

# Relaxation Behavior of Equilibrating Molecular Configurations. Application to the 2-Norbornyl Problem

Francis K. Fong

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. Received May 13, 1974

**Abstract:** In this paper, the principles of the quantum statistical mechanical theory of relaxation are applied to elucidate the general properties of intramolecular rearrangement processes in carbonium ions. An interplay of well-known chemical concepts is brought out in an analysis of the dynamical behavior of the Wagner–Meerwein shift in the bicyclic 2-norbornyl cations. The alternate roles of the activated rate process and quantum mechanical tunneling are explored in terms of theoretical limiting cases and experimental conditions. The relaxation behavior of the entire homologous series of norbornyl cations can be understood without invoking the role of the ground-state  $\sigma$ -bridged nonclassical ions. The low barrier to interconversion of classical structures is analyzed in terms of the electron deficiency at C-2. The theoretical estimate  $\sim 10^{12} \text{ sec}^{-1}$  for the rate constant of the Wagner–Meerwein shift in the 2-norbornyl cation is in agreement with earlier empirical estimates. The treatment given here appears to be generally applicable to all carbonium ions from saturated structures. The concept of the transition state is critically reexamined in terms of the present formulation. It is emphasized that the widespread usage of the transition state theory may have contributed to considerable confusion in the literature.

Recently, we developed a general theory for molecular relaxation.<sup>1-6</sup> This theory is based<sup>6</sup> on the fundamental postulates of quantum statistical mechanics and the concepts underlying Önsager's reciprocity theorem<sup>7,8</sup> for irreversible thermodynamics. The relaxation rate constants are calculated within the framework of the adiabatic approximation.<sup>1-6,9-11</sup> In the relaxation process, the zero-order Born–Oppenheimer states are coupled by the nondiagonal matrix elements of the nonadiabatic nuclear kinetic energy operator.<sup>1-6,10</sup>

We have applied the formal theory to a variety of relaxation phenomena.<sup>1-6,12-14</sup> Numerical fits of theory and experiment have been obtained for the radiationless relaxation rates of electronically excited rare-earth ions in crystals<sup>2,3,5</sup> and for the orientational relaxation rates of ion-defect pairs in  $\text{CaF}_2$ .<sup>4</sup> The theoretical analysis of the relaxation properties of chlorophyll molecules has led to a promising model<sup>12-14</sup> for the primary light reaction in plant photosynthesis. In this paper, the basic principles of the relaxation theory are applied to a description of the dynamical behavior of equilibrating molecular configurations.

All flexible molecules undergo intramolecular transitions between equilibrium configurations. The principles invoked in this work therefore should find broad areas of application. Examples include the ammonia molecule and the diphenyl ethers. Other familiar phenomena are exemplified by group rotations in nonrigid molecules, *cis-trans* isomerization of substituted alkenes, and intramolecular rearrangement reactions.

In the gaseous state, intramolecular rotations or configuration rearrangements are governed by the potential surfaces prescribed by the normal mode coordinates of the molecule. In condensed media, effects arising from solute–solvent interactions must also be considered. The majority of intramolecular transitions have thus far been examined in terms of the typical behavior of activated rate processes. However, the possible role of quantum mechanical tunneling in large nonrigid molecules remains mostly undetermined.

In the following, we explore the general properties of intramolecular relaxation. An interplay of important chemical concepts is brought out in an analysis of the dynamical behavior of bicyclic carbonium ions. Symmetry effects of the internal degrees of freedom and the effects of steric strain and electron delocalization are described. The alternate roles of the activated rate process and quantum me-

chanical tunneling are explored. The distinction between the rapid equilibration of enantiomorphs and electronic resonance is examined in terms of relaxation effects. The question of the activated complex is discussed.

## Theory of Activated Rate Processes. Molecular Relaxation in the Classical Limit

In the present treatment, we specialize the theory of molecular relaxation to processes involving discrete nuclear configurations. In a complete departure from earlier theories,<sup>15-22</sup> we have derived<sup>4</sup> a quantum statistical mechanical expression for the activated rate constant of the transition between two states corresponding to two equilibrium nuclear configurations. This derivation is made in the strong-coupling limit<sup>4</sup> in which the activation barrier  $E_a$  is large compared with the vibrational quantum  $\hbar\omega$  of the normal mode which promotes the transition. The rigorous result for the harmonic approximation reduces to the simplified high-temperature ( $kT \gg \hbar\omega$ ) expression for the transition rate constant<sup>4</sup>

$$W = A(T) \exp(-E_a/kT) \\ = (kT/h) [(2\pi MkT/h^2)^{1/2} \Delta R]^{-1} \times \\ [(2h\pi/M\omega) |S|^2 \Delta\epsilon^{-2}] \exp[-M\omega^2 (\Delta R)^2 / 8kT] \quad (1)$$

where  $h$  is the Planck constant,  $M$  and  $\omega$  are respectively the effective mass and the frequency of the promoting mode,  $\Delta R$  is the equilibrium separation of the two nuclear configurations measured in the coordinate of the promoting mode,  $S$  is a coupling parameter, and  $\Delta\epsilon$  is the vertical energy separation of the potential surfaces of the two nuclear configurations evaluated at the equilibrium configuration of the initial state (see Figure 1). In practice, it is convenient to treat  $|S|^2/\Delta\epsilon^2$  as a single parameter. The activation barrier

$$E_a = \frac{1}{8} M\omega^2 (\Delta R)^2 \quad (2)$$

is just the energy at which the two potential surfaces intersect.

The promoting mode corresponds to a normal mode vibration along the coordinate pathway of the configurational transformation. It may be exemplified by the torsional vibration about the  $\text{C}=\text{C}$  bond in the *cis-trans* isomerization of, say, the 1,2-dichloroethylene molecule. The significance of the promoting mode has been discussed previously.<sup>4</sup>

Equation 1 reproduces the empirical temperature dependence displayed in the Arrhenius equation with a weak preexponential temperature dependence ( $\sim T^{1/2}$ ) for the frequency factor  $A$ . Although this result can appropriately be envisioned in terms of a classical system undergoing a shift in the nuclear configuration by climbing the barrier which separates the two equilibrium positions, the underlying premises are derived directly from the postulates of quantum statistical mechanics.<sup>6</sup> This approach avoids the necessity to invoke an intermediate "activated complex state" and appears to be a reasonable approach to the activated rate process. Lin and Eyring<sup>23</sup> have also applied the quantum statistical mechanical method and arrived at a final result that is essentially identical with eq 1.

Equation 1 is particularly suited for dipolar reorientations in solids and restricted intramolecular rotations or rearrangement processes in which high barriers or activation are encountered. However, it fails for low-barrier intramolecular mechanisms in which  $E_a \lesssim \hbar\omega$ .

For the problem of overall molecular rotations, it is necessary to consider the average solute-solvent interactions. These interactions have been incorporated into a viscosity frictional constant  $\eta$ .<sup>15</sup> The dependence of the relaxation time on the molecular dimensions and on the macroscopic viscosity of the solvent medium has been extensively tested.<sup>24,25</sup> For example, it has been established that the dielectric relaxation times of the homologous series of halobenzenes generally increase with the size and polarizability of the halogen atom.<sup>26-33</sup>

Within the context of the quantum statistical theory, the rate constant for the rotation of a rigid molecule in a viscous medium has been cast<sup>4</sup> in a form similar to that given by Debye<sup>15</sup>

$$W = kT/4\pi\eta(\kappa_0, T)r_0^3 \quad (3)$$

in which

$$\eta(\kappa_0, T) = (\mu\delta\theta/4\pi\hbar)(\Delta\epsilon^2/|S|^2)(2\kappa_0kT)^{1/2} \times \exp[8\pi r_0^2 \kappa_0 (\delta\theta)^2/kT] \quad (4)$$

where  $\mu$  is the reduced mass of the rotating molecule,  $\kappa_0$  is an effective force constant corresponding to the intermolecular forces which stabilize a given spatial orientation of the molecule, and  $\delta\theta$  is the average angular displacement between two neighboring equilibrium orientations. In view of (4), the rate expression 3 approximately observes the expected exponential temperature dependence with the activation energy

$$E_A = 8\pi r_0^2 \kappa_0 (\delta\theta)^2 \quad (5)$$

We note that, in addition to the usual  $r_0^3$  dependence<sup>15</sup> of the rate constant, there is also an exponential dependence on  $r_0^2$  for a constant value of the average angular displacement  $\delta\theta$ .

The application of (1) and (3) in an analysis of the dynamical behavior of intramolecular rotations (or molecular rearrangements) and overall molecular rotations takes on the following significance. There is a minimum of encounter against the intermolecular forces when a nonrigid molecule relaxes predominantly through intramolecular mechanisms. In this case, eq 1 may be applicable. On the other hand, overall molecular rotations can only be achieved against the binding forces of the surrounding molecules. In this case, eq 3 becomes appropriate. In eq 3 and 4,  $r_0$  may be interpreted as the effective radius of the volume swept out by a 180° rotation of the molecule. If the molecule is approximately spherical, the act of overall rotation can be achieved with little or no disruption of the local array of solvent molecules. The effective force constant  $\eta$  and hence the activa-

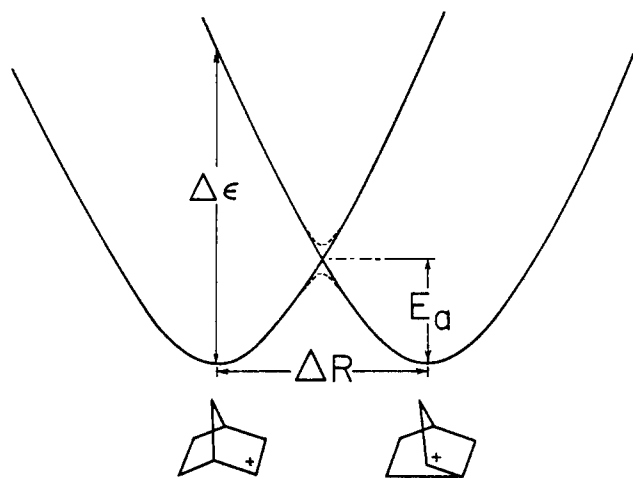


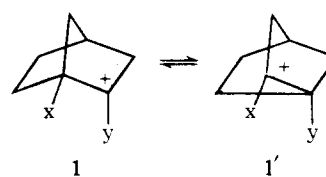
Figure 1. Schematic representation of intersecting adiabatic surfaces of two equivalent nuclear configurations exemplified by the two enantiomorphs of the 2-norbornyl cation. The molecular parameters  $\Delta\epsilon$ ,  $\Delta R$ , and  $E_a$  are given in eq 1 for the rate constant of the activated rate process. The dotted lines represent the lifting of electronic degeneracy at the intersection on account of nonadiabatic coupling.

tion energy  $E_A$  can be expected to be relatively low. On the other hand, if the molecule is irregularly shaped, the act of molecular rotation will be accompanied by a displacement of the surrounding molecules, leading to relatively large values for the activation energy  $E_A$ .

The explicit forms of eq 1 and 3 allow model calculations using the appropriate molecular parameters. Such a calculation has been performed in the simple case of dipole reorientations in crystals.<sup>4</sup> In the following, we first apply the qualitative features of (1) and (3) to a phenomenological description of the dynamics of the bicyclic 2-norbornyl cations. We then probe the limiting conditions under which eq 1 is valid in order to arrive at a quantitative understanding of intramolecular rearrangement processes.

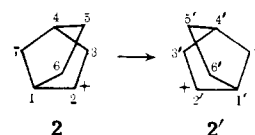
### Dynamical Behavior of the Wagner-Meerwein Rearrangement in 2-Norbornyl Cation Derivatives. A Classical Description

The physical and chemical properties of the 2-norbornyl cation derivatives have been the subject of extensive study in recent years.<sup>34</sup> The intense interest has resulted from the postulate of the concept of "σ participation" in the nonclassical σ-bridged carbonium ion.<sup>35,36</sup> We shall consider later the possible role of σ participation in the solvolysis of *exo*-norbornyl derivatives which leads to the formation of σ bridging. Here we specialize our discussion to the phenomenon of the intramolecular Wagner-Meerwein rearrangement characterized by the equilibrating pair

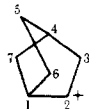


which has been established for a large number of 2-norbornyl derivatives.<sup>34b,37-42</sup>

**2-Norbornyl. Effects of Symmetry.** A close examination of the intramolecular shift



in the 2-norbornyl cation reveals that the promoting mode corresponds to a concerted intramolecular (CIM) *twist* vibration of C-5, C-6, and C-3, C-2 about the C-1, C-7, C-4 bridgehead. In this vibration, the C-5, C-6 and the C-3, C-2 bonds are kept as parallel as the restrictive geometry of the 2-norbornyl cation would allow in bringing the cation from the equilibrium configuration **2** to the instantaneous configuration



which may be considered to be the precursor to the transition. During the transition, the 1,6 C-C bond is broken to yield the 2,6 C-C bond as the positive charge shifts from C-2 to C-1. The indices 1', 2', 3', 4', 5', 6', and 7' in **2'** correspond to 2, 1, 7, 4, 5, 6, and 3 in **2**, respectively. The total angular momentum of the molecule is practically conserved in the CIM transition which results in a rather minor rearrangement within the spherical cluster of nuclei, leaving the intermolecular forces mostly undisturbed. Given the appropriate conditions of the strong coupling limit,<sup>4</sup> the rate constant  $W_{2 \rightarrow 2'}$  may be given by eq 1 (departures from this equation will be discussed later), with the corresponding energy barrier determined by the effective mass and the frequency of the promoting mode associated with the torsional oscillation along the coordinate of the CIM mechanism described above.

In ordinary solvents, the 2-norbornyl cation is probably closely associated with its counterion. The center of gravity of the ion pair can be kept stationary if the CIM transition **2**  $\rightarrow$  **2'** is accompanied by a slight *overall* tumbling of the cation such that the orientation of position 2 in **2** and **2'** remains constant with respect to the counterion. In this case, the overall molecular rotation may play a minor role. The rotations of nearly spherical rigid molecules are characterized by small activation energies  $\sim 1$  kcal.<sup>43-45</sup> Typical activation energies in the 0-3-kcal range have been found<sup>46-51</sup> for intramolecular group rotations in nonrigid molecules. The symmetrical diphenyl ether molecule is nonrigid and relaxes through CIM mechanisms. The symmetrical CIM mechanism, originally proposed<sup>52</sup> to account for the anomalously low dielectric relaxation times<sup>53,54</sup> ( $3-5 \times 10^{-12}$  sec) of diphenyl ether, is also thought to play an important role in the isomerization of diaryl compounds capable of restricted rotation of the aryl groups.<sup>55</sup>

In the present context, the relaxation behavior of the diphenyl ether molecule appears to provide an interesting comparison for that of the 2-norbornyl cation. Both molecules exhibit highly symmetrical internal flexibilities giving rise to rapid concerted intramolecular transitions. Based on the known relaxation behavior of rigid and nonrigid molecules,<sup>4,43-54</sup> it is reasonable to *speculate* that, if the CIM **2**  $\rightarrow$  **2'** transition in the 2-norbornyl cation resembles intramolecular rotations in nonrigid molecules, a relatively high rate constant on the order of  $10^{12}$  sec<sup>-1</sup> with an activation barrier  $< 3$  kcal may be characteristic of such a transition. Numerical estimates of these parameters will be made in the following section.

**2-Norbornyl Derivatives. Effects of Asymmetry.** The introduction of substituent groups at the 1 and 2 positions in **1** disrupts the near-spherical symmetry of the 2-norbornyl nuclear configuration. The loss of symmetry leads to the following consequences.

(A) In the nearly spherical norbornyl cation, intramolecular rearrangement can occur without disrupting the arrangements of the surrounding solvent molecules. The situation is different in the case of the substituted cation in which the CIM transition results in the displacement of surrounding solvent molecules by the protruding substituent groups. The transition rate constant is now determined by a combination of inter- and intramolecular interactions. This combination results in an effective increase in the internal barrier and hence retards the Wagner-Meerwein process. From eq 3-5, we note that this retardation effect should increase with the increasing size of the substituent groups. Where the substituent groups introduce large departures from the approximately spherical symmetry of the parent norbornyl cation, the retardation effect will be greatly enhanced.

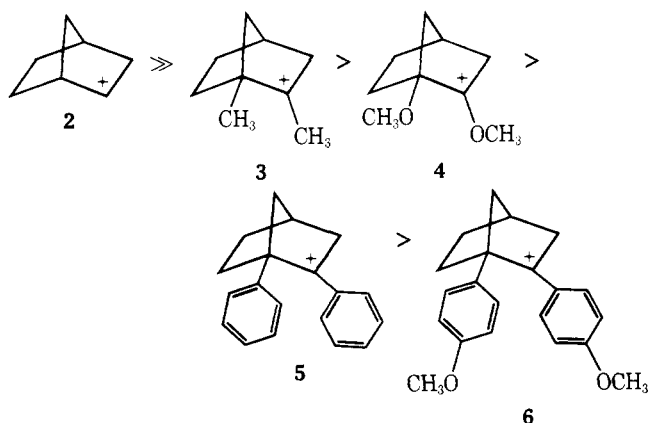
(B) The substituent groups increase the effective mass  $M$  of the CIM torsional mode, raising the barrier to the Wagner-Meerwein shift according to eq 2.

(C) The presence of bulky substituent groups at the 1,2 positions may introduce intramolecular steric hindrance, increasing the energy barrier to the CIM mechanism. This effect may be relatively unimportant except for the largest substituent groups.

The effects of asymmetry are well documented in the study of the dielectric behavior of nonrigid molecules.<sup>52</sup> Diphenyl ether, a symmetrical nonrigid molecule, has a relaxation time  $4.9 \times 10^{-12}$  sec in benzene solution at 20°. <sup>54</sup> The bis(*p*-nitrophenyl) ether molecule, being larger, is expected to exhibit a larger relaxation time according to B. This expectation is borne out by the experimentally observed relaxation time  $14 \times 10^{-12}$  sec for the bis(*p*-nitrophenyl) ether molecule at 20° in benzene solution.<sup>56</sup> If the CIM mechanisms<sup>52</sup> are blocked as in the bis(*o*-nitrophenyl) ether molecule, one would expect to observe a much larger relaxation time according to C, which is indeed the case as shown by the large observed value  $52 \times 10^{-12}$  sec for bis(*o*-nitrophenyl) ether at 20° in benzene.<sup>56</sup> When the symmetry of the CIM relaxation process is disrupted by the introduction of an asymmetrical component as in the *p*-bromophenyl phenyl ether and the *p*-pyridyl phenyl ether molecules, overall molecular relaxation becomes important. The conservation of angular momentum requires a counter displacement of the solvent molecules, giving rise to appreciably larger relaxation times according to A. The observed relaxation times for *p*-bromophenyl ether<sup>57</sup> and *p*-pyridyl phenyl ether<sup>58</sup> are  $72 \times 10^{-12}$  and  $52.2 \times 10^{-12}$  sec in benzene at 20°, respectively.

On the basis of a variety of physical and chemical properties, the 1,2-dimethylnorbornyl,<sup>38,39</sup> 1,2-dimethoxynorbornyl,<sup>41</sup> 1,2-di-*p*-anisylnorbornyl,<sup>40</sup> 2-*p*-anisylnorbornyl,<sup>34b</sup> 2-phenylnorbornyl,<sup>37</sup> and 1,2-diphenylnorbornyl<sup>59</sup> cations are all considered to exhibit classical behavior.<sup>42</sup> This behavior has been rationalized in terms of two well-established concepts: (D) stabilization of the tertiary carbonium ion due to strain release<sup>60-63</sup> at the site of substitution, and (E) stabilization or destabilization of the carbonium ion at the substitution site depending upon the electron-donating or electron-withdrawing nature of the substituent group. Within the framework of the present theoretical analysis, the effects A-C arising from asymmetry should also enhance the characteristics of classical behavior. In fact, it is not only possible to rationalize the retardation of the Wagner-Meerwein rearrangement in terms of A-C but also predict *trends* for the rate constants of the CIM transitions in the various 2-norbornyl derivatives.

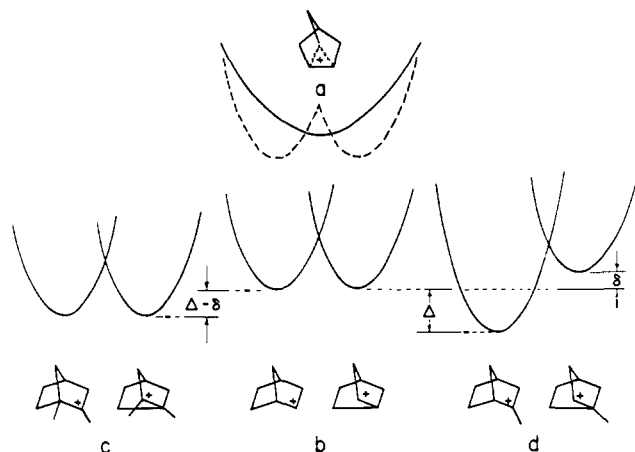
In ordinary solvents, the rate constants for the Wagner-Meerwein rearrangement should decrease in the order



In arriving at the above sequence, we have primarily made use of A and B. The discontinuity  $2 \gg 3$  results from the disruption of the symmetrical CIM Wagner–Meerwein rearrangement in **2** by the introduction of the methyl groups in **3**. The remaining order can be understood in terms of the increasing size of the substituent groups according to eq 3 and 4. In the last statement, we have assumed that the average intermolecular solute–solvent interactions (and hence  $\kappa_0$ ) remain approximately constant throughout the series 3–6.

In strongly polar solvents such as the “super acids”<sup>64,65</sup> (e.g.,  $\text{SbF}_5\text{-SO}_2$  and  $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2$ ) employed<sup>65</sup> to stabilize 2-norbornyl cations, polar substituent groups are expected to exert a pronounced retarding effect over nonpolar groups due to enhanced solute–solvent interactions. The expected order for the rate constants now becomes  $2 \gg 3 > 5 \gg 4 > 6$ . The large activation barrier<sup>41</sup> 13.2 kcal mol<sup>-1</sup> observed for **4** compared to the low barrier<sup>65</sup> for the 1,2 Wagner–Meerwein shift in **3** appears to be consistent with the above argument. The activation energy 13.2 kcal for **4** is comparable to the large activation energies 10–15 kcal mol<sup>-1</sup> for molecular rotations found in strongly hydrogen-bonded liquids such as glycerol.<sup>66</sup>

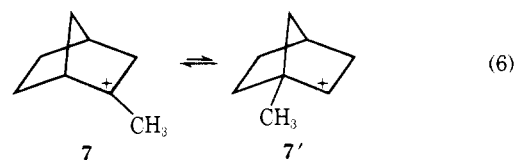
Actually, of course, the dynamical behavior of the 2-norbornyl cations must be interpreted in terms of an interplay of the five effects A–E. For example, the 2-*p*-anisyl-2-norbornyl cation is undoubtedly stabilized due to charge localization *via* the electron-donating *p*-anisyl group and the strain release at the tertiary site. Careful pmr studies have indeed revealed no 1,6 charge delocalization in 2-phenyl-2-norbornyl<sup>37</sup> and the same is doubtless true in the more stable 2-*p*-anisyl-2-norbornyl cation.<sup>34b</sup> However, neither charge delocalization nor steric strain effects are expected to significantly lower the internal barrier  $E_a$  in 1,2-disubstituted 2-norbornyl cations. The force constant of the proposed CIM vibration derives mainly from the strain arising from bending the bridgehead angles  $\angle\text{C-2,C-1,C-6}$  and  $\angle\text{C-3,C-4,C-5}$ . Stabilization and destabilization effects D and E are largely canceled in the symmetrical disubstituted cations. We take for example the effects of the methyl groups. We let  $\delta$  be the steric strain due to the introduction of a  $\text{CH}_3$  group on a tertiary carbon and  $-\Delta$  be the stabilization energy due to the delocalization of the positive charge in a tertiary cation. If we neglect any effects on the force constant of the CIM mode arising from the introduction of the  $\text{CH}_3$  groups, we arrive at a set of intersection adiabatic potential surfaces for the 1,2-dimethylnorbornyl and the monosubstituted methylnorbornyl cations relative to those of the 2-norbornyl cation (see Figures 2b–d). From Figures 2b and 2c, we observe that no substantial change in the barrier height is expected from the introduction of the two methyl groups in the 1,2-dimethylnorbornyl cation although there is a shift in the equilibrium energy with re-



**Figure 2.** Model adiabatic surfaces for several norbornyl cations illustrating (a) the question of  $\sigma$  bridging in the 2-norbornyl cation, (b) rapid equilibration of “classical” 2-norbornyl cations, and (c, d) steric strain and charge delocalization effects in methyl-substituted 2-norbornyl cations. The values of  $\delta$  and  $\Delta$  are arbitrary.

spect to that of the 2-norbornyl cation.

In monosubstituted derivatives, the situation is quite different. From Figure 2d, we observe that the combined effects of steric strain and charge delocalization in



renders **7** by far the more stable isomer in the equilibration in (6). The forward and backward rate constants in (6) are given by

$$W_{7'-7} = A \exp[-(\Delta + \delta - 4E_a)^2/16E_a kT] \quad (7)$$

$$W_{7-7'} = A \exp[-(\Delta + \delta + 4E_a)^2/16E_a kT] \quad (8)$$

where  $A$  is given by the preexponential factor in eq 1. Equations 7 and 8 have been derived from eq 36 and 37 of ref 4.  $E_a \gg \hbar\omega$  and  $kT \gg \hbar\omega$ . From (7) and (8), the equilibrium distribution of **7** and **7'** can be evaluated

$$N_7/N_{7'} = W_{7'-7}/W_{7-7'} = \exp[(\Delta + \delta)/kT] \quad (9)$$

which is exactly what one would expect from thermodynamic arguments and serves as a consistency check for the theoretical expressions employed herein.

On the basis of the qualitative analysis given above, we thus expect the 2-norbornyl cation to exhibit anomalous behavior, an exceptionally fast rate of equilibration. This anomaly is a result of the near-spherical symmetry of the 2-norbornyl cation. The CIM  $2 \rightarrow 2'$  process can take place without appreciable counter participation of the solvent medium. The rearrangement transition occurs between two electronically degenerate states whose potential minima are given by the two equivalent nuclear configurations with the cation charge localized at the 2 positions. Relaxation processes *predominated* by intramolecular mechanisms are characterized by low-activation barrier.<sup>46–51</sup> In the present case, only a minor nuclear rearrangement is needed for the  $2 \rightarrow 2'$  transition. In terms of eq 2, this means that a relatively small displacement  $\Delta R$  in the normal coordinate of the promoting mode is required for the transition, leading to a small activation barrier  $E_a$ . In the following, we develop a more quantitative treatment for the dynamical behavior of the Wagner–Meerwein shift. The expected quantum-mechanical behavior in the low-barrier limit is discussed as

well as the significance of  $\sigma$  bridging in the 2-norbornyl cation.

### Departure from the Arrhenius Behavior. Relaxation by Quantum Shuttling

Equation 1 is valid strictly for the limiting conditions

$$E_a \gg \hbar\omega \quad (10a)$$

$$kT \gg \hbar\omega \quad (10b)$$

If (10a) holds but (10b) is relaxed, such that  $kT \lesssim \hbar\omega$  as in low-temperature experiments, it is necessary to write, instead of (1), for the activated rate constant

$$W' = (2n + 1)(\hbar|S|^2/M\Delta\epsilon^2)[(2\pi MkT/\hbar^2)^{1/2}\Delta R]^{-1} \times \exp(-E_a/kT) \quad (11)$$

where

$$n = [\exp(\hbar\omega/kT) - 1]^{-1} \quad (12)$$

and  $E_a$  is given by eq 2. It is clear that for  $kT \gg \hbar\omega$ , (11) reduces directly to (1). In the limit  $kT \ll \hbar\omega$ , (11) simplifies to

$$W = (2\hbar|S|^2/M\Delta\epsilon^2)[(2\pi MkT/\hbar^2)^{1/2}\Delta R]^{-1} \exp(-E_a/kT) \quad (13)$$

where we have used condition 10a.

The important point here is that regardless of the temperature, the rate expression does not depart significantly from the Arrhenius behavior. At high temperatures, we have

$$W \propto T^{1/2} \exp(-E_a/kT) \quad (1a)$$

while at low temperatures, we have

$$W \propto T^{-1/2} \exp(-E_a/kT) \quad (13a)$$

so long as the activation barrier  $E_a$  is much larger than one quantum  $\hbar\omega$  of the promoting mode.

It is desirable to arrive at an estimate (a detailed discussion of which is given in a later section) of the rate constant for the  $2 \rightarrow 2'$  process in the 2-norbornyl cation. Assuming the values  $M \sim 2 \times 10^{-23}$  g (corresponding to an estimate for the reduced mass of the CIM oscillation),  $\omega \sim 4 \times 10^{13}$  sec $^{-1}$  (corresponding to a skeletal-twist vibrational energy  $\hbar\omega \sim 200$  cm $^{-1}$ ) and  $\Delta R \sim 4 \times 10^{-9}$  cm (corresponding to an estimated displacement of 0.4 Å in the CIM promoting mode coordinate), we obtain from (2)  $E_a \sim 1$  kcal mol $^{-1}$ . This falls in the range of activation barriers normally observed for sterically unhindered intramolecular group rotations.<sup>43-54</sup> Assuming the usual value  $10^{13}$  sec $^{-1}$  for the Arrhenius  $A$  parameter in eq 1, we arrive at the rate constant  $W \sim 10^{12}$  sec $^{-1}$  at 25° which, at first sight, appears to fall within the range  $2 \times 10^{12}$ – $2 \times 10^{13}$  sec $^{-1}$  at 25° estimated by Winstein<sup>67</sup> for the  $2 \rightarrow 2'$  process in the 2-norbornyl cation from pmr and solvolysis data.

The above calculation, however, is not valid. The estimated barrier  $E_a \sim 1$  kcal mol $^{-1}$  (350 cm $^{-1}$ ) is on the order of  $\hbar\omega$  which has been assumed to be 200 cm $^{-1}$ . Instead of (10a), we now have

$$E_a \sim \hbar\omega \quad (14)$$

as the classical Arrhenius behavior for the rate constant given by (1), and (16) gives way to the description of quantum mechanical tunneling.

In a general description of the double-minimum problem typified by the  $2 \rightarrow 2'$  Wagner–Meerwein rearrangement, the stationary eigenfunctions are given by the symmetrical combination

$$\Psi_1 = \frac{1}{\sqrt{2}}(\psi_2 + \psi_{2'}) \quad (15)$$

and the antisymmetrical combination

$$\Psi_2 = \frac{1}{\sqrt{2}}(\psi_2 - \psi_{2'}) \quad (16)$$

where

$$\psi_2 = \frac{1}{\sqrt{2}}(\Psi_1 + \Psi_2)$$

and

$$\psi_{2'} = \frac{1}{\sqrt{2}}(\Psi_1 - \Psi_2) \quad (17)$$

respectively, correspond to the instantaneous wave functions of the system with the 2-norbornyl cation assuming the classical structures **2** and **2'**. The rate constant for the intrinsic time evolution of  $\psi_2$  to  $\psi_{2'}$  corresponding to the Wagner–Meerwein shift  $2 \rightarrow 2'$  is given<sup>68</sup> by the approximate formula

$$W' = \tau'^{-1} = (2\omega/\pi)(2E_a/\pi\hbar\omega)^{1/2} \exp(-2E_a/\hbar\omega) \quad (18)$$

where  $E_a$  and  $\omega$  assume the same significance as in eq 1 for the activated rate constant  $W$ . We observe that under the conditions in (10) specialized to the Arrhenius behavior

$$W \gg W' \quad (19)$$

However, in the low-barrier case characterized by (14), the quantum mechanical shuttling rate  $W'$  can become significant.

In Figure 3, we plot the values of  $\log \omega\tau'$  calculated from (18) as  $E_a/\hbar\omega$  is parametrically varied. Also plotted in Figure 3 is an exact extrapolation to the zero-barrier limit using numerical solutions.<sup>68</sup> From Figure 3, we obtain the estimate  $\sim 10^{12}$  sec $^{-1}$  for the rate constant of  $2 \rightarrow 2'$  at  $\hbar\omega = 200$  cm $^{-1}$  for a 1-kcal mol $^{-1}$  barrier. This result is at the lower end of Winstein's estimated range  $2 \times 10^{12}$ – $2 \times 10^{13}$  sec $^{-1}$ .

### Evidence for $\sigma$ Bridging in the 2-Norbornyl Cation

In the preceding sections, the dynamical behavior of the 2-norbornyl cation derivatives has been discussed in terms of the double-minimum model. Here, we examine the evidence for the postulated nonclassical  $\sigma$ -bridged 2-norbornyl cation.<sup>55</sup>

Perhaps the most vigorous current proponents of the concept of  $\sigma$  bridging in the 2-norbornyl cation are Olah and his students who have reported massive evidence for the 2-norbornyl cation nonclassical structure **8** in terms of pmr,<sup>65,69</sup>  $^{13}\text{C}$  nmr,<sup>65a,70-73</sup> Raman,<sup>65a,71</sup> and ESCA<sup>72,73</sup> spectroscopic observations.



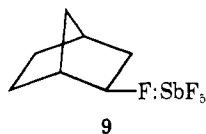
The temperature-dependent pmr studies<sup>64</sup> of the 2-norbornyl cation are of great interest. At  $-154^\circ$ , the low-field four-proton resonance is separated into two components at  $\delta$  3.05 and 6.59. This splitting may be suggestive of structure **8**, with the two components corresponding respectively to the two equivalent protons at the bridgehead and the two equivalent corner protons of **8**. However, since the time resolution of nmr is low ( $\sim 10^{-3}$  sec), the observed  $-154^\circ$  splitting could equally well be attributed to the two protons at positions 1 and 2 and the two methylene protons at position 6 of **2** and **2'**. Structural assignments<sup>64,65,69,70,73</sup> based on chemical shifts observed in the pmr and  $^{13}\text{C}$  nmr studies are thought to be unreliable.<sup>74</sup> No dependable theory is available at present which makes possible an unambiguous comparison of chemical shifts observed in strained bicyclic and in aliphatic compounds.

The weakest evidence for **8** advanced by Olah and co-

workers is based<sup>65a,71</sup> on a qualitative interpretation of the laser Raman spectra in terms of the symmetry properties of alternative models for the 2-norbornyl cation. In the absence of detailed normal mode analyses,<sup>75</sup> a definitive structural assignment is impossible. Qualitative symmetry determinations based on optical spectroscopy are seldom unique, and conclusions drawn from them without a proof of their uniqueness are almost invariably misleading.<sup>76</sup>

The experimental evidence offered for **8** in terms of the ESCA data has been disputed by Kramer.<sup>74</sup> According to Olah, *et al.*,<sup>72,73</sup> a curve resolver analysis of the C 1s binding energy spectrum gave an approximate peak area ratio of 5:2 in support of **8**. However, a careful reexamination of the first published spectrum<sup>72</sup> by Kramer<sup>74</sup> yielded an area ratio slightly larger than 6:1. The second published spectrum,<sup>73</sup> according to Kramer, differs from the first in the appearance of a new band on the high-energy shoulder of the supposed cation band. After a correction for this discrepancy, an area ratio 6:1 was again obtained,<sup>74</sup> in support of the classical structure **2**. The claim for the existence of **8** on the basis of the energy separation ( $\sim 1.5$  eV) of the two observed ESCA bands has also been questioned by Kramer.<sup>74</sup>

The Olah-Kramer disagreement notwithstanding, it appears that in view of existing data, it is safe at present to conclude that a certain distribution of C atoms exists in Olah's "norbornyl" samples. This distribution yields a main ESCA peak with a minor high-energy shoulder. It is desirable to establish on independent grounds that the observed spectrum does in fact originate from the 2-norbornyl cation. The possibility that the observed ESCA spectra may well have resulted from an addition compound of 2-norbornyl fluoride such as **9** has yet to be ruled out. It is not at all



clear that the area ratios claimed by Kramer and Olah are meaningful judging from the variability in Olah's published data.<sup>72,73</sup> In ESCA experiments, the probe penetration of the sample material is approximately 30 Å, and surface contamination may play an important role on the reproducibility of the measurements.

Attempts at resolving the question of  $\sigma$  bridging on the basis of quantum mechanical calculations have also been conflicting and inconclusive.<sup>76-80</sup> The uncertain nature of *ab initio* calculations can perhaps be summed up by Goetz and Allen's own assessment of their theoretical calculations.<sup>80</sup> These authors concluded that the total energy of **2** is 4.7 kcal mol<sup>-1</sup> lower than that of **8**. However, they also estimated that the "addition of polarization functions will produce a further lowering of the nonclassical relative to the classical structure, most likely making the nonclassical more stable."<sup>81</sup>

The confusion in the literature may perhaps be alleviated by an improved reexamination of the ESCA spectra. If an area ratio of 5:2 can be definitively attributed to the 2-norbornyl cation spectrum, the existence of the nonclassical structure **8** can then be established beyond question within the present framework of relaxation theory. The results displayed in Figure 3 are instructive. We find that irrespective of the barrier  $E_a$ , the expected relaxation time for the **2**  $\rightarrow$  **2'** process cannot assume values much less than  $\sim 10^{-13}$  sec. Within the present context, the nonclassical ion question thus reduces simply to whether or not the minimum of the adiabatic surface corresponding to the lowest electronic state of the nuclear configuration **8** lies below the cusp of

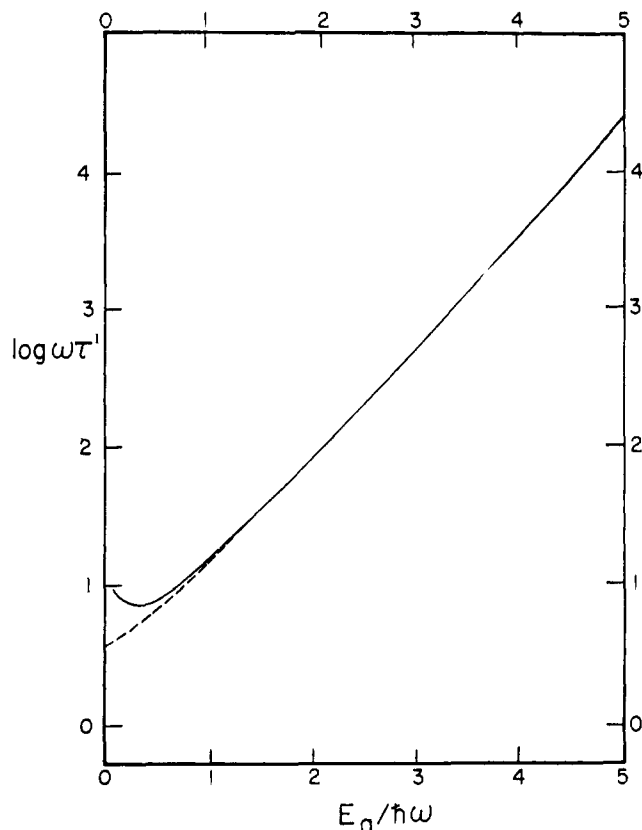
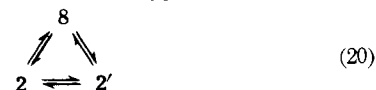


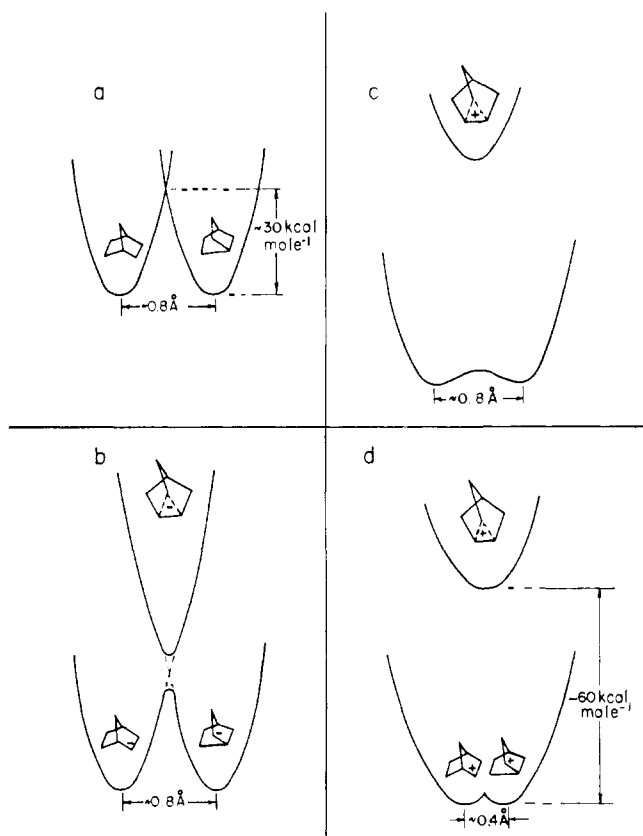
Figure 3. Parametric dependence of the shuttling time  $\tau'$  on the barrier height  $E_a$  separating the two equivalent potential wells in the double-minimum model for equilibrating 2-norbornyl cation configurations. The solid curve is calculated from the approximate expression in eq 4 for  $E_a \gg 0.25 \hbar\omega$ . The dotted line represents a numerical evaluation in the low-barrier limit involving the two lowest vibrational eigenvalues of the double-minimum well problem.

the intersecting adiabatic surfaces of **2** and **2'** (see Figure 2a). A dynamical equilibration of the type



must then be considered. Individual rate constants must be assigned to **2**  $\rightarrow$  **8** (**2'**  $\rightarrow$  **8**), **8**  $\rightarrow$  **2** (**8**  $\rightarrow$  **2'**), and **2**  $\rightarrow$  **2'** (**2'**  $\rightarrow$  **2**) transitions. Since the time resolution of ESCA spectroscopy is  $\sim 10^{-16}$  sec and the quantum mechanical shuttling time is  $\sim 10^{-12}$  sec, a definitive determination of the C 1s binding energy spectrum of the 2-norbornyl cation should yield the peak ratios 5:2 if there is a single stable configuration corresponding to **8**, 6:1 if there are two stable configurations corresponding to **2** and **2'**, and 17:2:2 if **2**, **2'**, and **8** are equally stable provided that Olah's qualitative interpretation of the ESCA spectral band separation is correct. A more quantitative description of (20) is developed later in terms of the theoretical expectations.

There appears to be unanimous agreement that all known examples of substituted norbornyl cations<sup>37-42,59</sup> exhibit classical behavior. The only disputed case is the 2-norbornyl cation. The postulated nonclassical behavior of the 2-norbornyl cation is thus presented as a unique chemical singularity. On the other hand, the present treatment provides a consistent description of the entire homologous series of norbornyl cations on the basis of the double-minimum model without invoking the creation of the nonclassical configuration **8**. The apparent anomaly in the relaxation behavior of **2** has been numerically accounted for in terms of the low-barrier CIM degree of freedom. The numerical estimates of the rate constant for the **2**  $\rightarrow$  **2'** process are shown



**Figure 4.** Summary of the theoretically deduced energy diagrams for (a) two noninteracting adiabatic surfaces; (b) two interaction surfaces with a small splitting at the cross-over point; (c) two strongly interacting surfaces with a large splitting at the intersection resulting in an excited potential with a single minimum and a ground-state double-minimum potential surface with a low barrier; and (d) the harmonic representation of the ground-state double-minimum well corresponding to a leaning of **2** and **2'** to the bridged structure **8**. The barrier in (d) corresponds to  $E_a$  in Figure 1.

to be consistent with the empirical estimates by Winstein.<sup>67</sup> Similar relaxation anomalies arising from low-barrier CIM mechanisms have been fully documented by the homologous series of diphenyl ethers.<sup>52</sup>

#### Barrier to the Wagner–Meerwein Shift

The values of  $M$ ,  $\omega$ , and  $\Delta R$  upon which we base the numerical analysis of the **2**  $\rightarrow$  **2'** transition have been arrived at in a relatively simple manner. The estimate  $M \sim 2 \times 10^{-23}$  g has resulted from the assumption that the collective motion of the nuclei at positions 2 and 3 is countered by that at positions 5 and 6. We have used the approximate equation

$$M = \mu_1 \mu_2 / (\mu_1 + \mu_2) \quad (21)$$

where  $\mu_1$  is the collective mass of the carbon and hydrogen atoms at positions 2 and 3 and  $\mu_2$  is that at positions 5 and 6 in **2**.

If the remainder of the molecule were to remain stationary, C-6 would be displaced by about 2.5 Å in the **2**  $\rightarrow$  **2'** shift assuming the nuclear configuration of the norbornyl cation is the same as that of norbornane. Since, however, the overall angular momentum of the molecule is conserved in intramolecular rearrangement and since the remainder of the molecule must readjust to an energy minimum, the pathway of C-6 is countered by the remainder of the molecule in **2**  $\rightarrow$  **2'**, and the normal mode displacement between the equilibrium positions of the adiabatic states is estimated to be only approximately 0.8 Å.

First, we consider the case in which there is zero interaction between the diabatic states (as in the norbornane molecule). The value  $\hbar\omega = 600 \text{ cm}^{-1}$  typically observed for skeletal vibrations in alkanes<sup>82</sup> is assumed for the torsional mode corresponding to the CIM degree of freedom described earlier for **2**  $\rightarrow$  **2'**. Using eq 2 with  $M = 2 \times 10^{-23}$  g,  $\hbar\omega = 600 \text{ cm}^{-1}$ , and  $\Delta R = 0.8 \text{ Å}$ , we find that the two harmonic surfaces intersect at  $\sim 30 \text{ kcal mol}^{-1}$ . This is a reasonable order-of-magnitude estimate for the energy required for the deformation of  $\angle\text{C-2,C-1,C-6}$  by  $\sim 50^\circ$ . The coordinate representation of the two noninteracting states is given in Figure 4a.

In the 2-norbornyl anion, there is electronic coupling between the diabatic states. Due to a nonbonding  $\sigma$ -electron repulsion in the anion, however, this coupling is weak and the splitting at the cross-over point is small (see Figure 4b). The barrier to a CIM rearrangement process corresponding to **2**  $\rightarrow$  **2'** is thus expected to be on the order of at least 30 kcal mol<sup>-1</sup>, which accounts for the fact that the anion does not rearrange under normal conditions.

In the 2-norbornyl cation, coupling between the diabatic states is strong due to the electronic deficiency at C-2. The splitting at the cross-over point is accordingly large, resulting in a depressed barrier for the **2**  $\rightarrow$  **2'** transition and an elevated minimum (located at  $\sim 60 \text{ kcal mol}^{-1}$  above the ground-state minima) for the  $\sigma$ -bridged configuration (see Figure 4c).

In the above description, the ground-state double-minimum hypersurface is composed of two shallow anharmonic wells. In practice, however, it is convenient to consider a readjustment of the equilibrium positions of **2** and **2'** such that the anharmonic double-minimum well is now replaced by two intersecting harmonic potentials corresponding to ground-state "classical" configurations leaning toward the "nonclassical" structure of **8**. While the primary motivation for this consideration is mathematical simplicity, the implications of such a proposal actually appear to make good physical sense in the present context. There is no justifiable reason to expect the norbornyl cation to assume the same nuclear coordinates as those of the neutral norbornane molecule. In view of the attraction of the electron-deficient carbon atom at position 2 for the bonding electrons of C-2 and C-6, a slight displacement of C-6 toward C-2 in the equilibrium configuration of **2** is most likely.

The above reasoning procedure leads to the  $\Delta R = 0.4 \text{ Å}$  estimate for the **2**  $\rightarrow$  **2'** transition in the 2-norbornyl cation. The value  $\hbar\omega = 200 \text{ cm}^{-1}$  assumed for the CIM promoting mode of **2**  $\rightarrow$  **2'** is characteristic of low-barrier double-minimum well problems as typified by the ring-puckering motion in trimethylene oxide.<sup>83,84</sup>

The foregoing discussion thus leads to the following picture for the 2-norbornyl cation problem, which is summarized in Figure 4d. The ground electronic state is prescribed by the harmonic double-minimum well corresponding to the two "classical" structures **2** and **2'**. The first excited state is the lowest lying state of the  $\sigma$ -bridged "nonclassical" ion **8**. This picture is reminiscent of the  $\text{NH}_3$  molecule for which the ground state is characterized by a double-minimum well corresponding to the two umbrella structures and the first excited state potential surface is given by a single-minimum well corresponding to a stable planar structure.<sup>85</sup> In exact analogy with the ground-state  $\text{NH}_3$  molecule, we have shown that the ground-state 2-norbornyl cation undergoes quantum shuttling between the two "classical" structures. The "nonclassical" structure **8** (in analogy with the planar  $\text{NH}_3$  molecule) is an unstable species at the crest of the barrier in the ground electronic state and exists only as a stable species (with a single energy minimum) in an excited state. In terms of this description, we would not expect the **2**  $\rightleftharpoons$  **8**

and  $2' \rightleftharpoons 8$  transitions in (20) to play any significant role in the ground-state chemistry of **2** and  $2'$ .

In the 1,2-disubstituted norbornyls, the  $1 \rightarrow 1'$  shift is retarded by the displacement of the surrounding solvent molecules. The barrier to the rearrangement process can no longer be simply evaluated from eq 2. This barrier can be approximated by a combination of (2) and (5). The summary given in Figure 4d is thus exemplary of all the norbornyl systems. The barrier  $\sim 1$  kcal mol<sup>-1</sup> estimated for the 2-norbornyl cation gives the lower limit for the  $1 \rightarrow 1'$  shift. For systems characterized by high activation energies (e.g., the 1,2-dimethoxy 2-norbornyl cation<sup>41</sup> in a superacid), the quantum shuttling process most probably becomes less important than the corresponding activated rate process, in which case the rate constant is best given by eq 1.

Other carbonium ion derivatives have been examined under stable ion conditions and shown to exhibit rapid equilibration between classical ions which cannot be frozen out at low temperatures. Such ions include 2-butyl, 2,3-dimethyl-2-butyl, 2,3,3-trimethyl-2-butyl, and cyclopentyl.<sup>86</sup> The inability to freeze out the interconversions means that the barriers for interconversion must be low, generally less than 4 kcal mol<sup>-1</sup>. It thus appears that the above analysis of the 2-norbornyl cations is generally applicable to all carbonium systems which can undergo intramolecular rearrangement.

### The Transition State Problem

The starting point of this paper is the complete departure from the activated complex theory which is basically invalid in the formal description of most activated rate processes.<sup>4,6,22,23</sup> The confusion which has contributed to the long-standing controversy of the classical-nonclassical 2-norbornyl cation problem<sup>67,87-90</sup> can be traced to the widespread usage of the activated complex theory. The transition state in Eyring's original theory is a thermodynamic state with energy minimum located on the reaction coordinate midway between the potential surfaces of the reactant and the product. This assumption of thermodynamic stability allows for the parameters of activation such as  $\Delta G^*$ ,  $\Delta S^*$ , and  $\Delta E^*$ , the free energy, entropy, and energy of activation, even though there is no basis of justification for such an assumption.<sup>6</sup> The situation is now complicated by an evolution of Eyring's concept into three variations. In common practice, the transition state is generally considered to be located at the maximum of the activation barrier, while the barrier with an energy trough is thought to be associated with a "metastable intermediate" or an "intermediate" depending on whether the energy trough is higher or lower than the energy minima of the reactant and the product (see, for example, the discussion of Figure 3 in ref 59). Olah and coworkers, for example, arbitrarily considered all the substituted norbornyl cations in their  $\sigma$ -bridged forms to be "transition states" or "metastable intermediates" and the 2-norbornyl cation in its  $\sigma$ -bridged form to be an "intermediate" (presumably due to exceptionally large " $\sigma$ -bridging stabilization") in the solvolysis of norbornyl derivatives.<sup>59</sup> Out of these considerations, Olah developed a "general concept of carbocations" based on the differentiation of the trivalent "carbenium" ("classical") ions from the "pentavalent" carbonium ("nonclassical") ions.<sup>34c</sup>

It has been argued that the low barrier to the interconversion of classical carbonium structures implies the existence of a low-lying transition state. This transition state is presumed to be equivalent to the  $\sigma$ -bridged nonclassical ion of Winstein. It is therefore reasoned that if the transition state is so stabilized in energy, why should one question the possibility that this may become a stabilized ground state?

The estimated<sup>67</sup> range  $2 \times 10^{12}$ – $2 \times 10^{13}$  sec<sup>-1</sup> for the rate constant of the  $2 \rightarrow 2'$  equilibration process suggested the bridged nonclassical structure **8** to Winstein<sup>67</sup> because such a rate constant appears to be "greater than  $kT/h$  in absolute rate theory, namely  $6 \times 10^{12}$  sec<sup>-1</sup> at 25°, the rate constant predicted for zero  $\Delta F^*$ ." Bartlett further elaborated<sup>90</sup> that the rate constant  $4 \times 10^{12}$  sec<sup>-1</sup> estimated for the  $2 \rightarrow 2'$  racemization process in SO<sub>2</sub>-SbF<sub>5</sub> at 25° "happens to be about the rate of passage of a transition state over the barrier in rate theory." In his view, "any reaction occurring so fast has zero activation energy and the migrating carbon would be at just as low an energy when midway in its migration as at the beginning or end." He concluded that "no such picture of decaying molecular structure results if we attribute the racemization to the direct formation of the bridged ion with planar symmetry, and no absurdly high rate constants are required."

In view of the detailed analysis given above, the estimated  $\sim 10^{12}$  sec<sup>-1</sup> rate constant in the low-barrier limit of the double-well model appears to be well within expectation. The postulate of the  $\sigma$ -bridged nonclassical structure **8** for the ground-state 2-norbornyl cation on the basis of the otherwise "absurdly high" rate constant is tantamount to the postulate of a ground-state *stable* planar structure for the NH<sub>3</sub> molecule on the basis of the rapid rate ( $\sim 10^{12}$  sec<sup>-1</sup>) of shuttling between its two pyramidal configurations.

We now see that the  $\sigma$ -bridged structure at the top of the barrier to interconversion does not correspond to a state since it is not a stable species. The creation of the low barrier to interconversion of ground-state classical structures is in fact accompanied by the elevation of the energy minimum of the stable bridged structure which exists as an excited electronic state. When the barrier to intramolecular rearrangement is low (i.e.,  $E_a \lesssim \hbar\omega$ ), as indeed appears to be the case in the 2-norbornyl cations, we envision a most elegant internal mode of quantum shuttling between the two "classical" wells, far from Bartlett's vision of a "decaying molecular structure" in which "C-6 flops about randomly" as if "in an untidy box."<sup>90</sup>

### Conclusion

In the above, we have provided the theoretical grounds for the apparent differences between 2-norbornyl and the mono- and 1,2-disubstituted norbornyls in terms of the solvent effects on the concerted intramolecular rearrangement process. A self-consistent description has been made without invoking the role of the ground-state  $\sigma$ -bridged nonclassical ion. Partial formation of the nonclassical ion in the transition state of the *exo*-norbornyl isomer was originally thought<sup>35</sup> to be responsible for the phenomenon of high *exo*/*endo* rate ratios in the solvolysis of the 2-norbornyl derivatives until Brown systematically established that such *exo*/*endo* rate ratios are not significantly different from those observed in tertiary 2-norbornyl derivatives yielding classical cationic intermediates.<sup>42</sup>

It was then argued<sup>67,90</sup> that the high degree of racemization observed in the solvolysis of 2-norbornyl derivatives required a seemingly absurd rate constant of  $\sim 10^{12}$  sec<sup>-1</sup> for the equilibration between the two classical ions. The present treatment now reveals that such a rate of equilibration is in fact expected of the norbornyl system and, indeed, can be estimated from well-accepted first principles.

The "classical" behavior established for all the known substituted 2-norbornyl cations<sup>34b,37-41,59</sup> and aliphatic cations<sup>86</sup> suggests that the description summarized in Figure 4 is generally valid. In this description, *the energy minimum of the  $\sigma$ -bridged structure must lie above the crest of the activation barrier to the equilibrating pair of "classical" ions*. The remaining debate over the nonclassical ion status



of the 2-norbornyl cation thus appears to boil down to the validity of the postulate that, in the singular case of **8**, the ground state is given by the single-minimum potential well corresponding to the structure that typically characterizes an excited state of all the other norbornyl systems. Such a postulate has not been supported by definitive theoretical or experimental evidence, and it clearly reaches beyond the rigorous confines of the present logical framework.

In itself, the question of nonclassical ions represents a specialized area of research. Since the publication of the collection of research reprints and commentaries by Bartlett in 1965,<sup>90</sup> the once-exalted position commanded by the concept of  $\sigma$ -bridged nonclassical ions, which at one time included practically all existing carbonium ions from saturated structures, has eroded to the debate over the singular case of the 2-norbornyl cation. Nevertheless, this debate is important because the problem points to the larger question of the transition state in chemical reactions. We have shown that decades of the controversy over the classical-nonclassical ions appear to have been sustained by a proliferation of ambiguous definitions and concepts derived mostly from the uncritical usage of the transition state theory. This usage has resulted from the tremendous influence exerted on generations of chemists by the transition state theory which, ironically, may have acted as the major deterrent in the progress of unraveling reaction mechanisms.

**Acknowledgments.** This paper was inspired by a stimulating lecture delivered by G. A. Olah at Purdue University on April 16, 1974. Throughout various stages of this work, the writer has benefited from extensive discussions and communications with H. C. Brown, G. L. Closs, M. Saunders, and C. L. Wilcox. Critical reading of earlier drafts of the paper by J. H. Brewster, D. J. Diestler, J. B. Grutzner, and N. Muller is also gratefully acknowledged.

## References and Notes

- F. K. Fong and M. M. Miller, *Chem. Phys. Lett.*, **10**, 408 (1971).
- F. K. Fong, S. L. Naberhuls, and M. M. Miller, *J. Chem. Phys.*, **56**, 4020 (1972).
- F. K. Fong and W. A. Wassam, *J. Chem. Phys.*, **58**, 956 (1973).
- F. K. Fong and D. J. Diestler, *J. Chem. Phys.*, **57**, 4953 (1972).
- H. V. Lauer and F. K. Fong, *J. Chem. Phys.*, **60**, 274 (1974).
- F. K. Fong, "Theory of Molecular Relaxation: Applications in Chemistry and Biology," Wiley-Interscience, New York, N.Y., 1975.
- L. Onsager, *Phys. Rev.*, **37**, 405 (1931); **38**, 2265 (1931).
- R. Kubo, M. Yokota, and S. Nakajima, *J. Phys. Soc. Jap.*, **12**, 1203 (1957).
- W. M. Gelbart, K. F. Freed, and S. A. Rice, *J. Chem. Phys.*, **52**, 2460 (1970).
- K. F. Freed and J. Jortner, *J. Chem. Phys.*, **52**, 6272 (1970).
- S. Fischer, *J. Chem. Phys.*, **53**, 3195 (1970).
- F. K. Fong, *J. Electrochem. Soc.*, **121**, c117 (1974).
- F. K. Fong, *J. Theor. Biol.*, **46**, 407 (1974).
- F. K. Fong, *Proc. Nat. Acad. Sci. U.S.A.*, **71**, 3692 (1974).
- P. Debye, "Polar Molecules," Chemical Catalog, New York, N.Y., 1929.
- S. Chandrasekhar, *Rev. Mod. Phys.*, **15**, 1 (1943).
- M. C. Wang and G. E. Uhlenbeck, *Rev. Mod. Phys.*, **17**, 323 (1945).
- H. Eyring, *J. Chem. Phys.*, **3**, 107 (1935).
- W. Kauzmann, *Rev. Mod. Phys.*, **14**, 12 (1942).
- S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of the Rate Processes," McGraw-Hill, New York, N.Y., 1941.
- R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge University Press, London, 1939.
- F. K. Fong, *J. Chem. Phys.*, **43**, 2572 (1965).
- S. H. Lin and H. Eyring, *Proc. Nat. Acad. Sci. U.S.A.*, **69**, 3192 (1972).
- R. J. Meakins, *Trans. Faraday Soc.*, **54**, 1160 (1958).
- D. A. Pitt and C. P. Smyth, *J. Amer. Chem. Soc.*, **81**, 783 (1959).
- D. H. Whiffen and H. W. Thompson, *Trans. Faraday Soc.*, **42A**, 114 (1946).
- J. F. Ambrose and W. E. Wallace, *J. Phys. Chem.*, **63**, 1536 (1959).
- D. H. Whiffen, *Trans. Faraday Soc.*, **46**, 130 (1950).
- W. Jackson and J. G. Powles, *Trans. Faraday Soc.*, **42A**, 101 (1946).
- E. J. Hennesly, W. M. Heston, and C. P. Smyth, *J. Amer. Chem. Soc.*, **70**, 4102 (1948).
- F. H. Branin and C. P. Smyth, *J. Chem. Phys.*, **20**, 1121 (1952).
- R. J. W. LeFevre and E. P. A. Sullivan, *J. Chem. Soc.*, 2873 (1954).
- S. K. Garg and C. P. Smyth, *J. Chem. Phys.*, **42**, 1397 (1965).
- For representative reviews, see (a) G. D. Sargent in "Carbonium Ions," Vol. 3, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1972, Chapter 24; (b) H. C. Brown, *Accounts Chem. Res.*, **6**, 377 (1973); (c) G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972).
- S. Winstein and D. S. Trifan, *J. Amer. Chem. Soc.*, **74**, 1147 (1952).
- J. A. Berson in "Molecular Rearrangement," Vol. 1, P. de Mayo, Ed., Interscience, New York, N.Y., 1963, Chapter 3.
- D. G. Farnum and G. Mehta, *J. Amer. Chem. Soc.*, **91**, 3256 (1969).
- H. L. Goering and K. Humski, *J. Amer. Chem. Soc.*, **90**, 6213 (1968).
- H. L. Goering and J. V. Cleveger, *J. Amer. Chem. Soc.*, **94**, 1010 (1972).
- P. v. R. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *J. Amer. Chem. Soc.*, **85**, 479 (1963).
- A. Nickon and Y. E. Lin, *J. Amer. Chem. Soc.*, **91**, 6861 (1969).
- H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N.Y., 1972, Chapters 10 and 11.
- C. Clemett and M. Davies, *Trans. Faraday Soc.*, **58**, 1705 (1962).
- Krishnaji and A. Mansingh, *J. Chem. Phys.*, **42**, 2503 (1965).
- A. J. Curtis, P. L. McGeer, J. B. Rathman, and C. P. Smyth, *J. Amer. Chem. Soc.*, **74**, 644 (1952).
- M. Davies and R. J. Meakins, *J. Chem. Phys.*, **26**, 1584 (1957).
- F. K. Fong and C. P. Smyth, *J. Phys. Chem.*, **67**, 226 (1963).
- M. Davies, *Z. Naturforsch. B*, **17**, 854 (1962).
- F. K. Fong and C. P. Smyth, *J. Amer. Chem. Soc.*, **85**, 548 (1963).
- F. K. Fong and C. P. Smyth, *J. Amer. Chem. Soc.*, **85**, 1565 (1963).
- F. K. Fong and C. P. Smyth, *J. Chem. Phys.*, **40**, 2404 (1964).
- F. K. Fong, *J. Chem. Phys.*, **40**, 132 (1964).
- E. Fischer, *Z. Elektrochem.*, **53**, 16 (1949).
- H. Hufnagel, *Z. Naturforsch. A*, **15**, 723 (1960).
- D. Gust and K. Mislow, *J. Amer. Chem. Soc.*, **95**, 1535 (1973).
- W. P. Purcell and C. P. Smyth, *J. Amer. Chem. Soc.*, **83**, 1063 (1961).
- J. E. Anderson, Ph.D. Dissertation, Princeton University, Princeton, N.J., 1963.
- H. Hufnagel, G. Klages, and P. Knoblock, *Z. Naturforsch. A*, **17**, 96 (1962).
- G. A. Olah and G. Liang, *J. Amer. Chem. Soc.*, **96**, 195 (1974).
- H. C. Brown, *Science*, **103**, 385 (1946).
- H. C. Brown and R. S. Fletcher, *J. Amer. Chem. Soc.*, **71**, 1845 (1949).
- H. C. Brown and H. L. Berneis, *J. Amer. Chem. Soc.*, **75**, 10 (1953).
- E. L. Eliel in "Steric Effects in Organic Chemistry," M. S. Newman, Ed. Wiley, New York, N.Y., 1956, Chapter 2.
- (a) M. Saunders and E. L. Hagen, *J. Amer. Chem. Soc.*, **90**, 2436 (1968); (b) M. Saunders, P. Vogel, E. L. Hagen, and J. Rosenfeld, *Accounts Chem. Res.*, **6**, 54 (1973); (c) G. A. Olah and J. A. Olah, ref 34a, Chapter 17.
- (a) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, **92**, 4627 (1970); (b) G. A. Olah, J. R. DeMember, C. Y. Lui, and R. D. Porter, *J. Amer. Chem. Soc.*, **93**, 1442 (1971).
- N. E. Hill, W. E. Vaughan, A. H. Price, and M. Davies, "Dielectric Properties and Molecular Behavior," Van Nostrand-Reinhold, London, 1969, p 328.
- S. Winstein, *J. Amer. Chem. Soc.*, **87**, 381 (1965).
- E. Merzbacher, "Quantum Mechanics," Wiley, New York, N.Y., 1961, Chapter 5.
- G. A. Olah, E. B. Baker, and M. B. Comisarow, *J. Amer. Chem. Soc.*, **86**, 1265 (1964).
- G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 6883 (1969).
- G. A. Olah, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, **90**, 3882 (1968).
- G. A. Olah, G. D. Mateescu, and J. L. Riemenschneider, *J. Amer. Chem. Soc.*, **94**, 2529 (1972).
- G. A. Olah, G. Liang, G. D. Mateescu, and J. L. Riemenschneider, *J. Amer. Chem. Soc.*, **95**, 8698 (1973).
- G. M. Kramer, *Advan. Phys. Org. Chem.*, in press.
- E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra," McGraw-Hill, New York, N.Y., 1955.
- R. H. Heist, C. R. Chilver, and F. K. Fong, *Phys. Rev. B*, **5**, 4237 (1972).
- R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964).
- W. S. Trahanovsky, *J. Org. Chem.*, **30**, 1966 (1965).
- G. Klopman, *J. Amer. Chem. Soc.*, **91**, 89 (1969).
- R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5350 (1969).
- D. W. Goetz and L. C. Allen, "XXIII International Congress of Pure and Applied Chemistry," Vol. 1, Boston, 1971.
- D. W. Goetz and L. C. Allen, "Electronic Structure of the 2-Norbornyl Cation," unpublished manuscript.
- L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, Wiley, New York, N.Y., 1958, p 31.
- S. I. Chan, J. Zinn, J. Fernandez, and W. D. Gwinn, *J. Chem. Phys.*, **33**, 1643 (1960).
- S. I. Chan, J. Zinn, and W. D. Gwinn, *J. Chem. Phys.*, **34**, 1319 (1961).
- A. D. Walsh, *J. Chem. Soc.*, 2306 (1953).
- For a general review, see D. M. Brouwer and H. Hogeveen, *Progr. Phys. Org. Chem.*, **9**, 179 (1972).
- S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *J. Amer. Chem. Soc.*, **87**, 376 (1965).
- A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *J. Amer. Chem. Soc.*, **87**, 378 (1965).
- R. Howe, E. C. Friedrich, and S. Winstein, *J. Amer. Chem. Soc.*, **87**, 379 (1965).
- P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, New York, N.Y., 1965, p 625.