9. S. Winstein, A. H. Fainberg, and E. Grunwald, *J. Am. Chem. Soc.*, **79**, 4146 (1957).
10. M. Fujio, M. Goto, T. Yoshino, K. Funatsu, Y. Tsuji, S. Ouchi, and Y. Tsuno, *Mem. Fac. Science, Kyushi University, Ser. C.*, **16**, 85 (1987); *Chem. Abstr.*, **109**, 148671j (1988).
11. J. Laureillard, A. Casadevall, and E. Casadevall, Herv. *Chim. Acya*, **67**, 352 (1984).
12. I. S. Koo, T. W. Bentley and H. C. Harris, *J. Org. Chem.*, **53**, 724 (1988).
13. T. W. Bentley and G. E. Carter, *J. Am. Chem. Soc.*, **104**, 5741 (1991).
14. T. W. Bentley and G. E. Gream, *J. Org. Chem.*, **50**, 1776 (1991).
15. T. W. Bentley and H. C. Harris, *J. Chem. Soc., Perkin Trans 2*, 619 (1986).
16. T. W. Bentley and H. C. Harris, *Adv. Phys. Org. Chem.* **17**, 121-158 (1990).
17. (a) K. T. Liu, H. C. Sheu, H. I. Chen, P. F. Chiu, and C. R. Hu, *Tetrahedron Lett.*, **31**, 3661 (1990); (b) K. T. Liu and H. C. Sheu, *J. Org. Chem.*, **56**, 3021 (1991).
18. A. Kivinen, *Acta. Chem. Scand.*, **19**, 835 (1965).
19. L. Senatore, E. Ciuffarin, and A. Fava, *J. Am. Chem. Soc.*, **92**, 3035 (1970).

Theory of Diffusion-Influenced Bimolecular Reactions in Solution: Effects of a Stochastic Gating Mode

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We have investigated the kinetics of diffusion-influenced bimolecular reactions in which one reactant has an internal mode, called the gating mode, that activates or deactivates its reactivity intermittently. The rate law and an expression for the time-dependent rate coefficient have been obtained from the general formalism based on the hierarchy of kinetic equations involving reactant distribution functions. The analytic expression obtained for the steady-state reaction rate constant coincides with the one obtained by Szabo *et al.*, who derived the expression by employing the conventional concentration-gradient approach. For the time-dependent reaction rate coefficient, we obtained for the first time an exact analytic expression in the Laplace domain which was then inverted numerically to give the time-domain results.

Introduction

When the inherent reaction step proceeds very rapidly upon the contact of reactant molecules, the diffusive encounter rate can influence the overall reaction rate. Examples can be found in radical or ion recombination reactions,[1,2] intermolecular energy transfer reactions,[3,4] enzyme-substrate reactions,[5] tunneling reactions of solvated electrons,[6] and the coagulation of colloid particles.[7]

A theory for the rate of diffusion-controlled reactions was first formulated by Smoluchowski.[7] Since then the theory has been refined and generalized in many aspects[8]: *e.g.*, refined modelings of the reaction event by the radiation boundary condition[9] or by the reaction sink function,[10] rigorous formulations of the rate theory based on hierarchical kinetic equations governing the evolution of reactant molecule distribution,[11,12] inclusion of the effects due to long-range intermoleuclar forces[13] and solvent-mediated hydrodynamic interactions,[14] consideration of orientation-dependent reactivity of reactant molecules,[15,16] and so on.

An interesting generalization of the theory that has attracted much attention recently is to include the effect of structural fluctuation in reactant molecules that may dynamically alter their intrinsic reactivity.[17-19]. In enzyme-substrate reactions, for example, the enzyme molecule may have side chains that can change the binding site accessibility. Motions of such side chains constitute a *gating mode* which *opens* and *closes* the binding site of substrate molecules.

One of the simplest model of gated diffusion-influenced reactions is that proposed by A. Szabo *et al.*[19] They considered a bimolecular reaction between molecules of species A and B,

$$A+B \longrightarrow P+B \tag{1.1}$$

where B molecules, which do not change in the course of reaction like an enzyme in enzyme-substrate reactions, have a fluctuating reactivity due the gating dynamics of an internal mode. For simplicity, they assumed that the fluctuations in the reactivity of B molecules can be described as a two-state process and that the dynamics of the gate between the two states, open and closed, can be described by the first-order rate equation

$$O \underset{k_o}{\overset{k_c}{\rightleftharpoons}} C \tag{1.2}$$

Here we designate the B molecules in the open state as molecules O while those in the closed state as molecules C. k_c and k_o are the rate constants, respectively, for the closing and opening of the gate. Molecules of species A can react only with molecules O:

$$A+O \longrightarrow P+O \tag{1.3}$$

where P denotes the product converted from A.

In the present work, we adopt the above model of gated diffusion-influenced reactions and reformulate the rate theory by starting from the hierarchical kinetic equations governing the reactant molecule distribution functions.[12] The rationale of this approach is to remove the limitations in the conventional theory that is based on the calculation of the reactive flux of O molecules into a sink molecule of species A fixed at the origin. The conventional approach based on such an analysis has two major difficulties. First, one cannot neglect the presence of nearby A molecules competing for the reaction partners with the central A molecule. Second, the cumulative flux of O molecules into the central A molecule must be less than one since the A molecule is destroyed after the reaction with one O molecule. One may avoid the second complication by considering the reactive flux of A molecules into a sink molecule of species O. But then another difficulty arises. The boundary condition imposed on the concentration field of A molecules at infinite separation from the central O molecule is to match its value with the bulk concentration of A molecules, which is time-dependent. This makes the analysis far more complicated. Hence the usual practice adopted in the conventional approach, as described in many textbooks on chemical kinetics,[8,20] is to neglect altogether the complications raised above. Obviously, the validity of such approximations needs to be checked.

In the next section we present the general formalism to deal with the gated diffusion-influenced reactions. A second-order rate equation that is expected for the molecularity of reaction (1.1) but which involves a time-dependent reaction rate coefficient is derived. A microscopic but formal expression obtained for the rate coefficient is then evaluated analytically for the steady-state kinetics in the third section. The result agrees with that obtained by Szabo, *et al.*[19] *via* the conventional approach. Errors due to the neglect of the *competition* and *reactivity saturation of the sink* as mentioned above are shown to be cancelled out. For the time-dependent reaction rate coefficient, we obtain for the first time an exact analytic expression in the Laplace domain which is then inverted numerically to give the time-domain results.

Derivation of the Reaction Rate Expression

We consider a solution which contains N_A° molecules of species A and N_B° molecules of species B including both O and C forms as $t=0$. We assume that A molecules have spherically symmetric reactivity with no gating mode and that B molecules with a gating mode also have spherically symmetric reactivity. Hence the molecular state may be described by the position vector. The kinetic equation governing the evolution of one particle probability density function $P_{A_i}(\mathbf{r}, t)$, which denotes the probability density that the ith A molecule has not undergone the reaction until time t and is located at the position $\mathbf{r}$, is then written as

$$\frac{\partial}{\partial t} P_{A_i}(\mathbf{r}, t)=L_A P_{A_i}(\mathbf{r}, t)-\sum_{j=1}^{N_B^\circ}\int d\mathbf{r}'\, S_{AO}(\mathbf{r}, \mathbf{r}')\, P_{A_iO_j}(\mathbf{r}, \mathbf{r}', t) \tag{2.1}$$

where the first term on the right hand side represents the evolution of $P_{A_i}(\mathbf{r}, t)$ due to the thermal motion of A_i in the absence of reaction. In the present work we approximate the evolution operator L_A by the Smoluchowski operator. In the absence of the external potential field, L_A is simply given by $D_A(\partial/\partial \mathbf{r})^2$ with D_A denoting the diffusion coefficient. The second term on the right hand side of Eq. (2.1) denotes the depopulation rate of A_i at $\mathbf{r}$ due to the reaction with any of the O molecules (B moecules in the open state). The sink function $S_{AO}(\mathbf{r}, \mathbf{r}')$ denotes the reaction probability per unit time between an A molecule at $\mathbf{r}$ and an O molecule at $\mathbf{r}'$. The two particle probability density function $P_{A_iO_j}(\mathbf{r}, \mathbf{r}', t)$ denotes the joint probability density that at time t the ith A molecule which has not undergone reaction is at $\mathbf{r}$ and the jth B molecule is at $\mathbf{r}'$ in the open state.

Kinetic equations governing the evolutions of one-particle probability density functions $P_{O_j}(\mathbf{r}, t)$ and $P_{C_j}(\mathbf{r}, t)$, which denote respectively the probability densities that the jth B moecule is located at $\mathbf{r}$ in the open and in the closed states at time t, are given by

$$\frac{\partial}{\partial t} P_{O_j}(\mathbf{r}, t)=L_O P_{O_j}(\mathbf{r}, t)-k_c P_{O_j}(\mathbf{r}, t)+k_o P_{C_j}(\mathbf{r}, t) \tag{2.2}$$

$$\frac{\partial}{\partial t} P_{C_j}(\mathbf{r}, t)=L_C P_{C_j}(\mathbf{r}, t)+k_c P_{O_j}(\mathbf{r}, t)-k_o P_{C_j}(\mathbf{r}, t) \tag{2.3}$$

Again, the first term on the right hand side of Eq. (2.2) or Eq. (2.3) represents the change due to diffusive thermal motion, and the second and the third terms represent the changes due to the gating dynamics. The evolution operators L_O and L_C are assumed to be given by the Smoluchowski operators.

Summation of $P_{A_i}(\mathbf{r}, t)$ over i gives the concentration (number density) field of A molecules at $\mathbf{r}$ at time t:

$$\sum_{i=1}^{N_A^\circ} P_{A_i}(\mathbf{r}, t)=C_A(\mathbf{r}, t)=[A] \tag{2.4}$$

where we further equate the concentration field to the bulk concentration of A molecules at time t. This should be true under usual experimental condition where there is no external potential field on A molecules. Similarly, we have

$$\sum_{j=1}^{N_B^\circ} P_{O_j}(\mathbf{r}, t)=C_O(\mathbf{r}, t)=[O] \tag{2.5}$$

$$\sum_{j=1}^{N_B^\circ} P_{C_j}(\mathbf{r}, t)=C_C(\mathbf{r}, t)=[C] \tag{2.6}$$

The two-particle probability density function $P_{A_iO_j}(\mathbf{r}, \mathbf{r}', t)$ can be expressed in the form

$$P_{A_iO_j}(\mathbf{r}, \mathbf{r}', t)=P_{A_i}(\mathbf{r}, t)\, P_{O_j(A_i)}(\mathbf{r}', t|\mathbf{r}) \tag{2.7}$$

where $P_{O_j(A_i)}(\mathbf{r}', t|\mathbf{r})$ denotes the conditional probability density that O_j is at $\mathbf{r}'$ at time t given that A_i is at $\mathbf{r}$. Summing Eq. (2.7) over i and j gives

$$\sum_{i=1}^{N_A^\circ}\sum_{j=1}^{N_B^\circ} P_{A_iO_j}(\mathbf{r}, \mathbf{r}', t)=\sum_{i=1}^{N_A^\circ} P_{A_i}(\mathbf{r}, t)\, C_{O(A_i)}(\mathbf{r}', t|\mathbf{r}) \tag{2.8}$$

where $C_{O(A_i)}(\mathbf{r}', t|\mathbf{r})$ is the conditional concentration field of O molecules at $\mathbf{r}'$ at time t given that A_i is at $\mathbf{r}$. It depends only on $|\mathbf{r}'-\mathbf{r}|$ and should be the same for all A molecules. Hence we can write

$$C_{O(A_i)}(\mathbf{r}',\ t|\mathbf{r})=[O]\,\rho_{AO}(|\mathbf{r}'-\mathbf{r}|,\ t) \tag{2.9}$$

where ρ_{AO} denotes the nonequilibrium pair correlation function for the relative distribution of A and O molecules, and

$$\sum_{i=1}^{N_A^\circ}\sum_{j=1}^{N_B^\circ} P_{A_iO_j}(\mathbf{r},\ \mathbf{r}',\ t)=[A]\,[O]\,\rho_{AO}(|\mathbf{r}'-\mathbf{r}|,\ t) \tag{2.10}$$

Summing Eq. (2.1) over i and using Eqs. (2.4) and (2.10), we obtain the rate equation:

$$\frac{d}{dt}[A]=-k_f^\circ(t)[A][O] \tag{2.11}$$

where

$$k_f^\circ(t)=\int d\mathbf{r}' S_{AO}(|\mathbf{r}'-\mathbf{r}|)\rho_{AO}(|\mathbf{r}'-\mathbf{r}|,\ t) \tag{2.12}$$

On the other hand, summing Eq. (2.2) or Eq. (2.3) over j and using Eqs. (2.5) and (2.6), we obtain

$$\frac{d}{dt}[O]=-\frac{d}{dt}[C]=-k_c[O]+k_o[C] \tag{2.13}$$

The usual phenomenological rate expression for the reaction in Eq. (1.1) is

$$\frac{d}{dt}[A]=-k_f[A][B] \tag{2.14}$$

Comparison of Eq. (2.14) with Eq. (2.11) shows that

$$k_f=([O]/[B])\,k_f^\circ(t) \tag{2.15}$$

The distribution of B molecules over the open and closed states and thus the ratio $[O]/[B]$ must be determined by solving the rate equation, (2.13) for an appropriate initial condition. For simplicity, we assume an equilibrium distribution; that is,

$$[C]/[O]=k_c/k_o=K_{eq} \tag{2.16}$$

In this case the bimolecular rate coefficient k_f has the expression

$$k_f=(1+K_{eq})^{-1}\,k_f^\circ(t) \tag{2.17}$$

To calculate $k_f^\circ(t)$ defined in Eq. (2.12), we need an explicit expression for the nonequilibrium pair correlation function $\rho_{AO}(|\mathbf{r}'-\mathbf{r}|,\ t)$. The kinetic equation governing the evolution of ρ_{AO} can be derived from the evolution equations for two-particle probability density functions. We have

$$\begin{aligned}\frac{\partial}{\partial t}P_{A_iO_j}(\mathbf{r},\ \mathbf{r}',\ t)&=L_{AO}P_{A_iO_j}(\mathbf{r},\ \mathbf{r}',\ t)-S_{AO}(\mathbf{r},\ \mathbf{r}')P_{A_iO_j}(\mathbf{r},\ \mathbf{r}',\ t)\\&\quad-k_cP_{A_iO_j}(\mathbf{r},\ \mathbf{r}',\ t)+k_oP_{A_iC_j}(\mathbf{r},\ \mathbf{r}',\ t)\\&\quad-\sum_{\substack{k=1\\k\neq j}}^{N_B^\circ}\int d\mathbf{r}''\,S_{AO}(\mathbf{r},\ \mathbf{r}'')\,P_{A_iO_jO_k}(\mathbf{r},\ \mathbf{r}',\ \mathbf{r}'',\ t)\end{aligned} \tag{2.18}$$

$$\begin{aligned}\frac{\partial}{\partial t}P_{A_iC_j}(\mathbf{r},\ \mathbf{r}',\ t)&=L_{AC}P_{A_iC_j}(\mathbf{r},\ \mathbf{r}',\ t)\\&\quad+k_cP_{A_iO_j}(\mathbf{r},\ \mathbf{r}',\ t)-k_oP_{A_iC_j}(\mathbf{r},\ \mathbf{r}',\ t)\\&\quad-\sum_{\substack{k=1\\k\neq j}}^{N_B^\circ}\int d\mathbf{r}''\,S_{AO}(\mathbf{r},\ \mathbf{r}'')\,P_{A_iC_jO_k}(\mathbf{r},\ \mathbf{r}',\ \mathbf{r}'',\ t)\end{aligned} \tag{2.19}$$

Each term in these equations has a similar meaning as the corresponding term in Eqs. (2.1)-(2.3). In Eq. (2.18), for example the first term on the right hand side represents the change due to diffusive thermal motions of A_i and O_j; the second term due to the reaction between A_i and O_j; the third and the fourth terms due to gating dynamics in O_j moecule; and finally the fifth term, involving the three-particle probability density functions, describes the change due to the reaction of A_i at $\mathbf{r}$ with O molecules at $\mathbf{r}''$ other than O_j.

One can note the hierarchical structure of evolution equations for reactant molecule distribution functions from Eqs. (2.1), (2.18), and (2.19); that is, the evolution equation for an n-particle probability density function involves $(n+1)$-particle probability density function. Writing higher-order equations is straightforward, but the solution to the whole hierarchy of kinetic equations is difficult to obtain. To truncate the hierarchy at the level of two-particle kinetic equations we need to approximate the three-particle probability density functions contained in Eq. (2.18) and (2.19) in terms of one-particle and two-particle probability density functions. In the superposition approximation,[12,21,22] we may write

$$P_{A_iO_jO_k}(\mathbf{r},\ \mathbf{r}',\ \mathbf{r}'',\ t)\cong P_{A_i}(\mathbf{r},\ t)\,P_{O_j(A_i)}(\mathbf{r}',\ t|\mathbf{r})\,P_{O_k(A_i)}(\mathbf{r}'',\ t|\mathbf{r}) \tag{2.20}$$

With this approximation, we have

$$\sum_{i=1}^{N_A^\circ}\sum_{j=1}^{N_B^\circ}\sum_{\substack{k=1\\k\neq j}}^{N_B^\circ} P_{A_iO_jO_k}(\mathbf{r},\ \mathbf{r}',\ \mathbf{r}'',\ t) \cong C_A(\mathbf{r},\ t)\,C_{O(A)}(\mathbf{r}',\ t|\mathbf{r})\,C_{O(A)}(\mathbf{r}'',\ t|\mathbf{r}) \tag{2.21}$$

Similarly,

$$\sum_{i=1}^{N_A^\circ}\sum_{j=1}^{N_B^\circ}\sum_{\substack{k=1\\k\neq j}}^{N_B^\circ} P_{A_iC_jO_k}(\mathbf{r},\ \mathbf{r}',\ \mathbf{r}'',\ t) \cong C_A(\mathbf{r},\ t)\,C_{C(A)}(\mathbf{r}',\ t|\mathbf{r})\,C_{O(A)}(\mathbf{r}'',\ t|\mathbf{r}) \tag{2.22}$$

Using the above approximation, we sum Eq. (2.18) over i from $i=1$ to N_A° and over j from $j=1$ to N_B°. The resulting equation is then simplified with Eqs. (2.4)-(2.10) and (2.12) to give

$$\begin{aligned}\frac{\partial}{\partial t}\{[A][O]\rho_{AO}(\mathbf{r},\ \mathbf{r}',\ t)\}&=[A][O]\,L_{AO}\,\rho_{AO}(\mathbf{r},\ \mathbf{r}',\ t)\\&\quad-[A][O]\,S_{AO}(\mathbf{r},\ \mathbf{r}')\rho_{AO}(\mathbf{r},\ \mathbf{r}',\ t)\\&\quad-[A][O]\,k_c\,\rho_{AO}(\mathbf{r},\ \mathbf{r}',\ t)+[A][C]\,k_o\,\rho_{AC}(\mathbf{r},\ \mathbf{r}',\ t)\\&\quad-[A][O]^2k_f^\circ(t)\rho_{AO}(\mathbf{r},\ \mathbf{r}',\ t)\end{aligned} \tag{2.23}$$

With Eqs. (2.11) and (2.16), we can expand the left hand side of this equation as

$$\begin{aligned}\frac{\partial}{\partial t}\{[A][O]\rho_{AO}(\mathbf{r},\ \mathbf{r}',\ t)\}&=-k_f^\circ(t)[A][O]^2\rho_{AO}(\mathbf{r},\ \mathbf{r}',\ t)\\&\quad+[A][O]\frac{\partial}{\partial t}\rho_{AO}(\mathbf{r},\ \mathbf{r}',\ t)\end{aligned} \tag{2.24}$$

We note that the last term in Eq. (2.23), which arises from the last term in Eq. (2.18) that represents the *competition* among O molecules for the reaction with A molecules, offsets the first term on the right hand side of Eq. (2.24), which is related to the *reactivity saturation* of the sink molecule as discussed in the introductory section. This observation justifies the neglect of *both* the *competition* and *reactivity saturation* of the sink molecules as done in the conventional theories of diffusion-influenced reactions. However, this shows also that attempts to account for only the competition effect or only the reactivity saturation effect would yield worse results.[23,24]

From Eqs. (2.23) and (2.24), we obtain

$$\frac{\partial}{\partial t}\rho_{AO}(\mathbf{r},\ \mathbf{r}',\ t)=L_{AO}\rho_{AO}(\mathbf{r},\ \mathbf{r}',\ t)-S_{AO}(\mathbf{r},\ \mathbf{r}')\,\rho_{AO}(\mathbf{r},\ \mathbf{r}',\ t)$$
$$-k_c\rho_{AO}(\mathbf{r},\ \mathbf{r}',\ t)+k_c\rho_{AC}(\mathbf{r},\ \mathbf{r}',\ t) \qquad (2.25)$$

where we have used Eq. (2.16) to equate $([C]/[O])k_o$ with k_c. Similar manipulation of Eq. (2.19) gives

$$\frac{\partial}{\partial t}\rho_{AC}(\mathbf{r},\ \mathbf{r}',\ t)=L_{AC}\rho_{AC}(\mathbf{r},\ \mathbf{r}',\ t)$$
$$+k_o\rho_{AO}(\mathbf{r},\ \mathbf{r}',\ t)-k_o\rho_{AC}(\mathbf{r},\ \mathbf{r}',\ t) \qquad (2.26)$$

Summarizing this section, we have derived the rate equation, Eq. (2.14) [or equivalently, Eq. (2.11)] that is expected for the molecularity of reaction (1.1) but which involves a time-dependent reaction rate coefficient given by Eqs. (2.12) and (2.17). To evaluate the rate coefficient, we should solve the coupled partial differential equations, Eqs. (2.25) and (2.26), for the nonequilibrium pair correlation function $\rho_{AO}(|\mathbf{r}'-\mathbf{r}|,\ t)$.

Calculation of the Rate Coefficient

We first rewrite Eqs. (2.25) and (2.26) as a matrix equation

$$\frac{\partial}{\partial t}\underset{\sim}{\rho}(r,\ t)=\mathbf{L}(r)\cdot\underset{\sim}{\rho}(r,\ t) \qquad (3.11)$$

where $r=|\mathbf{r}'-\mathbf{r}|$ and

$$\underset{\sim}{\rho}(r,\ t)=\begin{pmatrix}\rho_{AO}(r,\ t)\\ \rho_{AC}(r,\ t)\end{pmatrix}$$
$$\mathbf{L}(r)=\mathbf{L}_O(r)+\mathbf{L}_G-\mathbf{S}(r)$$
$$\mathbf{L}_O(r)=\begin{pmatrix}L_{AO}(r) & O\\ O & L_{AO}(r)\end{pmatrix}$$
$$\mathbf{L}_G=\begin{pmatrix}-k_c & k_c\\ k_o & -k_o\end{pmatrix}$$
$$\mathbf{S}(r)=\begin{pmatrix}S_{AO}(r) & O\\ O & O\end{pmatrix}$$

A formal solution to Eq. (3.1) is given by

$$\underset{\sim}{\rho}(r,\ t)=\exp[t(\mathbf{L}_O+\mathbf{L}_G-\mathbf{S})]\cdot\underset{\sim}{\rho}(r,\ O)$$
$$=\exp[t(\mathbf{L}_O+\mathbf{L}_G)]\cdot\underset{\sim}{\rho}(r,\ O)$$
$$-\int_O^t d\tau\exp[\tau(\mathbf{L}_O+\mathbf{L}_G-\mathbf{S})]\cdot\mathbf{S}$$
$$\cdot\exp[(t-\tau)(\mathbf{L}_O+\mathbf{L}_G)]\cdot\underset{\sim}{\rho}(r,\ O) \qquad (3.2)$$

where in writing the second line we used the well-known operator identity,[25]

$$e^{t(A+B)}=e^{tA}+\int_O^t d\tau\, e^{\tau(A+B)}Be^{(t-\tau)A} \qquad (3.3)$$

We now assume that the initial distribution of reactant molecules is an equilibrium one so that

$$\underset{\sim}{\rho}(r,\ O)=\mathbf{g}^{(2)}(r)=\begin{pmatrix}g_{AO}^{(2)}(r)\\ g_{AC}^{(2)}(r)\end{pmatrix} \qquad (3.4)$$

where $g_{AO}^{(2)}(r)$ and $g_{AC}^{(2)}(r)$ denote the equilibrium pair correlation functions for A-O and A-C pairs, respectively. We further assume that physical characteristics of O molecules are not much different from those of C molecules. For example, they have the same diffusion coefficient D_B and interact with A molecules through the same potential of mean force $U_{AB}(r)$. We then have[12]

$$g_{AO}^{(2)}(r)=g_{AC}^{(2)}(r)=\exp[-\beta U_{AB}(r)]\equiv g^{(2)}(r) \qquad (3.5)$$
$$L_{AO}(r)=L_{AC}(r)=\left(\frac{\partial}{\partial r}+\frac{2}{r}\right)d_{AB}(r)\left[\frac{\partial}{\partial r}+\beta\frac{\partial}{\partial r}U_{AB}(r)\right]$$
$$\equiv L_O(r) \qquad (3.6)$$

Here $\beta=1/k_BT$ with k_B the Boltzmann constant and T the absolute temperature. $d_{AB}(r)$ is the relative diffusion coefficient bewteen A and B molecules. If the hydrodynamic interaction is negligible, $d_{AB}(r)$ is simply given by the sum of the diffusion constants of A and B molecules; *i.e.*, $d_{AB}(r)=D_A+D_B$.

With the assumptions expressed in Eqs. (3.4)-(3.6), we have

$$\mathbf{L}_O(r)\cdot\mathbf{L}_G=\mathbf{L}_G\cdot\mathbf{L}_O(r) \qquad (3.7)$$

and thus

$$\exp[t(\mathbf{L}_O+\mathbf{L}_G)]\cdot\underset{\sim}{\rho}(r,\ O)=\exp(t\mathbf{L}_G)\cdot\exp(t\mathbf{L}_O)\cdot\mathbf{g}^{(2)}(r)$$
$$=\exp(t\mathbf{L}_G)\cdot\begin{pmatrix}\exp[tL_O(r)]g^{(2)}(r)\\ \exp[tL_O(r)]g^{(2)}(r)\end{pmatrix}=\exp(t\mathbf{L}_G)\cdot\begin{pmatrix}g^{(2)}(r)\\ g^{(2)}(r)\end{pmatrix}$$
$$=\mathbf{g}^{(2)}(r) \qquad (3.8)$$

With Eq. (3.8), Eq. (3.2) reduces to

$$\underset{\sim}{\rho}(r,\ t)=\mathbf{g}^{(2)}(r)-\int_O^t d\tau\exp[\tau(\mathbf{L}_O+\mathbf{L}_G-\mathbf{S})]\cdot\mathbf{S}\cdot\mathbf{g}^{(2)}(r) \qquad (3.9)$$

On the other hand, the expression for the rate coefficient $k_f^{\circ}(t)$ in Eq. (2.12) can be rewritten as

$$\mathbf{K}(t)\cdot\begin{pmatrix}1\\ 1\end{pmatrix}\equiv\begin{pmatrix}k_f^{\circ}(t) & O\\ O & O\end{pmatrix}\cdot\begin{pmatrix}1\\ 1\end{pmatrix}=\int d\mathbf{r}\ \mathbf{S}(r)\cdot\underset{\sim}{\rho}(r,\ t) \qquad (3.10)$$

Noting that

$$\mathbf{g}^{(2)}(r)=\begin{pmatrix}g^{(2)}(r)\\ g^{(2)}(r)\end{pmatrix}=\begin{pmatrix}g^{(2)}(r) & O\\ O & g^{(2)}(r)\end{pmatrix}\cdot\begin{pmatrix}1\\ 1\end{pmatrix}$$
$$\equiv\mathbf{G}^{(2)}(r)\cdot\begin{pmatrix}1\\ 1\end{pmatrix} \qquad (3.11)$$

and substituting Eq. (3.9) into Eq. (3.10), we obtain

$$\begin{aligned}\boldsymbol{K}(t) &= \int d\boldsymbol{r}\, \boldsymbol{S}(r)\boldsymbol{G}^{(2)}(r) \\ &\quad -\int_0^t d\tau \int d\boldsymbol{r}\, \boldsymbol{S}(r)\cdot \exp\{\tau[\boldsymbol{L}_O(r)+\boldsymbol{L}_G-\boldsymbol{S}(r)]\}\cdot \boldsymbol{S}(r)\cdot \boldsymbol{G}^{(2)}(r) \\ &\equiv \boldsymbol{K}_{eq} - \int_0^t d\tau\, \boldsymbol{Y}(\tau) \end{aligned} \tag{3.12}$$

where we have defined the equilibrium rate constant matrix $\boldsymbol{K}_{eq}$ and the matrix memory kernel $\boldsymbol{Y}(\tau)$.

Using the operator identity, Eq. (3.3), $\boldsymbol{Y}(\tau)$ can be rewritten as

$$\begin{aligned}\boldsymbol{Y}(\tau) &= \int d\boldsymbol{r}\, \boldsymbol{S}(r)\cdot \exp\{\tau[\boldsymbol{L}_O(r)+\mathbf{L}_G]\}\cdot \boldsymbol{S}(r)\cdot \boldsymbol{G}^{(2)}(r) \\ &\quad -\int_0^\tau d\tau_1 \int d\boldsymbol{r}\, \boldsymbol{S}(r)\cdot \exp\{\tau_1[\boldsymbol{L}_O(r)+\boldsymbol{L}_G-\boldsymbol{S}(r)]\}\cdot \boldsymbol{S}(r) \\ &\quad \cdot \exp\{(\tau-\tau_1)[\boldsymbol{L}_O(r)+\boldsymbol{L}_G]\}\cdot \boldsymbol{S}(r)\cdot \boldsymbol{G}^{(2)}(r) \end{aligned} \tag{3.13}$$

Introducing the Green's functions,

$$\begin{aligned}\boldsymbol{G}_R(r,\ t|r_O) &\equiv \exp\{t[\boldsymbol{L}_O(r)+\boldsymbol{L}_G-\boldsymbol{S}(r)]\} \\ &\quad \cdot \begin{pmatrix} \delta(r-r_O)/4\pi r_O^2 & O \\ O & \delta(r-r_O)/4\pi r_O^2 \end{pmatrix} \end{aligned} \tag{3.14}$$

$$\begin{aligned}\boldsymbol{G}^*(r,\ t|r_O) &\equiv \exp\{t[\boldsymbol{L}_O(r)+\boldsymbol{L}_G]\} \\ &\quad \cdot \begin{pmatrix} \delta(r-r_O)/4\pi r_O^2 & O \\ O & \delta(r-r_O)/4\pi r_O^2 \end{pmatrix} \end{aligned} \tag{3.15}$$

we can reexpress $\boldsymbol{Y}(\tau)$ as

$$\begin{aligned}\boldsymbol{Y}(\tau) &= \int \mathrm{d}\boldsymbol{r}\, \boldsymbol{S}(r)\cdot \int d\boldsymbol{r}_O\, \boldsymbol{G}_R(r,\ \tau|r_O)\cdot \boldsymbol{S}(r_O)\cdot \boldsymbol{G}^{(2)}(r_O) \\ &= \int \mathrm{d}\boldsymbol{r}\, \boldsymbol{S}(r)\cdot \int d\boldsymbol{r}_O\, \boldsymbol{G}^*(r,\ \tau|r_O)\cdot \boldsymbol{S}(r_O)\cdot \boldsymbol{G}^{(2)}(r_O) \\ &\quad -\int_0^\tau d\tau_1 \int d\boldsymbol{r}\, \boldsymbol{S}(r)\cdot \int d\boldsymbol{r}_1\, \boldsymbol{G}_R(r,\ \tau_1|r_1)\cdot \boldsymbol{S}(r_1) \\ &\quad \cdot \int \mathrm{d}\boldsymbol{r}_O\, \boldsymbol{G}^*(r_1,\ \tau-\tau_1|r_O)\cdot \boldsymbol{S}(r_O)\cdot \boldsymbol{G}^{(2)}(r_O) \end{aligned} \tag{3.16}$$

We assume that the reaction can occur when A and O molecules are brought into contact at the separation $r=\sigma$. Then the reaction sink function $S_{AO}(r)$ may be modelled by a delta function; that is,

$$S_{AO}(\mathrm{r}) = \kappa\, \delta(r-\sigma)/4\pi\sigma^2 \tag{3.17}$$

or

$$\boldsymbol{S}(r) = \frac{\delta(r-\sigma)}{4\pi\sigma^2} \begin{pmatrix} \kappa & O \\ O & O \end{pmatrix} \equiv \frac{\delta(r-\sigma)}{4\pi\sigma^2}\, \mathbf{K}_i \tag{3.18}$$

Putting this expression for $\boldsymbol{S}(r)$ into Eq. (3.16) and taking the Laplace transformation of the resulting equation, with the notation

$$\hat{\Psi}(z) = \int_0^\infty dt\, \Psi(t) e^{-zt} \tag{3.19}$$

for the Laplace-transformed quantity, we obtain

$$\hat{\boldsymbol{Y}}(z) = \boldsymbol{K}_i\cdot \hat{\boldsymbol{G}}_R(\sigma,\ z|\sigma)\cdot \boldsymbol{K}_i\cdot \boldsymbol{G}^{(2)}(\sigma) \tag{3.20}$$

with

$$\hat{\boldsymbol{G}}_R(\sigma,\ z|\sigma) = \hat{\boldsymbol{G}}^*(\sigma,\ z|\sigma)\cdot [\boldsymbol{I}+\boldsymbol{K}_i\cdot \hat{\boldsymbol{G}}^*(\sigma,\ z|\sigma)]^{-1} \tag{3.21}$$

where $\mathbf{I}$ is a 2×2 unit matrix.

Substituting Eq. (3.20) into Eq. (3.12), we finally obtain a general but still formal expression for the rate coefficient:

$$\begin{aligned}\hat{\boldsymbol{K}}(z) &= z^{-1}\boldsymbol{K}_i\cdot \boldsymbol{G}^{(2)}(\sigma) - z^{-1}\hat{\boldsymbol{Y}}(z) \\ &= z^{-1}[\boldsymbol{I}+\boldsymbol{K}_i\cdot \hat{\boldsymbol{G}}^*(\sigma,\ z|\sigma)]^{-1}\cdot \boldsymbol{K}_i\cdot \boldsymbol{G}^{(2)}(\sigma) \end{aligned} \tag{3.22}$$

Once the reaction-free Green's function $\boldsymbol{G}^*(r,\ t|r_O)$ is calculated, the rate coefficient $k_f^{\circ}(t)$ can be evaluated from this equation.

We will then derive a more explicit expression for $\boldsymbol{G}^*(r,\ t|r_O)$. Since $\boldsymbol{L}_O(r)$ and $\boldsymbol{L}_G$ commute [Eq. (3.7)], we can rewrite Eq. (3.15) as

$$\boldsymbol{G}^*(r,\ t|r_O) = \exp(\mathrm{t}\boldsymbol{L}_G)\cdot \boldsymbol{G}(r,\ t|r_O) \tag{3.23}$$

where

$$\begin{aligned}\boldsymbol{G}(r,\ t|r_O) &\equiv \exp[t\boldsymbol{L}_O(r)]\cdot \begin{pmatrix} \delta(r-r_O)/4\pi r_O^2 & O \\ O & \delta(r-r_O)/4\pi r_O^2 \end{pmatrix} \\ &= \begin{pmatrix} G(r,\ t|r_O) & O \\ O & G(r,\ t|r_O) \end{pmatrix} \end{aligned} \tag{3.24}$$

with

$$G(r,\ t|r_O) = \exp[tL_O(r)]\delta(r-r_O)/4\pi r_O^2 \tag{3.25}$$

A simple expression for the exponential operator $\exp(t\boldsymbol{L}_G)$ can be found once we find the transformation matrix $\boldsymbol{T}$ which diagonalizes $\boldsymbol{L}_G$. We have

$$\boldsymbol{T}^{-1}\cdot \boldsymbol{L}_G\cdot \boldsymbol{T} = \begin{pmatrix} -(k_c+k_o) & O \\ O & O \end{pmatrix} \equiv \boldsymbol{L}_G^D \tag{3.26}$$

where

$$\boldsymbol{T} = \begin{pmatrix} k_c & 1 \\ -k_o & 1 \end{pmatrix}\ ;\ \boldsymbol{T}^{-1} = \frac{1}{k_c+k_o} \begin{pmatrix} 1 & -1 \\ k_o & k_c \end{pmatrix} \tag{3.27}$$

With the relation in Eq. (3.26), we can write

$$\begin{aligned}\boldsymbol{T}^{-1}\cdot \exp(t\boldsymbol{L}_G)\cdot \boldsymbol{T} &= \exp(t\boldsymbol{T}^{-1}\cdot \boldsymbol{L}_G\cdot \boldsymbol{T}) = \exp(t\boldsymbol{L}_G^D) \\ &= \begin{pmatrix} \exp[-(k_c+k_o)t] & O \\ O & 1 \end{pmatrix} \end{aligned} \tag{3.28}$$

and

$$\begin{aligned}\boldsymbol{G}^*(r,\ t|r_O) &= \boldsymbol{T}\cdot \boldsymbol{T}^{-1}\cdot \exp(t\boldsymbol{L}_G)\cdot \boldsymbol{T}\cdot \boldsymbol{T}^{-1}\cdot \boldsymbol{G}(r,\ t|r_O) \\ &= \boldsymbol{T}\cdot \exp(t\boldsymbol{L}_G^D)\cdot \boldsymbol{G}(r,\ t|r_O)\cdot \boldsymbol{T}^{-1} \\ &= \boldsymbol{T}\cdot \begin{pmatrix} \exp[-(k_c+k_o)t]G(r,\ t|r_O) & O \\ O & G(r,\ t|r_O) \end{pmatrix} \\ &\quad \cdot \boldsymbol{T}^{-1} \end{aligned} \tag{3.29}$$

where in writing the second line we have used the fact that $\boldsymbol{T}^{-1}$ commutes with $\boldsymbol{G}(r,\ t|r_O)$ defined in Eq. (3.24). Taking the Laplace transformation of Eq. (3.29), we get

$$\hat{\boldsymbol{G}}^*(r,\ z|r_O) = \boldsymbol{T}\cdot \begin{pmatrix} \hat{G}(r,\ z+k_c+k_o|r_O) & O \\ O & \hat{G}(r,\ z|r_O) \end{pmatrix}\cdot \boldsymbol{T}^{-1} \tag{3.30}$$

Substituting this expression for $\hat{\boldsymbol{G}}^*(r,\ z|r_O)$ into Eq. (3.22), we obtain a general expression for the rate coefficient matrix

$\hat{K}(z)$:

$$\hat{K}(z)=\frac{\kappa g^{(2)}(\sigma)}{z[\kappa k_c\hat{G}(\sigma,\ z+\lambda|\sigma)+\kappa k_o\hat{G}(\sigma,\ z|\sigma)+\lambda]}\begin{pmatrix}\lambda & O\\ O & O\end{pmatrix} \tag{3.31}$$

where $\lambda=k_c+k_o$. Hence the bimolecular rate coefficient k_f, which is related to $k_f^o(t)$ by Eq. (2.17), is given by

$$\hat{k}_f(z)=\frac{k_o g^{(2)}(\sigma)}{z[k_c\hat{G}(\sigma,\ z+\lambda|\sigma)+k_o\hat{G}(\sigma,\ z|\sigma)+(\lambda/\kappa)]} \tag{3.32}$$

The Green's function $G(r,\ t|r_O)$ defined in Eq. (3.25) has been obtained analytically only for a very simple case[8] when (i) the potential of mean force $U_{AB}(r)$ vanishes for $r\geq\sigma$ and becomes infinite for $r<\sigma$ and (ii) the relative diffusion coefficient $d_{AB}(r)$ is simply given by (D_A+D_B):

$$\hat{G}(r,\ z|r_O)=\frac{1}{4\pi Drr_O}\left\{\frac{1}{2\alpha}\left[e^{-\alpha|r-r_o|}-e^{-\alpha(r+r_o-2\sigma)}\right]\right.$$
$$\left.+\frac{\sigma}{1+\sigma\alpha}e^{-\alpha(r+r_o-2\sigma)}\right\} \tag{3.33}$$

where $\alpha\equiv(z/D)^{1/2}$. Hence,

$$\hat{G}(\sigma,\ z|\sigma)=\{k_D[1+\sigma(z/D)^{1/2}]\}^{-1} \tag{3.34}$$

where $k_D=4\pi\sigma D$, the well-known expression for the rate constant of ungated diffusion-controlled reactions first derived by Smoluchowski.[7]

The Laplace transform expression for the time-dependent rate coefficient $k_f(t)$ in Eq. (3.32) together with Eq. (3.34) constitutes the principal result of the present work. The expression can be inverted numerically to give the time-domain results. For large t, a steady state is attained in which the rate coefficient has a constant value. An analytic expression for the steady-state rate constant can be readily obtained as follows[26]:

$$k_f^s\equiv\lim_{t\to\infty}k_f(t)=\lim_{z\to 0}z\hat{k}_f(z)$$
$$=\left(\frac{\kappa k_D}{\kappa+k_D}\right)\left\{1+\frac{K_{eq}k_D}{\kappa+k_D}+\frac{K_{eq}\kappa}{\kappa+k_D}\ \frac{1}{[1+\sigma(\lambda/D)^{1/2}]}\right\}^{-1} \tag{3.35}$$

This expression for k_f^s was obtained previously by Szabo *et al.*[19] but through a different analysis based on the consideration of concentration gradient around a sink.

It is of interest to consider some limiting expression for k_f^s. First, Eq. (3.35) reduces to the well-known expression, $[\kappa k_D/(\kappa+k_D)]$, for ungated diffusion-influenced reactions.[8] Second, for completely diffusion-controlled cases in which reaction takes place immediately upon the encounter of A and O molecules (*i.e.*, when $\kappa\to\infty$), we have

$$k_f^s=k_D\left\{1+\frac{K_{eq}}{[1+\sigma(\lambda/D)^{1/2}]}\right\}^{-1} \tag{3.36}$$

The factor in the curly brackets gives the correction to the Smoluchowski result. Finally, for the fast diffusion limit (*i.e.*, when $k_D\to\infty$), Eq. (3.35) reduces to

$$k_f^s=\kappa/(1+K_{eq}) \tag{3.37}$$

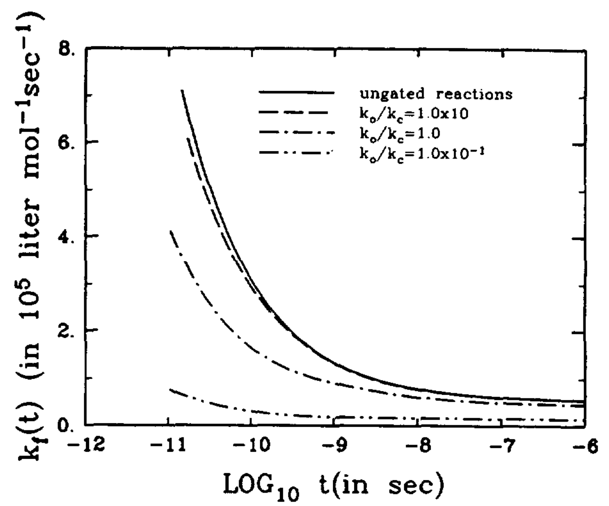

Figure 1. Variation in the transient kinetic behavior with the changes in the ratio of the gate-opening rate to the gate-closing rate.

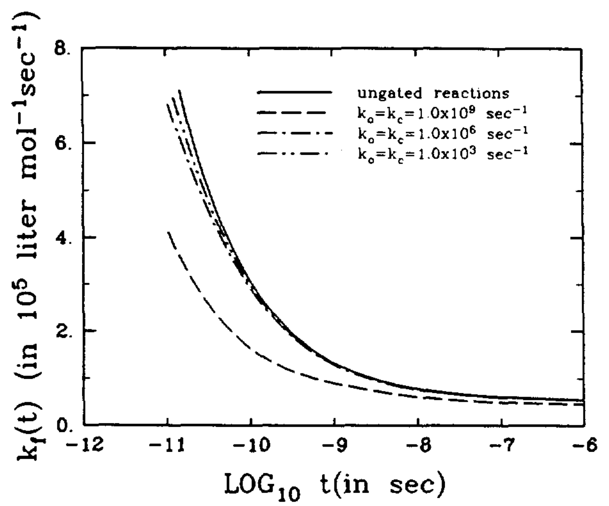

Figure 2. Variation in the transient kinetic behavior with the changes in the fluctuation rate of the gating mode.

which is the intuitively expected expression.

Numerical Calculation of the Time-Dependent Rate Coefficient

Inverse Laplace transformation of the expression for $\hat{k}_f(z)$ in Eq. (3.32) with $\hat{G}(\sigma,\ z|\sigma)$ given by Eq. (3.34) has been carried out numerically by using the IMSL subroutine FLINV.[27] In Figures 1 and 2, we display the variation of the rate coefficient $k_f(t)$ with time in gated diffusion-influenced reactions, and compare the results with that for the ungated reactions. The calculation was performed with the following model parameters: $\sigma=32$ Å, $D=131$ Å^2/ns, and $\kappa=3.0\times10^{12}$ l·mol^{-1}·s^{-1}. These values are taken to model the reaction between superoxide dismutase and O_2^-, which is one of the fastest enzyme-substrate reactions.[28,29] But no attempt has been made to analyze the experimental data since no transient kinetic data is available. For the present, we just take the above values for motional and reaction parameters as a reasonable choice for the input to model calculations to illustrate the possible effects of an gating mode in the transient kinetics.

Figure 1 shows that the transient time before reaching the steady state is shorter in general for gated reactions when compared with the ungated reactions. In particular, as the ratio of the gate-opening rate to the gate-closing rate decreases down to a factor of 1/10, the steady state is established within 100 ps. The value of k_c was fixed at 1.0 ns^{-1}.

In Figure 2, we fixed the ratio of k_o/k_c to unity, and instead changed the magnitudes of both rate constants. As the gating mode fluctuates more rapidly, the transiency in the dynamical variation of the bimolecular kinetics becomes less prominent.

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References

1. B. Otto, J. Schroeder, and J. Troe, *J. Chem. Phys.*, **81**, 202 (1984).
2. E. M. Eyring, in *Physical Chemistry*, ed. by H. Eyring (Academic, New York, 1970), Vol. IXB, Chap. 8.
3. D. P. Millar, R. J. Robbins, and A. H. Zeweil, *J. Chem. Phys.*, **75**, 3649 (1981).
4. S. Lee, M. Yang, K. J. Shin, K. Y. Choo, and D. Lee, *Chem. Phys.*, **156**, 339 (1991).
5. K. Chou and G. Zhou, *J. Am. Chem. Soc.*, **104**, 1409 (1982).
6. S. A. Rice and M. J. Pilling, *Prog. React. Kinet.*, **9**, 93 (1979).
7. M. Smoluchowski, *Ann. Phys.*, **48**, 1103 (1915); *Z. Phys. Chem. (Leipzig)*, **92**, 129 (1917).
8. S. A. Rice, *Comprehensive Chemical Kinetics 25, Diffusion-Limited Reactions* (Elsevier, Amsterdam, 1985).
9. F. C. Collins and G. E. Kimball, *J. Colloid Sci.*, **4**, 425 (1949).
10. G. Wilemski and M. Fixman, *J. Chem. Phys.*, **58**, 4009 (1973).
11. R. Kapral, *Adv. Chem. Phys.*, **48**, 71 (1981).
12. S. Lee and M. Karplus, *J. Chem. Phys.*, **86**, 1883 (1987).
13. E. W. Montroll, *J. Chem. Phys.*, **14**, 202 (1946).
14. H. L. Friedman, *J. Phys. Chem.*, **70**, 3931 (1966).
15. K. Solc and W. H. Stockmayer, *J. Chem. Phys.*, **54**, 2981 (1971).
16. S. Lee and M. Karplus, *J. Chem. Phys.*, **86**, 1904 (1987).
17. J. A. McCammon and S. H. Northrup, *Nature* **293**, 316 (1981).
18. S. H. Northrup, F. Zarrin, and J. A. McCammon, *J. Phys. Chem.*, **86**, 2314 (1982).
19. A. Szabo, D. Shoup, S. H. Northrup, and J. A. McCammon, *J. Chem. Phys.*, **77**, 4484 (1982).
20. S. H. Lin, K. P. Li, and H. Eyring, in *Physical Chemistry*, ed. by H. Eyring (Academic, New York, 1975), Vol. VII, Chap. 1.
21. L. Monchick, J. L. Magee, and A. H. Samuel, *J. Chem. Phys.*, **26**, 935 (1957).
22. T. R. Waite, *Phys. Rev.*, **107**, 463 (1957); *J. Chem. Phys.*, **28**, 103 (1958); *Ibid.*, **32**, 21 (1960).
23. H. L. Frisch and F. C. Collins, *J. Chem. Phys.*, **20**, 1797 (1952).
24. O. G. Berg, *Chem. Phys.*, **31**, 47 (1978).
25. J. T. Hynes and J. M. Deutch, in *Physical Chemistry*, ed. by D. Henderson (Academic, New York, 1976), Vol. XIB, Chap. 8.
26. I. N. Sneddon, *The Use of Integral Transforms* (McGraw-Hill, New York, 1972).
27. *IMSL Library Reference Manual*, 9th ed. (International Mathematical and Statistical Libraries, Inc., Houston, Texas, 1982).
28. J. Sines, S. A. Allison, A. Wierzbicki, and J. A. McCammon, *J. Phys. Chem.*, **94**, 959 (1990).
29. S. A. Allison, J. A. McCammon, and J. Sines, *J. Phys. Chem.*, **94**, 7133 (1990).

Preparation and Structure of $\overline{CH_2CH_2OOCC}HCH_2SnCl_3$

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A new estertin, $\overline{CH_2CH_2OOCC}HCH_2SnCl_3$, was prepared and its structure was determined by X-ray crystallography ($P2_12_12_1$; $a=9.439(1)$, $b=9.601(1)$, $c=10.779(1)$ Å, $Z=4$) and refined to $R=0.0356$. The coordination geometry around the tin atom approximates to a trigonal bipyramid with the intramolecularly coordinated oxygen O(1), (Sn-O(1), 2.482(6) Å) and Cl(2) occupying mutually *trans* positions (O(1)-Sn-Cl((2), 176.4(2)°).

Introduction

Since a novel synthetic route to "estertin" was reported[1], a large number of estertin compounds and their derivatives have been investigated because of their interesting bonding mode and industrial applicability[2-8].

In continuing efforts to extend the estertin chemistry[9], this paper reports the preparation and structure of the title compound.