

# A Successor to Transition-State Theory

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Few physical theories have influenced the development of modern chemistry as much as the transition-state theory.<sup>1-3</sup> The concept of the "transition state" permeates the chemical literature nearly as much as the first and second laws of thermodynamics and the fundamental concepts of chemical bonding. Yet through the four decades since the formulation of the transition-state theory, unsettled questions regarding the validity of the underlying assumptions of this theory have persisted.

In transition-state theory, the rate constant  $W$  of a thermally activated rate process is given by the expression

$$W = \tau^{-1} = \frac{kT}{h} F^\ddagger F^{-1} \xi \exp \frac{-V_0}{kT} \\ = \frac{kT}{h} \exp \frac{\Delta S^\ddagger}{R} \exp \frac{-\Delta H^\ddagger}{RT} \quad (1)$$

where  $F^\ddagger$  and  $F$  are the partition functions of the "transition state" and the equilibrium state, respectively,  $\xi$  is a dimensionless transmission coefficient, and  $V_0$  is the activation barrier height.  $\Delta S^\ddagger$  and  $\Delta H^\ddagger$  are the molar entropy and enthalpy changes, respectively, required to promote the initial equilibrium state to the transition state.

The derivation of eq 1 is based on the assumption that thermodynamic equilibrium is attained between the initial state and the transition state. It is considered that, so long as the molecules are activated and deactivated at a rate fast compared to that at which these molecules enter into the final state from the transition state, the equilibrium assumption may perhaps be justified.<sup>4</sup> Considerable attention has been focused<sup>5,6</sup> on the question of the assumed equilibrium that exists between the reactant state and the forward moving transition state. Implicit in this assumption is the transiency<sup>5b</sup> of the transition state and the unidirectional passage of the reactive system from the initial to the final state.<sup>5,6</sup>

In spite of the detailed arguments that rationalize the equilibrium assumption, it remains difficult to visualize the formation of an "activated complex" in the transition state (in view of its transiency) whose partition functions  $F^\ddagger$  are calculable in the framework of equilibrium statistical thermodynamics. Compelling motivations exist for the formulation of an alternate approach to the understanding of chemical rate processes. Decades of research based on the transition-state theory have resulted in scores of highly sophisticated theo-

retical developments<sup>5,6</sup> and have aided generations of chemists in the systematization of reaction mechanisms. Even so "the calculation from first principles of the rate of even the simplest chemical reaction has still not been accomplished".<sup>5a</sup>

That dynamical processes occur is a consequence of systems being *out of equilibrium*. It appears reasonable to suppose that the starting point in the conceptualization of reaction rates should be a closer look into the consequences of *nonequilibrium* conditions rather than an elaborate rationalization of the equilibrium assumption in transition-state theory. It is desirable to be able to describe rate processes in the framework of irreversible (nonequilibrium) thermodynamics. The new approach would thus amount to a complete departure from many of the currently established equilibrium rate theories.

The purpose of this Account is to reexamine the fundamental mechanisms responsible for rate processes in terms of the recently developed<sup>7-9</sup> quantum statistical mechanical (QSM) theory of molecular relaxation.<sup>10-12</sup> Special attention will be focused on what appears to be the universal role<sup>9</sup> of quantum tunneling in molecular processes underlying *all* double-minimum relaxation phenomena.<sup>13</sup>

Contrast and comparison between the QSM approach to activated rate processes and the transition-state theory were made by Fong and Diestler<sup>7</sup> in 1972. This new approach was subsequently elaborated by Lin and Eyring<sup>8,12</sup> and refined by Freed and Fong.<sup>9</sup> In 1974, the new rate theory was applied<sup>14</sup> to the treatment of Wagner-Meerwein rearrangements in carbocations with special focus on the low-barrier limit of double-minimum relaxation. Along this line of development, we proceed here to relate the transition-state problem to

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general questions of structural symmetries and electron delocalization interactions. It is hoped that this development brings a fresh view to some old problems in chemistry with the notion that the dynamical properties of a rate process depend not so much on the properties of the "transition state" as those of the initial equilibrium molecular configuration.

### Divergent Relaxation Behavior: Symmetrical or Unsymmetrical Structures?

Two thoroughly investigated examples of double-minimum (DM) relaxation are the molecular inversion of the ammonia molecule<sup>15</sup> and the migration of F<sup>-</sup> interstitials in CaF<sub>2</sub>.<sup>7,9,16-19</sup> The ammonia example is generally accepted as the prototype of quantum mechanical tunneling phenomena. The CaF<sub>2</sub> process gives the classical Arrhenius behavior with the usual exponential temperature dependence for the rate constant

$$W = A \exp(-E_a/RT) \quad (2)$$

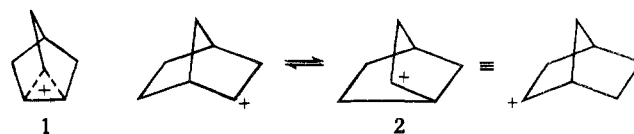
where  $E_a$  is the molar activation energy, and  $A$  is the "preexponential factor".

The Arrhenius behavior, depicted in eq 2, is conventionally interpreted in terms of transition-state theory, whereas departure from this "classical" behavior is often attributed to manifestations of ammonia-like quantum mechanical behavior. Transition-state theory does not account for the divergence in the two types of relaxation behavior, nor does it provide answers for the questions: Why does the NH<sub>3</sub> molecule differ so sharply from other double-minimum systems? Is there a transition state in the NH<sub>3</sub> inversion problem? Is quantum tunneling a molecular phenomenon unique to molecular systems containing protons?<sup>13</sup>

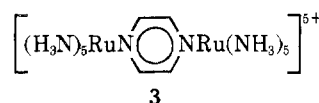
In the following sections we attempt to answer these questions, and show that Arrhenius behavior is in fact generically related to ammonia-like behavior. We choose to focus our attention on a correct model description of DM rate processes for two reasons. First, such a description provides a nice illustration of the new rate theory. Second, DM rate processes appear in virtually all areas of chemistry. The primary photoactivity of chlorophyll *a*-water adducts<sup>20-22</sup> in photosynthesis<sup>23,24</sup> and in solar conversion experiments<sup>24-26</sup> is believed to result from the formation of a charge-transfer state involving a DM tautomeric proton shift.<sup>10e,23,24</sup>

The question of low-barrier DM relaxation appears to lie<sup>14</sup> at the heart of the longstanding nonclassical ion controversy.<sup>10c,13,27-31</sup> Much of the current debate is

centered on the symmetry of the norbornyl cation which can either assume the single minimum (SM) structure<sup>13</sup> (1) or exist as a pair of "rapidly equilibrating" enantiomeric structures (2).<sup>29,31</sup> Of equal significance are



the question of the ground-state symmetry of cyclobutadiene,<sup>32-38</sup> which can be either square<sup>32,36</sup> or rectangular,<sup>33-35,37,38</sup> and the electron delocalization problem in the mixed-valence  $\mu$ -pyrazine-decaamminediruthenium ion<sup>39-42</sup> (3) which can either assume a DM con-



figuration in which the two Ru ions are different<sup>39-41</sup> or a SM configuration in which extensive charge delocalization results in an equalization of the two Ru ions.<sup>42</sup> Most theoretical considerations of the norbornyl cation,<sup>43-45</sup> the cyclobutadiene molecule,<sup>35-37</sup> and the  $\mu$ -pyrazine-decaamminediruthenium(5+) ion<sup>42</sup> have been concerned with the stationary properties of the ground-state electronic configurations. The present work relates the equilibrium molecular configuration with its relaxation dynamics.

### The Quantum Statistical Mechanical Theory of Rate Processes

The QSM theory of rate processes is so called because it has its origin in the time-dependent perturbation theory in quantum mechanics and in the entropy production postulate of irreversible statistical thermodynamics. The starting point is the proper definition of the initial (reactant) and final (product) states. In the DM problem we define the reaction coordinate  $R$  to be along the pathway of configuration interconversion. Molecular vibrations along this coordinate are known as libron motions. All other degrees of freedom of the molecular system and the surrounding host (solvent) medium are collectively called phonon motions or "bath modes"

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because they serve as the temperature bath for the libron motions.

When the libron motions are very slow compared to phonon motions, we envisage the instantaneous adjustment of the bath modes to the libration. It is then possible to invoke adiabatic libron-phonon separation and write

$$[T(\mathbf{r}) + T(\mathbf{Q}) + V(\mathbf{r}, \mathbf{Q}, R)]|\alpha(\mathbf{r}, \mathbf{Q}, R)\rangle = U_\alpha(R)|\alpha(\mathbf{r}, \mathbf{Q}, R)\rangle \quad (3)$$

where  $\mathbf{r}$  and  $\mathbf{Q}$  collectively represent the electron and phonon coordinates, and  $T$  and  $V$  respectively denote kinetic and potential energies. The phonon adiabatic states  $|\alpha(\mathbf{r}, \mathbf{Q}, R)\rangle$  with energies  $U_\alpha(R)$  are labeled by the configuration  $\alpha$ , and vary parametrically with the librational coordinate  $R$ . The librational nuclear eigenfunctions  $\mu_{\alpha n}$  and energies  $E_n$  are accordingly evaluated from

$$[T(R) + U_\alpha(R)]|\eta_{\alpha n}(R)\rangle = E_{\alpha n}|\eta_{\alpha n}(R)\rangle \quad (4)$$

In the above, the adiabatic approximation is in essence applied twice. First, the electrons are regarded as the "fast" subsystem with the lattice phonons regarded as the "slow" subsystem. Then, the lattice phonons are considered to be the fast subsystem with respect to the libration. This double separation preserves the integrity of the libration in a prescribed molecular configuration and gives physical meaning to invoking the single-minimum potential surfaces for the adiabatic "configuration" states  $|\alpha(\mathbf{r}, \mathbf{Q}, R)\rangle$ .

In irreversible thermodynamics, the regression of nonequilibrium fluctuations occurs with a corresponding production of entropy since by postulate entropy is at a maximum in equilibrium. In the linear response theory<sup>46</sup> this entropy production postulate results in the QSM time-correlation function for the rate constant expression<sup>47</sup>

$$W_{\alpha\alpha'} = (\beta \langle \mathbf{N}_\alpha \rangle)^{-1} \times \int_0^\infty dt \int_0^\infty d\lambda \langle \dot{\mathbf{N}}_\alpha(-i\hbar\lambda - t) \dot{\mathbf{N}}_\alpha(0) \rangle \quad (5)$$

where  $W_{\alpha\alpha'}$  is the rate constant for the  $\alpha \rightarrow \alpha'$  transition and  $\beta = kT$ .  $\mathbf{N}_\alpha$  and  $\dot{\mathbf{N}}_\alpha$  are the population and current operators for the configuration  $\alpha$  related through the Heisenberg equation of motion

$$\dot{\mathbf{N}}_\alpha = \frac{i}{\hbar} [\mathbf{H}, \mathbf{N}_\alpha] \quad (6)$$

where  $\mathbf{H}$  is the total Hamiltonian operator. In eq 5 the angular brackets denote a thermal average that signifies the calculation of the stochastic properties in the quasi-thermodynamic scheme.

In this scheme the population flow from  $|\alpha\rangle$  to  $|\alpha'\rangle$  may be likened to matter flow between two heterogeneous phases. In this sense the reactant ( $\alpha$ )-product ( $\alpha'$ )-system may be considered in terms of a quasi-thermodynamic grand canonical ensemble with an assumed form for the time-dependent density operator that is directly analogous to the grand canonical density operator in equilibrium statistics.<sup>10d</sup>

It follows from (3) and (4) that the nonadiabatic couplings between the zeroth-order states  $|\alpha(\mathbf{r}, \mathbf{Q}, R)\rangle$  occur through the off-diagonal elements of the nuclear kinetic energy operator  $T(R)$  for the librions. The nonadiabatic libron kinetic energy operator accordingly gives rise to nonvanishing contributions to the commutator in eq 6, leading to the rate process  $|\alpha\rangle \rightarrow |\alpha'\rangle$ . The above statements can be verified by the usual procedure in adiabatic theory.<sup>10b</sup> In this case, we may think of the stationary states as characterized by rapid lattice vibrations in fixed configurations and transitions between these states as being initiated by a "kick" from the slow libron system.

Assuming harmonic behavior for  $U_\alpha(R)$  and carrying the perturbation expansion to first order, making use of operator algebra in the evaluation of eq 5, we obtain in the simplest form the rate constant expression<sup>7</sup> for interconversion from one configuration,  $\alpha$ , to the other,  $\alpha'$ :

$$W = A(T) \exp(-\epsilon_a/kT) = (kT/h)[(2\pi MkT/h^2)^{1/2} \Delta R]^{-1} \times [(2h\pi/M\omega)|S|^2 \Delta\epsilon^{-2}] \exp[-M\omega^2(\Delta R)^2/8kT] \quad (7)$$

where  $h$  is Planck's constant,  $M$  and  $\omega$  are respectively the effective mass and the frequency of the libron mode (vibration along the reaction coordinate),  $\Delta R$  is the separation of the two equilibrium configurations along this coordinate,  $S$  is the matrix element  $\langle \alpha | (\partial V / \partial R) | \alpha' \rangle$ , and  $\Delta\epsilon$  is the vertical energy separation of the two assumed harmonic surfaces for the two configurations evaluated at the equilibrium configuration of the initial state (see Figure 7.11 of ref 10). In practice, it is convenient to treat  $|S|^2/\Delta\epsilon^2$  as a single parameter.

The activation barrier

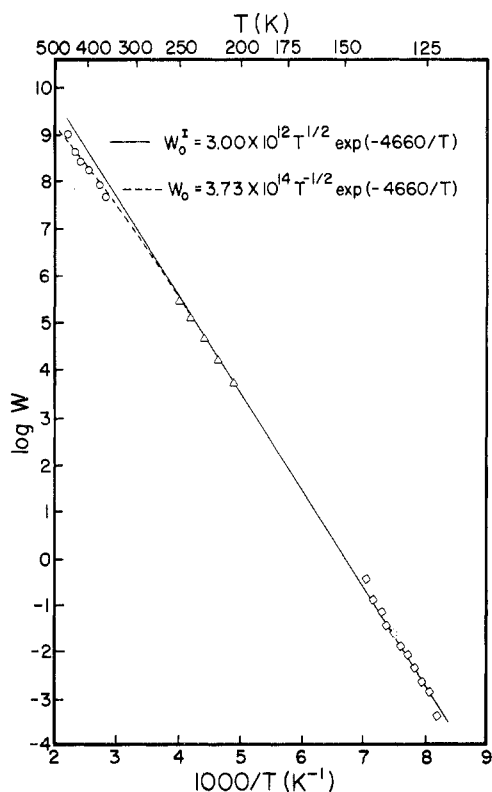
$$\epsilon_a = \frac{1}{8} M \omega^2 (\Delta R)^2 \quad (8)$$

is just the energy at which the two harmonic surfaces intersect. Equation 7 has been derived for the conditions (i)  $\epsilon_a \gg \hbar\omega$  and (ii)  $kT \gg \hbar\omega$ . Relaxing condition ii results in a rate expression that manifests the full quantum scattering features of the underlying tunneling mechanism (see eq 7.31 of ref 10). The removal of condition i gives rise to ammonia-like tunneling (see below).

Equation 7 reproduces the empirical temperature dependence displayed in the Arrhenius equation (eq 2) with a weak preexponential temperature dependence ( $\sim T^{1/2}$ ) for the frequency factor  $A$  and  $E_a = N_0 \epsilon_a$ , where  $N_0$  is the Avogadro number. This result should be valid for cases in which the potential surfaces of the reactant-product system can be closely imitated by two intersecting harmonic curves. In many real systems, however, the crossover regions between the two configurations  $\alpha$  and  $\alpha'$  are highly anharmonic, the activation energy barriers being formed in the shape of gently curving rounded tops. The assumption of a pointed cusp formed by two intersecting harmonic curves (which are fitted as the best approximation for the actual DM potential surface) in the crossover region thus suggests yet another important mechanism for the  $\alpha \rightarrow \alpha'$  transition. The perturbation in this case is the potential energy difference  $V'$  between the area under the pointed cusp of the two intersecting harmonic curves and that underlying the actual rounded energy barrier.

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**Figure 1.** Plot of the logarithm of the relaxation rate  $W$  ( $\text{s}^{-1}$ ) vs.  $10^3/T$  ( $\text{K}^{-1}$ ) for  $\text{F}^-$  interstitial motion in  $\text{CaF}_2$  doped with trivalent impurity cations. Symbols:  $\circ$ , paramagnetic data of Franklin and Marzullo;<sup>18</sup>  $\Delta$ , dielectric relaxation data of Franklin and Marzullo;<sup>18</sup>  $\diamond$ , thermal depolarization data of Stott and Crawford;<sup>19</sup> —, least-squares fit according to the functional form  $W = AT^{1/2} \exp(-b/T)$  in eq 7; - - -, least-squares fit according to the functional form  $W = A'T^{-1/2} \exp(-b'/T)$  in eq 9. The relaxation data are interpreted in terms of the jump of the nearest-neighbor (nn)  $\text{F}^-$  interstitial about the stationary  $\text{M}^{3+}$  cation between two of the four adjacent equivalent orientations along the  $\{100\}$  axes. In the numerical fits the preexponential constants  $A$  and  $A'$  are empirically determined as additive constants in the log  $W$  vs.  $1/T$  plots. The exponential temperature coefficient is given by  $b = M\omega^2(\Delta R)^2/8k = I\omega(\delta\theta)^2/8k$  where  $M$  and  $\Delta R$  in eq 7 and 9 are explicitly replaced by  $I$ , the moment of inertia of  $\text{F}^-$  librating about the stationary  $\text{M}^{3+}$  cation, and  $\delta\theta = \delta/2$ , the angular displacement between two nn interstitial positions. The moment of inertia is given by  $I = mr_0^2$ , where  $m = 3.18 \times 10^{-23}$  g is the mass of  $\text{F}^-$  and  $r_0 = 2.726$  Å is the nn  $\text{M}^{3+}$ - $\text{F}^-$  interstitial separation. Using known molecular constants  $I$  and  $\delta\theta$ , the least-squares fit parameter  $b = 4.66 \times 10^3$  K corresponds to the frequency  $\omega = 9.45 \times 10^{12} \text{ s}^{-1}$  for the  $\text{F}^-$  interstitial libration in the  $\{100\}$  plane, which compares favorably with values ( $\sim 10^{13} \text{ s}^{-1}$ ) usually observed for atomic vibrations in ionic crystals. The better fit of eq 9 in the high-temperature region suggests that the anharmonic perturbation may be the dominant mechanism. For a detailed description of the crystalline defect problem, see ref 10, section 7.3.

It is clear that  $V'$  is nondiagonal in the  $\{\alpha\}$  basis and accordingly may contribute to the commutator in (6) leading to the rate process. The anharmonic perturbation  $V'$  gives rise to a rate expression<sup>9</sup> that is closely similar to (7):

$$W_{\alpha\alpha'} = (|V'|^2/\hbar^2) [(M\omega^2(\Delta R)^2 kT/2\pi\hbar^2)^{-1/2} \times \exp[-M\omega^2(\Delta R)^2/8kT]] \quad (9)$$

where  $|V'|^2$  is a coupling parameter associated with the anharmonic perturbation. In writing (9) we have assumed that the effects of the reorganization of the bath modes accompanying the rate process are negligibly small. Equation 9 differs from (7) in that the weak preexponential temperature dependence is  $T^{-1/2}$  rather than  $T^{1/2}$ . The rate constant expressions 7 and 9 are explicitly given in terms of the equilibrium molecular

configuration, viz.,  $M$ ,  $\omega$  and  $\Delta R$ , that can be determined from independent experiments. Using 7 and 9 and known molecular parameters, we have obtained an excellent fit<sup>7,9</sup> for the experimental observations on  $\text{F}^-$  interstitial relaxation in  $\text{CaF}_2$ , for which data points over a large temperature range are available (see Figure 1).

The Arrhenius-type temperature behavior given in (7) and (9) is not applicable for the low-barrier DM configuration in which  $\epsilon_a \sim \hbar\omega$ . The rate constant in this case is given by the approximate formula<sup>14,15</sup>

$$W = (2\omega/\pi)(2\epsilon_a/\pi\hbar\omega)^{1/2} \exp(-2\epsilon_a/\hbar\omega) \quad (10)$$

which carries no explicit temperature dependence, and the system thus cannot be captured in one of the two minima by the lowering of temperature. In spite of the dramatically different temperature dependence, the Arrhenius and ammonia-like relaxation processes are generically related in that quantum mechanical tunneling through the barrier  $\epsilon_a$  is the underlying mechanism for the  $\alpha \rightarrow \alpha'$  transition in arriving at eq 7, 9, and 10. The divergence of temperature dependence given in (7) or (9) and (10) originates from the fact that, whereas ammonia-like behavior is an intrinsic property of the low-barrier DM model independent of the phonon modes of the heat bath, Arrhenius-type relaxation is a result of coupling of the libron systems to the phonon motions.<sup>9</sup>

The above statement can be readily appreciated in terms of simple physical concepts. From elementary physical chemistry we know that the libron nuclear wavefunctions can penetrate into the finite energy barrier  $\epsilon_a$ . Each libronic wavefunction in the initial configuration  $\alpha$  is thus overlapped with libronic wavefunctions of the final configuration  $\alpha'$ . The coupling of the DM configuration to the heat bath ensures a Boltzmann distribution over the libronic levels in the initial well. The "kick" from the libron motion is responsible for promoting the  $\alpha \rightarrow \alpha'$  interconversion, whereas the coupling of the DM configuration to the bath modes ensures a proper Boltzmann average over the population of the initial vibronic levels. The exponential temperature dependence in (7) and (9) thus signifies a Boltzmann average of the quantum tunneling rates from these individual vibronic levels.

### Time-Averaged Symmetry Effects and Structural Determinations

The equivalence of configurations  $\alpha$  and  $\alpha'$  in the DM problem demands an equivalence of the forward and backward interconversion processes. That is, the  $\alpha \rightarrow \alpha'$  and  $\alpha' \rightarrow \alpha$  transitions must be equal and indistinguishable. When the transitions occur on a time scale short compared to that of the measurement, the DM system may assume a time-averaged symmetry. This simple principle was the basis for the proposal<sup>23</sup> and in vitro characterization<sup>21</sup> of the symmetrical dimer ( $\text{Chl a-H}_2\text{O}$ )<sub>2</sub> for the photosystem I primary chlorophyll a molecular adduct in plant photosynthesis.<sup>24</sup> Symmetry consideration of the in vivo adduct has led to a general interpretation<sup>20,22</sup> of intermolecular  $\text{Chl a-Chl a}$  and  $\text{Chl a-H}_2\text{O}$  bonding interactions.

The low-temperature observation<sup>13</sup> of a symmetrical norbornyl cation on the time scale ( $\sim 10^{-3}$  s) of NMR experiments has been interpreted in terms of either the

$\sigma$ -bridged ion<sup>13</sup> 1 or a low-barrier DM configuration (2) on the basis of time-averaged symmetry.<sup>14,48</sup> Likewise vibrational analysis of the matrix-isolated cyclobutadiene molecule has led to the assignment<sup>32</sup> of either a square equilibrium geometry or an effective square geometry corresponding to a low-barrier DM configuration exhibiting ammonia-like relaxation behavior (the vibrational spectra were measured at cryogenic temperatures).<sup>49</sup> The observation of two distinguishable ESCA peaks in the Ru (3d) binding energy was offered<sup>41</sup> as evidence for the mixed valence states of two non-equivalent Ru ions in the  $\mu$ -pyrazine-decaaminediruthenium(5+) ion (3). On the other hand the same observation has been interpreted<sup>42</sup> in terms of the symmetrical structure by invoking electronic relaxation effects in the ionized final state.<sup>50</sup>

From the dependence of the rate constant on equilibrium structures in the present development there emerges a simple set of guidelines for the classification of possible equilibrium structures in terms of the ratio parameter  $\rho = \epsilon_a/\hbar\omega$ : (i)  $\rho \gg 1$ , high-barrier DM configurations in which the unsymmetrical species can be frozen out at low temperatures according to eq 7; (ii)  $\rho \sim 1$ , low-barrier DM configurations in which the ammonia-like behavior of eq 10 gives rise to stationary symmetrical configuration;<sup>51</sup> and (iii)  $\rho = 0$ , SM configurations.

In the norbornyl question, classification iii corresponds to the  $\sigma$ -bridged symmetry historically assigned to the nonclassical ion.<sup>48</sup> In recent developments the presence of any  $\sigma$  delocalization is often accepted as nonclassical behavior.<sup>28</sup> On this basis only those cations in which structural deformation due to the presence of the electron-deficient center is totally absent would be considered to be classical. If this position were to be accepted it becomes clear that we would have reached a happy resolution of the nonclassical ion problem because apparently the problem is in fact nonexistent by definition: it has always been argued that the 2-norbornyl cation can exist either as the bridged ion 1 or as a pair of rapidly equilibrating unsymmetrical ions (2), and it has been established<sup>14,52</sup> that rapid interconversion in 2 could not have taken place had it not been for the extensive intramolecular electronic (" $\sigma$  delocalization") effects that are responsible for the relatively low barriers to Wagner–Meerwein (WM) shifts even in

carbocations that exhibit Arrhenius relaxation behavior.

We can appreciate the preceding statement by a consideration of eq 8, where the activation energy barrier  $\epsilon_a$  is given in terms of  $\Delta R$ , the separation between the two equilibrium configurations for the unsymmetrical structures along the reaction coordinate for the WM shift.<sup>14</sup> It is clear that the  $\sigma$ -bridged configuration would be given by eq 8 for  $\epsilon_a = \Delta R = 0$ , the asymptotic limit at which the two minima merge into a single minimum. The decrease in value from the "classical" limit of  $\Delta R$  for the hypothetical classical ion therefore represents a tendency toward the  $\sigma$ -bridged configuration.<sup>14</sup> I tend to agree with Professor George Olah who has argued<sup>13</sup> that the DM description in the low-barrier limit is effectively indistinguishable from the SM assignment in that either description is a result of extensive  $\sigma$  delocalization.<sup>53</sup>

However, I have some semantic reservations regarding the terms "classical" and "nonclassical" ions because this historical and still fashionable nomenclature tends to emphasize a difference between carbocations that really does not exist. For example, the 1,2-dimethylnorbornyl cation is generally accepted as a "rapidly equilibrating" pair of classical (carbenium?) ions, whereas the very act of rapid equilibration in carbocations, as I have stated earlier, would represent a drastic departure from the definition of the hypothetical classical ion. This classical ion corresponds to the zeroth-order state in the *adiabatic* approximation detailed in ref 10c, and is not expected to equilibrate rapidly at all, its estimated activation barrier to the WM shift being on the order of 25 kcal mol<sup>-1</sup>.<sup>52</sup> If structural departures from the classical tetrahedral C–C or C–H bond angles resulting from  $\sigma$  delocalization were to be accepted as nonclassical, then all carbonium ions, including the planar methyl cation, must be considered nonclassical. Along the same line of argument, we might consider the Kekulé structures for benzene as classical, in which case it follows that the ground-state equilibrium  $D_{6h}$ -symmetric configuration of benzene must be nonclassical.

On the basis of Professor H. C. Brown's definition of a classical ion being one characterized by a "rapidly equilibrating" pair (or set) of equivalent structures, it would appear that the overwhelming majority of the carbocations are classical, including the *norbornyl cation*.<sup>14,48</sup> The continuing debate is thus a matter of resolving the intricate differences between rapidly equilibrating (low barrier, double minimum) and bridged (no barrier, single minimum) systems in particular cases. With the objectives thus defined, I propose that we converge on an agreement on the established facts and bring the overdrawn nonclassical ion controversy to an end. This should be an occasion for celebration since the major experimental findings from the contending laboratories seem to be mostly supportive of each other.

The relatively recent extension of the fully developed QSM theory<sup>10,11</sup> for photophysical processes<sup>54</sup> to chemical systems<sup>7,8,12,14</sup> is still in its embryonic stage.

(48) For a detailed formulation of the nonclassical ion problem, see ref 10c. See, in particular, Section 8.6 for a definition of the nonclassical ion in organic chemistry.

(49) However, the latter possibility was ruled out on the basis of *ab initio* calculations of the triplet state and the expectation that the "equilibrium singlet corresponds to a strongly distorted square".<sup>32</sup> On the other hand, a recent study shows that considerations of electron repulsion effects in open-shell systems can lead to stabilization of ground-state cyclobutadiene in a square or effectively square configuration.<sup>36</sup>

(50) The Hush interpretation may have far-reaching consequences because it would appear to cast doubt on the validity of attributing observed binding energy differences to different chemical environments, a widely accepted premise underlying most ESCA determinations. This interpretation was based on the assumed effects of one-electron relaxation, however, and deserves a more detailed theoretical analysis that incorporates many-electron effects. I am grateful to Professor N. Winograd for this comment.

(51) For further elaboration on this point and a formal theoretical treatment of time-averaged symmetry specialized to the norbornyl cation, see Section 8.5 of ref 10c. In this discussion, the relatively high barrier ( $\sim 11.5$  kcal mol<sup>-1</sup>) for the 3,2 hydride shift in the norbornyl cation is shown to be a consequence of the time-averaged symmetry.

(52) Section 8.4, ref 10c. See, in particular Figures 8.3 and 8.4 for the formal relationship between the assumed zeroth-order states in the adiabatic approximation and the actual low-barrier DM configurations in carbocations. In the adiabatic approximation, the electronic delocalization effects are neglected in the zeroth order.

(53) However, based on the available experimental data, it seems unreasonable<sup>14</sup> that with the single exception of 2-norbornyl the great majority of equilibrating cations under stable ion conditions are now assigned "classical" (DM) structures by Olah and other workers in the field. See Summary in Table 8.1, ref 10c.

Major unsolved problems await the adventurous. The rate constant expressions 7 and 9 should be refined to include explicit solvent effects. The concept of phonon-induced vacancies<sup>55</sup> may have to be incorporated into a rate theory addressed to the liquid state. The normalization of the overcomplete basis sets<sup>9</sup> in the intersecting harmonic approximation for the DM configuration requires further consideration. The QSM rate theory has been applied to electron-transfer reactions

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in condensed media<sup>56,57</sup> and surface diffusion phenomena.<sup>58</sup> Further generalization to chemical reactions is mostly an exercise in the proper choice of  $R$  and an appropriate perturbation to promote the transition between the equilibrium reactant and product configurations.

Parting from the transition-state theory of rate processes in condensed media has opened up a research field that is still virtually untouched. Hopefully this Account will serve to focus attention on the future of this exciting new field.

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## Phenomena in Homogeneous Chemical Systems Far from Equilibrium

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During the course of a chemical reaction the concentration of the chemical species either passes through a single extremum or else attains monotonically a steady-state concentration. This statement is still widely believed by chemists, except for some chemical engineers more familiar with instabilities occurring in continuous chemical reactors.<sup>1,2</sup> Indeed, in some critical conditions these reactors may exhibit striking oscillations in temperature and composition due to the heat of reaction; in these systems rate constants are very sensitive to temperature, and these reactions may be involved in a feedback loop. Such instabilities are known as thermokinetic phenomena and are treated in chemical engineering texts. They are not the subject of our present attention.

Other known physicochemical oscillations, such as Liesegang rings, periodic crystallizations, periodic dissolution of metals in acid, catalytic decomposition of hydrogen peroxide by mercury, periodic adsorption of

gas, enzymatic reactions in colloidal solutions, and electrochemical oscillations, take place in heterogeneous medium.<sup>3-6</sup>

Oscillations in homogeneous media were long considered impossible, although there seems to have been some early experimental evidence of homogeneous oscillating reactions. The reaction of hydrogen peroxide and potassium iodate in dilute aqueous sulfuric acid solution observed by Caulkins and Bray in 1917 and published in 1921 by Bray<sup>7</sup> is the first experimental evidence of oscillating behavior in an homogeneous chemical reaction, if one suspects, as Bray does, the periodic evolution of carbon monoxide during the dehydration of formic acid in sulfuric acid described by Morgan<sup>8</sup> in 1916 to be heterogeneous. More recently, Belousov<sup>9</sup> (1959) reported sustained oscillations in the oxidation of citric acid by potassium bromate catalyzed by ceric sulfate in dilute aqueous sulfuric acid. This reaction and its variants were extensively investigated

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