Reversible Reactions Regarded as a Series of Irreversible Reactions

By PER AHLBERG* and MARIANNE EK

(*Institute of Chemistry, University of Uppsala, P.O. Box* 531, S-751 21 *Uppsala, Sweden*)

Summary The usefulness of regarding reversible reactions as a series of irreversible reactions is pointed out and demonstrated for symmetric reactions, racemizations, and related reactions.

REVERSIBLE first order reactions [(A) $\rightleftharpoons$ (B)] are characterized by the rate constants of the forward (k_1) and reverse (k_{-1}) processes and by the equilibrium constant K ($=k_1/k_{-1}$). The approach to equilibrium, *i.e.* the time-dependence of [(A)] and [(B)], is described by equations (1) and (2).[1]

$$[(\text{A})] - [(\text{A})]_\infty = \{[(\text{A})]_0 - [(\text{A})]_\infty\}\exp[-(k_1 + k_{-1})t] \quad (1)$$

$$[(\text{A})] + [(\text{B})] = \text{const.} \quad (2)$$

Recently we wished to estimate the enantiospecificity of 1,3-proton transfer in (+)-(*R*)-3-phenyl-1-(*o*-tolyl)cyclohexene (A), to give mainly (+)-(*S*)-1-phenyl-3-(*o*-tolyl)-cyclohexene (B) which is presumably at least partially bifunctionally catalysed, by the secondary amidine, 1,2,3,4,4a,5,6,7-octahydro-1,8-naphthyridine.[2] It was possible to make this estimation by using the time-dependence of the specific rotation of (A) ($[\alpha_A]$) [only partially resolved (A) is required for this purpose] and the two rate constants of the reversible reaction. Equation (3) has been derived[3]

$$[\alpha_A]/[\alpha_{A_0}] = \{\sum_{i=0}^{\infty}[(A)_{B_i}]x^iy^i\}/\sum_{i=0}^{\infty}[(A)_{B_i}] \qquad (3)$$

in which $[\alpha_{A_0}]$ is the specific rotation of unchanged (A), $[(A)_{B_i}]$ is the concentration of (A) molecules that have been (B) i times, and x and y are the stereospecificities of the reactions (A) → (B) and (B) → (A), respectively.

Thus for an accurate estimate of the enantiospecificity it is not sufficient to know only the fraction of (A) at time t that has been (B) during the reaction. One also needs to know the fraction of (A) which has been (B) once, twice, three times *etc.* In other words, knowledge of the fates of the molecules during reactions is required in detail and it is necessary to divide them into appropriate classes. A molecule of (A) which has been (B) i times cannot again become (A) which has been (B) $i - 1$ times. This way of looking at a reversible reaction transforms it into a series of irreversible reactions as shown in Scheme 1, where $(B)_{A_i}$ is analogous to $(A)_{B_i}$. The formal similarity of Scheme 1 with the radioactive series in Scheme 2 is obvious. The solutions of the differential equations for the sequence of first order processes in Scheme 2 are well known and a variety of cases are discussed by Rutherford, Chadwick, and Ellis.[4] Other cases, unlikely to be applicable to the radioactive series, in which the rate constants in the chain of irreversible reactions alternate (*i.e.*, $K \neq 1$), or the cases in which all rate constants are equal, do not seem to have been treated. The latter covers reversible reactions for which $K = 1$, *e.g.* racemizations, when (A) and (B) are enantiomers, or symmetric reactions where (A) and (B) are identical. This is outlined in Scheme 3, where $(A)_i$ represents those (A) molecules that have reacted i times to give (A) again [$(A)_{2i+1}$ and $(A)_{2i}$ in Scheme 3 correspond to $(B)_{A_{i+1}}$ and to $(A)_{B_i}$, respectively, in Scheme 1]. In this communication only the solution to the important special case in which $K = 1$ will be presented because of its simplicity. A full account of the $K \neq 1$ case will be published elsewhere.[3]

$$(A)_{B_0} \xrightarrow{k_1} (B)_{A_1} \xrightarrow{k_{-1}} (A)_{B_1} \xrightarrow{k_1} (B)_{A_2} - - - \xrightarrow{k_{-1}} (A)_{B_{i-1}}$$
$$\xrightarrow{k_1} (B)_{A_i} \xrightarrow{k_{-1}} (A)_{B_i} \xrightarrow{k_1} (B)_{A_{i+1}} \xrightarrow{k_{-1}} etc.$$

SCHEME 1

$$(C) \xrightarrow{k_2} (D) \xrightarrow{k_3} (E) \xrightarrow{k_4} (F) \xrightarrow{k_5} - - - -$$

SCHEME 2

$$(A)_0 \xrightarrow{k} (A)_1 \xrightarrow{k} (A)_2 - - - \xrightarrow{k} (A)_i - - - \xrightarrow{k} (A)_{2i} \xrightarrow{k} (A)_{2i+1} \xrightarrow{k} etc.$$

SCHEME 3

By solving the equation $d[(A)_0]/dt = -k[(A)_0]$, one obtains the time-dependence of $[(A)_0] = [(A)]\exp.(-kt)$ in which $[(A)]$ represents the total concentration of (A) in a symmetric reaction or, when (A) and (B) are different types of molecules, $[(A)] + [(B)] = $ const. The differential equation for $[(A)_1]$ is $d[(A)_1]/dt = k[(A)_0] - k[(A)]_1]$ and is solved using the solution of $[(A)_0]$ just obtained yielding $[(A)_1] = [(A)]kt\ \exp.(-kt)$. This result is then used to solve for $[(A)_2]$ and so on. By induction, the recursion formula $[(A)_i] = [(A)](k^it^i/i!)\exp.(-kt)$ is obtained. The dependence of $[(A)_0]$ to $[(A)_8]$ on time is shown in the Figure. Except for $[(A)_0]$ which only decays, the $[(A)_i]$ grow in turn to their maximum values and then decline. The maxima appear at regular time intervals. By differentiation of the recursion formula they are shown to appear at $t = i/k$. Furthermore, the maxima decrease in size with time as the curves become broader. The area under any $(A)_i$ curve is of course equal to $[(A)]/k$.

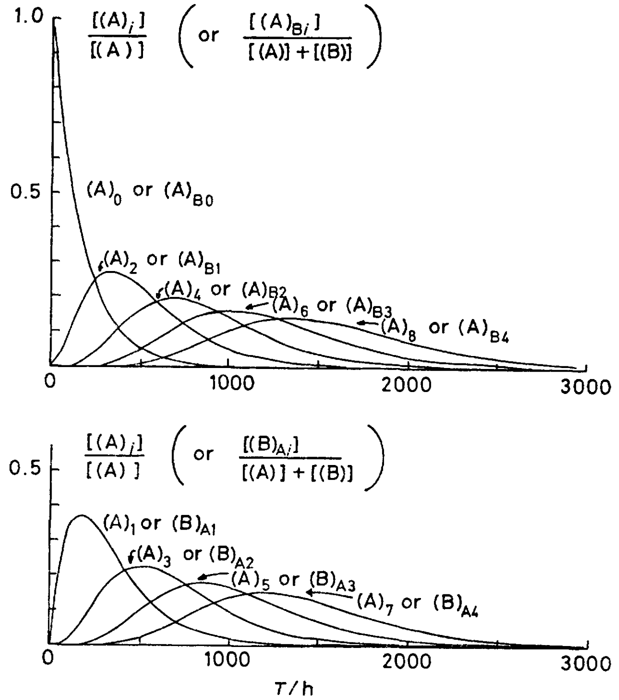

FIGURE. Time dependence of the fractions of reactants of reversible reactions, (A) ⇌ (A) [or (A) ⇌ (B)] with $K = 1$ and $k = 5{\cdot}88 \times 10^{-3}\ h^{-1}$, regarded as a series of irreversible reactions.

The above way of regarding reversible reactions might prove to be of use in the analysis of reversible processes in general.

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[3] M. Ek and P. Ahlberg, unpublished results.

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