Competitive Reversible Binding: A Bimolecular Boundary Condition for the Diffusion Equation

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I. Introduction

The competition of many diffusing particles over a single binding site is a difficult many-body problem that occurs in the kinetics of physical, chemical, and biological systems. When binding is irreversible, the attachment of a single particle to the site effectively eliminates that site. This leads to the Smoluchowski limit for pseudounimolecular reactions as applied, for example, to fluorescence quenching.1-2 When the site is stationary, the Smoluchowski theory is exact3 while it is only approximate when the site moves, in which case some extended approximations may be obtained.3,4

Unlike the familiar case of irreversible binding, only little was done to treat reversible binding.5,6 This includes some approximate theories that were not yet tested against stochastic simulations. Reversible binding is evidently more complicated than the irreversible case, because the binding site has to be considered even after the first binding event, so that correlations between the diffusing particles are introduced. Reversible binding is nevertheless quite relevant to experiment: Proton detachment from an excited solvated pyranine molecule was recently shown to be reversible.7 At low pH, the dissociated proton will compete with the homogeneous, randomly distributed protons for rebinding to the excited anion. The first step in the Michaelis–Menten mechanism of enzymatic catalysis is often reversible8 and therefore involves the competition of many substrate molecules over the catalytic site. It can be anticipated that the development of the subject of reversible competitive binding will be useful in analyzing this important class of biochemical reactions.

The simple chemical kinetic description of a pseudounimolecular binding reaction is via the appropriate rate equation. Let \( c \) be the concentration of the particles, denote by \( k_d \) and \( k_b \) the dissociation and recombination rate coefficients, respectively, and let \( P^*(t) \) be the probability that a particle is bound at time \( t \). (Throughout this work, we use script symbols for denoting many-body properties and an asterisk to denote the bound state. This conforms to notations in ref 6.) The binding probability is assumed to obey the kinetic equation

\[
dP^*(t)/dt = c(k_d P^*(t) - k_b P(t))
\]

For the initial condition \( P^*(0) = 0 \), its solution is

\[
P^*(t) = \frac{cK_{eq}}{1 + cK_{eq}} \left[ 1 - \exp\left(-k_d + c k_d \right) t \right]
\]

where \( K_{eq} = k_b / k_d \). Hence, the fraction bound at equilibrium is

\[
P^*(\infty) = \frac{cK_{eq}}{1 + cK_{eq}}
\]

and the decay to equilibrium is exponential. For a single particle, namely, geminate recombination, the long-time decay of the bound state is a power law rather than exponential.9,10 We would like to determine whether for a constant concentration of particles the decay to equilibrium becomes, asymptotically at least, exponential or whether it is still a power law.

In the present work we consider \( n \) noninteracting particles initially randomly distributed on the line in the presence of a static binding site. The particles are random walkers, and only one of them can bind to the site at any given instance. For given recombination and dissociation rate parameters, the occupancy of the site increases monotonically with time until it reaches its equilibrium value. We have simulated this process by Brownian dynamics for varying values of the dissociation rate parameter. The partial differential equation that describes the process is a \( n \)-dimensional diffusion equation (for the \( n \) particles) with the appropriate boundary conditions. This equation is very difficult to solve. Here we approximate it by a single-particle diffusion equation with the back-reaction (reversible) boundary condition, extended, in the "mean-field" sense, to allow for blocking of the...
binding of a particular particle by all other particles. This “bimolecular boundary condition” is exact in the limit of low site occupancy and enables us to investigate the long-time behavior in the approach to equilibrium. Additional approximations are considered in the work of Szabo and Zwanig.6

II. Theory

We consider a static, reversible binding site on the line, which can bind at most one particle at any given instant. Without loss of generality, we assume that the site is at the origin of the coordinate, x = 0, and denote it by an asterisk. The particles are diffusing with a diffusion constant D and are noninteracting and completely “transparent” to each other. The only interaction between the particles occurs at the “entrance” to the binding site, which allows a particle to enter only if no other particle is currently bound. The particles are initially uniformly (randomly) distributed, with a concentration c. Practically, one takes a finite segment of length l on which n particles are diffusing. The constant-concentration case is the limit l → ∞ and n → ∞ such that n/l → c. We consider an initially out-of-equilibrium situation where either no particle or exactly one particle is bound.

Let us discuss first the case n = 1, for which the many-body problem reduces to (particle-site) pair dynamics.6,7 We denote by p(x,t) the probability density that the distance from the binding site is x at time t. The probability density evolves in time according to the diffusion equation

$$\frac{\partial p(x,t)}{\partial t} = D \frac{\partial^2 p(x,t)}{\partial x^2}, \quad x > 0 \tag{4}$$

This equation may be generalized to include particle–site interactions, distance-dependent diffusion coefficient, and the like. We have chosen the simplest possible case in order to focus on the many-body effect. The case where particles diffuse on both sides of the site (x < 0 as well as x > 0) is a trivial extension involving factors of 2.

Let us denote by S(t) the probability that the particle survives recombination or, more accurately, that it is still separated from the site, by time t. It is defined by

$$S(t) = \int_0^\infty p(x,t) \, dx \tag{5}$$

Hence S(0) = 1 if the particle was initially unbound while S(0) = 0 for an initially bound particle. We will also denote the probability that the particle is bound by P(*,t) = 1 − S(t). The upper case symbol indicates a probability, as opposed to a probability density, and an asterisk denotes the bound state. In most cases it is the binding probability, rather than the density p(x,t), that corresponds to an experimentally observable quantity.

The reaction rate is defined as the fraction of particles that bind per unit time. By integrating the diffusion equation once and using the condition that the flux vanishes at infinity, we obtain

$$\frac{\partial P(*,t)}{\partial t} = \frac{\partial S(t)}{\partial t} = \frac{\partial}{\partial x} p(x,t) |_{x=0} \tag{6}$$

The “back-reaction” boundary condition6,10 can now be written as a simple kinetic equation for the time evolution of the binding probability

$$\frac{\partial P(*,t)}{\partial t} = \kappa_r p(0,t) - \kappa_b P(*,t) \tag{7a}$$

This extends eq 1 to a situation where the distance between the reacting partners is monitored in addition to their identity. Note that the rate coefficients, κr and κb, in eq 1 were replaced by the rate parameters, κr and κb, in the boundary condition, eq 7a. To verify that eq 7a is indeed a boundary condition (for a partial differential equation), we insert it into eq 6 to yield

$$D \frac{\partial^2 p(x,t)}{\partial x^2} |_{x=0} = \kappa_r p(0,t) - \kappa_b [1 - S(t)] \tag{7b}$$

It is now easy to verify that eq 7b is a simple generalization of known boundary conditions for the diffusion equation.1 In the limit that κr → ∞, eq 7b reduces to an absorbing boundary condition, p(0,t) = 0, while when κb → 0 it becomes the radiation boundary condition. A formulation involving the reversible boundary condition in eq 7 has been used to interpret experimental data on excited-state proton-transfer reactions.7

While the solution for one-dimensional diffusion with back-reaction can be obtained analytically for any initial location of the diffusing particle,10 for higher dimensionality, d > 1, or in the presence of a particle–site interaction potential, this may be impossible. In such cases one can still derive the asymptotic long-time decay law for the binding probability.6,7 In an infinite space, one finds a power law decay, P(*,t) ∝ t^{-d/2}, reflecting the probability of return to the origin of a random walker. For example, from eq 7a one may obtain

$$P(*,t) \sim \frac{\kappa_r}{\kappa_b} p(0,t) \sim \frac{K_{eq}}{(\pi D t)^{1/2}} \tag{8}$$

as the asymptotic behavior for t → ∞. The second relation follows from the asymptotic solution of eq 4, since p(x,t) will tend to a Gaussian distribution at long times. K_{eq} is the equilibrium binding constant, defined by

$$K_{eq} = \kappa_r / \kappa_b \tag{9}$$

In this one-dimensional case it can be verified that eq 8 is indeed the long-time limit of the full solution given in Appendix C of ref 7b.

We now consider the many-body problem of n particles diffusing on a line segment of length l. As stated above, we are interested in the “thermodynamic limit” of n → ∞, l → ∞, and n/l → c. In a given system there would always be either zero or one particle in the binding site. In an ensemble of such systems, the probability of observing a bound particle evolves with time. Following ref 6, we denote a many-body property by a script symbol, so that the binding probability will be denoted by P(*,t). Unlike the case of a single particle in infinite space, where the binding probability P(*,t) necessarily decays to zero according to eq 8, P(*,t) will decay to its equilibrium value which is a function of the concentration c.

In ref 6, an approximation was proposed for describing the time dependence of the binding probability. While we do not dwell on this approximation here, we mention two of its conclusions, which we envisage to be general. The first is that the equilibrium value of the binding probability is still given by eq 3. It is evidently independent of the initial condition and agrees with the thermodynamic expression for the equilibrium constant, namely, K_{eq} = P(*,∞)/[c(1 − P(*,∞))]. A question to be answered is whether the decay of the binding probability to its equilibrium value, P(*,t), will still be a power law, as in eq 8, or an exponential, as in eq 2.

The second result connects the binding probability for the two initial conditions considered below. Following ref 6, we denote the case where all particles are initially equilibrated (uniformly distributed) and the site vacant by (...)eq, while the case where the site is initially occupied (and the remaining n − 1 particles are equilibrated) by (...)*. By assuming that convolution relations connecting solutions for these two initial conditions, and derived for the single particle reversible-binding process, can be generalized to the many body case, one obtains

$$P(*,t|eq) = c K_{eq} [1 - P(*,t|eq)] \tag{10}$$

This result is consistent with the equilibrium limit in eq 3 being independent of the initial condition. Insertion of eq 3 into eq 10 indeed produces an identity. The “initial condition reciprocity relation” in eq 10 has recently been proven by Szabo and Zwanig.8

We are now in a position to consider a novel approximation for the time dependence of the binding probability. The reason an approximation is needed is that the full solution involves a diffusion equation for the joint probability density of having particle 1 at x_1, particle 2 at x_2, etc., with the appropriate boundary

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condition. This $n$-dimensional diffusion equation is too complicated to solve, even numerically, when $n$ is large. It is therefore useful to reduce the $n$-dimensional equation to an effective one-dimensional equation. This will lead to a nonlinear boundary condition that we call the "bimolecular boundary condition". It is the intuitive generalization of the back-reaction boundary condition, eq. 7, to a many-body case.

In our approximation we assume that particle $i$ obeys a diffusion equation similar to eq. 4, namely

$$\frac{\partial p(x,t)}{\partial t} = D\frac{\partial^2 p(x,t)}{\partial x^2}, \quad x > 0, 1 \leq i \leq n$$  \hspace{1cm} (11)

subject to its initial location. In eq. 11, $p(x,t)$ is the probability density for particle $i$ to be at a distance $x$ from the binding site. Thus, a $n$-dimensional diffusion equation has been replaced by $n$ one-dimensional equations. The binding of each particle is blocked if any of the other particles is bound. Hence, we extend the back-reaction boundary condition, eq. 7, to

$$D(\partial/\partial x)p(x,t)|_{x=0} = \kappa_i F_i(t) p_i(0,t) - \kappa_0 I_i(1 - S_i(t))$$  \hspace{1cm} (12)

$F_i(t)$ is the probability that at time $t$ the site is free from any of the other $n-1$ particles. Denoting, again, by $P(i,t)$ = $1 - S_i(t)$ the probability that the $i$th particle is bound, we have

$$F_i(t) = 1 - \sum_{j \neq i}^n S_j(t)$$  \hspace{1cm} (13)

while the probability that a particle is bound will be given by

$$P(i,t) = \sum_{j \neq i}^n p_j(t)$$  \hspace{1cm} (14)

The partial sum in eq. 13 reflects the fact that a particle does not block its own binding. The summation in eq. 14 is due to the fact that the individual binding probabilities are not independent variables. As seen from eq. 12, the only term that couples the $n$ diffusion equations (11) is $F_i$. When $n = 1$, eq. 13 reduces to $F_i = 1$, and the approximation becomes exact. In general, we expect that it improves as the coupling diminishes, $F_i \to 1$.

In the thermodynamic limit of an infinite system, the approximation improves as $c \to 0$ and becomes exact in the limit of infinite dilution. It is also expected to become exact in the limit of $K_{eq} \to 0$, namely, for vanishing site occupancy. This is just the opposite limit than that of the Smoluchowski approximation, which is valid when $K_{eq} = 0$, since it requires small $x_i$ and large $K_{eq}$. Hence, we conclude that our approximation becomes exact as $K_{eq} \to 0$. In the limit of large $n$ but small site occupancy ($c K_{eq} \to 0$), one may extend the sum in eq. 13 over all particles including the $i$th. Then, from eq. 14, $F_i(t) = 1 - P(i,t)$ is the concentration of free sites and the term $\kappa_0 I_i(1 - P(i,t))$ represents a (local) bimolecular recombination rate in the classical chemical kinetic sense. Thus, in this limit, the terminology "bimolecular boundary condition" is justified.

So far we have not addressed the question of the initial condition. When all particles start from the same initial condition, the $n$ equations become identical. Hence, we can eliminate the subscript $i$ from eqs 11 and 12 and solve a single, one-dimensional equation. Equation 12 becomes a nonlinear boundary condition, with

$$F(t) = 1 - (n-1)P(*)$$  \hspace{1cm} (15)

and the $n$-particle binding probability

$$P(*) = nP(*)$$  \hspace{1cm} (16)

is simply $n$ times the single-particle binding probability. We will apply these equations below to describe the binding probability for the case where all particles are initially randomly distributed and the binding site is empty, $P(*) = 0$.

III. Numerical Procedures

Simulation. We have simulated the random motion of $n = 20$ particles on $l = 100$ lattice sites arranged on a circle (i.e. periodic boundary conditions). Site 0 is the binding site (*), which can initially be empty or occupied by a (single) particle. At each step in the simulation of the reaction process, there are two possibilities depending on whether the binding site is occupied or not. If all particles are free, then one particle is chosen at random and moved to one of its neighboring sites (irrespective of whether that site is already occupied or not). This constitutes an elementary Monte Carlo (MC) step. In one time unit, $\Delta t$, each of the $n$ particles performs, on the average, two such elementary steps. (The factor of 2 arises because each particle on the line can move in one of two opposite directions.) Therefore, the time increment for this elementary MC step is $\Delta t = 1/(2n)$. This corresponds to taking the diffusion constant to be $D = 1$ (in units of lattice spacing squared per unit time).

If one particle is bound, the time increment to the next elementary MC step is $\Delta t = 1/[2(n - 1 + c K_{eq})]$, where $c K_{eq}$ is the dissociation rate parameter of the bound particle. Under this condition, with probability $2(n - 1)\Delta t$ the next elementary MC step leads to diffusion of a free particle as described above, whereas with probability $2c K_{eq}\Delta t$ the bound particle is released. Whenever a free particle hits the binding site, it is either captured, if the binding site is not occupied by another particle, or else it is reflected. This corresponds to a recombination rate parameter $c K_{eq} = 1$. In each simulation, the occupancy of the binding site was monitored as a function of time. Since the occupancy is either 0 or 1, some 100,000 simulations were needed to obtain reasonable statistics.

Propagation. The one-dimensional diffusion equation (11) is solved by an algorithm similar to that of ref. 7. In accordance with the Brownian simulations, the interval $[0,\Delta t]$ is discretized so that $\Delta x = 1$ and periodic boundary conditions are used. The diffusion equation becomes a master equation with jump frequencies $D = D/\Delta x^2$ between neighboring points, except between the points at $x = 1$ and the binding site at $x = 0$. Denoting by $P(t) = p(x=1,t)$ the probability that a single particle is located at $x = i$, and by $P(t) = P(*)$ the binding probability, we solve

$$\frac{\partial P(*,t)}{\partial t} = D[P(*,t) + P(t) - 2P(*,t)], \quad 2 \leq i \leq l - 1$$  \hspace{1cm} (17a)

$$\frac{\partial P(*,t)}{\partial t} = \kappa_i P(*,t) + D P(*) - \left[D + F(t)\right] P(*)$$  \hspace{1cm} (17b)

$$\frac{\partial P(t)}{\partial t} = \kappa_i P(t) + D P(t) - \left[D + F(t)\right] P(t) - 2\kappa_i P(t)$$  \hspace{1cm} (17c)

with $F(t) = 1 - (n - 1)P(*)$ and $P(*) = nP(*)$; see eqs 15 and 16. The initial uniform distribution translates into

$$P(0) = 0, \quad P(l) = 1/l, \quad i = 1, \ldots, l$$  \hspace{1cm} (18)

The propagation in time is based on the same Chebyshev algorithm used earlier. The nonlinearity introduced when $F(t) < 1$ is treated by taking an average value between the two time steps. To do so, each time step is iterated five times. In each iteration a new value for $F(t+\Delta t)$ is calculated until a self-consistent solution is obtained.

The equilibrium limit of the above model is easy to obtain, using the property that all fluxes vanish at equilibrium. From eq 17a we have

$$P(0) = P(\infty) = \ldots = P(l) = 1 - P(0)$$ \hspace{1cm} (19)

while from eq 17d we get the following quadratic equation for $P(0)$

$$s_i - (n_i + c K_{eq})P(0) + (n - 1)\kappa_i P(0)^2 = 0$$  \hspace{1cm} (20)

In the limit of low site occupancy (small $n_i$, $c K_{eq}$, large $l$, $\kappa_i$), the last term on the left-hand side becomes negligible and (after taking the thermodynamic limit) we retrieve the equilibrium binding probability of eq. 3. In general, it follows from eq 20 that for the present model $P(*) = c K_{eq}/(1 + c K_{eq})$. This indicates that the model is not only the exact small site-occupancy limit but possibly also an upper bound for $P(*)$. 

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Figure 1. Binding probability, $P(*,\tau_{eq})$, for competitive reversible binding in one dimension. A reversible, static binding site can bind at most one particle at any given time. $n = 20$ particles are initially randomly distributed over a $l = 100$ grid points arranged in a circle (periodic boundary conditions), while the binding site is initially vacant. The particle diffusion coefficient and binding rate parameter are arbitrarily assumed to be unity, $D = 1$ and $\epsilon = 1$, while the dissociation rate parameter, $K_d$, is varied. Full curves are stochastic simulations of 100,000 realizations each. Dashed curves are the solution of the single-particle master equation (17), involving a nonlinear, locally bimolecular, boundary condition. (a) Linear time scale; (b) logarithmic time scale.

Figure 2. Binding probability, under the conditions of Figure 1, for the two initial conditions. Upper and lower curves are $P(*,\tau_{eq})$ and $P(*,\tau_{eq})$, respectively. Full curves are exact simulations; see Figure 1. Superimposed dashed curves are the simulations transformed according to eq 10.

IV. Results

Figure 1 shows the binding probability, $P(*,\tau_{eq})$, as a function of time (in both linear and logarithmic scales) for an initially vacant site. Full curves are the result of the simulation while the dashed curves are the approximation using the new "bimolecular boundary condition" and calculated by propagation of eq 17. As expected, the difference between the full and dashed curves vanishes for small $P(*,\tau_{eq})$. For $K_d = 1$, this corresponds to all times while for $K_d = 0.1$ it corresponds only to the initial behavior.

We have also carried out simulations beginning with one bound particle (and 19 randomly distributed particles). $P(*,\tau_{eq})$ thus obtained is compared with $P(*,\tau_{eq})$ in Figure 1. For both initial conditions all other parameters were equal. The chosen value of $K_d = 0.1$ is that for which the approximation is least accurate in Figure 1. We note that both initial states indeed evolve toward the same equilibrium value $P(*,\infty)$. It is calculated to be 0.667 and 0.681 from eqs 3 and 20, respectively. This difference is just sufficient to allow us to conclude that the simulation tends toward the asymptotic value of eq 3 rather than that of eq 20. In addition, we test the initial condition reciprocity relation, eq 10. From each one of the two curves, $P(*,\tau_{eq})$, and $P(*,\tau_{eq})$, we obtain the other using eq 10. The results are plotted as dashed curves in Figure 2. Since the dashed curves are hardly discernible on the background of the full curves, we conclude that eq 10 is most likely exact.

For $K_d = 0.5$, $P(*,\infty) = 0.286$ and the difference between the predictions of eqs 3 and 20 differs by no more than 0.001. Hence, we can use the approximate solution to check the asymptotic behavior. Figure 3 shows the deviation from equilibrium, $cK_d/(1 + cK_d) - P(*,\tau_{eq})$, both on a semilog and log-log scales. From Figure 3a (semilog scale) it is clear that, in contrast to the kinetic result of eq 2, decay to equilibrium is nonexponential at either short or long times. Figure 3b (log-log scale) shows that the approach to equilibrium is a power law. The data over most of the range are in a straight line with a slope somewhat larger than -0.5. At extremely long times ($t > 200$), the curve bends down, tending to an exponential decay. This is due to the finite number of grid points, $l$, involved in both simulation and propagation. When both $l$ and $n$ are doubled, we obtain the dotted curve which shows a power law behavior over an even larger time range.

V. Conclusions

In this work we have concentrated on the competitive reversible binding of many diffusing particles to an immobile reacting partner, placed at the origin of the coordinate system. As usual with such problems, one may either use the diffusion equation approach (a deterministic approach) or use simulations based on (stochastic) random walks. The diffusion method is simpler to handle for a small number of particles, in low-dimensionality spaces and in regions devoid of complexly shaped traps. It requires a thorough analysis when the role of the reaction partners has to be implemented, even approximately, through (judiciously chosen) boundary conditions. The random-walk procedure is more straightforward to implement (especially insofar as the description of the many-body reaction is concerned) but requires extensive calculations to minimize stochastic fluctuations. Here we have used both methods in order to gain good understanding of the complex process investigated.
Starting from the boundary condition rigorously valid for a pair of diffusing and reacting particles, we have advanced a boundary condition of bimolecular character, eq 12, to approximate the back-reaction in the presence of many particles. As demonstrated through comparison with the simulation results, this heuristically determined bimolecular form performs extremely well in the case of moderately to strong dissociation coefficients ($k_d > 0.5$). But even for smaller values of $k_d$ the agreement between approximate diffusion approach and random-walk simulation is encouraging, as may be seen from Figure 1. Furthermore, our method allows us to study the initial condition effect as well as the region of long times and approach to equilibrium. Evidently, determination of the long-time behavior is difficult, because we have to monitor smaller deviations with increasing stochastic fluctuations. Nevertheless, the combination of stochastic and deterministic methods renders us confident in our result, namely, the power law approach to equilibrium. Hopefully, more elaborate statistical mechanics methods will allow an analytic derivation of this result in the future.

Note Added in Proof. Recently, Burlatsky et al. (Burlatsky, S. F.; Oshanin, G. S.; Ovchinnikov, A. A. Chem. Phys. 1991, 152, 13) have analyzed a mean-field approximation similar to ours, showing that approach to equilibrium indeed obeys a $t^{-\theta}$ power law. A similar conclusion was reached by Szabo and Zwanzig$^2$ for the "superposition" approximation.

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FTIR Study of the Mechanism of the Cl and Br Atom Initiated Oxidation of Acetylene

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FTIR analysis of the products of the Cl and Br atom initiated oxidation of C$_2$H$_2$ at 700 Torr total pressure of N$_2$/O$_2$ diluent and 296 ± 2 K has shown that the (halovinyl)peroxy radical (XCH=CHOO; X = Cl or Br) formed primarily undergoes isomerization followed by unimolecular dissociation to (a) HC(O)X + HCO, (b) H(CO)CHO + X, and (c) HX + CO + HCO. The branching ratios determined were $a:b:c = 0.26:0.21:0.53$, for $X = \text{Cl}$, and $0.17:0.09:0.74$, for $X = \text{Br}$, independent of O$_2$ pressure in the range 10–700 Torr. The formation of O$_3$ in ca. 10% yield, depending on O$_2$ pressure, was observed in both the Cl and Br atom initiated oxidations, and it is proposed that a small fraction of the (halovinyl)peroxy radicals reacts with O$_2$ to form O$_3$ and a (halovinyl)oxy radical (XCH=CHO). It is noted that addition of a halogen atom to acetylene can produce both cis and trans isomers of both the halovinyl and (halovinyl)peroxy radicals. On sterio grounds, the isomerization rate may be slower for the cis form of the (halovinyl)oxy radical than for the trans form, thereby leading to the formation of O$_3$ preferentially via (cis-halovinyl)oxy radical. Evidence for the formation of HO radical was also obtained in both the Cl and Br atom initiated oxidations, and this has been attributed to the O$_2$ reaction of the (halovinyl)oxy radical: XCHCHO + O$_2$ → [XCH(OO)CHO] → HC(O)X + CO + HO.

Br and Cl atoms are known to react with C$_2$H$_2$ by forming an addition complex which can be collisionally stabilized to form a substituted vinyl radical (I):$^6$

$$X + C_2H_2 \xrightarrow{<} XCH=CH \quad X = \text{Cl or Br} \quad (1, -1)$$

By analogy with the vinyl radical,$^8$ I is expected to form an adduct (II) by reaction with O$_2$:

$$XCH=CH + O_2 \xrightarrow{<} XCH=CHOO \quad (2)$$

The rate of reaction of halogen atoms with C$_2$H$_2$ in air is determined by reactions 1 and 2. In the case of Cl atoms, re-dissociation of radical I is very slow, and therefore the apparent

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Introduction

There is evidence to suggest that reaction with halogen atoms (Cl and Br) may be significant for C$_2$H$_2$ in certain regions of the troposphere. For instance, in the marine troposphere Cl atom concentrations are estimated to be 1–2 orders of magnitude smaller than that of HO radical; however, this may be offset by the fact that the rate constant for reaction of C$_2$H$_2$ with Cl atoms is more than an order of magnitude larger than with HO radical. The atmospheric reactions of Br atoms in the arctic troposphere are of current interest because of their potential involvement in the catalytic destruction of O$_3$ at ground level by BrO$_3$ species during the arctic spring. Recent observations made during the polar sunrise have shown that O$_3$ depletion occurs concurrently with depletion of light unsaturated hydrocarbons present, such as C$_2$H$_2$ and C$_2$H$_4$, which are known to be reactive toward Br atoms in atmospheric pressures of air. Since the Br-catalyzed destruction of O$_3$ proceeds via a chain reaction, it may be sensitive to the presence of unsaturated hydrocarbons if their Br atom reactions function as chain-termination steps. Thus, quantitative product studies of the Br atom initiated oxidation of C$_2$H$_2$ are required to assess the role of C$_2$H$_2$ in the ground-level O$_3$ destruction observed at polar sunrise. To date, there have been no apparent quantitative studies of either the mechanism or the product distributions of both the Cl and Br atom initiated oxidation reactions of C$_2$H$_2$.

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