Intermolecular Force Effects on Geminate Combinations

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Abstract: Koenig has developed a mathematically simple model of diffusion controlled geminate combinations which ignored direct intermolecular force effects on the diffusing fragments. We have extended this theory to provide approximately for such effects, particularly in the two limiting cases when the intermolecular forces are either very weak or very strong in comparison with the thermal fluctuation force responsible for the diffusion. In the former limit one finds only small perturbations from the Koenig yield function which is proportional to the reciprocal square root of viscosity. In the large force limit substantial deviations from this proportionality could obtain. Experimental implications of our calculations are considered.

Many models[1-5] have been proposed for the efficiency of geminate combination reactions, which have been recently reviewed by Koenig and Fischer.[6] Previous treatments have ignored the effects of intermolecular forces between the combining (or diffusing) fragments. We examine these effects in this paper using the simplest version of the theory. In view of the many approximations which we will be forced to make, and which will be more fully discussed below, we will be able to obtain only semiquantitative results. Anticipating this we will replace the mathematically complex, real forces between the fragments by simplified, radial forces acting on the centers of mass of the fragments. Our starting point will be the simplified theory of Koenig and Deinzer[7] (KD) whose justification has been provided by the more accurate treatment of Koenig.[2] We will adopt both the terminology and notation of the KD article.

Specifically, we will treat two cases of diffusion controlled dissociation subject to forces between the diffusing fragments which will be generally electrostatic in origin:

Case I

$$\text{A-X-B} \xrightarrow{k_d} \text{A}\|\text{B}$$

(with the motion of X immaterial and forces considered only between A and B)

or

Case II

$$\text{A-X-B} \xrightarrow{k_d} \text{A}\|\text{X}\|\text{B}$$

(with forces between A and B, A and X, and B and X)

Following KD,[7] the rate constant k_d is given by

$$k_d = \frac{r(\tau)}{(\rho - R_0)\tau} \tag{1}$$

where τ is the effective reduced lifetime of the pair defined by eq 6 of KD, $r(\tau)$ is the root mean square displacement distance of the fragments, $\rho - R_0$ is the distance they must travel to effectively escape one another with ρ the effective (cage) collision diameter and R_0 the initial distance of separation. As shown in ref 7 for diffusion not restricted by any interfragment forces $r(\tau) = (2D\tau)^{1/2}$. In the next section we will present a classical phenomenological theory of $r(\tau)$ in the presence of such forces. We make the following assumptions which also underlie the KD theory: (1) All effective molecular parameters such as local, effective diffusion coefficients D, viscosities η, and dielectric constants ϵ can be approximated by their macroscopic bulk values. Clearly the actual molecular environment of the reaction site is "grainy" on a molecular scale; thus our theory can be used at best as a data-correlation scheme with the bulk properties of the medium. (2) All other complications such as, e.g., discussed by Carapellucci[8] are ignorable for the systems to which we restrict our considerations. (3) All separations between the fragments can be treated as if they occurred along a straight line connecting the center of mass of A and B in case I and an effective straight line connecting the centers of mass of A, X, and B in case II. Clearly the latter assumption is a drastic approximation to simplify the mathematics.

In Appendix A we will test this approximation for an exactly soluble instance of case I. Subject to these assumptions the calculation of k_d given by eq 1 reduces to a calculation of $r(\tau)$ using Smoluchowski's equation rather than Fick's second law equation for pure diffusion in the absence of forces. In the final section of this paper we will very briefly relate the theory to some of the available experimental data.

Theory of the Root Mean Square Displacement Distance in the Presence of Forces. In case I let us fix the coordinate system on the center of mass (CM) fragment B and let x be the distance from the CM of the fragment A. The probability of finding the CM of A at a distance lying between x and $x + \mathrm{d}x$ at time t is $p(x,t)\mathrm{d}x$, which satisfies the Smoluchowski equation

$$\frac{\partial p}{\partial t} = D \frac{\partial}{\partial x}\left(\frac{\partial p}{\partial x} - \frac{F(x)}{kT}p\right), \quad -\infty < x < \infty \tag{2}$$

subject to the initial condition

$$p(x,0) = \delta(x - R_0)$$

where $D = \hat{D}_A + \hat{D}_B$ ($\hat{D}_A$, $\hat{D}_B$ being the binary diffusion coefficients of the A and B fragment, respectively, which are presumably inversely proportional to the medium viscosity) and $F(x)$ is the force between fragments A and B (e.g., a Coulomb force if A and B are charged, dipole-dipole force, etc.). Denote by

$$\langle f(x)\rangle = \int_{-\infty}^{\infty} f(x)p(x,t)\mathrm{d}x$$

then multiplying eq 2 by x, x^2 and $xF(x)$, respectively, and integrating by parts one finds ($r^2 = \langle x^2\rangle$)

$$\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} = \frac{D}{kT}\langle F(x)\rangle \tag{3}$$

$$\frac{\mathrm{d}\langle x^2\rangle}{\mathrm{d}t} = 2r(t)\frac{\mathrm{d}r(t)}{\mathrm{d}t} = 2D\left[1 + \frac{\langle xF(x)\rangle}{kT}\right] \tag{4}$$

$$\frac{\mathrm{d}\langle xF(x)\rangle}{\mathrm{d}t} = D\left\{\left\langle \frac{\mathrm{d}^2}{\mathrm{d}x^2}[xF(x)]\right\rangle + \frac{1}{kT}\left\langle F(x)\frac{\mathrm{d}}{\mathrm{d}x}[xF(x)]\right\rangle\right\} \tag{5}$$

respectively, using the facts that p and its derivatives vanish as $|x| \to \infty$.

Equation 5 shows that in general an exact closure relation for eq 4 is not possible except for some special cases. We deal with these first: (a) For very small displacements all analytic potentials with a single minimum lead to a harmonic oscillator force $F(x) = -\gamma(x - x_0)$ where the equilibrium distance x_0 need not equal R_0 and γ is the effective spring constant. In this case eq 3 and 4 become

$$\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} = \frac{D\gamma}{kT}\langle x\rangle + \frac{x_0 D\gamma}{kT}$$

$$\frac{\mathrm{d}\langle x^2\rangle}{\mathrm{d}t} = 2D\left[1 - \frac{\gamma}{kT}\langle x^2\rangle + \frac{\gamma x_0}{kT}\langle x\rangle\right]$$

which can be successively integrated (subject to $\langle x\rangle = \sqrt{\langle x^2\rangle} = R_0$ as $t \to 0$) to give

$$\langle x\rangle = R_0 e^{-D\gamma t/kT} + x_0[1 - e^{-D\gamma t/kT}]$$

$$\langle x^2\rangle = \left(R_0^2 + 2x_0R_0 - 3x_0^2 - \frac{kT}{\gamma}\right)e^{-2D\gamma t/kT} - 2x_0(R_0 - x_0)e^{-D\gamma t/kT} + \left(\frac{kT}{\gamma} + x_0^2\right) \quad (6)$$

Finally

$$r(\tau) = \sqrt{\left(R_0^2 + 2x_0R_0 - 3x_0^2 - \frac{kT}{\gamma}\right)e^{-2D\gamma\tau/kT} - 2\,x_0(R_0 - x_0)e^{-D\gamma\tau/kT} + \left(\frac{kT}{\gamma} + x_0^2\right)} \quad (7)$$

Equation 7 simplifies for $x_0 \sim R_0 \sim 0$ to

$$r(\tau) = \sqrt{\frac{kT}{\gamma}(1 - e^{-2D\gamma\tau/kT})} \quad (8)$$

Thus $r(\tau)$ is independent of D if $\tau \gg kT/2D\gamma$ and behaves as

$$r(\tau) = \sqrt{2D - \frac{4D^2\tau^2\gamma}{kT}}$$

for $\tau \ll kT/2D\gamma$ (the more likely possibility if the process is diffusion controlled).

(b) The second exactly soluble case can be encountered when the B fragment is a long cylindrical polyelectrolyte and the A fragment a point charge q, where

$$F(x) = \frac{-\partial}{\partial x}\left[\frac{\gamma q}{\epsilon}\ln(x/a)\right]$$

with γ the change per unit length of the polyelectrolyte, ϵ the dielectric constant, and a the radius of the cylinder. Using eq 4 one finds

$$\langle x^2\rangle = R_0^2 + 2Dt(1 - 2\lambda qa/\epsilon) \quad (9)$$

and thus

$$r(\tau) = \sqrt{R_0^2 + 2D\left(1 - \frac{2\lambda qa}{\epsilon}\right)} \quad (10)$$

Equation 10 is of the same form as the free diffusion result except that the diffusion coefficient is replaced by an effective constant

$$D_{\mathrm{eff}} = D\left(1 - \frac{2\lambda qa}{\epsilon}\right)$$

In other cases we must resort to further approximations. Clearly two limiting cases can exist for eq 4: either $\langle xF\rangle < kT$ (weak field limit) or $\rangle \gg kT$ (strong field limit). In the weak field limit we can replace eq 4 by the perturbation approximation ($\sqrt{\langle x^2\rangle} = r(t)$)

$$r\frac{\mathrm{d}r}{\mathrm{d}t} \simeq D\left[1 + \frac{r_0(t)F(r_0(t))}{kT}\right] \quad (11)$$

where $r_0(t) = \sqrt{R_0^2 + 2Dt}$ is the free diffusion separation of the fragments. Integration of eq 11 yields explicitly

$$r(\tau) \simeq \sqrt{R_0^2 + 2D\tau + \frac{2D}{kT}\int_0^\tau r_0(t)F(r_0(t))\mathrm{d}t} \quad (12)$$

In the strong field limit $r(t) \simeq \langle x\rangle$ and $\langle F\rangle \simeq F(r)$ as determined by setting

$$r\frac{\mathrm{d}r}{\mathrm{d}t} \simeq D\left[1 + \frac{rF(r)}{kT}\right] \quad (13)$$

We note that eq 13 is indeed consistent with the physically intuitive requirement that now $\langle x\rangle \simeq r(t)$ since neglecting 1 in comparison to rF/kT we have

$$\frac{\mathrm{d}r}{\mathrm{d}t} = \frac{D}{kT}F(r) \quad (14)$$

which is eq 3 with $\langle F\rangle = F(r)$, a further approximation. From eq 13 one obtains $r(\tau)$ implicitly from the quadrature

$$\int_{R_0}^{r(\tau)} \frac{r\mathrm{d}r}{\left[1 + \frac{rF(r)}{kT}\right]} = D\tau \quad (15)$$

In the case of a Coulomb force between the fragment charges q_A, q_B

$$F(x) = q_A q_B/\epsilon x^2, \qquad \alpha = q_A q_B/\epsilon kT$$

one finds from eq 15

$$D\tau = \int_{R_0}^{r(\tau)} \frac{r^2\mathrm{d}r}{r + \alpha} = \left\{\frac{r^2(\tau)}{2} - \alpha r(\tau) - \frac{R_0^2}{2} + \alpha R_0 + \alpha^2 \ln\left[\frac{\alpha + r(\tau)}{\alpha + R_0}\right]\right\}$$

$$= \frac{r^3(\tau)}{3\alpha} - \frac{R_0^3}{3\alpha} + 0\left(\frac{1}{\alpha^2}\right) \quad (16)$$

The last expression in eq 16 is the same result as is obtained by integrating eq 14 directly to obtain

$$r(\tau) = \sqrt[3]{R_0^3 + \frac{3q_Aq_BD}{\epsilon kT}} \quad (17)$$

The viscosity and dielectric constant variation with changing solvent of the effective yield y satisfies now (see eq 1 in KD)

$$\frac{1}{y} - 1 = \frac{k_d}{k_c} + \frac{k_2}{k_c}$$

$$\cong \sqrt[3]{\frac{\text{constant}}{\epsilon\eta}} + \text{constant}' \quad (18)$$

instead of a linear relation in $\eta^{-1/2}$ as for free diffusion. In the weak field limit one has from eq 12

$$r^2(\tau) = R_0^2 + 2D\tau + 2\alpha[\sqrt{R_0^2 + 2D\tau} - R_0]$$

which reduces for small α and $2D\tau \gg R_0$ to

$$r(\tau) = \sqrt{2D\tau} + \alpha$$

Thus the weak field limit, via eq 12, predicts that

$$\frac{1}{y} - 1 = \sqrt{\frac{\text{constant}}{\eta}} + \frac{\text{constant}'}{\epsilon} + \text{constant}'' \quad (19)$$

Unfortunately a Coulomb field cannot really be weak for any realistic physical situation.

The dependence on η of the yield is even weaker for dipole-dipole forces $F(x) = C\mu_A\mu_B/x^4$ with μ_A the dipole moment of A and C containing the orientation averaged angular factors. The strong field limit gives

$$r(\tau) \simeq \sqrt[5]{R_0{}^5 + \frac{5C\mu_A\mu_B D}{kT}}$$

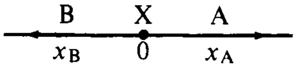
$$\text{or } \frac{1}{y} - 1 = \text{constant} \left(\frac{C\mu_A\mu_B}{\eta}\right)^{1/5} + \text{constant}' \quad (20)$$

The weak field limit, via eq 12, yields

$$r(\tau) \simeq \sqrt{R_0{}^2 + 2D\tau} - \frac{C\mu_A\mu_B}{kT\sqrt{R_0{}^2 + 2D\tau}}\left[\frac{1}{\sqrt{R_0{}^2 + 2D\tau}} - \frac{1}{R_0}\right]$$

$$\frac{1}{y} - 1 = \text{constant } \eta^{-1/2} + \text{constant } C\mu_A\mu_B\eta^{1/2} \times [1 - \text{constant}''\ \eta^{1/2}] + \text{constant}''' \quad (21)$$

We now turn to case II. Professor M. Szwarc[9] thought that this would be an important case for charge transfer in an organic medium with induced dipole forces between the fragments A, X, B. We fix our coordinate system on the fragment X on a line through the CM of A and B, viz.



The arrows indicate the positive direction of the distance x_A, x_B. We need $r(t)$ where

$$r^2(t) = \langle(x_A + x_B)^2\rangle = \int_{-\infty}^{\infty}\int (x_A + x_B)^2 p(x_A,x_B,t)\mathrm{d}x_A\mathrm{d}x_B$$

with $p(x_A,x_B,t)\mathrm{d}x_A\mathrm{d}x_B$ the joint probability of finding fragment A between x_A and $x_A + \mathrm{d}x_A$ and fragment B between x_B and $x_B + \mathrm{d}x_B$ at time t. This joint probability satisfies a Smoluchowski equation involving two diffusion coefficients

$$D_A = \hat{D}_A + \hat{D}_X$$
$$D_B = \hat{D}_B + \hat{D}_X$$
$$(D = D_A + D_B)$$

and the forces $F_A(x_A)$ between A and X, $F_B(x_B)$ between B and X, and $F_{AB}(x_A + x_B)$ between A and B. We will not supply here computational details (interested readers can apply to us to supply this to them); instead we merely quote the results for the strong and weak field limit for induced dipole forces, where $F(x) = Kx^{-7}$, K being the appropriate force parameter K_A, K_B, or K_{AB}.

In the strong force limit one has

$$r(\tau) \simeq [R_0{}^8 + 8\{K_A\phi^{-7} + K_B(1 - \Phi)^{-7} + K_{AB}D\tau\}]^{1/8} \quad (22)$$

with ϕ obtained from the numerical solution of

$$\frac{\phi^2}{(1 - \phi)^2} = \left(\frac{D_A}{D_B}\right)\frac{K_A\phi^{-6} + \phi K_{AB}}{K_B(1 - \phi)^{-6} + (1 - \phi)K_{AB}} \quad (23)$$

If the second term in the eighth root in eq 22 is dominant then

$$\frac{1}{y} - 1 = \text{constant} \times [\{K_A\phi^{-7} + K_B(1 - \phi)^{-7} + K_{AB}\}\eta^{-1}]^{1/8} + \text{constant}'$$

Unless exceptionally large differences arise in the viscosities or K's with changing solvent one would essentially observe eq 23 as $^1/y - 1$ being roughly constant.

In the weak field limit one finds, with $\phi_0 = \sqrt{D_A/D_B}/(1 + \sqrt{D_A/D_B})$,

$$r(\tau = \sqrt{R_0{}^2 + 2D\tau} \times \left\{1 + \frac{(K_A\phi_0{}^{-7} + K_B(1 - \phi_0)^{-7} + K_{AB})}{4(R_0{}^2 + 2D\tau)} \times \left[\frac{1}{R_0{}^4} - \frac{1}{(R_0{}^2 + 2D\tau)^2}\right]\right\} \quad (24)$$

or if $R_0{}^2 \ll 2D\tau$

$$\frac{1}{y} - 1 = \text{constant } \eta^{-1/2}\{1 + \eta(K_A\phi_0{}^{-7} + K_B(1 - \phi_0{}^{-7}) + K_{AB})[1 - \text{constant}''\ \eta^2]\} + \text{constant}''' \quad (25)$$

Equation 25 exhibits explicitly the small, solvent-dependent correction terms to the Koenig-Deinzer result.

Discussion

The experimental data currently available indicate that several decompositon reactions obey the reciprocal square root dependence on viscosity as originally derived by Koenig and Deinzer,[7] and that the additional terms in Koenig's later approximation[2] or in the weak field limit represented in eq 19 above are not important.[10]

Among the types of compounds whose decompositions obey this relationship are peresters,[2,7] *N*-nitrosohydroxylamines,[7] and azo compounds.[10] When deviations from linearity occur they appear as upward curvatures at lower viscosities. Thus, with the data presently available it is reasonable to expect that the weak field approximation will usually hold for systems involving decompositions of neutral molecules.

Recently it has been reported that the second-order reaction between trimethylstannylsodium and aryl bromides displays the characteristics of a cage effect, the caged species being shown as the products of the following equation:[11]

$$\text{ArBr} + \text{Me}_3\text{SnNa} \rightarrow \{\text{ArNa}, \text{Me}_3\text{SnBr}\}$$

Because of the highly polar nature of ArNa one might anticipate behavior approximating the strong field case represented by eq 18. However, in mixtures of tetraglyme and 1,2-dimethoxyethane the viscosity behavior obeys the reciprocal square root behavior very nicely, and the linear plot required by eq 18 is strongly curved.[12] This observation suggests that either the species in the cage are not those proposed[13] or that ArNa and Me_2SnBr behave like the dipolar free radicals of the more familiar examples of the cage effect.

Perhaps a suitable system for testing the effect of intermolceular forces on cage behavior could be obtained with a system such as that represented in case I in which A and B are ions and X is sufficiently large that they are well separated in the cage at the moment of formation.

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Appendix A

If the fragments A and B of case I are treated as points diffusing in three dimensions, with the coordinate system again fixed on fragment B, and r the radial distance to fragment A, one can replace eq 2 by

$$\frac{\partial p}{\partial t} = \frac{D}{r^2}\frac{\partial}{r}\left\{r^2\left[\frac{\partial p}{\partial r} - \frac{F(r)}{kT}p\right]\right\} \quad (\text{A1})$$
$$p(r,0) = \frac{\delta(r - R_0)}{4\pi r^2}$$

Denoting by

$$\langle f(r)\rangle = 4\pi \int_0^\infty f(r)p(r,t)r^2\,\mathrm{d}r$$

one finds now by multiplying eq A1 by r and r^2 and integrating by parts that

$$\frac{\mathrm{d}\langle r\rangle}{\mathrm{d}t} = \frac{D}{kT}\langle F(r)\rangle + 2D\left\langle \frac{1}{r}\right\rangle$$
$$\frac{\mathrm{d}\langle r^2\rangle}{\mathrm{d}t} = 2D\left[3 + \frac{1}{kT}\langle rF(r)\rangle\right] \qquad \text{(A2)}$$

essentially similar relations to our previous linear (one-dimensional) Smoluchowski equation results (3 and 4). The term $2D\langle 1/r\rangle$ prevents loss of particles to a necessary singularity at the origin. To see the similarity of the predictions of these equations to those of eq 3 and 4 consider the special case when eq A2 can be exactly integrated, say when $F(r) = -\gamma r$. For mathematical simplicity we set $R_0 \sim r_0 \sim 0$ and compare with eq 8. From eq A2 we have

$$\frac{\mathrm{d}\langle r^2\rangle}{\mathrm{d}t} = 2D\left[3 - \frac{\gamma}{kT}\langle r^2\rangle\right]$$

Thus

$$\sqrt{\langle r^2\rangle} = r(\tau) = \sqrt{\frac{3kT}{\gamma}\left[1 - e^{-2D\gamma\tau/kT}\right]} \qquad \text{(A3)}$$

which differs only by the factor $\sqrt{3}$ from eq 8. In view of the many approximations inherent in our starting formula such a numerical factor is negligible.

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Photodetachment of Electrons from Enolate Anions. Gas Phase Electron Affinities of Enolate Radicals

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Abstract: Photodetachment cross sections are measured as a function of photon energy for enolate anions formed by proton abstraction in the gas phase, using an ion cyclotron resonance spectrometer to trap and detect the ions. Electron affinities are determined from the photodetachment thresholds for the enolate anions from acetaldehyde, propionaldehyde, butyraldehyde, 3-pentanone, pinacolone, methyl acetate, acetophenone, 4-heptanone, 1,1,1-trifluoroacetone, diisopropyl ketone, phenylacetaldehyde, acetyl fluoride, acetone, 3,3-dimethylbutanal, and 2-butanone. The cross section shapes are analyzed in terms of a theoretical model for photodetachment, and we conclude that each cross section is composed of many vibronic transitions. We find evidence for electronic transitions in some of these anions in the blue and UV regions of the spectrum. Finally, substituent effects on anion stabilities are discussed and compared with the corresponding effects in solution.

The reactions of enolate anions are of major importance in synthetic organic chemistry as well as in the study of organic reaction mechanisms. An understanding of their thermochemical and spectroscopic properties is useful both in devising synthetic schemes employing enolate anions and in mechanistic studies of reactions involving enolate anions. The thermodynamic stability of an enolate anion is reflected in the acidity of its parent carbonyl compound. Since the acidity is strongly dependent on the relative solvation of the anion and the neutral compound, it is often difficult to evaluate the intrinsic effects of small changes in molecular structure on the stabilities of anions in solution. It is not unusual that small changes in the stabilities of anions in solution may be completely dominated by large variations in the degree of their solvation. For example, the acidity order observed in solution is reversed from that observed in the gas phase for aliphatic alcohols.[2] Although the acidities of some simple carbonyl compounds have been measured in solution,[3,4] in most cases it is difficult to determine to what extent acidity changes are the result of solvation effects.

Recent measurements by Kebarle and co-workers[5] of the acidities of some carbonyl compounds in the gas phase have been used to note substituent effects on the stabilities of enolate anions. While the application of these acidity measurements to simple carbonyl compounds was limited to acetone, acetophenone, and trifluoroacetone, they clearly showed the potential of the technique for investigating the intrinsic thermodynamic stabilities of these compounds. Grunwell and Sebastian[6] have made a CNDO/2 study of the relative stabilities of the two possible enolate anions derived from 2-butanone, finding the most highly substituted anion to be energetically more stable by 11.0 kcal/mol. However, it is not clear that CNDO is capable of accurately predicting small changes in stability, especially when variations from "standard" geometries are not considered.

The object of this work was to investigate the stabilities of