dihedral near 0°, while the half-chair is characterized by one large torsional angle near 48°. Table I shows the calculated torsional angles for cyclopentane from the literature and from MM3 for comparison.[15]

The presence of the two cyclopentene rings in **2** makes the envelope conformer in the saturated ring unattainable. In order for the saturated ring in dihydrotriquinacene to achieve the envelope conformation, one torsion angle running along the backbone would have to be zero and the neighboring torsion angle would have to be at least 25°. Geometrical constraints therefore enforce a half-chair conformation on the saturated portion of dihydrotriquinacene. This is the major difference between **2** and **3** or **4**. Thus, the saturated ring in dihydrotriquinacene (**2**) has the half-chair conformation, and the saturated rings in tetrahydrotriquinacene (**3**) and perhydrotriquinacene (**4**) are in envelope conformations (Figure 5). The consequence of the enforced half-chair in **2** is larger nonbonded 1,4-interactions relative to those in compounds **3** and **4**. A detailed analysis of the MM3 energy components revealed that the increase in steric energy between triquinacene and the optimized dihydrotriquinacene is mainly due to nonbonded 1,4-interactions such as those involving endo hydrogens on the saturated cyclopentane and carbons attached to the cyclopentane ring. The cyclopentanes in **3** and **4** can have envelope conformations because of increased backbone flexibility, not found in **2**. These envelope conformations are preferred because 1,4-interactions are reduced by the more even distribution of saturated ring dihedrals. The hydrogenation energies of **2** and **3** are larger than **1** primarily for this reason.

This simple analysis shows that geometrical constraints of dihydrotriquinacene prevent it from relaxing in the same way that **3**, **4**, or cyclopentane does relative to unsaturated analogues. There is still a small discrepancy between the MM3 calculated heat of hydrogenation of **1** (25.7 kcal/mol) and that found experimentally (21–25 kcal/mol).[16] The calculated heat of formation is 0.7 kcal/mol above the experimental range, but computations or experiment could easily be in error by this amount. Homoaromaticity in triquinacene, and in other neutral hydrocarbon systems, is vanishingly small.[17]

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Registry No. 1, 6053-74-3; **2**, 31678-74-7; **3**, 57595-39-8; **4**, 17760-91-7.

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(15) Fuchs, B. In *Tropics in Stereochemistry*; Eliel, E. L., Allinger, N. L., Eds; John Wiley & Sons: New York, 1978; Vol. 10, p 1.

(16) There are no major differences in MM3 entropies (85.4, 85.9, 86.2, and 82.7 cal/(mol·K), respectively) calculated from vibrational analysis of **1–4**.

(17) N. L. Allinger, private communication, reports the MM3 π-stabilization energy for triquinacene to be 0.52 kcal/mol versus the calculation with no π energy included. This corroborates our conclusion that homoaromatic stabilization is very small.

Effects of Geminate Recombination in Measurements of Rate Constants in Perturbation/Relaxation and NMR Line-Shape Experiments on Fast Bimolecular Reactions in Solution

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Abstract: Geminate recombination plays an important role in the kinetics of a reversible bimolecular association $A + B \rightleftarrows C$ in solution. Since geminate pairs usually have mean lifetimes of 10^{-10} s or less, a pseudo-steady flux through geminate pairs is closely approached within about 10^{-9} s, after which the rate of geminate recombination is first order in C. Thus, geminate pairs behave as if they were sparsely populated subspecies of C, not independent molecules A and B. As a consequence, when reaction relaxation times longer than 10^{-9} s are measured, as in classical perturbation/relaxation or NMR line-shape experiments, geminate recombination is not detected, and the rate constants determined are those for the global forward and backward reactions, which consist, respectively, of nongeminate combination of A and B and of those bond cleavages in C that are followed by escape to independent A and B molecules. The global rate constants are the diffusion-influenced constants that are measured in many conventional kinetic experiments. These conclusions do not support the recent suggestion that perturbation/relaxation and NMR line-shape experiments measure the diffusion-independent, activation-control rate constants (Keizer, J. *J. Am. Chem. Soc.* **1990**, *112*, 7952).

The rate of a fast bimolecular reaction in solution, such as an association

$$A + B \rightleftarrows C \tag{1}$$

is often determined through a perturbation/relaxation experiment on a system that is at equilibrium initially. In "classical" methods of this type, e.g., T-jump, E-jump, ultrasonic relaxation, etc., the measured relaxation times are greater than 10^{-9} s (and usually greater than 10^{-7} s).[1]

According to Eigen and others,[1,2] the value so determined is that of the diffusion-influenced or global rate constant k_G, which is analogous to the long-time, steady-state rate constant k_{SCK} of the theory of Smoluchowski, Collins, and Kimball (SCK) or Noyes.[3,4] Keizer proposes instead that it is the value of the

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(1) See, for example: Cauldin, E. F. *Fast Reactions in Solution*; Wiley: New York, 1964.

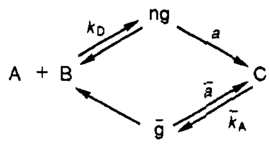
(2) (a) Eigen, M. *Angew. Chem.* **1964**, *3*, 1. (b) Eigen, M.; Kruse, W.; Maass, G.; De Maeyer, L. *Prog. React. Kinet.* **1964**, *2*, 286. (c) Eigen, M. *Z. Phys. Chem.* (*Munich*) **1954**, *1*, 176.

(3) For a recent review, see: Rice, S. A. *Comprehensive Chemical Kinetics. Diffusion-Limited Reactions* Vol. 25. Bamford, C. H., Tipper, C. F. H., Compton, R. G., Eds.; Elsevier: Amsterdam, 1985.

(4) (a) Noyes, R. M. *J. Chem. Phys.* **1954**, *22*, 1349. (b) Noyes, R. M. *Prog. React. Kinet.* **1961**, 129.

0002-7863/92/1514-1168$03.00/0

Scheme I



intrinsic or activation-control rate constant k_A, that is, the rate constant describing the initial rate of the irreversible reaction of A and B when they are initially distributed in space as they would be at equilibrium.[3-7] Indeed, the systems in perturbation/relaxation experiments are always close to equilibrium, where k_A can be used to describe the forward rate.[5a,6]

The measured rate constants for fast proton transfers in aqueous solutions approach or even exceed 10^{11} M^{-1} s^{-1}.[1,2] Under Eigen's interpretation, these are values k_D of the global rate constants for reactions under diffusion control. To account for the fact that the measured values are higher than the calculated values of k_D, a special mechanism of proton transfer through hydrogen-bonded chains has been proposed.[1,2] If the measured values were those of activation-control rate constants k_A, then no special interpretation would be required; 10^{11} M^{-1} s^{-1} is a plausible value at least two orders of magnitude below the theoretical upper limit.

Even so, the analysis given here indicates that classical perturbation/relaxation experiments give values of k_G, not those of k_A.

Keizer also suggests that values of k_A are determined by analyses of NMR line shapes for bimolecular reactions at equilibrium.[5a] Again, the present treatment indicates instead that values of k_G are determined.

The critical points concern the behavior of geminate AB pairs, each of which consists of A and B molecules formed simultaneously from the same C molecule. Because geminate pairs are very short-lived (typical mean lifetime $\approx 10^{-10}$ s), a pseudo-steady flux through them is established within about 10^{-9} s. After this, the rate of geminate recombination is first order in C, not second order in A and B. Thus, geminate pairs behave at long times ($>10^{-9}$ s) as if they were sparsely populated subspecies of C. This behavior is manifest in both classical perturbation/relaxation experiments and NMR line-shape analyses, both of which detect nongeminate combination but not geminate recombination. The global forward reaction consists of nongeminate combination only, and these experiments determine the corresponding second-order rate constant k_G.

Case of Spin-Free, Isotropically Reactive, Spherical Molecules

Physical Model. The equations developed by Keizer, with which some of those in the present treatment can be compared, are for A and B molecules that are spin-free, isotropically reactive, and spherical, as in the SCK treatment.[3,4,7] This case is treated first; the general case is outlined later. Complicating features that are not relevant to the issues are neglected: (a) activity coefficients are unity; (b) internal relaxation among the ground and excited states of A, B, and C is fast.

Associated Pairs. Associated AB pairs include geminate pairs $\bar{g}$ and nongeminate pairs ng. Geminate pairs $\bar{g}$ are formed in bond cleavages in C, while nongeminate pairs ng are formed in initial collisions of A and B molecules not born of the same C (Scheme I).

An associated pair lives until its members suffer mutual reaction (probability a for nongeminate pairs, $\bar{a}$ for geminate pairs) or escape (probability $1 - a$ for nongeminate pairs, $1 - \bar{a}$ for geminate pairs). Escape occurs when the members of a pair gain diffusion trajectories that would never bring them into contact again (in a medium of infinite extent), even if their lifetimes were infinite.[3,4,6,7] For three-dimensional diffusion, the possibility of escape is guaranteed by the recurrence theorem of Polyā.[8]

Isolated Pair Approximation. When the probability of a collision of a member of an associated pair with any potentially reactive molecule (other than its partner) is negligible, associated pairs in actual systems will behave as if they were isolated. This will be an appropriate approximation at sufficient dilution.

According to Noyes, the isolated-pair approximation is appropriate for solutions less than about 10^{-2} M in A and B.[4] For ordinary small molecules in ordinary fluid solvents, the value of the rate constant k_D for nongeminate pair formation is $\approx 10^{10}$ M^{-1} s^{-1}, and the median lifetimes of associated pairs are $\approx 10^{-10}$ s (or less).[4,9] At 10^{-2} M, the mean lifetime of an A or B between collisions that form nongeminate pairs is $1/k_D[A] \approx 10^{-8}$ s, about 10^2 times the median lifetime of an nongeminate pair. Thus, almost all nongeminate pairs suffer reaction or escape before a collision of either partner with some other A or B. The same argument applies to geminate pairs.

The restriction to solutions that are 10^{-2} M or less in A and B is not very significant. The concentrations of very reactive species are usually much less than this in actual systems.

Pseudo-Steady States of Associated Pairs. In a solution that is 10^{-2} M in A and B, the effective relaxation time for nongeminate pair formation is $\approx 10^{-8}$ s. This is the minimum value under conditions where the isolated-pair approximation is appropriate. As noted above, the median lifetime of a nongeminate pair is $\approx 10^{-10}$ s. The much longer relaxation time for nongeminate pair formation than destruction leads to a pseudo-steady state of flux through nongeminate pairs. The characteristic time for approach to this steady state is $\approx 10^{-10}$ s. The similar treatment of geminate pairs requires that the rate constant for bond cleavage be about 10^8 s^{-1} or less. In the pseudo-steady states, the concentrations of associated pairs can be neglected.

Global and Local Reactions. The distinction between global and local reactions, as defined by Berg (and alluded to earlier by Noyes),[4,7] is critical. The global forward reaction consists of nongeminate combination (combination in nongeminate pairs) only. Similarly, the global backward reaction consists of bond cleavage in C that is not followed by geminate recombination. Thus, the global forward and backward reactions are described by the upper and lower branches, respectively, of Scheme I. On the other hand, the local forward reaction includes all bond formation to give C, including that in geminate pairs, and the local backward reaction includes all bond cleavages in C, whether or not they are followed by geminate recombination.

In the pseudo-steady state of the global forward reaction

$$\text{global forward rate} = ak_D[A][B] \qquad (2)$$

and

$$k_G = ak_D \qquad (3)$$

where k_G is the global forward rate constant. In the limit as $a \rightarrow 1$, the reaction is strictly diffusion controlled. The global rate constant k_G is the diffusion-influenced rate constant that might be measured in an experiment.

For spin-free, isotropically reactive, spherical molecules (but not in the general case),[6] $\bar{a} = a$ and

$$\text{local forward rate} = ak_D[A][B] + a\bar{k}_A[C] \qquad (4)$$

where $\bar{k}_A$ is the rate constant for bond cleavage in C (forming geminate AB pairs) and the second term on the right side is the rate of geminate recombination in the pseudo-steady state of the

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(5) (a) Keizer, J. *J. Am. Chem. Soc.* **1990**, *112*, 7952. Related recent works include: (b) Lee, S.; Karplus, M. *J. Chem. Phys.* **1987**, *86*, 1883. (c) Naumann, W. *Chem. Phys.* **1991**, *150*, 187. (d) Szabo, A. *J. Chem. Phys.* **1991**, *95*, 2481.

(6) (a) Garst, J. F. *J. Chem. Soc., Chem. Commun.* **1987**, 589. (b) Garst, J. F. *J. Chem. Soc., Chem. Commun.* **1987**, 1440. (c) Garst, J. F. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 1245.

(7) Berg, O. G. *Chem. Phys.* **1978**, *31*, 47.

(8) The recurrence theorem states that some of the trajectories followed by a walker B in a three-dimensional random walk will never lead to a site labeled A, no matter how small the initial (nonzero) separation of B from the site A. Pōlya, G. *Math. Ann.* **1921**, *84*, 149.

(9) The median lifetime is easily calculated for the SCK model: Swift, B. L.; Garst, J. F., unpublished results.

(10) Burshtein, A. I.; Khudyakov, I. V.; Yakobson, B. I. *Prog. React. Kinet.* **1984**, *13*, 221.

flux through geminate pairs. If

$$Q = [\mathrm{C}]/[\mathrm{A}][\mathrm{B}] \tag{5}$$

then

$$\text{local forward rate} = ak_{\mathrm{D}}[\mathrm{A}][\mathrm{B}] + a\bar{k}_{\mathrm{A}}Q[\mathrm{A}][\mathrm{B}] \tag{6}$$

and

$$k_{\mathrm{L}} = k_{\mathrm{G}} + a\bar{k}_{\mathrm{A}}Q \tag{7}$$

where k_{L} is the local forward rate coefficient.

Similarly, for the backward reaction (when $\bar{a} = a$),

$$\text{global backward rate} = (1 - a)\bar{k}_{\mathrm{A}}[\mathrm{C}] \tag{8}$$

$$\bar{k}_{\mathrm{G}} = (1 - a)\bar{k}_{\mathrm{A}} \tag{9}$$

$$\text{local backward rate} = \bar{k}_{\mathrm{A}}[\mathrm{C}] \tag{10}$$

$$\bar{k}_{\mathrm{L}} = \bar{k}_{\mathrm{A}} \tag{11}$$

There are several important aspects of eqs 2–11. First, they apply whenever the system is at least $\approx 10^{-9}$ s old, no matter what the initial state, since only then are the pseudo-steady-state approximations for the fluxes through associated pairs, used in eqs 2–11, appropriate. Second, they apply to reactions that are displaced from equilibrium, as well as to those that are at equilibrium. Third, k_{G}, $\bar{k}_{\mathrm{G}}$, and $\bar{k}_{\mathrm{L}}$ are rate *constants*, independent of [A], [B], and [C], but k_{L} is a variable rate *coefficient* whose value depends on the concentration quotient Q.

Identification of k_{A} with $k_{\mathrm{L}}{}^0$. At equilibrium, A, B, C, and all substates of the system are equilibrated. In particular, A, B, and C have equilibrium spatial distributions. Bond formation, then, is strictly under activation control. The total rate of bond formation is the local forward rate and $k_{\mathrm{L}}{}^0 = k_{\mathrm{A}}$. Here and elsewhere in this work, superscript zeroes denote equilibrium values.

Relationship to SCK Treatment. In the SCK treatment, the reaction of A with B is treated as irreversible. A system with equilibrium (random) spatial distributions of A and B is created suddenly at time zero. AB pairs with A and B initially in close proximity disappear rapidly, depleting A and B near one another and leaving radial concentration gradients of potential reactants around A and B. As a consequence, the rate coefficient $k(t)$ decreases with time. The initial rate constant $k(0)$ has the value k_{A}, but eventually the steady-state rate constant k_{SCK} is approached.[3]

The relationship of k_{G} to k_{SCK} can be made obvious as follows. Consider a system in which the reversible reaction of A with B is at equilibrium. Now suddenly remove C. This leaves the system in exactly the same state as the initial state of the SCK treatment. The geminate pairs disappear rapidly and are not replenished, while the global forward reaction continues unperturbed (except to enter a relatively slow decaying pseudo-steady state, replacing the actual steady state present at equilibrium). Thus, the global forward rate constant k_{G} is identical with the SCK rate constant k_{SCK}.

Relationship to Noyes Treatment. Noyes treats the same physical model as SCK, but where the SCK treatment uses the differential equations of diffusion, describing many molecules, the Noyes treatment uses reaction and escape probabilities of individual molecular pairs.[4] When these probabilities are evaluated from diffusion equations, the two treatments become equivalent,[3] but the Noyes framework is more general and can be supplemented with any theory (including computational simulation) for reckoning the appropriate probabilities.

In Noyes theory, the time dependence of the forward rate coefficient $k(t)$ is given by

$$k(t) = k_{\mathrm{A}}\left[1 - \int_0^t h(x)\,\mathrm{d}x\right] \tag{12}$$

where $h(t)$ is the probability per unit time that a geminate pair formed at time zero will suffer geminate reaction at time t.[4,6b] Thus, the entire time dependence of the rate coefficient is assigned to depletion by geminate recombination or, if the initial state is prepared in such a way that geminate pairs cannot be identified, to depletion by reactions of pairs whose behavior is identical with that of geminate pairs ("geminate-cognate" pairs).[6b]

The initial value, $k(0)$, is k_{A}. As t approaches infinity, $\int_0^t h(x)\,\mathrm{d}x$ approaches the geminate recombination probability a and $k(t)$ approaches k_{G} ($=k_{\mathrm{SCK}}$).

Relationships among Observable and Limiting Rate Constants. Using $K = k_{\mathrm{A}}/\bar{k}_{\mathrm{A}}$, along with definitions and equations given above, some relationships among the various observable and limiting rate constants can be established.

$$\begin{aligned}\text{equilibrium local forward rate}\\ &= k_{\mathrm{L}}{}^0[\mathrm{A}]^0[\mathrm{B}]^0\\ &= k_{\mathrm{A}}[\mathrm{A}]^0[\mathrm{B}]^0 = ak_{\mathrm{D}}[\mathrm{A}]^0[\mathrm{B}]^0 + a\bar{k}_{\mathrm{A}}[\mathrm{C}]^0\\ &= ak_{\mathrm{D}}[\mathrm{A}]^0[\mathrm{B}]^0 + a\bar{k}_{\mathrm{A}}\mathrm{K}[\mathrm{A}]^0[\mathrm{B}]^0\end{aligned} \tag{13}$$

$$k_{\mathrm{A}} = ak_{\mathrm{D}}/(1 - a) = k_{\mathrm{G}}/(1 - a) \tag{14}$$

$$k_{\mathrm{G}} = (1 - a)k_{\mathrm{A}} \tag{15}$$

$$\bar{k}_{\mathrm{G}} = (1 - a)\bar{k}_{\mathrm{A}} \tag{16}$$

$$a = k_{\mathrm{A}}/(k_{\mathrm{D}} + k_{\mathrm{A}}) \tag{17}$$

Net Rates. In a system that may or may not be at overall equilibrium, but for which the fluxes through associated pairs are in pseudo-steady states, the net forward rate can be expressed as the balance of forward and backward rates, either global or local. For both choices, the result is the same.

$$\begin{aligned}\text{net forward rate} &= \mathrm{d}[\mathrm{C}]/\mathrm{d}t\\ &= ak_{\mathrm{D}}[\mathrm{A}][\mathrm{B}] - (1 - a)\bar{k}_{\mathrm{A}}[\mathrm{C}] \qquad \text{(global – global)}\\ &= ak_{\mathrm{D}}[\mathrm{A}][\mathrm{B}] + a\bar{k}_{\mathrm{A}}[\mathrm{C}] - \bar{k}_{\mathrm{A}}[\mathrm{C}] \qquad \text{(local – local)}\end{aligned} \tag{18}$$

At equilibrium, eq 18 leads to an equation for the equilibrium constant K. The parameters that make up the expression for K can be grouped in several ways to express K as the quotient of forward and backward global, activation-control, or diffusion-control rate constants.

$$K = ak_{\mathrm{D}}/(1 - a)\bar{k}_{\mathrm{A}} = k_{\mathrm{G}}/\bar{k}_{\mathrm{G}} = (1 - a)k_{\mathrm{A}}/(1 - a)\bar{k}_{\mathrm{A}} = k_{\mathrm{A}}/\bar{k}_{\mathrm{A}} = k_{\mathrm{D}}/\bar{k}_{\mathrm{D}} \tag{19}$$

It is impossible, of course, for a reaction to be strictly diffusion controlled ($a = 1$). In that event, $\bar{k}_{\mathrm{G}}$ (and $\bar{k}_{\mathrm{D}}$) would be zero and K would be infinite. Thus, the quotient $k_{\mathrm{D}}/\bar{k}_{\mathrm{D}}$ must be interpreted as the limit of the quotient $k_{\mathrm{G}}/\bar{k}_{\mathrm{G}}$ as $a \rightarrow 1$. With this understanding,

$$\bar{k}_{\mathrm{D}} = (1 - a)\bar{k}_{\mathrm{A}}/a \tag{20}$$

and

$$a = \bar{k}_{\mathrm{A}}/(\bar{k}_{\mathrm{D}} + \bar{k}_{\mathrm{A}}) = k_{\mathrm{A}}/(k_{\mathrm{D}} + k_{\mathrm{A}}) \tag{21}$$

At equilibrium, the net rate is zero and eq 18 can be rewritten in two equivalent ways.

$$0 = k_{\mathrm{G}}[\mathrm{A}]^0[\mathrm{B}]^0 - \bar{k}_{\mathrm{G}}[\mathrm{C}]^0 \qquad \text{(global – global)} \tag{22}$$

$$0 = k_{\mathrm{L}}{}^0[\mathrm{A}]^0[\mathrm{B}]^0 - \bar{k}_{\mathrm{L}}[\mathrm{C}]^0 = k_{\mathrm{A}}[\mathrm{A}]^0[\mathrm{B}]^0 - \bar{k}_{\mathrm{A}}[\mathrm{C}]^0 \qquad \text{(local – local)} \tag{23}$$

Classical Perturbation/Relaxation Experiments. An appropriate analysis of a classical perturbation/relaxation experiment will answer the question, "Which rate constant is measured, k_{G} or k_{A}?" In such an experiment, the deviation α from equilibrium, or any observable that is proportional to α, is monitored.

$$\alpha = [\mathrm{A}]^0 - [\mathrm{A}] = [\mathrm{B}]^0 - [\mathrm{B}] = [\mathrm{C}] - [\mathrm{C}]^0 \tag{24}$$

The relaxation of α is described by an equation obtained from eq 18.

$$\begin{aligned}\mathrm{d}\alpha/\mathrm{d}t = \mathrm{d}[\mathrm{C}]/\mathrm{d}t &= ak_{\mathrm{D}}[\mathrm{A}][\mathrm{B}] - (1 - a)\bar{k}_{\mathrm{A}}[\mathrm{C}]\\ &= ak_{\mathrm{D}}([\mathrm{A}]^0 - \alpha)([\mathrm{B}]^0 - \alpha) - (1 - a)\bar{k}_{\mathrm{A}}([\mathrm{C}]^0 + \alpha)\end{aligned} \tag{25}$$

For small values of α,

$$\mathrm{d}\alpha/\mathrm{d}t = -\{ak_\mathrm{D}([\mathrm{A}]^0 + [\mathrm{B}]^0) + (1 - a)\bar{k}_\mathrm{A}\}\alpha \qquad (26)$$

so the decay has a relaxation time τ.

$$\tau^{-1} = ak_\mathrm{D}([\mathrm{A}]^0 + [\mathrm{B}]^0) + (1 - a)\bar{k}_\mathrm{A} = k_\mathrm{G}([\mathrm{A}]^0 + [\mathrm{B}]^0) + \bar{k}_\mathrm{G} \qquad (27)$$

From measured values of τ, K, and concentrations, or from values of τ measured at several known concentrations, the coefficient k_G of $([\mathrm{A}]^0 + [\mathrm{B}]^0)$ and the constant term $\bar{k}_\mathrm{G}$ of eq 27 are determined.

This is the result that was sought. According to this reasoning, a classical perturbation/relaxation experiment yields values of the global (diffusion-influenced) rate constant k_G, not that of the equilibrium value of the local rate constant, $k_\mathrm{L}{}^0$ or k_A. As a approaches unity, the experimentally determined forward rate constant approaches k_D.

Comparison of Treatments. Keizer treats nonequilibrium systems maintained in steady states by added sources and sinks of A, B, and C, while the present treatment deals with pseudo-steady states of the global forward and backward reactions in the absence of such sources and sinks. This is not an essential difference. When Keizer's steady-state systems are treated by the present methods, the key equations that result are the same as for the pseudo-steady states used here.

Keizer's analysis begins with eq 28, where Keizer's "k^obs" is

$$k_\mathrm{L} = \text{“}k^\mathrm{obs}\text{”} = k_\mathrm{A}g(R) \qquad \text{(ref 5a, eq 4)} \qquad (28)$$

identified here with the local rate constant k_L. Here $g(r)$ is the steady-state radial distribution function of B about A (or A about B), normalized by the bulk concentration of B (or A) and evaluated at the reaction radius R, centered on A (or B). Since the function $g(r)$ describes the radial distributions of all potential reactants, making no distinctions among them, it contains contributions from both nongeminate and geminate pairs. Therefore, "k^obs" governs all bond making in the system and must be identified with the local rate constant k_L. Keizer's derived expression for "k^obs" is identical with that found here for k_L.

$$k_\mathrm{L} = k_\mathrm{G}[1 + (k_\mathrm{A}/k_\mathrm{D})(Q/K)] \qquad \text{(from eqs 3, 7, and 19)} \qquad (29)$$

$$\text{“}k^\mathrm{obs}\text{”} = k_\mathrm{G}[1 + (k_\mathrm{A}/k_\mathrm{D})(Q/K)] \qquad \text{(ref 5a: eq 1)} \qquad (30)$$

Turning now to perturbation/relaxation experiments, eq 25 could have been framed initially as follows (the "global – global" rate difference).

$$\begin{aligned}\mathrm{d}\alpha/\mathrm{d}t = \mathrm{d}[\mathrm{C}]/\mathrm{d}t &= k_\mathrm{G}[\mathrm{A}][\mathrm{B}] - \bar{k}_\mathrm{G}[\mathrm{C}] \\ &= k_\mathrm{G}([\mathrm{A}]^0 - \alpha)([\mathrm{B}]^0 - \alpha) - \bar{k}_\mathrm{G}([\mathrm{C}]^0 + \alpha)\end{aligned} \qquad (31)$$

Since k_G and $\bar{k}_\mathrm{G}$ are independent of α, they are constant as α relaxes toward zero and eq 27 follows directly. However, eq 25 could have been written alternatively as the "local – local" rate difference, eq 32, where β is the deviation in the value of k_L from

$$\begin{aligned}\mathrm{d}\alpha/\mathrm{d}t = \mathrm{d}[\mathrm{C}]/\mathrm{d}t &= k_\mathrm{L}[\mathrm{A}][\mathrm{B}] - \bar{k}_\mathrm{L}[\mathrm{C}] \\ &= (k_\mathrm{A} + \beta)([\mathrm{A}]^0 - \alpha)([\mathrm{B}]^0 - \alpha) - \\ &\qquad \bar{k}_\mathrm{A}([\mathrm{C}]^0 + \alpha)\end{aligned} \qquad (32)$$

its equilibrium value k_A.

The critical difference between treatments is that β is zero in Keizer's formalism,[5a] which is based on fluctuation theory, so that k_A and $\bar{k}_\mathrm{A}$ become the rate constants in the derived expression, analogous with eq 27, for the relaxation time, while in the present treatment β is not zero. The approach through eq 32, using eq 29 to establish β, gives the same final result (eq 27) as the approach through eq 25 or 31.

Relationships between $g(R)$ and a. By comparing eq 28 with equations from the present treatment, the function $g(R)$ can be related to the probability a. In this way, $g(R)$ can be separated into contributions from nongeminate and geminate AB pairs ng and $\bar{g}$.

From eqs 7, 15, 19, and 28,

$$g(R) = 1 - a + (Q/K)a \qquad (33)$$

At equilibrium, $Q = K$ and $g^0(R) = 1$, so that $k_\mathrm{L} = k_\mathrm{A}$ as required. In the limit far from equilibrium, $Q = 0$ and only nongeminate pairs contribute to $g(R)$

$$g_\mathrm{non}(R) = 1 - a \qquad (34)$$

where $g_\mathrm{non}(R)$ is the nongeminate-pair contribution to $g(R)$. Since $g_\mathrm{non}(R)$ is the same whether or not geminate pairs are present,

$$g(R) = g_\mathrm{non}(R) + g_\mathrm{gem}(R) = g_\mathrm{non}(R) + (Q/K)a \qquad (35)$$

and

$$g_\mathrm{gem}(R) = (Q/K)a \qquad (36)$$

where $g_\mathrm{gem}(R)$ is the contribution of geminate pairs to $g(R)$. As expected, $g_\mathrm{gem}(R)$ depends on Q. At equilibrium,

$$g^0{}_\mathrm{gem}(R) = a \qquad (37)$$

Using these relationships, eq 28 can be rewritten

$$\begin{aligned}k_\mathrm{L} = k_\mathrm{A}[g_\mathrm{non}(R) + g_\mathrm{gem}(R)] &= k_\mathrm{A}[(1 - a) + (Q/K)a] = \\ &\qquad k_\mathrm{G} + ak_\mathrm{A}(Q/K)\end{aligned} \qquad (38)$$

which is equivalent to eq 7. Also, $g(R)$ can be expressed in terms of the limiting rate constants and the deviation from equilibrium.

$$g(R) = [k_\mathrm{D} + (Q/K)k_\mathrm{A}]/(k_\mathrm{D} + k_\mathrm{A}) \qquad (39)$$

Time Scales and Multiple Relaxations. Time scales are a critical element of the analysis presented here. All of the equations used, beginning with eq 2, are for pseudo-steady states of the global forward and backward reactions that require up to $\approx 10^{-9}$ s to be established. Since classical perturbation/relaxation experiments are limited to relaxations with longer characteristic times than 10^{-9} s, the pseudo-steady-state approximation is appropriate.

Measurements of relaxations at shorter times could provide other information. Such relaxation is related, possibly in a complex fashion, to the activation-control rate constants k_A and $\bar{k}_\mathrm{A}$.

Three distinct relaxations are likely. Within 10^{-11} s contact AB pairs, that is, those executing quasi-vibrational collisions within the same cavity of solvent molecules, will relax to a pseudo-steady state. Within 10^{-9} s associated pairs will relax to pseudo-steady states, establishing the concentration gradients that result in diffusion-influenced rate constants. Finally, on a longer time scale (for sufficiently slow reactions), the deviation of the reaction from equilibrium will relax toward zero. This is the only relaxation that is detected in a classical perturbation/relaxation experiment.

Relationships among Equilibrium and Rate Constants. Keizer points out that the quotient $k_\mathrm{G}/\bar{k}_\mathrm{A}$ is not equal to the equilibrium constant K.[5a] Several other ratios of forward and backward rate constants, $k_\mathrm{A}/\bar{k}_\mathrm{A}$, $k_\mathrm{G}/\bar{k}_\mathrm{G}$, and $k_\mathrm{D}/\bar{k}_\mathrm{D}$, *are* equal to K (eq 19).[6]

General Case

Perturbation/Relaxation Experiments. The analysis presented here requires neither the adoption of the SCK model of spin-free, isotropically reactive, spherical molecules nor the assumption of any particular equations of molecular transport.[6] In the general case, the value of the probability $\bar{a}$ of geminate recombination can differ from that of the probability a of nongeminate combination, with the value of $\bar{a}$ being greater than or equal to that of a.[6]

Equation 15 is replaced by

$$k_\mathrm{G} = (1 - \bar{a})k_\mathrm{A} \qquad (40)$$

and eq 7 by

$$k_\mathrm{L} = k_\mathrm{G} + \bar{a}k_\mathrm{A}Q \qquad (41)$$

the right side of which can be expressed in terms of k_G and k_A to give

$$k_\mathrm{L} = k_\mathrm{G} + (k_\mathrm{A} - k_\mathrm{G})Q/K \qquad (42)$$

which reduces, as required, to $k_\mathrm{L}{}^0 = k_\mathrm{A}$ at equilibrium ($Q = K$).

The treatment of a classical perturbation/relaxation experiment proceeds exactly as before (eqs 25 and 26), with $(1 - \bar{a})$ replacing $(1 - a)$, and gives the same final result (eq 27).

The well-known relationship

$$k_G = k_Dk_A/(k_D + k_A) \qquad (43)$$

which is obtained in every treatment of spin-free, isotropically reactive, spherical molecules A and B,[3,4,7] follows immediately from eqs 3 and 17. However, it is not a general relationship. In the general case, eq 43 is replaced by

$$k_G = k_Dk_A/(k_D + bk_A) \qquad (44)^{6}$$

where $b = \bar{a}/a$.

In the general case, eq 28 loses some of its clarity. The contact separation R is hard to define for irregularly shaped molecules. In addition, owing to spin, orientational, and conformational factors, not all pairs in contact are poised to react. As a consequence, $g(R)$ is not easily defined. Nonetheless, if $g(R)$ is taken to be the distributional quantity that makes eq 28 correct, it can be identified as before with parameters of the present treatment. The results are:

$$g_{\text{non}}(R) = 1 - \bar{a} \qquad (45)$$

$$g_{\text{gem}}(R) = (Q/K)\bar{a} \qquad (46)$$

$$g^0{}_{\text{gem}}(R) = \bar{a} \qquad (47)$$

$$g(R) = [k_D + bk_A(Q/K)]/(k_D + bk_A) \qquad (48)$$

Acid–Base Neutralization Reactions. There are some conceptual difficulties with rate measurements and fast acid–base neutralization reactions, where A and B are the acid and base (often ions) and C is the neutralization product. The fact that the neutralization products are usually two neutral molecules in proton-transfer reactions is of no consequence here, provided that the neutralization products are highly favored at equilibrium.

In a scheme proposed by Eigen and discussed by Keizer,[2,5a] contact ion pairs P are intermediates.

$$A + B \rightleftarrows P \rightleftarrows C \qquad (49)$$

Suppose that the equilibrium constant K_P for the formation of such ion pairs from free ions can be estimated from theory. The major conceptual problem in applying K_P in the analysis of rate data lies in distinguishing contact ion pairs from associated pairs ng and $\bar{g}$. These various types of pairs have overlapping populations but are not exactly the same.

In the present analysis, nongeminate and geminate pairs are distinguished, but contact ion pairs are not. If K_C is the equilibrium constant for C formation from contact ion pairs, then $K = K_PK_C$ and

$$\bar{k}_G = k_G/K_PK_C \qquad (50)$$

This might be a useful relationship when $k_G = k_P$, where k_P is the rate constant for the nongeminate formation of contact ion pairs, so that

$$k_G/K_P = k_P/K_P = \bar{k}_P \qquad (51)$$

If contact ion pairs are formed at the diffusion-controlled rate, then

$$\bar{k}_P = k_D/K_P \qquad (52)$$

Great care must be taken in interpreting these equations. In particular, $\bar{k}_P$ must not be interpreted as the rate constant for contact ion-pair separation. It is instead the rate constant for contact ion-pair separation and escape; that is, it is the *global* rate constant for ion-pair dissociation, not the local rate constant for ion-pair separation. With this understanding, these equations appear to be consistent with Eigen's interpretation, discussed by Keizer. This consistency vanishes if the overall reaction is not diffusion controlled.

NMR Experiments. NMR line-shape measurements are made at equilibrium, and once again the net rate can be described as either the difference between global rates (eq 22) or between local rates (eq 23) of reaction. In deciding whether line-shape analysis gives values of k_A or k_G, one must decide whether or not the broadening effect "sees" geminate pairs and geminate recombination.

The effect depends on lifetimes of a nucleus in two environments, those of A (or B) and C in the present case. Consider a sample consisting of C only, and consider the exchange between C and geminate pairs. Although geminate recombination is not governed by a first-order rate constant but rather by a time-dependent first-order rate coefficient,[3-7] it is surely an adequate approximation for present qualitative purposes to treat it as if it were first-order with a constant rate coefficient of $\approx 10^{10}$ s^{-1}. The standard equations of two-site exchange can then be applied.[11]

Let τ_A be the lifetime of the geminate pair, and let τ_C be the lifetime of the C molecule. The effective relaxation time for the equilibration of C with geminate pairs AB is very short, on the order of 10^{-10} s, which is also the effective lifetime of a geminate pair. C and geminate pairs will be at the rapid exchange limit, and a single signal will be observed, the frequency of which will be the population-weighted average of the frequencies for pure geminate AB pairs and pure C.[11] In all cases in which geminate recombination is significant, the population of C will far outweigh that of geminate pairs, so the NMR signal will be, in effect, that of C only. In contrast, the lifetimes of independent molecules A and B, that is, those that have suffered escape from geminate pairs, can be much longer than those of geminate pairs.

Consequently, NMR line shapes reflect nuclear exchanges between C and independent molecules A and B, that is, those which occur in the global reaction. Thus, NMR line-shape analyses, like classical perturbation/relaxation experiments, give values of the global (diffusion-influenced) rate constants k_G.

Limitations of Mass Action. In chemistry, "mass action" denotes proportionality to the product of the concentrations of reactants. There is both equilibrium mass action, as in

$$[C] = K[A][B] \qquad (53)$$

and kinetic mass action, as in

$$\text{global rate} = k_G[A][B] \qquad (54)$$

and

$$\text{local rate} = k_A[A]^0[B]^0 \qquad (55)$$

However, the validities of eqs 54 and 55 are limited, with eq 54 being valid only at long times and eq 55 only at equilibrium. Thus, kinetic mass action is valid only under appropriate restrictions.

Determination of k_A. If classical perturbation/relaxation experiments do not give values of k_A, how can these be determined?

If it can be assumed safely that $\bar{a} = a$, then one can obtain a as the quotient of a measured k_G and an estimated k_D, $a = k_G/k_D$. Then $k_A = k_G/(1 - a)$ (eq 14). However, in the general case $\bar{a} > a$.[6]

In the general case, a measurement of k_G and an estimate of k_D are not sufficient. One must somehow obtain $\bar{a}$ or b as well. The fundamental problem is that the parameters $\bar{a}$ and $\bar{k}_A$ seem to be inextricably bound together, so that only their product is available experimentally [as $\bar{k}_G = (1 - \bar{a})\bar{k}_A$].

There is hope in the steady increase in computational and simulational powers. In the future, accurate calculations of k_A might be possible. Together with a calculation of k_A, a measurement of k_G, and an estimate of k_D, for example, eq 44 could be used to obtain values of $\bar{a}$ and b.

Alternatively, perhaps b could be calculated without calculating k_A. This seems possible because b is sometimes determined by factors that have more to do with A and B than with the transition state for bond making. Thus, b can reflect spin factors (constant or time-dependent), rotational anisotropies in the reactivity, and conformational differences between an A and B approaching the transition state and those not so involved in solution.[6,10] If b can be calculated more easily than k_A, without calculating k_A, then

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[11] Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High-Resolution Nuclear Magnetic Resonance*; McGraw-Hill: New York, 1959; pp 218–224.

a measurement of k_G and an estimate of k_D would suffice for the calculation of k_A from eq 44.

Experimentally, estimates of b may be available from detailed studies of the variations of experimentally determined values of k_G with factors such as viscosity and temperature,[10] allowing the use of eq 44 to determine k_A. Finally, picosecond kinetic methods can provide direct illumination the problem.

Asking for the value of k_A for a fast bimolecular reaction in solution might not be a very meaningful question. This constant is defined in theory as the rate constant for the reaction at equilibrium, but it is not accessible directly in experiments, at least not easily. Even if the forward and backward rates could be measured at equilibrium, some decision would have to be made as to exactly what constitutes reaction. Different types of experiments might have the effect of defining reaction differently. Thus, the value of k_A might depend on the nature of experiment or on a somewhat arbitrary decision concerning the analysis of data. In this sense, k_A could be an illusion.

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Note Added in Proof. There now appears to be agreement on diffusion effects on fast bimolecular reactions in the presence of the backward reactions. In addition to the present work and refs 5a–d, see: (a) Burlatskii, S. F.; Ovchinnikov, A. A.; Oshanin, G. S. *Sov. Phys. JETP* **1989**, *68*, 1153. (b) Burlatskii, S. F.; Oshanin, G. S.; Ovchinnikov, A. A. *Phys. Chem.* **1991**, *152*, 13. (c) Keizer, J.; Molski, A. *Trends in Chemical Physics*, in press. (d) Molski, A.; Keizer, J. *J. Chem. Phys.*, in press.

The Hydrosodalite System $Na_{6+x}[SiAlO_4]_6(OH)_x{\cdot}nH_2O$: Formation, Phase Composition, and De- and Rehydration Studied by ^1H, ^{23}Na, and ^{29}Si MAS–NMR Spectroscopy in Tandem with Thermal Analysis, X-ray Diffraction, and IR Spectroscopy

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Abstract: Hydrosodalites of general composition $Na_{6+x}(SiAlO_4)_6(OH)_x{\cdot}nH_2O$ have been prepared from kaolinite and aqueous NaOH solution by hydrothermal synthesis under various conditions and subsequent NaOH extraction with water and/or thermal dehydration. Detailed characterization of the products by ^{29}Si, ^{23}Na, and ^1H MAS–NMR spectroscopy in combination with thermal analysis, powder X-ray diffraction, and infrared spectroscopy verifies the composition of the following five distinct hydrosodalite phases: $Na_8[SiAlO_4]_6(OH)_2{\cdot}2H_2O$, $Na_8[SiAlO_4]_6(OH)_2$ ("basic hydrosodalites"), $Na_6[SiAlO_4]_6{\cdot}8H_2O$, $Na_6[AlSiO_4]_6{\cdot}4H_2O$, and $Na_6[SiAlO_4]_6H$ ("nonbasic hydrosodalites"). Hydrosodalite phases of other compositions such as "superbasic sodalites" $Na_{10}[SiAlO_4]_6(OH)_4$ and basic sodalite hydrates $Na_8[SiAlO_4]_6(OH)_2{\cdot}nH_2O$ with $n > 2$ proposed by several authors could not be identified. The primary product of hydrothermal synthesis is always the basic hydrosodalite $Na_8[SiAlO_4]_6(OH)_2{\cdot}2H_2O$. However, the latter is partially transformed into nonbasic $Na_6[SiAlO_4]_6{\cdot}8H_2O$ sodalite due to intracage NaOH/H_2O exchange during the washing of the crude product with water, generally applied to remove NaOH impurities from the outer surface of the crystallites. The extent of the exchange depends on the washing conditions and is very effective for microcrystalline powders but strongly reduced for large single crystals of 0.5–1 mm in size. Thus the basic hydrosodalites of composition $Na_8[SiAlO_4]_6(OH)_2{\cdot}nH_2O$ with $n > 2$ described previously are in fact mixtures of basic and nonbasic hydrosodalites. In contrast to the highly hydrophilic anhydrous nonbasic sodalite $Na_6[SiAlO_4]_6$, the dehydrated basic sodalite $Na_8[SiAlO_4]_6(OH)_2$ is hydrophobic and cannot be rehydrated. During slow rehydration of the former an intermediate phase of composition $Na_6[SiAlO_4]_6{\cdot}4H_2O$ has been positively identified. This study clearly demonstrates the power of combined application of multinuclear MAS–NMR spectroscopy, X-ray diffraction, IR spectroscopy, and thermal analysis for providing detailed information on the specific cage fillings and host/guest chemistry in sodalites.

Introduction

The framework of 1:1 aluminosilicate sodalites consists of a perfectly periodic array of all-space filling $[4^66^8]$ polyhedra ("β-cages") formed by a network of alternating and corner-sharing SiO_4 and AlO_4 tetrahedra with a unit cell content of $[SiAlO_4]_6^{6-}$ (two β-cages).[1] Besides the cations M^+ compensating the negative charge of the framework, the β-cages may contain a large variety of encapsulated salt M^+A^-, hydroxide M^+OH^-, and/or water molecules. The general unit cell composition of aluminosilicate sodalites can be given by $M_{6+x}[SiAlO_4]_6A_x{\cdot}nH_2O$ where M and A are single-charged cations and anions, respectively. Sodalites have attracted considerable attention because of their structural relationship with the well-known A- and X, Y-type zeolites, their cathodochromic, photochromic, and ion-conducting properties, and, more recently, their application as matrices for semiconductor superstructures in the quantum size regime (nanocomposites).[2] A large number of different sodalites has been synthesized, and their composition and structure have been characterized by chemical and thermal analysis, X-ray and neutron diffraction, and spectroscopic methods. Nevertheless there are still open questions concerning, e.g., the optimum synthesis conditions and procedures

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