

Orientation Effects in Bimolecular Ionic Reactions

Julian M. Sturtevant

Citation: [The Journal of Chemical Physics](#) **3**, 295 (1935); doi: 10.1063/1.1749656

View online: <http://dx.doi.org/10.1063/1.1749656>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/3/5?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Pressure effects on bimolecular recombination and unimolecular dissociation reactions](#)

J. Chem. Phys. **114**, 9807 (2001); 10.1063/1.1370552

[Excimer formation in pyrene molecular crystal: Femtosecond dynamics of an oriented bimolecular reaction](#)

J. Chem. Phys. **87**, 7346 (1987); 10.1063/1.453331

[Kinetics of diffusioninfluenced bimolecular reactions in solution. II. Effects of the gating mode and orientationdependent reactivity](#)

J. Chem. Phys. **86**, 1904 (1987); 10.1063/1.452757

[The effect of dipole moment on diffusion controlled bimolecular reaction rates](#)

J. Chem. Phys. **84**, 5536 (1986); 10.1063/1.449911

[Effects of Chemical Reactions on the Bimolecular Rate Constant](#)

J. Chem. Phys. **46**, 1316 (1967); 10.1063/1.1840850



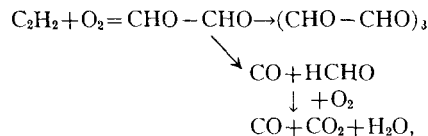
kinetic standpoint. The main interest in the results, however, lies in the fact that previous assumptions regarding the simple nature of the glyoxal decomposition have been shown to be incorrect.

In the oxidation of acetylene no appreciable quantity of carbon or tar is formed.^{1, 6} It therefore follows that while glyoxal may be formed and *oxidized* in the acetylene oxidation, it cannot *decompose* during the course of this reaction as has been previously assumed.

It also follows that the scheme proposed by

⁶ Steacie and McDonald, unpublished work.

Lenher for the oxidation of acetylene catalyzed by the oxides of nitrogen, *viz.*:



is not a possible mechanism, although certain *ad hoc* modifications could be made to bring it into line with the present work.

An investigation of the glyoxal oxidation is in progress.

MAY, 1935

JOURNAL OF CHEMICAL PHYSICS

VOLUME 3

Orientation Effects in Bimolecular Ionic Reactions

JULIAN M. STURTEVANT, *Sterling Chemistry Laboratory.*

(Received January 15, 1935)

It is shown on the basis of accepted views concerning second order ionic reactions in solution that the variation with concentration of the electrostatic orientation effects in such a reaction arising from the lack of symmetry of a spheroidal ion is negligible in dilute solution. Deviations from Brönsted's law must be attributed to other causes.

IT has been observed that certain bimolecular ionic reactions deviate very considerably from the requirements of the limiting Brönsted formula, which is, for water as solvent and at 25°C,

$$\log k'' = \log k_0 + z_1 z_2 (\mu)^{\frac{1}{2}}. \quad (1)$$

In this equation k'' is the observed bimolecular specific reaction rate, k_0 is a quantity independent of concentration, z_1 , z_2 are the valences of the reacting ions, and μ is the ionic strength. In many instances these deviations are probably due to failure of the simple Debye-Hückel limiting law for ions of high valence, but there are a few cases where this explanation cannot hold. Outstanding among these is the one observed by LaMer and Kamner.¹ These authors found that the reaction between α -bromopropionate and thiosulfate ions follows the Brönsted formula accurately, while the analogous reaction involving the β -bromopropionate ion leads to a slope of the

$\log k''$ vs. $(\mu)^{\frac{1}{2}}$ curve which does not even have the expected sign. After an exhaustive study had indicated that the effect is not due to side-reactions or other such causes, LaMer and Kamner suggested that purely electrostatic effects resulting from a comparatively large separation of charge and center of reaction (the bromine atom) in the unsymmetrical organic ion might lead to the observed results. It is the purpose of the present note to examine this suggestion a little more closely. It will appear from the study of a fairly general case that this explanation is not valid, if one accepts present views concerning second order ionic reactions in solution.

Christiansen² developed a statistical theory of bimolecular ionic reactions which he showed to be in formal agreement with Eq. (1) in very dilute solutions. His treatment led to a general result which may be written

$$k'' = k_0 \exp(-\epsilon z_2 \varphi_1 / kT) \cdot \Omega \cdot (1 + \sum \chi_i f_i). \quad (2)$$

¹ LaMer and Kamner, J. Am. Chem. Soc. **53**, 2832 (1931).

² Christiansen, Zeits. f. physik. Chemie **113**, 35 (1924).

The term in parentheses expresses an approximation to the effect of deactivating collisions, and may be considered as practically independent of concentration at low total concentrations. Ω is a factor introduced to allow for orientation effects, and was also considered by Christiansen to be independent of concentration in very dilute solutions. The quantity φ_1 is the electrostatic potential due to an ion of type 1 and its atmosphere, at a distance r from its point charge ϵz_1 ; r is to be taken as the separation of the charges of the ions at the moment of reaction. Christiansen used for the value of φ_1 the value obtained by Debye and Hückel³ for spherically symmetrical ions of negligible diameter in a solution of low ionic strength,

$$\varphi_1 = (\epsilon z_1 / Dr) e^{-\kappa r} \approx -\epsilon z_1 \kappa / D + (\epsilon z_1 / Dr) (\kappa r \ll 1). \quad (3)$$

D is the dielectric constant of the medium and κ is defined by

$$\kappa^2 = (\pi \epsilon^2 N / 125 D k T) \mu, \quad (4)$$

N being Avogadro's number.

Eq. (2) will be used as the basis of an extension to the case that the ions of type 1 are not spheri-

cally symmetrical. In order to make the treatment reasonably simple the ions of type 1 are assumed to be prolate spheroidal, with semiaxes a and b ($a > b$). These dimensions define a spheroidal surface beyond which, on the average, the charges of the other ions in the solution do not penetrate. A coordinate system is taken with origin at the center of an ion of type 1, the semimajor axis of which lies along the z -axis. Then in the confocal coordinates, η , ϑ , φ , defined by the relations

$$\begin{aligned} x &= c \sinh \eta \sin \vartheta \cos \varphi & 0 \leq \eta < \infty, \\ y &= c \sinh \eta \sin \vartheta \sin \varphi & 0 \leq \vartheta \leq \pi, \\ z &= c \cosh \eta \cos \vartheta & 0 \leq \varphi < 2\pi, \end{aligned} \quad (5)$$

the "surface" of the ion corresponds to $\eta = \eta_0$ such that

$$\cosh \eta_0 = a/c; \quad \sinh \eta_0 = b/c$$

where $2c$ is the separation of the foci. The point charge ϵz_1 is located at $(\eta', \vartheta', \varphi')$.

If ψ_1' is the potential inside the ion due to its atmosphere and ψ_1'' is that due to the charge ϵz_1 , then the total potential for $\eta < \eta_0$ is $\psi_1 = \psi_1' + \psi_1''$. Now ψ_1' satisfies Laplace's equation and is bounded at the origin, so that it has the form⁴

$$\psi_1' = \sum_{n=0}^{\infty} \sum_{m=0}^n P_n^m(\cosh \eta) P_n^m(\cos \vartheta) [C_{nm} \cos m\varphi + D_{nm} \sin m\varphi] \quad (6)$$

where the P_n^m are the associated Legendre functions of the first kind and the C_{nm} , D_{nm} are constants. Expansion⁵ of the reciprocal of the distance between $(\eta, \vartheta, \varphi)$ and $(\eta', \vartheta', \varphi')$ gives

$$\begin{aligned} \psi_1'' &= \sum_{n=0}^{\infty} \sum_{m=0}^n Q_n^m(\cosh \eta) P_n^m(\cos \vartheta) E_{nm} \cos m\varphi, \\ E_{n0} &= (2n+1)(\epsilon z_1 / Dc) P_n(\cosh \eta') P_n(\cos \vartheta'), & \eta > \eta' \quad (7) \\ E_{nm} &= (-1)^m 2(2n+1)(\epsilon z_1 / Dc) [(n-m)! / (n+m)!]^2 P_n^m(\cosh \eta') P_n^m(\cos \vartheta') \cos m\varphi' \end{aligned}$$

if we take $\varphi' = 0$. Here the Q_n^m are the associated Legendre functions of the second kind and D is the dielectric constant inside the ion, assumed to be the same as that of the surrounding medium.

The potential ψ_2 for $\eta > \eta_0$ is a solution of $\Delta \psi_2 = \kappa^2 \psi_2$. Assuming that $\psi_2 = H(\eta) \Theta(\vartheta) \Phi(\varphi)$, we obtain

$$\Phi = \alpha \cos m\varphi + \beta \sin m\varphi, \quad m = 0, 1, 2, \dots \quad (8)$$

$$(1-x^2)y'' - 2xy' + (k^2x^2 + \mu - m^2/(1-x^2))y = 0. \quad (9) \text{ and } (10)$$

In Eq. (9) $y = \Theta$, $x = \cos \vartheta$ and $-1 \leq x \leq 1$; in Eq. (10) $y = H$, $x = \cosh \eta$, and $1 \leq x < \infty$. m and μ are

³ Debye and Hückel, *Physik. Zeits.* **24**, 185 (1923).

⁴ Cf. Hobson, *Spherical and Ellipsoidal Harmonics*, Cambridge, 1931, p. 412.

⁵ Hobson, reference 4, p. 416.

separation constants. Since the parameter $k = \kappa c$ is small, (9) and (10) may be treated by perturbation methods, taking $\mu = n(n+1) + O(k^2)$. We thus set

$$\Theta_n^m = \sum c_j P_j^m(\xi), \quad \xi = \cos \vartheta, \quad m = 0, 1, 2, \dots, n. \quad (11)$$

Using the formula

$$\xi^2 P_n^m = \frac{(n-m+2)(n-m+1)}{(2n+1)(2n+3)} P_{n+2}^m + \frac{2n^2+2n-1-2m^2}{(2n-1)(2n+3)} P_n^m + \frac{(n+m)(n+m-1)}{(2n-1)(2n+1)} P_{n-2}^m$$

we readily find that, aside from constant factors

$$\begin{aligned} \Theta_n^m &= P_n^m + k^2 \left[\frac{(n-m+2)(n-m+1)}{2(2n+1)(2n+3)^2} P_{n+2}^m - \frac{(n+m)(n+m-1)}{2(2n-1)^2(2n+1)} P_{n-2}^m \right] + O(k^4) \\ &= P_n^m + \alpha_{n+2}^m P_{n+2}^m + \beta_{n-2}^m P_{n-2}^m + O(k^4). \end{aligned} \quad (12)$$

An approximate solution of Eq. (10) can now be found by consideration of the unseparated equation involving $y = \Theta H$ as dependent variable. This equation is satisfied by

$$y = \sin^m \vartheta \sinh^m \eta e^{-k \cosh \vartheta \cosh \eta} \equiv K(\vartheta, \eta),$$

so that we have

$$H_n^m(\zeta) = \int_1^\infty K(\xi, \zeta) \Theta_n^m(\xi) d\xi, \quad \zeta = \cosh \eta. \quad (13)$$

We thus have to evaluate integrals of the type

$$I_n^m = i^m (\zeta^2 - 1)^{m/2} \int_1^\infty (\xi^2 - 1)^{m/2} e^{-k\xi} P_n^m(\xi) d\xi. \quad (14)$$

When ξ is not real and between -1 and $+1$,

$$P_n^m(\xi) = \frac{(n+m)!}{(n-m)!} P_n^{-m}(\xi) = \frac{(n+m)!}{(n-m)!} \frac{1}{2^n n!} (\xi^2 - 1)^{-m/2} \frac{d^{n-m}}{d\xi^{n-m}} (\xi^2 - 1)^n.$$

Introducing this relation into Eq. (14) and integrating m times by parts gives

$$I_n^m = i^m \frac{(n+m)!}{(n-m)!} \frac{(\zeta^2 - 1)^{m/2}}{(k\zeta)^m} \int_1^\infty e^{-k\xi} P_n(\xi) d\xi.$$

It can be shown that

$$\int_1^\infty e^{-k\xi} P_n(\xi) d\xi = \frac{i^{n+1}}{(k\xi)^4} \left(\frac{\pi}{2} \right)^{1/2} H^{(1)}_{n+1/2}(ik\zeta),$$

where $H^{(1)}_{n+1/2}$ is the Hankel function of the first kind,⁶ and enters here because it is the only type of Bessel function which vanishes for infinite positive imaginary argument.

To complete the calculation of the solution of Eq. (10) it is necessary to extend the computation of the coefficient α_{n+2}^m in Eq. (12), since the fact that $H^{(1)}_{n+1/2}(ik\zeta)/H^{(1)}_{n+1/2}(ik\zeta) = O(1/k^2)$ necessitates the inclusion of more terms to obtain the desired accuracy. The result obtained is, omitting unessential constant factors,

$$H_n^m(\zeta) = \frac{(\zeta^2 - 1)^{m/2}}{(k\zeta)^{m+1/2}} \left[H^{(1)}_{n+1/2}(ik\zeta) + \sum_{j=1}^\infty (-1)^j a_{n,j}^m H^{(1)}_{n+2j+1/2}(ik\zeta) \right] + \text{relative } O(k^4),$$

⁶ The definition of $H_{n+1/2}^{(1)}$ used here is that given in Jahnke-Emde, *Funktionentafeln*, 2nd ed., Berlin, 1933, p. 202. In evaluating the potential about a spherical ion the point charges of which are not located at its center, Kirkwood (J. Chem. Phys. 2, 599 (1934)) was led to the functions $e^{-\kappa r} K_n(\kappa r) r^{-n-1}$ where the K_n are polynomials. These functions are identical, aside from constant factors, with the functions $r^{-1/2} H_{n+1/2}^{(1)}(i\kappa r)$.

$$a_{n, 2j} = k^2 i \frac{(n+m+1)(n+m+2) \cdots (n+m+2j)}{2 \cdot 4 \cdots (2j)(2n+1)(2n+3)^2(2n+5)^2 \cdots (2n+2j+1)^2(2n+2j+3) \cdots (2n+4j-1)} \\ \times \left[1 + \frac{2jk^2(4m^2-1)}{(2n-1)(2n+3)^2(2n+4j+3)} \right] + \text{relative } O(k^4). \quad (15)$$

The general expression for the potential outside the ion is taken in the form

$$\psi_2 = \sum_{n=0}^{\infty} \sum_{m=0}^n H_n^m (\cosh \eta) \Theta_n^m (\cos \vartheta) [A_{nm} \cos m\varphi + B_{nm} \sin m\varphi]. \quad (16)$$

The coefficients A_{nm} and B_{nm} may be calculated from the boundary conditions that

$$\psi_1 = \psi_2 \quad \text{and} \quad \nabla \psi_1 = \nabla \psi_2 \quad \text{at} \quad \eta = \eta_0. \quad (17)$$

We thus find that

$$A_{nm} = E_{nm} \left\{ \frac{d Q_n^m}{d \zeta P_n^m} \right\}_{\zeta=\zeta_0} - \alpha_n^m F_{n-2, m} \left\{ \frac{d Q_{n-2}^m}{d \zeta P_{n-2}^m} \cdot \frac{d H_{n-2}^m}{d \zeta P_n^m} \right\}_{\zeta=\zeta_0} - \beta_n^m F_{n+2, m} \left\{ \frac{d Q_{n+2}^m}{d \zeta P_{n+2}^m} \cdot \frac{d H_{n+2}^m}{d \zeta P_n^m} \right\}_{\zeta=\zeta_0} \\ + \text{relative } O(k^4), \quad B_{nm} = \text{relative } O(k^4). \quad (18)$$

In order to simplify the formulae somewhat we will specify that the charge $e z_1$ is located on the z axis at a distance ρ from the origin, so that $\cosh \eta' = \rho/c$, $\cos \vartheta' = 1$ or $\cosh \eta' = 1$, $\cos \vartheta' = \rho/c$, according to whether $\rho > c$ or $\rho < c$. There is no significant loss in generality in this restriction since we are mainly interested in the extreme case of a long thin ion in which the charge could not be far removed from the major axis. In this case the potentials are independent of the coordinate φ , so that m is to be set equal to zero in all the above formulae.

Now if $c \leq 3 \times 10^{-8}$ cm and we restrict ourselves to the consideration of solutions in which $\mu^{\frac{1}{2}} \leq 0.1$ we may write that

$$H_{n+1}^{(1)}(ik\zeta) \approx \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{i^{n+1}} \left(\frac{2}{\pi} \right)^{\frac{1}{2}} (k\zeta)^{-n-1}, \quad H_1^{(1)}(ik\zeta) \approx \frac{1}{i^{\frac{1}{2}}} \left(\frac{2}{\pi} \right)^{\frac{1}{2}} \frac{1-k\zeta}{(k\zeta)^{\frac{1}{2}}}, \\ a_{n, 2j} \approx k^2 i \frac{(n+1)(n+2) \cdots (n+2j)}{2 \cdot 4 \cdots (2j)(2n+1)(2n+3)^2(2n+5)^2 \cdots (2n+2j+1)^2(2n+2j+3) \cdots (2n+4j-1)}. \quad (19)$$

The relative error in these approximations is less than 0.5 percent if $\zeta < 1.2$. We thus obtain the simple result that

$$H_n(\zeta) = k^{-n-1} Q_n(\zeta), \quad H_0(\zeta) = -1 + k^{-1} Q_0(\zeta), \quad (20)$$

so that the expression for $\psi_2(\zeta_0, \vartheta)$, omitting certain negligible terms, is

$$\psi_2(\zeta_0, \vartheta) = -\frac{e z_1 K}{D} + \frac{e z_1}{D} \sum_{n=0}^{\infty} \left\{ (2n+1) P_n \left(\frac{\rho}{c} \right) Q_n(\zeta_0) \right. \\ \left. + \frac{k^2}{2} \frac{n(n-1)}{(2n-1)^2} P_{n-2} \left(\frac{\rho}{c} \right) \left[Q_{n-2} + (\zeta^2 - 1) (P_n)^2 Q_n \frac{d}{d\zeta} \frac{Q_{n-2}}{P_n} \right]_{\zeta=\zeta_0} \right. \\ \left. - \frac{k^2}{2} \frac{(n+1)(n+2)}{(2n+3)^2} P_{n+2} \left(\frac{\rho}{c} \right) \left[Q_{n+2} + (\zeta^2 - 1) (P_n)^2 Q_n \frac{d}{d\zeta} \frac{Q_{n+2}}{P_n} \right]_{\zeta=\zeta_0} \right\} P_n(\cos \vartheta). \quad (21)$$

It can be shown by using the asymptotic values

$$Q_n(\zeta) \approx \left(\frac{\pi}{n}\right)^{\frac{1}{2}} \frac{e^{-(n+\frac{1}{2})\eta}}{(2 \sinh \eta)^{\frac{1}{2}}},$$

$$P_n(\zeta) \approx \frac{1}{(n\pi)^{\frac{1}{2}}} \frac{e^{(n+\frac{1}{2})\eta}}{(2 \sinh \eta)^{\frac{1}{2}}}, \quad n \gg 1$$

valid for $\zeta = \cosh \eta > 1$, that the relative error introduced into each term of the sum in (21) by omitting the k^2 terms vanishes with increasing n . Moreover these errors are certainly monotonic functions of n for values of ζ_0 and ρ/c sufficiently near unity and for n greater than 5 or 6. We can thus obtain an estimate of the total error involved in neglecting these terms by examining the first few. Taking $\zeta_0 = 1.1$ and $\rho/c = 1.05$, we find that the error is certainly considerably less than 1 percent. This value of ζ_0 corresponds to an ion having a major axis about $2\frac{1}{2}$ times as long as its minor axis. Thus even in quite extreme cases we may write with sufficient accuracy,

$$\psi_2(\zeta_0, \vartheta) = -\epsilon z_1 \kappa / D + (\epsilon z_1 / D) \sum_{n=0}^{\infty} (2n+1) \\ \times P_n(\rho/c) Q_n(\zeta_0) P_n(\cos \vartheta); \quad (22)$$

the first term is the potential due to the ionic atmosphere and the second term is that due to the charge ϵz_1 , so that we obtain again the simple Debye-Hückel result.

To evaluate the orientation factor Ω appearing in Eq. (2) we assume that the irreversible chemical reaction between an ion of type 1 and one of type 2 (the latter being spherically symmetrical) can take place only when the charge of the ion 2 is located on the spheroid defined by $\eta = \eta_0$, and the line joining the centers of the ions is contained within a solid angle $\Delta\omega$ determined by the finite reactive portion of the surface of the ion 1. This picture should serve as a simplified representation of a reaction between a comparatively simple inorganic ion and a complicated organic ion, the reaction involving one particular group

present in the latter. Then Ω is the fraction of the ions of type 2 with charges located on the spheroid which have the orientation necessary for reaction. If we assume a Boltzmann distribution⁷ we have

$$\Omega(\eta_0) = \frac{\int_{\vartheta'}^{\vartheta''} \int_{\varphi'}^{\varphi''} \exp(-\epsilon z_2 \psi_2 / kT) dS}{\int_0^\pi \int_0^{2\pi} \exp(-\epsilon z_2 \psi_2 / kT) dS}, \quad (23)$$

where the limits ϑ' , ϑ'' , φ' , φ'' , correspond to $\Delta\omega$, dS is the element of surface, and k is Boltzmann's constant.

It is at once apparent that a potential of the form of (22) will lead to an Ω which is independent of κ . Furthermore, if we use ψ_2 in place of φ_1 in Eq. (2) we obtain, after introducing appropriate numerical values,

$$d \log k'' / d(\mu)^{\frac{1}{2}} = z_1 z_2, \quad (24)$$

again in agreement with Brönsted's formula.

As might be expected, exactly the same result is obtained in the consideration of the simpler case of a spherical ion whose charge is not located at its center. It seems quite safe to draw the conclusion that no reasonable type of dissymmetry could lead to purely electrostatic orientation effects that would be observable at concentrations within the range where the Debye-Hückel theory may be applied with any degree of confidence. The observations of LaMer and Kammerl¹ on the β -bromopropionate-thiosulfate reaction can only be reconciled with the theory of Brönsted by assuming that the $\log k''$ vs. $\mu^{\frac{1}{2}}$ curve has a maximum just below the last experimental point.

In conclusion, it is a pleasure for the author to express his gratitude to Professor Lars Onsager for many helpful suggestions given in connection with the treatment of the differential equations in this paper.

⁷ See Christiansen, reference 2, p. 43.