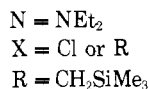


II



The relative concentration of g-I at $t = 22$ min, $[g-I]/[a-I] \approx 0.25$, is ca. 10% larger than that expected from isomerization of the initially formed a-I. The presence of significant⁹ concentrations of *gauche*-W₂Cl₂(NEt₂)₄ in equilibrium with *anti*-W₂Cl₂(NEt₂)₄, or anti to *gauche* isomerization of an intermediate such as W₂Cl(CH₂SiMe₃)(NEt₂)₄, could contribute to the formation of g-I.

The above, together with previous findings,⁷ indicate that compounds containing metal-to-metal triple bonds may be systematically synthesized by metathetic reactions involving compounds already containing metal-to-metal triple bonds. Moreover, in the present study the stereochemical course of the substitution reaction leading to I implies that cleavage of the tungsten-to-tungsten bond does *not* occur during the alkyl-for-chlorine exchange process. It seems likely that reactions analogous to that reported here are responsible for the ultimate formation of the dinuclear compounds M₂L₆ (M = Mo or W, L = CH₂SiMe₃ or NR₂) from metathetic reactions involving molybdenum and tungsten halides.

The mechanism of isomerization reactions of type 1 is currently under investigation.¹⁰

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$$\text{Re}_2\text{Cl}_8^{2-} \xrightarrow[\text{CH}_3\text{CN}]{h\nu} 2\text{ReCl}_4(\text{CH}_3\text{CN})_2^-$$
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- (8) Standard techniques for the manipulation of air-sensitive compounds were used at all times. D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
- (9) If a *g* ⇌ *a* isomerization were facile for W₂Cl₂(NEt₂)₄ and the *gauche* rotamer were kinetically more labile to substitution than the *anti* rotamer, then significant concentrations of g-I would be formed initially.
- (10) We thank Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant No. MPS 73-05016) for their support of this work.

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Reaction Ergodography. Methane-Tritium Reaction

Sir:

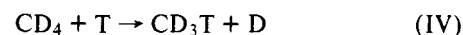
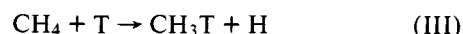
Detailed description of chemical reactions has long been one of the goals of theoretical chemistry. Since chemical reactions are usually attended with much complexity in the modes of nuclear rearrangements corresponding to the change of the reacting system from initial to final, the concept of the reaction coordinate has been conveniently utilized to abstract the essential feature for the rationalization of chemical reactions. Many theoretical attempts have been made to determine the reaction coordinate or the minimum energy path of various types of chemical reactions with the aid of semiempirical and ab initio molecular orbital procedures.¹ The only difficulty in this direction of research is the multidimensionality of the potential-energy surfaces. In this connection, a proposal was made previously about the theoretical formulation of the reaction coordinate and it is named the intrinsic reaction coordinate.² Such a theoretical formulation of the reaction coordinate enables a theoretical tracing of the change of geometry of the reacting system along the reaction path, which was called reaction ergodography.³ Also an analysis was made on the potential-energy gradient on the reaction coordinate to discuss the favorableness or the unfavorableness of a given reaction path in relation to the mode of interaction between two reacting species.⁴

Another utility of the reaction coordinate is demonstrated in the description of the reactive collision process. Marcus⁵ defined the natural collision coordinate in the three-body reactive scattering. In order to treat the dynamics of a polyatomic system, a more generalized definition of the reaction coordinate is required. The intrinsic reaction coordinate is suitable for such a purpose.

In this communication, we illustrate the intrinsic reaction coordinate of the methane-tritium reaction system and its isotopic analogy.⁶ Both the abstraction,



and the substitution,



were examined.

Since the formulation of the intrinsic reaction coordinate was given previously,²⁻⁴ we give a brief description here. Consider a reacting system composed of N atoms, the reaction coordinate is defined in terms of the gradient of the potential-energy function, $W(\xi_1, \xi_2, \dots, \xi_f)$, in which ξ_i is the independent internal coordinate such as the bond length or the bond angle, and f is the number of the internal degrees of freedom. At a nonequilibrium point on the reaction coordinate, the direction of the displacement vector along the reaction coordinate is defined as

$$\frac{\sum_{j=1}^f g_{ij}(\xi) d\xi_j}{\partial W / \partial \xi_i} = \text{constant} \quad (i = 1, 2, \dots, f) \quad (1)$$

and

$$g_{ij}(\xi) = \sum_{k=1}^{3N} \frac{\partial x_k}{\partial \xi_i} \frac{\partial x_k}{\partial \xi_j}$$

where x_k is the mass-weighted Cartesian coordinate which represents the position of an atom in the configuration space. Equation 1 can be rewritten with the mass-weighted Cartesian coordinates as follows,

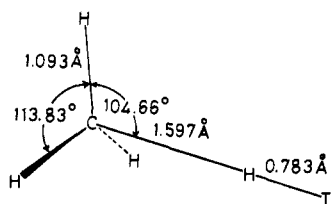


Figure 1. The geometry of the transition state for the abstraction mode.

$$\frac{dx_i}{dS} = \frac{\partial W / \partial x_i}{dW/dS} \quad (i = 1, 2, \dots, 3N) \quad (2)$$

and

$$\frac{dW}{dS} = \pm \sqrt{\sum_{k=1}^{3N} \left(\frac{\partial W}{\partial x_k} \right)^2} \quad (3)$$

In eq 2, S means the length measured along the reaction coordinate. The sign of eq 3 is adopted to be plus for the ascending path and to be minus for the descending path, respectively. The Eckart condition⁷ to fix the translation and the rotation about the center of gravity is automatically satisfied in eq 2. At an equilibrium point on the reaction coordinate, the gradient of the potential energy vanishes and the displacement vector becomes one of the normal coordinates at that point. When we solved the simultaneous differential equation, eq 2, by setting the initial condition such that the solution conforms to one of the normal coordinates of an equilibrium point, the nuclear configuration along the reaction coordinate is given.

For the potential-energy function of $\text{CH}_4 + \text{T}$ and $\text{CD}_4 + \text{T}$ systems, we adopted the analytical function proposed by Raff.⁸ He adjusted the results of the ab initio and the INDO⁹ calculations of the potential-energy surface to a simple analytic function and performed a classical trajectory calculation of these systems.

We first calculated the reaction coordinate of the abstraction mode, I and II. The geometry of the transition state was obtained by means of Powell's function minimization procedure,¹⁰ where the mean square of the gradient vector was made to be zero. The normal coordinates were given as the eigenvectors of the secular equation,

$$\det \left(\frac{\partial^2 W}{\partial x_i \partial x_j} - \kappa \delta_{ij} \right) = 0$$

The masses of atoms used here are 12.0 for C, 1.008 for H, 2.014 for D, and 3.016 for T, respectively. The displacement vector on the reaction coordinate at the transition state is the eigenvector whose eigenvalue is uniquely negative. The geometry of the transition state is shown in Figure 1. We solved eq 2 by imposing the displacement vector at the transition state as the initial condition. As to the integration, we employed the variable step-size Runge-Kutta-Gill method.¹¹ Figure 2 (top) illustrates the nuclear configuration and the displacement vector at several points on the reaction coordinate of reaction mode I. The magnitude of vectors is scaled to the Cartesian coordinate representation. The change of the potential energy for modes I and II is also shown in Figure 2 (bottom). The displacement vector along the reaction coordinate varies gradually and converges well at the initial and the final states. At the initial stage of reaction ($S < -2.0$), the component of the reaction coordinate is the relative translational mode between the centers of gravity of CH_4 and T. With the approach of T to CH_4 , the CH bond lengthens and the methyl group tends to be slightly planar ($-2.0 < S < -0.8$). At $S = -0.73$, the tritium reverses its direction and the stripping of the hydrogen atom is accelerated. After crossing over the transition state, the displacement vector is a combination of the leaving mode of H_2 and the bending mode of the methyl group to the planar form, and becomes the relative translation between the centers of gravity of CH_3 and H_2 at the final state. As seen in

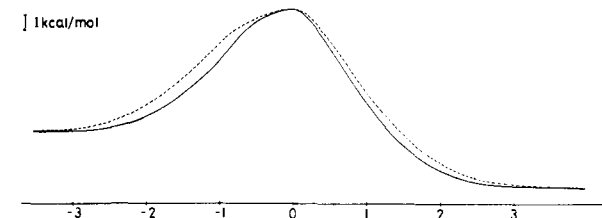
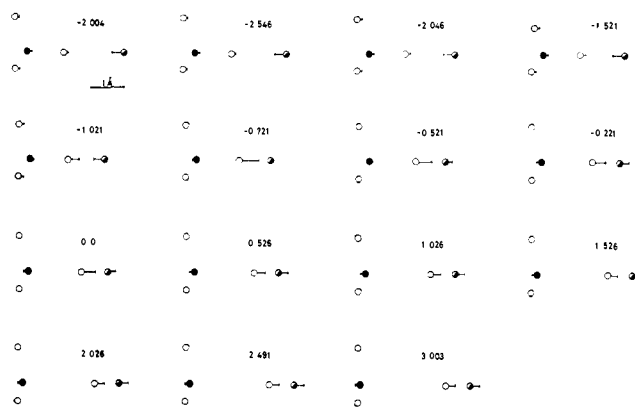


Figure 2. The change of nuclear configuration, displacement vector, and energy along the reaction coordinate of the abstraction mode. The scale of the reaction coordinate is $\sqrt{M_n}$ au, where M_n is the ratio of the atomic mass unit with the mass of electron. The location of atom is represented by: ●, C; ○, T; and ○, H. The dashed line is for reaction II, while the solid line is for reaction I.

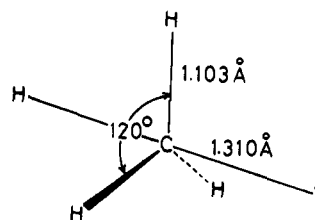


Figure 3. The geometry of transition state for the substitution mode.

Figure 2 (bottom), the potential barrier along the reaction coordinate is widened by the deuteration.

Next, the calculation was performed on the substitution mode, III and IV. Since the transition state corresponds to a cusp point of the potential surface with this approximation, we minimized the energy within the framework of the D_{3h} point group in the nuclear configuration space to calculate the geometry of the transition state. The optimization was carried out by Powell's procedure. In Figure 3, the nuclear configuration of the transition state is given. A set of nuclear configurations and the displacement vectors for mode III are shown in Figure 4 (top) and the comparison is made on the potential energies of III and IV in Figure 4 (bottom). Figure 4 (top) indicates a typical mode of the methyl inversion and the bond interchange in the substitution reaction mechanism. It should be noted that the difference of the masses of tritium and hydrogen atoms brings the difference of the magnitude of the displacement vectors. The effect of deuteration is more remarkable than in the case of abstraction mode. The width of the potential barrier is much affected by the deuteration in the region between the transition state and the final state, while it does not change remarkably in the region between the initial and the transition states. This is easily understood from the fact that, at the former region, the displacement is mainly constituted by the leaving mode of the deuterium and the inversion of the CD_3 group in reaction IV so that the ratio of the masses of deuterium and hydrogen reflects directly. This isotope effect

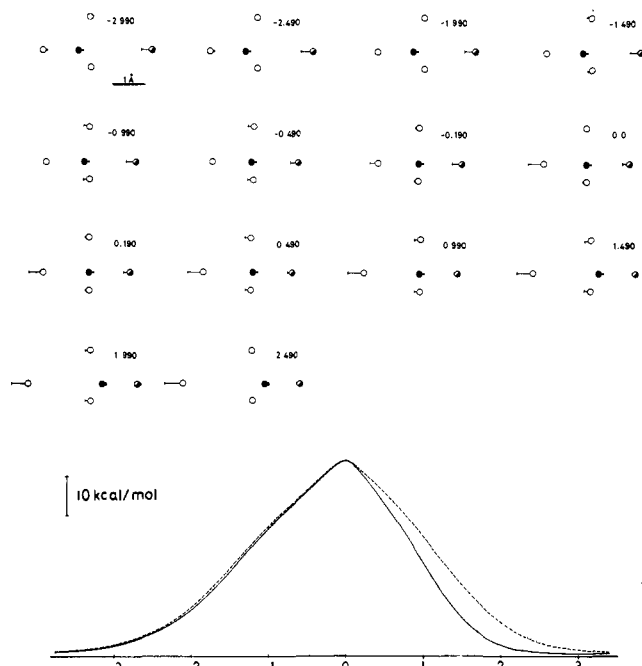


Figure 4. The change of nuclear configuration, displacement vector, and energy along the reaction coordinate of the substitution mode. The solid line is for reaction III and the dashed line is for reaction IV. Others are the same as in Figure 2.

on the width of potential barrier becomes important when the tunneling effect is discussed. The tunneling is expected not to be negligible near the top of the potential barrier even in the polyatomic reaction.

Many calculations of the trajectories of chemical reactions have been performed and afforded valuable information with respect to dynamic features of reactions.¹² Wang and Karplus¹³ applied the trajectory method to the quantum mechanical surface. The trajectory, nevertheless, depends on the initial condition chosen. The intrinsic reaction coordinate is independent of the initial condition and is uniquely determined for a given reaction path on a given potential surface.

Applications of the intrinsic reaction coordinate to the dynamic problems of polyatomic reacting systems also have some advantages. The reaction coordinate automatically includes the reduced mass of the reacting system, and we can easily construct the equation of motion or the Hamiltonian of the system with considering the coordinate system perpendicular to the reaction coordinate. As shown in the present calculation, the effect of isotopic nuclei is directly realized in the width of the potential barrier. An application to the dynamics of polyatomic systems will be presented in the near future.

Acknowledgment. The authors express their appreciation to the Data Processing Center, Kyoto University, for the generous permission to use the Facom 230-75 computer. This work was supported by a Grant-in-Aid for Scientific Research for the Ministry of Education of Japan (No. 047068).

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Geometries of Nitrilium Betaines. The Clarification of Apparently Anomalous Reactions of 1,3-Dipoles

Sir:

Frontier molecular orbital (FMO) theory correctly rationalizes the regioselectivity of most 1,3-dipolar cycloadditions,¹ and successfully predicts regioselectivity in others.^{1c,2} Previous generalizations about the frontier MO's of 1,3-dipoles, based on a variety of calculations using linear or planar geometries, are summarized in Figure 1. For unsymmetrical 1,3-dipoles, Z is always predicted to be the more nucleophilic terminus, and X the more electrophilic terminus.^{3,4} However, using these generalizations, regioselectivity predictions for the HOMO controlled^{1c,5} cycloadditions of nitrile ylides are incorrect. We concluded that "this case can only be rationalized by assuming that the calculations give the wrong result; this is, the larger [HOMO] coefficient must be on the "neutral" carbon (X in Figure 1)."^{1c} Using this ad hoc assumption, regioselectivity data known at the time were rationalized,^{5,6} and subsequent experimental work supported this unorthodox prediction of a theoretical result from experimental data.⁷⁻⁹

Optimizations of the geometries of the parent nitrilium betaines by ab initio LCAO-MO-SCF calculations,¹⁰⁻¹³ reported here, indicate that the geometries of nitrile ylide and, to a lesser extent, of the imine are appreciably different from those commonly accepted.¹⁴ Figure 2 shows the optimized geometries and a second geometry of interest for each species. The HCN-bent nitrile ylide geometry is favored over the planar, but otherwise optimized, geometry by 11.1 kcal/mol. Thus, this species resembles a bent allenyl anion rather than a planar propargyl anion.¹⁵ By contrast, the linear structure is favored for fulminic acid, in fair agreement with experi-

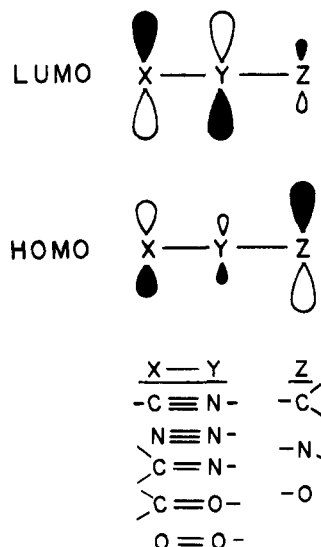


Figure 1. Frontier molecular orbitals of linear and planar 1,3-dipoles.