leads directly to the symmetric transition state **8**. The energy difference between the two barriers is too small for the present level of calculation to exclude either possibility. Both barriers are higher than the barrier **2** without hydration.

In the reaction of the complex **10** with a dihydrated chloride **9**, two H_2O migrations and a CH_3 transfer-inversion can take place one by one, two by one, or all three simultaneously. We find that the most favorable path is the initial migration of one H_2O with little or no barrier $(\mathbf{11})^{5b}$ to form the intermediate complex **12**, followed by the CH_3 inversion through the transition state **13** and the final migration **12** → **11** → **10** of the other H_2O molecule. The first H_2O migration ensures that Cl^- is hydrated throughout the reaction and keeps the potential energy low. The initial simultaneous H_2O migration–CH_3 inversion, **10** → **14** → **12**, has a slightly larger barrier but cannot be excluded. The overall barriers **13** and **14** for $n = 2$ are higher in energy than the corresponding barriers for $n = 1$, which in turn is higher than the barrier for $n = 0$.

One notes that H_2O migrations, **6** → **7** → **4** and **12** → **11** → **10**, proceed with little or no barrier. The geometry of **11′** in Figure 2,[5b] which is on the path connecting **12** and **10**, reveals an important role of Cl^- in the H_2O migration; Cl^- moves away from the C_{3v} axis to accompany the migrating H_2O until H_2O is delivered to the opposite Cl atom, and then it flips back onto the C_{3v} axis. This close association of Cl^- keeps the potential energy low for the process.

From the above results, we can suggest even for larger clusters that the first and the last steps are the H_2O migration possibility simultaneously with the CH_3 inversion. When n is large and the first solvation shell of halide is completed, the initial interaction involves dehydration and a new feature of the potential surface is expected to appear.

Further studies are in progress and will be published elsewhere.[7]

Acknowledgment. I am grateful to Drs. S. Kato, K. Kitaura, and S. Obara for much advice and discussion. Numerical calculations have been carried out at the IMS Computer Center.

Registry No. Cl^-, 16887-00-6; CH_3Cl, 74-87-3; H_2O, 7732-18-5.

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(7) Morokuma, K., to be submitted for publication.

Intramolecular Carbocyclic [3 + 2] Cycloaddition via Organopalladium Intermediates

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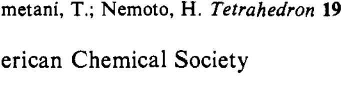
Received December 14, 1981

The intramolecular Diels–Alder reaction offers a powerful solution to many problems in complex natural products synthesis.[1] Converting olefin geometry into the stereochemistry of saturated carbon combined with forming two rings simultaneously from acyclic precursors accounts for the popularity of this approach. With the increasing importance of cyclopentanoid natural products, an intramolecular cycloaddition-like process that focuses on five-membered ring formation would complement the Diels–Alder reaction in some cases (e.g., toward perhydroindanes) and offer a unique approach in other cases (e.g., toward pentalenes, hirsutanes, etc.). As in eq 1 diyls generated from azo precursors



(1)

represent such an approach.[2,3] We wished to examine an approach

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(1) For recent reviews see: Brieger, G.; Bennett, J. N. *Chem. Rev.* **1980**, *80*, 63. Kametani, T.; Nemoto, H. *Tetrahedron* **1981**, *37*, 3.

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