Ion Pairs as Intermediates in Irreversible Reactions of Electrolytes[1a]

By F. MARSHALL BERINGER AND E. MELVIN GINDLER[1b]

Kinetic expressions are developed for a system in which free ions are in mobile equilibrium with ion pairs, which may collapse irreversibly to products. If the concentration of such ion pairs is substantial, even at constant ionic strength the experimental second-order rate constant depends on reagent concentrations. As the concentration of ion pairs decreases, the rate constant becomes independent of reagent concentrations, and its behavior may approach that of the Debye–Hückel limiting law. Relevant published equations and data are discussed.

Introduction

Results obtained in this Laboratory indicate that in water–dioxane mixtures ion pairs are intermediates in the irreversible reaction of diphenyliodonium and phenoxide ions to give diphenyl ether and iodobenzene. A preliminary report of these results already has been made[2]; a fuller exposition directly follows this paper.[3]

The results have prompted a formulation of the kinetics of irreversible reactions of ions of opposite charge on the basis of the following assumptions.

1. Free ions in solution are in equilibrium with ion pairs. This equilibrium is described by a mass action law formulated in terms of activities; the requisite activity coefficients are approximated by equations in the literature.

2. The ion pairs decompose irreversibly to products by way of an activated complex or transition state, the concentration of which determines the rate of the reaction.

Ion Pair Equilibria: Historical.—The incomplete dissociation of the electrolytes has long been proposed by Bjerrum,[4] Onsager,[5] Nernst,[6] Fuoss and Kraus[7] and others.[8,9] More recently Wicke and Eigen[10] have developed a new distribution formula for the ionic atmosphere in the theory of Debye and Hückel, have applied it to the incomplete dissociation of electrolytes in water and have obtained substantiating data from sound absorption measurements. Likewise Marshall and Grunwald[11] have used ion association in an interpretation of the activity coefficients of hydrogen chloride in methanol, ethanol and dioxane–water mixtures. Other workers have found it convenient to consider ion associa-

(1) (a) This paper is taken from a dissertation submitted by E. Melvin Gindler in partial fulfillment of the degree of Doctor of Philosophy, June, 1956. (b) Du Pont Postgraduate Fellow, 1953–1955.

(2) American Chemical Society Meeting, New York City, September 13–18, 1954; see Abstracts of Papers, p. 11R.

(3) F. M. Beringer and E. M. Gindler, THIS JOURNAL, 77, 3203 (1955).

(4) N. Bjerrum, Kgl. Danske Videnskab Selskab, Math-fys. Medd., 7, 9 (1926).

(5) L. Onsager, Physik. Z., 28, 277 (1927).

(6) W. Nernst and W. Orthmann, Z. physik. Chem., 135, 199 (1928).

(7) R. M. Fuoss and C. A. Kraus, THIS JOURNAL, 55, 476, 2387, 3614 (1933).

(8) For a detailed exposition see H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Second Ed., Reinhold Publ. Corp., New York, N. Y., 1950.

(9) For a recent survey of ion association see C. A. Kraus, J. Phys. Chem., 58, 673 (1954)

(10) E. Wicke and M. Eigen, Naturwiss., 38, 453 (1951); Z. Elektrochem., 56, 551 (1952); Z. Naturforsch., 8a, 161 (1953); Z. Elektrochem., 57, 219 (1953); M. Eigen and E. Wicke, J. Phys. Chem., 58, 702 (1954).

(11) H. P. Marshall and E. Grunwald, J. Chem. Phys., 21, 2143 (1953).

tion in kinetic studies of the reactions of ions.[12–18] It seems established that ion pair formation is of frequent occurrence and may be described in terms of a mass action law.

Symbols.—For the reaction

$$\overset{+}{A} + \overset{-}{B} \rightleftharpoons \overset{+}{A}\overset{-}{B} \longrightarrow \text{Products}$$
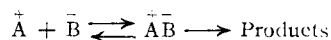
and related reactions let the symbols be

A = concn. of free $\overset{+}{A}$

a = $A + C$

B = concn. of free $\overset{-}{B}$

b = $B + C$

C = concn. of ion pairs $\overset{+}{A}\overset{-}{B}$

D = dielectric constant

f_i = activity coefficient of the ith species, referred to zero ionic strength

f^* = activity coefficient of the activated complex in the irreversible decomposition of ion pairs to products

k_0 = first-order rate constant for the irreversible decomposition of ion pairs to products, in terms of activities

k = $(f_c/f^*)k_0$

k_1 = exptl. first-order rate constant for the over-all reaction

k_2 = exptl. second-order rate constant for the over-all reaction

k_3 = rate constant for the reaction of $\overset{+}{A}\overset{-}{B}$ with $\overset{-}{B}$ at ionic strength u

$K_0 = K^0{}_{AB} = \dfrac{C}{AB} \times \dfrac{f_c}{f_A f_B}$ (In general the subscripts on K indicate the associating ions)

$K = K_0 \dfrac{f_A f_B}{f_c} = \dfrac{C}{AB}$ (1)

m = $a - b$

p = coefficient for dependence of $\ln f^* - \ln f_A f_B$ on $u^{1/2}$; see (30)

q = coefficient for dependence of $\ln f^* - \ln f_A f_B$ on u; see (30)

r = coefficient for dependence of $\ln f^* - \ln f_c$ on u; see (31)

T = absolute temperature in $^\circ K$.

$W = A + B + C = a + b - C$

X = concn. of free $\overset{+}{X}$

Y = concn. of free $\overset{+}{Y}$

Concentration of Ion Pairs.—Equation 1 may be expanded and rearranged.

$$C = K(a - C)(b - C) = Kab - KC(a + b - C) \quad (2)$$

(12) V. K. La Mer and M. E. Kamner, THIS JOURNAL, 57, 2662 (1935).

(13) G. Scatchard, J. Chem. Phys., 7, 657 (1939).

(14) C. W. Davies and P. A. H. Wyatt, Trans. Faraday Soc., 45, 770 (1949).

(15) P. A. H. Wyatt and C. W. Davies, ibid., 45, 774 (1949).

(16) A. R. Olson and T. R. Simonson, J. Chem. Phys., 17, 1167 (1949); see also F. Daniels, "Annual Review of Physical Chemistry", 1, 250 (1950).

(17) M. G. Evans and G. H. Nancollas, Trans. Faraday Soc., 49, 363 (1953).

(18) A. W. Adamson and R. G. Wilkins, THIS JOURNAL, 76, 3379 (1954).

$$C = \frac{Kab}{1 + K(a + b - C)} = \frac{Kab}{1 + KW} \qquad (3)$$

$$C = \frac{(a + b + 1/K)}{2} \left(1 - \left[1 - \frac{4ab}{(a + b + 1/K)^2} \right]^{1/2} \right) \qquad (4)$$

Expansion of the term in square brackets in (4) gives (5)

$$C = \frac{Kab}{1 + K(a + b)} \left(1 + \frac{K^2ab}{[1 + K(a + b)]^2} + \ldots \right) \qquad (5)$$

If C is small compared to a and b, (2)–(5) simplify to (6)

$$C = \frac{Kab}{1 + K(a + b)} \qquad (6)$$

The Kinetic Order.—Assumption 2 may in part be formulated

$$-da = -db = kC\, dt \qquad (7)$$

$$-d(A + C) = kC\, dt = kKAB\, dt \qquad (8)$$

If $a = b$ and, consequently, $A = B$, and if (8) is divided by C (or its equivalent KA^2)

$$d(1/A) - Kd \ln C = kK\, dt \qquad (9)$$

or

$$\text{or } d(1/A) - 2Kd \ln A = kK\, dt \qquad (10)$$

where

$$A = \left(\frac{1}{2K} \right) (\sqrt{1 + 4Ka} - 1) = (C/K)^{1/2} \quad (11)$$

Similarly, if $a = b + m$ and $m > 0$

$$(1/m)d \ln (A/B) - Kd \ln C = kK\, dt \qquad (12)$$

or

$$(1/m)d \ln \left(\frac{A}{A - m} \right) - Kd \ln A(A - m) = kK\, dt \quad (13)$$

where

$$A = \frac{1}{(2K)}(Km - 1 + [(1 - Km)^2 + 4Ka]^{1/2}) \quad (14)$$

It is to be noted with the above equations that as K goes to zero (*i.e.*, as $A \rightarrow a$ and $C \rightarrow 0$), the kinetic expressions approach the forms well-known for simple second-order reactions, (15) and (16).

$$d(1/a) = kK\, dt \qquad (15)$$

$$(1/m)d \ln (a/b) = kK\, dt \qquad (16)$$

On the other hand as K increases toward infinity (*i.e.*, as $A \rightarrow 0$ and $C \rightarrow a$), the equations approach the first-order form, (17).

$$-d \ln a = kdt \qquad (17)$$

This pure first-order kinetic behavior is approached as $1/K \rightarrow 0$. There is a region, however, where $1/K$ is still appreciable and k_1, the experimental first-order rate constant, drifts during the course of a run or from run to run. Similarly, there is a region where K is appreciable and k_2, the experimental second-order rate constant, will drift. One of the aims of this paper is to interpret mathematically the drift of k_1 or k_2 in terms of K.

The Over-all Reaction.—Substitution of (3) in (7) gives

$$\frac{-da}{dt} = \frac{-db}{dt} = \frac{kKab}{1 + K(a + b - C)} = \frac{kKab}{1 + KW} \quad (18)$$

If K is small and the kinetics are accordingly of approximately second order, the over-all rate is also k_2ab, giving

$$k_2 = \frac{kK}{1 + K(a + b - C)} = \frac{kK}{1 + KW} \qquad (19)$$

According to equation 19 even with u, D and T held constant k_2 is a function of reagent concentrations, decreasing as these concentrations are increased. Only when KW approaches zero, *i.e.*, when C is vanishingly small, does k_2 become independent of W.

At constant u, D, T:

$$\lim_{W \rightarrow 0} k_2 = kK \qquad (20)$$

Taking the natural logarithm of (19) gives

$$\ln k_2 = \ln kK - \ln(1 + KW) \qquad (21)$$

which when $KW < 0.1$ simplifies to (22)

$$\ln k_2 = \ln kK - KW \qquad (22)$$

On the other hand when K is large, when $a < b$, and when the kinetics are approximately of the first order in a, then

$$k_1 = kC/a = \frac{k}{1 + A/C} = \frac{k}{1 + 1/KB} \qquad (23)$$

Here k_1 will increase with K.

The Determination of k and K.[19-22]—Since k_2 depends linearly on k and non-linearly on K, it is possible to separate them by the variation of k_2 with reagent concentrations at constant ionic strength. One approach is to invert both sides of (19), arrange terms and divide by a.

$$\frac{1}{k_2 a} = \frac{1}{kKA} + \frac{1}{k} \qquad (24)$$

Data suitable for analysis might be obtained, for example, by determining k_2 in different runs in which b was small while a varied in different runs from $\sim b$ to $\sim 10b$, all runs (initially) at the same ionic strength. Such data may be conveniently analyzed by successive approximations. Suitable equations for finding rough values of k and K are

$$\frac{1}{k_2 a} = \frac{1}{kK(a - b)} + \frac{1}{k} \qquad (25)$$

$$\frac{1}{k_2} = \frac{1}{kK} + \frac{a}{k} \qquad (26)$$

Thus a plot of $1/k_2 a$ against $1/(a - b)$ gives a line of slope $\sim 1/kK$ and an intercept $\sim 1/k$. Alternatively, when $a \gg C$, a plot of $1/k_2$ against a gives a line of slope $\sim 1/k$ and an intercept of $\sim 1/kK$.

Once an approximate value of K is known, A is available and $1/k_2 a$ may be plotted against $1/A$ according to (24). The new value of K from this plot gives A more accurately, and a new plot may be made. While such a series of approximations may be continued indefinitely, convergence on final values is rapid. Usually after a rough value of K has been determined with (25) or (26), two plots accordingly to (24) will give values of k and K not appreciably improved by further approximations.

Thus it is possible by graphical methods to de-

(19) Equations in part similar to those developed in this section have recently been used to detect complex formation both in an experimentally first-order process (the oxidation of glycols with periodic acid, ref. 20) and in two experimentally second-order processes (the reaction of aniline with 2,4-dinitrochlorobenzene, ref. 21, and the bromination of mesitylene, ref. 22).

(20) J. E. Taylor, THIS JOURNAL, **75**, 3912 (1953); F. R. Duke and V. C. Bulgrin, *ibid.*, **76**, 3803 (1954); G. J. Buist and C. A. Bunton. *J. Chem. Soc.*, 1406 (1954).

(21) S. D. Ross and I. Kuntz. THIS JOURNAL. **76**, 3000 (1954).

(22) R. M. Keefer, J. H. Blake, 111, and L. J. Andrews, *ibid.*, **76**, 3062 (1954).

termine K, the equilibrium constant for ion pair formation, and k, the rate constant for irreversible collapse of ion pairs at a given u, D and T.[23]

The Determination of k_0 and K_0.—From definitions given previously

$$\ln k_0 = \ln k - \ln f_c + \ln f^* \qquad (27)$$

$$\ln K_0 = \ln K + \ln f_c - \ln f_A f_B \qquad (28)$$

$$\ln k_0 K_0 = \ln kK - \ln f_A f_B + \ln f^* \qquad (29)$$

Thus k_0 and K_0 represent values at zero ionic strength. To calculate k_0 and K_0 from k and K determined as in the preceding section, the usual procedure would be to determine k and K at various ionic strengths and to assume a simple dependence of the activity coefficients on u. Thus if

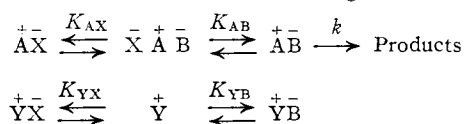$$\ln f^* - \ln f_A f_B = pu^{1/2} - qu \qquad (30)$$

where $pu^{1/2} > qu$, and if

$$\ln f^* - \ln f_c = ru \qquad (31)$$

then plots of $\ln K$ vs. $u^{1/2}$ and of $\ln k$ vs. u extrapolated to $u = 0$ should give K_0 and k_0.

An alternate procedure depends on prior knowledge of p, q and r, as from theoretical equations, and might be used when values of k and K could not be obtained at values of u small enough to allow extrapolations as above. Thus expressions for $\ln f_A f_B$ are given by Wicke and Eigen[10] and by Marshall and Grunwald[11] with the stipulation that the activity coefficients are those of the free ions and are not averaged over free ions and ion pairs. Similarly, if the activity coefficient of an ion pair or activated complex may be calculated as that of a dipolar molecule, the simple expression of Bateman, et al.,[24] or one of the more refined expressions of Kirkwood[25] might be used.

Parasitic Equilibria.—In the present section the situation is considered in which the ions which combine to give the reactive ion pairs also combine with other ions to give inert ion pairs. The effect of these added parasitic equilibria is to decrease the concentration of those ions which give reactive ion pairs, and thus the rate of the reaction rate is decreased. Consider the situation diagrammed below.

$$\overset{+\,-}{AX} \underset{}{\overset{K_{AX}}{\rightleftharpoons}} \overset{-\,+\,-}{X\,A\,B} \overset{K_{AB}}{\underset{}{\rightleftharpoons}} \overset{+\,-}{AB} \overset{k}{\longrightarrow} \text{Products}$$

$$\overset{+\,-}{YX} \underset{}{\overset{K_{YX}}{\rightleftharpoons}} \overset{+}{Y} \overset{K_{YB}}{\underset{}{\rightleftharpoons}} \overset{+\,-}{YB}$$

In a manner similar to that which gave (3) and (19) it can be shown that

$$C_{AB} = \frac{K_{AB}(a - C_{AX})(b - C_{YB})}{1 + K_{AB}[a + b - (C_{AB} + C_{AX} + C_{YB})]} \qquad (32)$$

and that

$$k_2 = \frac{kK_{AB}}{1 + K_{AB}(a + b - C_{AB}) + K_{AX}X + K_{YB}Y + K_{AX}K_{YB}XY} \qquad (33)$$

Additional Reaction Paths.—In the following example the ion pair is assumed to give products both by collapse and by reaction with $\overset{-}{B}$

(23) Note added in proof.—This analysis may determine the concentration of complexes between reactants but not the nature of these complexes, e.g., whether or not they are ion pairs.

(24) L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 979 (1940).

(25) J. G. Kirkwood, *Chem. Revs.*, **24**, 253 (1939).

$$k_2 ab = kC + k_3 BC \qquad (34)$$

In analogy with (18) it may be shown that

$$k_2 = kK \left[\frac{1}{1 + KW} + \frac{k_3}{kK} \times \frac{KB}{1 + KW} \right] \qquad (35)$$

If $b \gg a$, then $B \simeq b \simeq W$, and

$$k_2 = kK \left[\frac{1}{1 + Kb} + \frac{k_3}{kK} \times \frac{Kb}{1 + Kb} \right] \qquad (36)$$

If the reaction between $\overset{+\,-}{AB}$ and $\overset{-}{B}$ proceeds by formation and decomposition of an ion triplet $\overset{-\,+\,-}{BAB}$, then k_c is equivalent to the product of the equilibrium constant for ion triplet formation from ion pair and $\overset{-}{B}$ and the rate constant for ion triplet decomposition. If the cation were doubly charged, i.e., $\overset{+\,+}{A}$, then we would expect ion triplet formation, of $\overset{-\,+\,+\,-}{B\ \ AB}$, to be of more importance, such that the second term of (35) or (36) might contribute appreciably.

Other Ionic Reactions.—It is a well-known fact that in reactions of ions of the same charge type the rate is increased by the addition of ions of opposite charge. In some cases this is in part the result of ion pair formation between one reacting ion and an oppositely charged ion of added "inert salt" followed by reaction of the ion pair with the other reacting ion. Wyatt and Davies[15] have shown this to be the cause of metal ion catalysis of the much-studied thiosulfate-bromoacetate reaction.[12–15] The greater effect of barium and calcium ions over sodium ions arises from the greater tendency for ion pair formation.

In other cases it seems possible that the acceleration of reaction of ions of similar charge type by oppositely charged ions of an "inert salt" arises from an ionic atmosphere effect. Consider for instance the acceleration by perchlorate ions of the reaction between mercuric and bromopentammine-cobaltic ions.[16] Increasing perchlorate ion concentration will increase negative ionic atmosphere around the two reacting ions, decreasing their net charges and facilitating their approach and reaction. The positive sodium or lanthanum ions added with the perchlorate ions will be at a distance from the reacting ions and will have only a small effect and one nearly independent of the number of positive charges on each ion. Thus Olson and Simonson[16] found that the effect was to be correlated with the concentration of perchlorate ion, not with ionic strength.

Actually, there is no evidence in this latter case as to whether the acceleration by perchlorate ion arises from ion pair formation or from ionic atmosphere effects. All usual changes of charge type, concentration and dielectric constant which favor the one also favor the other. From a series of kinetic runs, then, in which the concentration of "inert" salt is increased it seems difficult, if not impossible without outside non-kinetic evidence, to attribute the change to ion pair formation or an ionic atmosphere effect.

For reactions of ions of opposite charge both ions from an inert salt will be effective in slowing the rate either by parasitic ion pair formation or by

building up ionic atmospheres about the ions which decrease their net charges and their tendency to approach each other and react. Olson and Simonson[16] have studied the reaction of very small concentrations of bromopentamminecobaltic bromide with excess sodium hydroxide in water. A plot of log k_2 vs. $u^{1/2}$ is linear. Since sodium hydroxide is the major component determining ionic strength, the plot of log k_2 vs. $[HO^-]^{1/2}$ or $[Na^+]^{1/2}$ is also linear. Further, the authors have developed a three parameter equation which also reasonably fits the data.

$$k = k_a \left[\frac{1}{1 + K(X)} + k' \frac{K(X)}{1 + K(X)} \right] \quad (37)$$

For (37) Olson and Simonson[16] define k as the sec-

ond-order rate constant, k_a as the rate constant when hydroxide ion concentration is low, k' and K' as adjustable parameters and (X) as the concentration of hydroxide ions. Finally, it will be noted that (37) is very similar to (35) and (36), derived for the case where ion pairs might give product both directly and by reaction with one of the free ions.

It is possible, however, by working at constant ionic strength and by varying the concentrations of reagents and "inert" salts to assess the importance of ion pair formation. Such an analysis, for the reaction of diphenyliodonium and phenoxide ions, is reported in the following paper.[3]

Brooklyn 1, N. Y.

Diaryliodonium Salts. III. Kinetics of the Reaction of Diphenyliodonium and Phenoxide Ions[1]

By F. Marshall Beringer and E. Melvin Gindler[2]

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In continuation of studies on the synthesis[3] and reactions[4] of diphenyliodonium salts the reaction of diphenyliodonium and phenoxide ions to give diphenyl ether and iodobenzene has been found to be of second order in most dioxane–water mixtures, with the order decreasing at high dioxane concentration.[1] Second-order rate constants in 1:1 dioxane–water at 45–70° gave Arrhenius parameters log $PZ = 12.8$ and $E_a = 25.9$ kcal./mole. At 65.1° a plot of log k_2 vs. $u^{1/2}$ had a slope of -2.7, while with u constant, log k_2 varied linearly with $1/D$. At constant u, D and T variation of k_2 with reagent concentration allowed calculation of the association constant for formation of the diphenyliodonium phenoxide ion pairs and the rate constant for irreversible decomposition of the ion pairs to products under a variety of conditions.

Introduction

Previous papers have reported improved syntheses[3] of diphenyliodonium salts and have shown that under relatively mild conditions organic and inorganic bases effect nucleophilic displacement on the 1-carbons of diphenyliodonium ions to form new bonds with carbon, hydrogen, oxygen, sulfur, selenium, nitrogen, phosphorus, arsenic, antimony and the halogens.[4] Thus iodonium salts show promise as general phenylating agents.

In the present work the reaction of diphenyliodonium and phenoxide ions to give diphenyl ether and iodobenzene[4] was examined cursorily in water and more intensively in dioxane–water mixtures.[5] Runs were made by preparing a thermostatted solution of diphenyliodonium chloride or nitrate and phenol in water or dioxane–water, adding a known amount of thermostated solution of sodium

(1) This paper is taken from a dissertation submitted by E. Melvin Gindler in partial fulfillment of the requirements of the degree of Doctor of Philosophy, June, 1956. The preceding paper developed the theory and equations for the kinetics of reactions of oppositely charged ions which occur by the formation and decomposition of ion pairs: F. M. Beringer and E. M. Gindler, This Journal, 77, 3200 (1955). The symbols here used are as defined in the preceding paper, with specialization to the present reaction. Equations are numbered as one series through both papers.

(2) Du Pont Postgraduate Fellow, 1953–1955.

(3) F. M. Beringer, M. Drexler, E. M. Gindler and C. C. Lumpkin, This Journal, 75, 2705 (1953).

(4) F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler and C. C. Lumpkin, ibid., 75, 2708 (1953).

(5) (a) These results were presented at the American Chemical Society Meeting, New York City, September 13–18, 1954; see Abstracts of Papers, p. 11R. (b) Recently a note has appeared in which the present reaction in water was discussed: E. S. Lewis and C. A. Stout, This Journal, 76, 4619 (1954).

hydroxide in the same solvent and analyzing aliquots removed at intervals for unreacted base. Excess phenol repressed the hydrolysis of the phenoxide ion.

Solvents.—Exploratory runs showed that while the reaction in water had a convenient rate at 80°, the kinetics were complicated by the fact that the finely dispersed second phase of insoluble reaction products effected a considerable acceleration of the reaction. In a typical run a zeroth order plot is linear from about 3–70% reaction. The reaction caused by the second phase cannot be equally distributed throughout the second phase, for the bulk of this second phase increased at least 20-fold during this portion of the reaction. Possibly surface effects are operative, small drops being initially formed but coalescing to larger drops having a smaller surface-volume ratio.

It might be noted that in the copper-catalyzed reaction of diphenyliodonium chloride to give chlorobenzene and iodobenzene in water or water–dioxane the presence of a finely dispersed second phase of products has a similar accelerating effect.[6] (Copper salts do not catalyze the reaction between diphenyliodonium ions and phenoxide ions.)

To maintain homogeneity, dioxane–water mixtures were used in all subsequent runs.[7]

Arrhenius Parameters.—In 1:1 dioxane–water reactions were considerably faster than in water and

(6) F. M. Beringer, E. J. Geering and I. Kuntz, Abstract of Papers, American Chemical Society Meeting, New York City, September 13–18, 1954, p. 90–O.

(7) Failure to maintain homogeneity probably helped make the results given in reference 5b erratic and difficult to interpret.