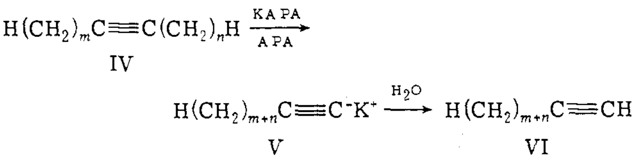
Table I. "Contrathermodynamic" Isomerization of Alkynes with KAPA[a]

Compound	Product[b]	Yield, %[c]
3-Hexyne	1-Hexyne	96
4-Octyne	1-Octyne	93
5-Decyne	1-Decyne	74
7-Tetradecyne	1-Tetradecyne	93 (89)
2-Methyl-4-nonyne	8-Methyl-1-nonyne	100
3-Methyl-4-nonyne	7-Methyl-1-nonyne	84
	3-Methyl-1-nonyne	0
2,2-Dimethyl-3-nonyne	8,8-Dimethyl-1-nonyne	94

[a] 20°, 1.2-1.5 equiv of KAPA (~1.0 *M* in APA), 2-10 min. There appears neither benefit nor detriment to the longer reaction times. [b] Purified by glpc and identified by comparison with authentic samples and/or from spectra. New compounds possessed consistent spectra and microanalyses. [c] After work-up and extraction, by glpc, ( ) = isolated yield.

essentially quantitative yield. Although multiposition migrations are reported to be generally unsatisfactory or very slow,[4,5] even 7-tetradecyne (IV, $m = n = 6$) was rapidly and quantitatively isomerized (Scheme I). These migrations are totally unprecedented regarding rate, mildness of conditions, and number of positions. Isomerization of 7-tetradecyne requires a *minimum* of 13 proton transfers and probably substantially more considering the presumably random nature of migration before the triple bond is "trapped" at the end.[12]

Scheme I



$$\underset{\text{IV}}{H(CH_2)_mC{\equiv}C(CH_2)_nH} \xrightarrow[\text{APA}]{\text{KAPA}} \underset{\text{V}}{H(CH_2)_{m+n}C{\equiv}C^-K^+} \xrightarrow{H_2O} \underset{\text{VI}}{H(CH_2)_{m+n}C{\equiv}CH}$$

Presence of a single chain branch blocks migration completely, consistent with the alkyne-allene migration mechanisms suggested in other base systems.[13] In no case were dienes observed in the products.[14]

The procedure is exceedingly simple. With cooling (15-20°) under argon or nitrogen, 7-tetradecyne (4.9 g, 25 mmol) was injected rapidly to a vigorously stirred solution of KAPA[15] (30 ml of 1.2 *M* in APA). The reaction mixture darkened and precipitation of potassium 1-tetradecynide was observed almost immediately. After 1-2 min the mixture was quenched by addition of 30 ml of water, extracted with pentane (backwash with 10% HCl), dried ($MgSO_4$), and evaporated under vacuum to yield 4.4 g, 89%, of 1-tetradecyne, ir 3310 ($\equiv$C—H) and 2120 cm^{-1} (terminal C$\equiv$C), one peak on glpc (DC 710), identical by coinjection with authentic material. Starting material was absent, and quantitative glpc with an internal standard confirmed the absence of nonvolatile products.

"Contrathermodynamic" isomerizations of various hydrocarbons with KAPA are summarized in Table I.

This remarkably facile migration—the "acetylene zipper"—represents a novel movement of functionality from the center to the terminus of a chain under exceptionally mild conditions.[16] We are currently exploring applications of this reaction to functional alkynes and synthesis.

Acknowledgment. Support from Research Corporation, the Cornell Chemistry Department, and Exxon Research and Engineering Co. are gratefully acknowledged.

References and Notes

(1) Saline Hydrides and Superbases in Organic Reactions. IX. Part VII: see ref 15b.

(2) A. Favorsky, *Ber.*, **21**, 177 (1888).

(3) F. Kraft and L. Reuter, *Ber.*, **25**, 2243 (1892).

(4) M. Bourguel, *Ann. Chim.* (*Paris*), **3**, 325 (1925).

(5) L. Brandsma, "Prepative Acetylene Chemistry," Elsevier, New York, N.Y., 1971, p 143. Ethylated and higher alkynes are reported to yield polymers.

(6) J. Klein and E. Gurfinkle, *Tetrahedron*, **26**, 2127 (1970).

(7) However, these do isomerize 1-alkynes to 2-alkynes smoothly.[5,6]

(8) (a) T. L. Jacobs, R. Akawie, and R. C. Cooper, *J. Am. Chem. Soc.*, **73**, 1273 (1951). (b) W. Smadja, *Ann. Chim.* (*Paris*), **10**, 105 (1965); (c) W. Smadja, *C. R. Acad. Sci.*, **258**, 546 (1964); (d) B. Wojkowiak and R. Romanet, *Bull. Soc. Chim. Fr.*, 805 (1962); (e) J. Bainvel, B. Wojkowiak, and R. Romanet, *ibid.*, 938 (1963).

(9) W. R. Moore and H. R. Ward, *J. Am. Chem. Soc.*, **85**, 86 (1963).

(10) (a) Dreiding models show the geometry of II to be highly favorable to such a process. (b) Similar mechanisms have been proposed for monofunctional bases associated with solvent ("asymmetric solvation") in both exchange[10c,d] and isomerization reactions.[10e] (c) A nine-membered difunctional transition state has been suggested for allene-alkyne equilibration by $NaNH_2$-ethylenediamine.[10g] (d) A. Streitwieser, Jr., W. C. Langworthy, and D. E. Van Sickle, *J. Am. Chem. Soc.*, **84**, 251 (1962). (e) A. Streitwieser, Jr., D. E. Van Sickle, and L. Reif, *ibid.*, **84**, 258 (1962). (f) D. J. Cram, C. A. Kingsbury, and B. Rickborn, *ibid.*, **83**, 3688 (1961). (g) J. H. Wotiz, P. M. Barelski, and D. F. Koster, *J. Org. Chem.*, **38**, 489 (1973).

(11) These conditions appear more vigorous than necessary; 7-tetradecyne is completely converted to 1-tetradecyne in less than 60 sec at 0°.

(12) (a) Such a process ("random walk") requires that the mean time for passage of the triple bond (and the number of proton transfers) be proportional to the square of the number of positions involved.[13b] Preliminary competitive studies appear to provide experimental confirmation but are complicated by differing solubilities of alkynes (with substantially different chain lengths) in the amine. (b) We are indebted to Professor Michael Fisher of the Cornell University Chemistry and Physics Departments for helpful discussions relating to the "random walk" problem.

(13) (a) R. J. Bushby, *Quart. Rev., Chem. Soc.*, 585 (1970); (b) J. H. Wotiz, W. E. Billups, and D. T. Christian, *J. Org. Chem.*, **31**, 3069 (1966).

(14) (a) Alkyne-diene isomerization has been observed in conjugated systems.[14b] There are conflicting reports regarding the conversion of simple alkynes to dienes with K-O-*t*-Bu-DMSO, in which Δ^1 to Δ^2 isomerization is observed.[5,6] (b) J. P. C. M. Van Dongen, A. J. DeJong, H. A. Selling, P. P. Montijn, J. H. Van Boom, and L. Brandsma, *Recl. Trav. Chim. Pays-Bays*, **86**, 1077 (1967).

(15) (a) The preparation of potassium alkylamides and handling of KH has been discussed;[15b] (b) C. A. Brown, *J. Org. Chem.*, **39**, 3913 (1974).

(16) (a) Two other such processes—the Willgerodt-Kindler reaction[16b] and borane isomerizations[16c]—both require prolonged elevated temperatures. (b) M. Carmack and M. G. Spielman, *Org. React.*, **3**, 83 (1946); L. Cavalieri, D. B. Pattison, and M. Carmack, *J. Am. Chem. Soc.*, **67**, 1783 (1945), reports that extensions to purely aliphatic systems are generally unsatisfactory. (c) H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N.Y., 1972, p 304.

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Received May 31, 1974

Accuracy of Transition State Theory for the Threshold of Chemical Reactions with Activation Energy. Collinear and Three-Dimensional H + H_2

Sir:

One of the major failures of the classical trajectory description of chemical reactions is the inability to deal correctly with the threshold region of a reaction with an activation barrier, for here quantum effects (i.e., tunneling) become important. This is a serious shortcoming, too, since it is primarily this threshold region which determines the thermally averaged rate constant.[1]

For low energies, however, the fundamental assumption[2] of transition state theory—namely, that flux through a particular surface in configuration space which divides reactants from products can be identified as the reactive flux—becomes valid. As has been recently emphasized,[3,4] though, the additional assumption of separability of motion along a reaction coordinate, which is invoked in traditional transition state theory, is a poor approximation in the threshold region. The suggestion has been made,[3] therefore, that transition state theory should provide an accurate description of the threshold region provided it can be applied quantum mechanically and without invoking additional approximations such as separability.

To gain a more quantitative feeling about the validity of transition state theory for the threshold region, we have carried out, and report here, classical calculations for the collinear and for the three-dimensional $H + H_2 \rightarrow H_2 + H$ reaction on the Porter–Karplus[5] potential surface. The classical trajectory calculations were *not* with the usual "quasi-classical" initial conditions,[6] which are designed to approximate the quantized aspect of the vibrational degree of freedom, but rather involved a classical mirocanonical average over all initial conditions, including vibration; it is this latter type of classical trajectory calculation to which classical microcanonical transition state theory corresponds. Collinear calculations of this type have been carried out previously by Morokuma and Karplus,[7] and, although their transition state results involved a harmonic approximation to the potential function about the saddle point, our collinear results are very similar to theirs.

The relevant theoretical expressions are the microcanonical version of the classical rate expressions given in ref 3, and the necessary phase space integrals have been evaluated without any subsidiary approximation (e.g., harmonic approximations to the potential function, neglect of rotation–vibration coupling, etc.) The dynamically exact microcanonical cross section for the three-dimensional case, for example, is given by

$$\sigma(E) = F(E)/F_0(E)\,. \qquad (1)$$

where F and F_0 are microcanonical averages of the reactive flux and incident flux per unit area, respectively. More explicitly, these quantities are

$$F(E) = \int d_3\mathbf{r} \int d_3\mathbf{R} \int d_3\mathbf{p} \int d_3\mathbf{P}\,\delta(E - H)\delta[f(\mathbf{r},\mathbf{R})] \times \frac{1}{2}\left|\frac{\partial f}{\partial \mathbf{r}}\cdot\mathbf{p}/m + \frac{\partial f}{\partial \mathbf{R}}\cdot\mathbf{P}/\mu\right|\frac{1 + (-1)^N}{2(N + 1)} \qquad (2)$$

$$F_0(E) = \int d_3\mathbf{r} \int dZ \int d_3\mathbf{p} \int d_3\mathbf{P}\,\delta(E - H_0) \times \delta(Z - Z_0)\frac{1}{2}\left|P_Z/\mu\right| \qquad (3)$$

where H and H_0 are the classical Hamiltonian functions for the complete A – BC system and for the noninteracting A + BC system, respectively; N is the number of times the trajectory which begins with initial conditions $(\mathbf{r},\mathbf{R},\mathbf{p},\mathbf{P})$ recrosses the surface defined by $f(\mathbf{r},\mathbf{R}) = 0$ as time is run forward and backward. The coordinates $\mathbf{r}$ and $\mathbf{R}$ are those for the relative B–C separation and A relative to BC, respectively, with $\mathbf{p}$ and $\mathbf{P}$ being their conjugate momenta and m and μ the corresponding reduced masses. The dynamically exact flux $F(E)$ is actually independent of the particular "dividing surface" which separates reactants from products, but the transition state approximation—i.e., $N \equiv 0$—depends on it. Our choice for the dividing surface is the usual one, the symmetric line; i.e., the function $f(\mathbf{r},\mathbf{R})$ is

$$f(\mathbf{r},\mathbf{R}) = r_a - r_b = r - \left|\mathbf{R} - \frac{1}{2}\mathbf{r}\right| = r - \left(R^2 + \frac{1}{4}r^2 - rR\cos\gamma\right)^{1/2} \qquad (4)$$

where r_a and r_b are the two interatomic distances from the central H atom, and γ is the angle between $\mathbf{r}$ and $\mathbf{R}$. Equation 2 can be reduced to a seven-dimensional integral in the dynamically exact case for which one actually computes trajectories to determine N for each set of initial conditions $(\mathbf{r},\mathbf{R},\mathbf{p},\mathbf{P})$; this seven-dimensional integral was evaluated by Monte Carlo methods. For the transition state approximation, $N \equiv 0$, it can be reduced to the following two-dimensional integral which was evaluated by Gaussian quadrature

$$F_{\mathrm{TST}}(E) = \frac{128\pi^3}{45}\left(\frac{2}{3}\right)^{1/2} 2\pi \int dr \int d(\cos\gamma)\, r^4(\cos\gamma + \sqrt{3 + \cos^2\gamma})^2 [m_{\mathrm{H}}(E - V)]^{5/2}\left(1 + \frac{\cos\gamma}{\sqrt{3 + \cos^2\gamma}}\right)^{1/2} \qquad (5)$$

where m_{H} is the mass of a hydrogen atom, and $V \equiv V(r, \cos\gamma)$ is the total potential energy on the symmetric line $r_a = r_b$. The incident flux is given in either case by

$$F_0(E) = \frac{128\pi^3}{45} \int dr\, r^2\{m_{\mathrm{H}}[E - v(r)]\}^{5/2} \qquad (6)$$

where $v(r)$ is the potential function for the H_2 molecule. The relevant expressions for the collinear case are similar (but simpler).

Microcanonical transition state theory has been discussed earlier by Marcus[8] from quite a different point of view. He also emphasized the value of comparing classical transition state theory with classical trajectory calculations, but in making such comparisons[8] he was forced to invoke the assumption of vibrational adiabaticity since the only classical trajectory results then available were with quasi-classical initial conditions.

Although these classical calculations are not of direct physical significance—because they ignore quantum effects which are important in the threshold region of this reaction—they do provide a rigorous and meaningful test of the fundamental assumption of transition state theory, i.e., that all the flux through the specially chosen dividing surface is reactive flux. To the extent that this assumption is valid classically, one expects it also to be valid quantum mechanically.

Figure 1 shows the reaction probability of the collinear $H + H_2$ reaction as a function of total energy above the barrier height, for the microcanonical classical trajectory calculation (CL DYN = classical dynamics) and for microcanonical transition state theory (CL TST). Pechukas and McLafferty[9] devised an ingenuous geometrical criterion which showed that classical transition state theory is formally *exact* in this case for energies up to about 0.1 eV above the barrier height. The present numerical results show it to be essentially exact to over 0.2 eV above the barrier height, and then it begins to fail substantially, being over a factor of 2 too large at 1 eV.

The three-dimensional trajectory and transition state results for the microcanonical reactive cross section of $H + H_2$ are shown in Figure 2. The transition state approximation is seen to be essentially exact up to a few tenths of an electron volt, and even as it begins to fail, the failure is much less drastic than in the collinear version; at 1 eV above the barrier height the transition state theory cross section is only about 10% too large.

These classical results provide extremely encouraging support for the accuracy of transition state theory for the threshold region of chemical reactions with activation energy, and the outlook is substantially better in three dimensions than for the collinear model. Should this accuracy be maintained for the quantum mechanical version of transition state theory,[3] then one will have a quantitative description of rate constants for such reactions. Work in progress seems to indicate this to be the case.

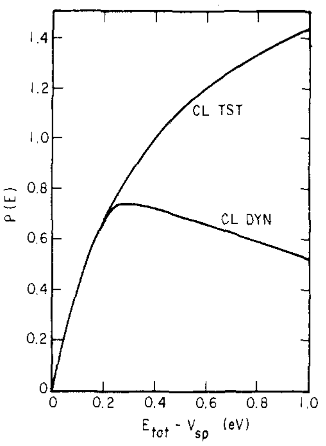

Figure 1. Reaction probability for the collinear H + H_2 reaction on the Porter-Karplus potential surface from a microcanonical classical trajectory calculation (CL DYN) and microcanonical classical transition state theory (CL TST), as a function of total energy above the barrier height (1 eV = 23.06 kcal/mol).

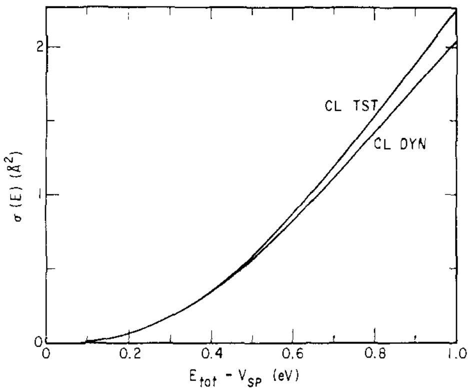

Figure 2. Same as Figure 1, except that σ(*E*) is the reactive cross section for the three-dimensional H + H_2 reaction.

Acknowledgment. Support by the U.S. Atomic Energy Commission, the National Science Foundation (GP-41509X), and a Teacher-Scholar grant to W.H.M. from the Camille and Henry Dreyfus Foundation are gratefully acknowledged. The computations reported herein were performed on a Datacraft 6024/4 minicomputer funded by NSF Grant GP-39317.

References and Notes

(1) See, for example, R. Wolfgang, *Acc. Chem. Res.*, **2**, 248 (1969).
(2) See E. Wigner, *Trans. Faraday Soc.* **34**, 29 (1938); my "fundamental assumption" is Wigner's "third assumption" discussed on pages 33 and 39. See also the formulation by J. C. Keck, *Adv. Chem. Phys.*, **13**, 85 (1967); *Adv. At. Mol. Phys.*, **8**, 39 (1972).
(3) W. H. Miller, *J. Chem. Phys.*, **61**, 1823 (1974).
(4) Johnston and Rapp (H. S. Johnston and D. Rapp, *J. Am. Chem. Soc.*, **83**, 1 (1961)) have earlier discussed the weakness of the separability assumption and suggested an approximate way of dealing with it.
(5) R. N. Porter and M. Karplus, *J. Chem. Phys.*, **40**, 1105 (1964).
(6) M. Karplus, R. N. Porter, and R. D. Sharma, *J. Chem. Phys.*, **43**, 3259 (1965).
(7) K. Morokuma and M. Karplus, *J. Chem. Phys.*, **55**, 63 (1971).
(8) R. A. Marcus, *J. Chem. Phys.*, **45**, 2138 (1966).
(9) P. Pechukas and F. J. McLafferty, *J. Chem. Phys.*, **58**, 1622 (1973).

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Reversible Electron Transfer to the Nitrosyl Group in Ruthenium Nitrosyl Complexes

Sir:

In transition metal nitrosyl complexes the electronic distribution in the metal-nitrosyl bond and the assignment of formal oxidation states, remain areas of some controversy.[1] However, in an appropriate coordination environment (one in which the ν(NO) stretching frequency is relatively high) the nitrosyl group has been shown to react chemically as the nitrosonium ion (NO^+).[2-10] The nitrosyl group in complexes like *cis*-$Ru(bipy)_2(NO)Cl^{2+}$ (bipy is 2,2′-bipyridine) reacts with nucleophiles like OH^- and N_3^-,[2,3] diazotizes primary amines,[7] and acts as an electrophile in aromatic substitution reactions.[8]

The free nitrosonium ion is also a strong oxidant.[11,12] Although the nitrosyl group has been reported to act as an oxidant in net redox reactions,[13-15] with the exception of nitroprusside ion,[16] the reactions do not involve simple electron transfer. We have prepared the series of nitrosyl complexes $[Ru(bipy)_2(NO)A]^{3+}$ (A is N_3^-, Cl^-,[2] NO_2^-, NH_3, py,[2] and CH_3CN). From voltammetry and cyclic voltammetry experiments at a platinum bead electrode, we find that the nitrosyl complexes undergo electrochemically reversible one-electron reduction reactions in acetonitrile in the potential range 0.2-0.6 V (*vs.* the saturated sodium chloride calomel electrode at 25 ± 2°), and a second irreversible one-electron reduction at more cathodic potentials. ν(NO) and voltammetric $E_{1/2}$ values are dependent upon the ligand A cis to the nitrosyl group in a systematic way: for $Ru(bipy)_2(NO)Cl^{2+}$, $E_{1/2}$ = 0.20 V, ν(NO) = 1940 cm^{-1} (in acetonitrile); for $Ru(bipy)_2(NO)(CH_3CN)^{3+}$, $E_{1/2}$ = 0.56 V, ν(NO) = 1970 cm^{-1} (in acetonitrile).

The nitrosyl complexes can be reduced chemically (using I^- as reductant) or electrochemically (*n* = 1.00 ± 0.05) to give one-electron reduction products, e.g., $Ru(bipy)_2(NO)Cl^+$ and $Ru(bipy)_2(NO)(CH_3CN)^{2+}$. In deaerated acetonitrile, acetone, or water solutions the reduction products are stable indefinitely; however, they do react slowly with oxygen in solution. The stable black iodide salt, $[Ru(bipy)_2(NO)Cl]I$, which gives excellent elemental analyses,[17] has been isolated in good yield.

The results of several experiments show that the electron transfer properties of the nitrosyl complexes are carried mainly by the nitrosyl ligand. (1) Upon reduction ν(NO) shifts dramatically to lower energies (1650 cm^{-1} for $Ru(bipy)_2(NO)(CH_3CN)^{2+}$ and 1610 cm^{-1} for $Ru(bipy)_2(NO)Cl^+$) as shown by ^{15}N labeling studies. The magnitude of the shifts in ν(NO), ~300 cm^{-1}, are in the same range as when NO^+ is reduced to NO.[4] (2) In contrast to normal bis(2,2′-bipyridine)ruthenium(III)/(II) couples, $E_{1/2}$ values for the nitrosyl complexes are sensitive to medium effects. In acetonitrile, $E_{1/2}$ for the $[Ru(bipy)_2(NO)Cl]^{2+/+}$ couple shifts 0.1 V to a lower potential when the supporting electrolyte is changed from 0.1 *M* $N(n\text{-}C_4H_9)_4PF_6$ to 0.1 *M* $LiClO_4$. Specific medium effects might be expected if electron transfer occurs to and from a group on the periphery of the complex rather than to and from metal d orbitals. (3) The epr spectrum of $[Ru(bipy)_2(NO)Cl]^+$ in frozen acetone at 170°K is qualitatively identical with the frozen solution spectrum of the one-electron reduced nitroprusside ion, $Fe(CN)_5NO^{3-}$.[18a] For both $Fe(CN)_5NO^{3-}$ and $Ru(bipy)_2(NO)Cl^+$ the expected ^{14}N hyperfine splittings are observed. In neither case has evidence been found for metal hyperfine interactions. The epr results and the results of a magnetically perturbed Mössbauer study on $[Fe(CN)_5NO]^{3-}$ [19] show that the unpaired spin density is confined largely to the nitrosyl ligand. This is