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Kinetics and Distribution in Hydrogen Isotope Exchange and Redistribution

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A method is described for the solution of an extensive class of problems concerning the kinetics of isotope exchange and redistribution reactions. Analytical expressions for the isotope distribution in the course of the exchange reaction of a hydrocarbon having equivalent hydrogen atoms are derived, both for the consecutive single-step (Section I) and for the multiple exchange reaction (II).

The effects of variations in the reaction mechanism on the isotope distribution are discussed (III). A simple recipe is given for finding the distribution for any exchange mechanism, if the initial state contains only undeuterated compound and the deuterating agent is present in large excess.

The kinetics of redistribution reactions are discussed and a redistribution rate law is formulated (IV).

Each of the sections (I–IV) is concluded by a discussion which recapitulates the results presented in that section.

INTRODUCTION

Isotopes are used in the study of mechanisms of chemical reactions in various ways, e.g., as tracers and by measuring kinetic isotope effects. Another application is the study of isotope interchange reactions: reactions in which no chemical change occurs except the substitution of one isotope for another one. The last-mentioned reactions form the subject of this paper, in which moreover we limit ourselves to protium–deuterium* interchange of hydrocarbons, although the treatment is of more general applicability.

There exist two classes of interchange reactions:

(a) Between chemically different species, e.g.,

$$D_2SO_4 + C_6H_6 \rightarrow C_6H_5D + C_6H_4D_2 + \ldots + C_6D_6$$

These are called *exchange reactions* and are dealt with in Sections I–III.

(b) Between chemically identical positions in identical species, e.g.

$$CH_4 + CD_4 \rightarrow CH_3D + CH_2D_2 + CHD_3.$$

They are called *redistribution* (*equilibration*) *reactions*† and are dealt with in Section IV.

Mass-spectrometric analysis allows of a determination of the distribution of the isotope over the various isotopic species: It yields the fractions of molecules containing 0, 1, 2, . . i, . . . deuterium atoms (denoted by $d_0, d_1, d_2, \ldots d_i, \ldots$; the molecules themselves are denoted by a capital D_i). These data in principle contain detailed information on reaction mechanisms. However, their correct interpretation in some instances runs into mathematical complications.

As far as we know only partial solutions of the problems involved have been obtained. We propose to give a general method of solution which seems to be valid for many problems in this field, although in some cases isotope effects are difficult to handle.

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* We shall use the following nomenclature: H^1 = *protium;* $H^2 = D$ = deuterium; hydrogen = protium and/or deuterium.

† The term "homomolecular exchange" has been proposed for this type of reaction (*1*). This term has also been used in a different sense (*2*).

It can readily be seen that the formalism of redistribution reactions is completely analogous to that of exchange reactions when the redistribution occurs via exchange with a chemically different species present in the system, e.g. a catalyst. We shall restrict ourselves to this type of redistribution and hence, we have only to deal with various types of exchange reactions.

From numerous reported data it is known that essentially two types of isotope distributions occur, corresponding to different situations in the exchange process (*3*).

The first type of exchange reaction is called *stepwise* exchange: A molecule after passing through the transition state for exchange of *one* hydrogen atom has a chance for further exchange which is equal to the chance of all other molecules in the system. Section I deals with this type, of which the exchange between benzene and a deuterated acidic solvent is an example.

The second possibility arises when a small part of all the molecules in the system are in a particular situation or converted to a particular structure and are then capable of undergoing exchange. Such processes, dealt with in Sections II and III, are called *multiple* exchange reactions since the molecule, in its particular situation, may exchange more than one hydrogen atom before returning to the normal, nonreactive state. The exchange between isoparaffins and deuterated, liquid or solid, acids is of this type (further examples are given in Section II).

It is possible to treat the stepwise process as a special case of the multiple process. We prefer, however, to discuss the stepwise process separately. It is simpler than the more general one, thus allowing among other things a rigorous discussion of isotope effects and the effect of sites of different reactivities in the deuterating agent (which might particularly apply to heterogeneous catalysts). This simplicity also makes the stepwise reaction well-suited for demonstrating our method for solving the differential equations.

The method will further be applied to some problems of varying complexity which together cover a large part of the field of isotopic exchange. Unless otherwise stated we confine ourselves to a hydrocarbon with equivalent exchangeable hydrogen atoms, their number being N. Extension to other cases is possible (cf. Sections I,3.3 and III).

List of Symbols

a	Ratio of number of exchangeable hydrogen atoms in hydrocarbon to number of ditto in deuterating agent
$\mathbf{A}$	Matrix whose elements are related to those of $\mathbf{R}$ by: $A_{i,j} = R_{i,j}r^j$
$\mathbf{d},\mathbf{d}^*$	Column vectors with elements d_i and d_i^*, respectively ($i = 0,1, \ldots, N$)
d_i,d_i^*	Fractions of normal and reactive molecules, respectively, containing i deuterium atoms per molecule
d_{2a},d_{2b}	Fractions of *cis*-1,2-$C_2H_2D_2$ and *trans*-1,2-$C_2H_2D_2$ + 1,1-$C_2H_2D_2$
D_i,D_i^*	Normal and reactive molecules, respectively, containing i deuterium atoms
$\mathbf{e}_j$	jth column of unit matrix
$\mathbf{e}'_j$	Transposed of $\mathbf{e}_j$
$\mathbf{f}'$	Row vector with elements $f_j = jx(1 - sx)(1 - x)^{j-1} - Nsx(1 - x)^j$
$\mathbf{F}$	Matrix whose elements are defined by: $F_{i,i-1} = (N - i + 1)s$; $F_{i,i} = -(N - i)s - ir$; $F_{i,i+1} = (i + 1)r$
$\mathbf{g}$	Column vector related to $\mathbf{f}$ by: $\mathbf{f} = \mathbf{Rg}$ ($\mathbf{f}'$ is the transposed of $\mathbf{f}$)
$\mathbf{G}$	Matrix whose elements are defined by: $G_{i,i-1} = -(N - i + 1)s$; $G_{i,i} = -i$
h	$= a(k' - k'')/(1 + a)$
$\mathbf{I}$	Unit matrix with elements $I_{i,j} = \delta_{i,j}$
$\mathbf{J}$	Diagonal matrix with elements $J_{i,i} = r^i$
k	Rate constant, in stepwise exchange, per hydrocarbon molecule, in arbitrary concentration units
k',k''	Rate constants of deuteration and dedeuteration, respectively
$\bar{k}$	$= \{k'[a\rho(\infty) + s(\infty)] + k''[a\sigma(\infty) + r(\infty)]\}/(1 + a)$
k_{-1},k_1	Rate constants for deactivation and activation, respectively, in multiple exchange
k_2	Rate constant for deuterium exchange of reactive molecule, in multiple exchange
$\mathbf{L}$	Diagonal matrix with elements $L_{i,i} = -i$

m_i	$= i\gamma/(1 + i\gamma)$
$\mathbf{M}$	Diagonal matrix with elements $M_{i,i} = \exp(-m_i\tau)$
N	Number of exchangeable hydrogen atoms in a molecule
p	$= 1 - \sigma$ or $= 1 - (\sigma/s)$
$p_{j,i}$	Chance that D_i is formed from D_j*
$\mathbf{P}$	Matrix with elements defined by $P_{i,j} = (-1)^i \binom{j}{i}$
q_j	1 − chance that, on reaction of D_j, D_j is formed back
Q_j	$= \exp(-q_j k_1 t)$
$\mathbf{Q}$	Matrix with elements defined by $Q_{i,j} = \binom{N-j}{i-j}(-s)^{i-j}$
r	$= 1 - s$
$\mathbf{R}$	$= \mathbf{PQ}$
s	Fraction of deuterium in deuterating agent
S	$= Te^{-\tau}$
t	Time
T	$= \int_{\tau'=0}^{\tau} s(\tau')e^{\tau'}d\tau'$
$\mathbf{u},\mathbf{u}^*$	Column vectors equal to $\mathbf{Pd}$ and $\mathbf{Pd}^*$, respectively
u	$= d_{2a} + d_3 + 2d_4$
$\mathbf{v}$	Column vector related to $\mathbf{d}$ by $\mathbf{d} = \mathbf{Rv}$
w_i	$= u_i e^{i\tau}$
$x,y,z,\hat{z}$	Variables in characterizing relations; $y = x/(1 - sx)$; $z = [x/(1 - Sx)]e^{-\tau}$; $\hat{z} = \{(1 - x)/[1 - S(1 - x)]\}e^{-\tau}$
β	Ratio of rate of exchange of reactive species and rate of deactivation $= k_2/k_1$
γ	$= \beta/N$
Δ_i	Fraction of ethylene molecules with i deuterium atoms in one of the CH_2 groups
ϵ	Fraction of molecules present in reactive state
λ	Eigenvalue
ξ	$= \sigma - \sigma(\infty)$
ρ	$= 1 - \sigma$
$\sigma(t)$	Mean deuterium content of hydrocarbon at time t
τ	$= \int_{t'=0}^{t} (k(t')/N)dt'$
Φ_i	Fraction of molecules that have reacted i times

I. Stepwise Exchange Reactions

1. The Rate Equations

We have already defined d_i as the fraction of hydrocarbon carrying i deuterium atoms per molecule.

Evidently,

$$\sum_{i=0}^{N} d_i = 1 \qquad (1)$$

We further define the mean deuterium fraction, σ, of the hydrocarbon

$$\sigma = \frac{1}{N}\sum_{i=1}^{N} id_i \qquad (2)$$

and the ratio a by

$$a = \frac{\text{total number of hydrogen atoms in the hydrocarbon}}{\text{ditto in the deuterating agent}}$$

The fraction of deuterium in the total hydrogen of the deuterating agent will be denoted by s. Generally, s is a function of t.

Then the material balance for deuterium reads

$$s + a\sigma = \text{constant} \qquad (3)$$

If $AH_{N-i}D_i$ is a hydrocarbon molecule containing i deuterium atoms, the reactions in the system can be written as

$$AH_{N-i}D_i + D \rightleftarrows AH_{N-i-1}D_{i+1} + H \qquad i = 0, 1, \ldots, N-1 \qquad (4)$$

Provided there is no kinetic (and equilibrium) isotope effect, the corresponding rate equations* are

$$(d/dt)d_i = (k/N)[(N - i + 1)d_{i-1}s - (N - i)d_i s - id_i r + (i + 1)d_{i+1}r] \qquad (5)$$
$$i = 0, 1, \ldots, N$$

terms with indices beyond that range must be discarded; k = rate constant per hydro-

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* Throughout this paper the rates of the various isotopic species are assumed to be governed by statistical factors only, which implies the absence of secondary isotope effects. This type of isotope effect is known to be very small and this assumption can, for the present purpose, be considered to be valid.

carbon molecule and in arbitrary concentration units; $r = 1 - s$.

Before discussing the system of equations (5) we first introduce a simplification by dividing both members by k/N and defining a new time-scale by

$$\tau = \int_{t'=0}^{t} \frac{k(t')\,dt'}{N} \tag{6}$$

We admit a time-dependent k here. The operation $d/(k/N)dt$ reduces to $d/d\tau$ and Eq. (5) becomes

$$\begin{aligned}(d/d\tau)d_i &= (N - i + 1)sd_{i-1} \\ &\quad - [(N - i)s + ir]d_i + (i + 1)rd_{i+1} \qquad (7)\\ &\qquad i = 0, 1, \ldots, N\end{aligned}$$

It is now convenient to consider the d_i as the elements of a column vector $\mathbf{d}$

$$\mathbf{d} = \begin{pmatrix} d_0 \\ d_1 \\ \vdots \\ d_N \end{pmatrix} \tag{8}$$

and to use matrix algebra.*

For that purpose we introduce the matrix $\mathbf{F}$, having elements $F_{i,j}$ (i = row number; j = column number; $i,j = 0, 1, \ldots, N$), such that we can write the rate Eqs. (7) in the condensed form

$$d/d\tau(\mathbf{d}) = \mathbf{Fd} \tag{9}$$

Comparison with (7) yields immediately

$$\begin{aligned} F_{i,i-1} &= (N - i + 1)s \\ F_{i,i} &= -(N - i)s - ir \\ F_{i,i+1} &= (i + 1)r \end{aligned} \tag{10}$$

the indices running from 0 to N. The remaining elements of $\mathbf{F}$ are zero.

2. General Solution of the Rate Equations

2.1. Plan of Solution

The Eqs. (9) contain the quantities s and r, which are related to the $\mathbf{d}$ by Eqs. (2) and (3). So the complete system of equations consists of (9) together with (3).

One might try to obtain a solution by deriving first, from (9) and (3), an equation for s. When we have succeeded in solving s from this equation, (9) is a complete system since then s is a known function of τ. We might then attempt to simplify (9) by means of a linear transformation

$$\mathbf{d} = \mathbf{Pu} \tag{11}$$

where $\mathbf{P}$ is a nonsingular matrix whose elements are constant.

When we make the calculations it turns out that we may equally well start with simplifying the system (9): Any useful simplification automatically yields an equation for s.

To find a useful transformation we substitute (11) in (9):

$$(d/d\tau)(\mathbf{Pu}) = \mathbf{FPu} \tag{12}$$

If the elements of $\mathbf{P}$ are constant we may write

$$\mathbf{P}(d/d\tau)\mathbf{u} = \mathbf{FPu} \tag{13}$$

or, by premultiplication by $\mathbf{P}^{-1}$

$$(d/d\tau)\mathbf{u} = \mathbf{Gu} \text{ with } \mathbf{G} = \mathbf{P}^{-1}\mathbf{FP} \tag{14}$$

We hope to find a transformation $\mathbf{P}$ such that $\mathbf{G}$ is simpler than $\mathbf{F}$. The most advantageous result would be a $\mathbf{G}$ having diagonal form. In that case Eqs. (14) could be solved separately. As we shall see in Section II, $\mathbf{P}$ should in that case have the eigenvectors of $\mathbf{F}$ as its columns, and it appears that these eigenvectors contain s. So this procedure applies only when s is constant, which means that a must be very small (large excess of deuterating agent).

In the general case of time-dependent s it is therefore impossible to find a $\mathbf{P}$ such that $\mathbf{G}$ has diagonal form. We have found, however, that transformations exist which, though less ambitious, are highly useful. One of these which we shall use throughout all our calculations is the transformation

$$P_{i,j} = (-1)^i \binom{j}{i} \equiv (-1)^i \frac{j!}{i!(j-i)!} \tag{15}$$

(We adopt the convention that

$$\binom{j}{i} = 0$$

if i is beyond the range $0 \leqq i \leqq j$.)

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* As an aid to the reader the explicit expressions for a number of frequently used matrices are given, for the case $N = 4$, in the Appendix.

2.2. Matrix Calculations

We shall not try here to derive the properties of linear transformations. They form the subject of linear algebra on which excellent textbooks exist, while an extensive discussion, directed to problems of reaction kinetics, has recently been given by Wei and Prater (*4*). We shall only recall the concept of characterizing relations, which are extensively used in the following calculations.

An arbitrary matrix **F** can be described by defining all of its elements $F_{i,j}$. For applications it will be convenient to employ an alternative description of **F** by means of a characterizing relation. Consider the product:

$$(1, x, \ldots, x^N)\mathbf{F} = (f_0, f_1, \ldots, f_N)$$

For each f_j we find a polynomium in x, with the elements of the jth column of **F** as coefficients:

$$f_j = \sum_{i=0}^{N} F_{i,j}x^i = (1, x, \ldots, x^N)\mathbf{F}\mathbf{e}_j \quad (16)$$

where $\mathbf{e}_j$ denotes the jth column of the unit matrix **I**.

As an example, we apply this procedure to the particular **F** defined by (10) and find:

$$(1, x, \ldots, x^N)\mathbf{F}\mathbf{e}_j = x^{j-1}(1 - x)[jr - (N - j)sx] \quad (17)$$

The matrix **P** defined by (15) can be described by the following characterizing relation:

$$(1, x, \ldots, x^N)\mathbf{P} = [1, (1 - x), \ldots, (1 - x)^N] \quad (18)$$

If we post-multiply expression (18) by **P**, we find:

$$(1, x, \ldots, x^N)\mathbf{P}^2 = [1, (1 - x), \ldots, (1 - x)^N]\mathbf{P} = (1, x, \ldots, x^N)$$

since $1 - (1 - x) = x$. So $\mathbf{P}^2 = \mathbf{I}$ (= identical transformation)

or
$$\mathbf{P} = \mathbf{P}^{-1} \quad (19)$$

The matrix **G**, defined by (14), can be found by carrying out the matrix multiplications **PFP**, but the calculations become much simpler when we apply the characterizing relations (17) and (18) for **F** and **P**, respectively. Thus we have to find:

$$(1, x, \ldots, x^N)\mathbf{G} = (1, x, \ldots, x^N)\mathbf{PFP}$$

Straightforward application of (17) and (18) yields

$$(1, x, \ldots, x^N)\mathbf{PF} = (f_0, f_1, \ldots, f_N) = \mathbf{f}'$$

where

$$f_j = jx(1 - sx)(1 - x)^{j-1} - Nsx(1 - x)^j$$

The product $\mathbf{f}'\mathbf{P}$ is evaluated by means of (18) and its derivative with respect to x

$$(0, 1, 2x, \ldots, Nx^{N-1})\mathbf{P}\mathbf{e}_j = -j(1 - x)^{j-1} \quad (20)$$

(in the application under consideration here we replace x by $1 - x$). The result is

$$(1, x, \ldots, x^N)\mathbf{G}\mathbf{e}_j = x^j[-j - (N - j)sx] \quad (21)$$

from which we read immediately the jth column of **G**. For application in the rate equations for u_i it is more convenient to write the rows of **G**. Thus, for row i

$$G_{i,i} = -i \qquad G_{i,i-1} = -(N - i + 1)s \quad (22)$$

The other elements are zero.

2.3. The Rate Equations in the New Variables **u**

Making use of the results of *2.2* we can now express the variables **u**, defined by (11) and (15), in the **d**. Since $\mathbf{P} = \mathbf{P}^{-1}$ according to (19) we find that

$$\mathbf{u} = \mathbf{Pd} \quad (23)$$

We can further write the rate equations for **u**

$$(d/d\tau)u_i + iu_i = -(N - i + 1)su_{i-1} \quad (24)$$

(here, as usual, terms with an index beyond the range $(0,N)$ must be discarded).

***a.* Solution of the equations for u_0 and u_1.** We shall first consider the equations for $i = 0$ and $i = 1$. From (23) we obtain

$$u_0 = \sum_{i=0}^{N} d_i, \qquad u_1 = -\sum_{i=1}^{N} id_i$$

and, in combination with (1) and (2):

$$u_0 = 1, \qquad u_1 = -N\sigma \tag{25}$$

It is therefore not surprising to find for $i = 0$ in (24):

$$(d/d\tau)u_0 = 0$$

For $i = 1$ we obtain from (24):

$$(d/d\tau)u_1 + u_1 = -Ns$$

or, using (25):

$$(d/d\tau)\sigma + \sigma = s \tag{26}$$

In (26) and the deuterium balance (3) we have a complete and very simple system of equations for solving both s and σ. For the constant in (3) we may put the initial value $s(\text{o}) + a\sigma(\text{o})$ or the equilibrium value $s(\infty) + a\sigma(\infty)$.

After some rearrangement we obtain

$$(d/d\tau)(s - \sigma) = -(1 + a)(s - \sigma)$$

which on integration gives

$$s - \sigma = [s(\text{o}) - \sigma(\text{o})] \exp[-(1 + a)\tau] \tag{27}$$

We see that the difference between the deuterium fraction in the hydrocarbon and in the deuterating agent vanishes exponentially. Thus

$$s(\infty) = \sigma(\infty)$$

Using this result we obtain from (27) and (3)

$$\begin{aligned} s - s(\infty) &= [s(\text{o}) - s(\infty)] \exp[-(1 + a)\tau] \\ \sigma - \sigma(\infty) &= [\sigma(\text{o}) - \sigma(\infty)] \exp[-(1 + a)\tau] \end{aligned} \tag{28}$$

The above equations show how the deuterium contents of hydrocarbon and deuterating agent change with τ. If k is constant, i.e. $\tau = (k/N)t$ [see Eq. (6)] this result represents the well-known rate law for isotope exchange (*5*).

To obtain information on the distribution of deuterium over the various isotopic species we must integrate the system (24) for $i = 2,3,\ldots,N$. These equations can now be integrated since—s being known as a function of time—they can successively be put in the form

$$(d/d\tau)u_i + iu_i = f(\tau)$$

However, this is a laborious procedure and we prefer to apply another transformation of variables to simplify the calculations.

The reader not interested in the formalism of these transformations should ignore the next section and pass directly to 2.4.

***b.* Complete integration of the *u* equations.** If we multiply Eqs. (24) by $e^{i\tau}$, we recognize the left-hand member as the derivative of $u_ie^{i\tau}$, which suggests the transformation

$$w_i = u_ie^{i\tau} \tag{29}$$

This turns (24) into

$$(d/d\tau)w_i = -(N - i + 1)se^{\tau}w_{i-1} \tag{30}$$

A further simplification is obtained by dividing (30) by se^{τ} and introducing a new time-scale T such that the operation $d/se^{\tau}d\tau$ turns into d/dT. Therefore we put

$$T = \int_{\tau'=0}^{\tau} s(\tau')e^{\tau'}d\tau' \tag{31}$$

which turns (30) into

$$(d/dT)w_i = -(N - i + 1)w_{i-1} \tag{32}$$

for $i = 1,2,\ldots,N$ with $w_0 = 1$ for all T.

We now integrate the Eqs. (32) successively, which results in expressions for w_i as functions of T and the initial values $w_i(\text{o})$, which are obviously the same as $u_i(\text{o})$

$$w_i = \sum_{j=0}^{i} (-1)^{i-j} \binom{N-j}{i-j} u_j(\text{o})T^{i-j}$$

and for u_i

$$u_i = \sum_{j=0}^{i} (-1)^{i-j} \binom{N-j}{i-j} u_j(\text{o})(Te^{-\tau})^{i-j}e^{-j\tau} \tag{33}$$

The connection of $Te^{-\tau}$ with the physical quantities of the system appears when we consider (33) for $i = 1$

$$u_1 = -N(Te^{-\tau}) + u_1(\text{o})e^{-\tau}$$

or, using (25)

$$\sigma = Te^{-\tau} + \sigma(\text{o})e^{-\tau} \tag{34}$$

or, introducing S by $S = Te^{-\tau}$:

$$S = \sigma - \sigma(\text{o})e^{-\tau} \tag{35}$$

In view of (28), Eq. (35) gives us S as a function of τ.

We can now write the solution in the form

$$u_i = \sum_{j=0}^{i} (-1)^{i-j} \binom{N-j}{i-j} S^{i-j} u_j(\mathrm{o}) e^{-j\tau}$$

or

$$\left.\begin{aligned} &(1,x,\ldots,x^N)\mathbf{u} \\ &\qquad = (1-Sx)^N(1,z,\ldots,z^N)\mathbf{u}(\mathrm{o}) \\ &\text{with} \qquad z = [x/(1-Sx)]e^{-\tau} \end{aligned}\right\} \quad (36)$$

This equation is obtained as follows:

$$(1,x,\ldots,x^N)\mathbf{u} = \sum_{i=0}^{N} u_i x^i$$

$$= \sum_{i=0}^{N} x^i \sum_{j=0}^{i} (-1)^{i-j} \binom{N-j}{i-j} S^{i-j} e^{-j\tau} u_j(\mathrm{o})$$

$$= \sum_{j=0}^{N} x^j e^{-j\tau} u_j(\mathrm{o}) \sum_{i-j=0}^{N-j} (-1)^{i-j} \binom{N-j}{i-j}$$

$$S^{i-j} x^{i-j} = \sum_{j=0}^{N} x^j e^{-j\tau} u_j(\mathrm{o})(1-Sx)^{N-j}$$

$$= (1-Sx)^N \sum_{j=0}^{N} z^j u_j(\mathrm{o})$$

The Eqs. (36) contain all the necessary information. In actual practice one will prefer the **d** representation of the solution, that is a set of equations expressing **d** as a function of **d**(o) and τ. To obtain this we write (36) in the form

$$\mathbf{u} = \mathbf{K}\mathbf{u}(\mathrm{o}) \text{ with } (1,x,\ldots,x^N)\mathbf{K} = (1-Sx)^N(1,z,\ldots,z^N)$$

Applying (11), (18), and (19) we find:

$$\mathbf{d} = \mathbf{M}\mathbf{d}(\mathrm{o}) \text{ with } \mathbf{M} = \mathbf{PKP}$$

The result is:

$$(1,x,\ldots,x^N)\mathbf{M} = (1-S+Sx)^N[1,(1-\hat{z}),\ldots,(1-\hat{z})^N]$$

$$\text{with} \quad \hat{z} = [(1-x)/(1-S+Sx)]\, e^{-\tau}$$

$$\text{or} \quad (1,x,\ldots,x^N)\mathbf{M}\mathbf{e}_j = (1-S+Sx)^{N-j}[(1-S-e^{-\tau}) + (S+e^{\tau})x]^j \quad (37)$$

We find **d** as:

$$\begin{aligned} (1,x,\ldots,x^N)\mathbf{d} &= (1-S+Sx)^N [1,(1-\hat{z}),\ldots,(1-\hat{z})^N]\mathbf{d}(\mathrm{o}) \\ &= (1-S+Sx)^N \Sigma d_j(\mathrm{o})(1-\hat{z})^j \end{aligned} \quad (38)$$

The d_i is the coefficient of x^i in the right-hand form.

2.4. The Solution in Terms of the d_i

From the general solution (38) explicit formulae for the d_i can be obtained, but this is a laborious process leading to rather intricate expressions. We shall not give these here since they are hardly ever needed. One usually has special initial conditions which often lead to considerably simpler expressions.

We shall use Eq. (38) firstly, to obtain such simple expressions in a particular case (Section I,2.4,a) and, secondly, to draw some important conclusions with respect to the rôle of the binomial distribution (I,2.4,b). We shall further briefly discuss a few results that can be obtained by using the methods of Sections I,2.2 and I,2.3, omitting the derivations which, although straightforward, are often lengthy.

***a.* The solution for special initial conditions.** The technique most frequently used is the deuteration of a compound that contains no deuterium in the initial state. In this case, $d_0(\mathrm{o}) = 1$ [and, consequently, $d_i(\mathrm{o}) = 0$ for $i = 1,2,\ldots,N$]. We then have [Eq. (35)] $S = \sigma$, so (38) becomes

$$(1,x,\ldots,x^N)\mathbf{d} = (\rho + \sigma x)^N$$

where $\rho = 1 - \sigma$,

$$\text{or} \qquad d_i = \binom{N}{i} \sigma^i \rho^{N-i} \qquad (39)$$

The two equivalent expressions of (39) represent a binomial distribution* of deuterium over the molecules, with the average deuterium content, σ, as defined by (2), as the parameter. Since by (28) σ is a known function of time, Eqs. (39) describe the step-

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* In chemical literature this distribution is often denoted as "statistical." The term binomial is to be preferred, since binomial statistics is but one type of statistics. Other types of statistics result from other assumptions on probabilities.

wise deuteration reaction for this particular case completely.

***b.* Some remarks on the binomial distribution.** We now return to the general solution (38). Since both $\hat{z}$ and $S - \sigma$ disappear as $e^{-\tau}$ [see (35) and (28)], we have at equilibrium

$$(1,x,\ldots,x^N)\mathbf{d}(\infty) = [\rho(\infty) + \sigma(\infty)x]^N(1,1,\ldots,1)\mathbf{d}(o) = [\rho(\infty) + \sigma(\infty)x]^N$$

Hence, $\mathbf{d}(\infty)$ is a binomial distribution, and the difference $\mathbf{d} - \mathbf{d}(\infty)$ disappears as $e^{-\tau}$.

A further conclusion concerns the behavior of the difference, $\boldsymbol{\delta}(\tau)$, between the actual $\mathbf{d}(\tau)$ and the corresponding binomial $\mathbf{d}(\tau)_{\text{bin}}$, having the same σ. From this definition: $\boldsymbol{\delta}(\tau) = \mathbf{d}(\tau) - \mathbf{d}(\tau)_{\text{bin}}$ it follows that $(1,1,\ldots,1)\boldsymbol{\delta} = 1 - 1 = 0$ and $(0,1,\ldots,N)\boldsymbol{\delta} = N\sigma - N\sigma = 0$ for all τ.

We shall show that:

(a) If $\boldsymbol{\delta}(o) = 0$ then $\boldsymbol{\delta}(\tau) = 0$ for all τ. This means that a distribution which is binomial in the initial state maintains its binomial character to equilibrium. Note that the initial state discussed in Section I,2.4,a is also binomial, with $\sigma(o) = 0$. This result has recently been discussed by Mikovsky and Wei (*6*).

(b) For arbitrary $\boldsymbol{\delta}(o)$ the $\boldsymbol{\delta}(\tau)$ disappears as $e^{-2\tau}$, which we may consider as a precise statement concerning the stability of the binomial distribution.

For the proof we consider

$$\begin{aligned}(1,x,\ldots,x^N)\boldsymbol{\delta} &= (1,x,\ldots,x^N)\mathbf{d} - (\rho + \sigma x)^N \\ &= (1 - S + Sx)^N [1,1-\hat{z},\ldots,(1-\hat{z})^N][\mathbf{d}(o)_{\text{bin}} + \boldsymbol{\delta}(o)] - (\rho + \sigma x)^N \\ &= (1 - S + Sx)^N[\rho(o) + \sigma(o)(1-\hat{z})]^N + (1 - S + Sx)^N [1,1-\hat{z},\ldots,(1-\hat{z})^N]\boldsymbol{\delta}(o) - (\rho + \sigma x)^N\end{aligned}$$

Because

$$\begin{aligned}(1 - S + Sx)[\rho(o) + \sigma(o)(1-\hat{z})] &= (1 - S + Sx)[1 - \sigma(o)\hat{z}] \\ &= (1 - S + Sx) - \sigma(o)(1-x)e^{-\tau} \\ &= 1 - [S + \sigma(o)e^{-\tau}] + x[S + \sigma(o)e^{-\tau}] \\ &= 1 - \sigma + \sigma x = \rho + \sigma x\end{aligned}$$

the terms not containing $\delta(o)$ cancel out, and we have

$$(1,x,\ldots,x^N)\boldsymbol{\delta} = (1 - S + Sx)^N [1,1-\hat{z},\ldots,(1-\hat{z})^N]\boldsymbol{\delta}(o)$$

The conclusion (a) is now evident. We prove (b) by expanding in powers of $\hat{z}$: Up to the first order we have:

$$\begin{aligned}(1,x,\ldots,x^N)\boldsymbol{\delta} &= (1 - S + Sx)^N (1,1-\hat{z},1-2\hat{z},\ldots,1-N\hat{z})\boldsymbol{\delta}(o) \\ &= (1 - S + Sx)^N[(1,1,\ldots,1)\boldsymbol{\delta}(o) - \hat{z}(0,1,2,\ldots,N)\boldsymbol{\delta}(o)] = 0\end{aligned}$$

and this proves the statement under (b).

3. Extensions

The methods of Sections I,2.2 and I,2.3 can still deal with the stepwise exchange reaction if there are complications. We shall briefly discuss some of the results obtained [for the case $d_0(o) = 1$], omitting the derivations.

3.1. Isotope Effects

If the rate constants $k' = k(\text{deuteration})/N$ and $k'' = k(\text{dedeuteration})/N$ are not equal the kinetics will be changed. It is found, however, that the deuterium *distribution* over the various isotopic species as given by (39) is not affected. The only difference is in the time-dependence of σ. Equation (28) for σ must be replaced by

$$\xi[\bar{k} - h\xi(o)] = \xi(o)(\bar{k} - h\xi)\exp[-(1+a)\bar{k}t] \qquad (40)$$

where

$$\begin{aligned}\xi &= \sigma - \sigma(\infty), \\ (1+a)\bar{k} &= k'[a\rho(\infty) + s(\infty)] + k''[a\sigma(\infty) + r(\infty)] \\ (1+a)h &= a(k' - k'')\end{aligned}$$

3.2. Nonequivalent Hydrogen Atoms in the Deuterating Agent

Nonequivalence of the hydrogen atoms in the deuterating agent may occur, for instance, in the exchange reaction between a hydrocarbon and deuterium on a solid catalyst. It can be shown that the distribution of deuterium over the isotopic species will again be binomial. This even holds when the hydrogen atoms on the catalyst surface cannot move freely and local s values may consequently differ widely during the reaction. In this case σ is not a simple function of time.

3.3. Nonequivalent Hydrogen Atoms in the Hydrocarbon Molecule

In many molecules not all exchangeable hydrogen atoms are equivalent. They can then be divided in groups of different reactivities. It has been shown that in this case the distribution of deuterium within each group is binomial with as parameter the mean deuterium content of that group.

The average deuterium content for any group is not a simple function of time. The distribution of deuterium over the total molecule is given by combination of the distributions of the groups and is itself not binomial (except at infinite time).

A more detailed discussion for the case of two groups has been given elsewhere (*7*).

4. Discussion

In this section (I) a formula has been derived for the time-dependence of each isotopic species d_i in a stepwise exchange reaction of a hydrocarbon with N equivalent exchangeable hydrogen atoms [Eq. (38)]. For arbitrary conditions at $t = 0$, the expression is very complicated. If, however, at $t = 0$ the distribution of deuterium over the various d_i's is binomial (which notably applies for ordinary starting material), then the distribution at any time during the exchange will also be binomial (Section I,3): It is completely determined by one parameter, σ, the average degree of deuteration [Eq. (39)]. This result is affected neither by isotope effects (I,3.1) nor by the occurrence of different deuterating reagents in the system (I,3.2).

In the absence of isotope effects σ changes exponentially with time [Eq. (28)]. For the special initial conditions mentioned, combination of Eq. (28) and the binomial distribution [Eq. (38)] readily yields the time-dependence of each individual d_i.

Usually exchange experiments are made to find the reaction mechanism and rate constants. In this connection we may briefly outline how we evaluate experimental results. By a least-squares calculation we ascertain whether the binomial expression can be fitted to the distribution in a sample. If so, it can be concluded that a stepwise process is involved and each sample yields a value for σ. From the change of σ with time the rate constant is derived.

Though other methods can be envisaged (e.g., using the time-dependence of every individual d_i), use of the present one, consisting of reducing the information on each sample to a value for σ and next considering σ as a function of time, seems imperative in more complicated cases. Thus for a hydrocarbon with different types of hydrogen atoms, the time-dependence of each d_i is complicated. However, from the experimental distribution a value of σ for every group of hydrogen atoms can be obtained. The change of each σ with time will, by an exact or approximate method, give a rate constant for that particular group of hydrogen atoms.

II. Multiple Exchange Reactions

In accordance with what was said in the Introduction a multiple exchange reaction is defined as a process in which a molecule after (before) passing through the transition state for the exchange of one hydrogen atom does not necessarily return to (come from) the normal state, but to (from) a relatively stable and, with respect to exchange, reactive state. As an illustration we mention the following cases:

(a) The behavior of an isoparaffin (*8*, *9*, *10*), e.g. isobutane, in homogeneous acidic solutions containing D^+. This system—owing to reactions not further discussed here—contains a number of t-butyl carbonium ions, $t\text{-}C_4H_9^+$, in addition to the normal isobutane molecules. These carbonium ions, which contain nine hydrogen atoms, are relatively stable and readily exchange according to

$$C_4H_9^+ \xrightarrow{D^+} C_4H_8D^+ \xrightarrow{D^+} C_4H_7D_2^+ \rightarrow \ldots \rightarrow C_4D_9^+$$

By reaction with another isobutane molecule these ions return to their normal state with formation of a new carbonium ion

$$C_4D_9^+ + C_4H_{10} \rightarrow C_4D_9H + C_4H_9^+$$

(b) In the gas-phase reaction between D atoms and methane (*11*), methyl radicals are formed. The latter are relatively stable and exchange with the surrounding deuterium gas. Finally the methyl radicals are converted again into methane molecules, themselves not capable of exchange.

(c) If an aromatic hydrocarbon, say benzene, is added to a two-phase system consisting, e.g., of D_2SO_4 and a normal paraffin, a small fraction of the benzene molecules are dissolved in the D_2SO_4 phase and are capable of undergoing exchange. They stop exchanging by passing the phase boundary. In spite of the stepwise character of the exchange in the acidic phase, the net result is that of multiple exchange, since there are some molecules in a privileged position, viz. in the acidic phase.

(d) In the exchange between a solid (e.g., a catalyst) and a gaseous hydrocarbon (*12*, *13*, *14*) some molecules may be chemisorbed and the chemisorbed species may be capable of exchange on the surface. The molecules become unreactive by desorption. Isoparaffins on a silica-alumina cracking catalyst show this behavior.

These processes can all be described by saying that, in the steady state, a small constant fraction, ϵ, of the molecules is present in a reactive state. The reactive species exchange protium for deuterium and vice versa, and occasionally return to the normal, nonreactive state, normal molecules taking their place in the reactive state.

It is possible, but not necessary, for the latter reactions to be coupled: The transition from normal to reactive state may take place by a bimolecular reaction between a normal and a reactive molecule [hydride-ion transfer in example (a)]. In case (c) the transition is clearly a monomolecular process.

The present discussion is limited to the case that the transition from normal to reactive state and vice versa can be described by

$$D_i \rightleftarrows D_i^*$$

where the * denotes the active state.

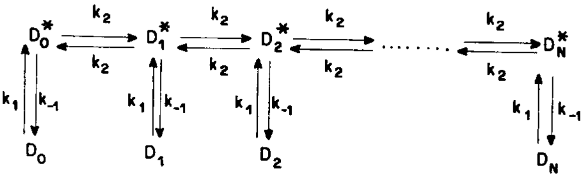
Other processes are discussed in Section III.

We further assume that no isotope effects manifest themselves.

An obvious difference between stepwise and multiple exchange is that in the latter process two parameters are required to characterize the reaction and, consequently, to describe the deuterium distribution. First, as in the stepwise process, there is the mean deuterium content, σ. Secondly, the distribution depends on a parameter, β, which is the ratio of the probability (reaction rate) that a molecule in the reactive state undergoes (further) exchange to the probability (reaction rate) that it gives the normal molecule.

The problem of calculating the isotope distribution in reactions of this type can be approached in two ways, viz. by solving the set of differential equations or by means of calculation of (transition) probabilities. The first method is discussed in Section II,1, the second in II,2, both for the mechanism defined above. The second method gives a solution only when $s = 1$ and the hydrocarbon is undeuterated in the initial state.

1. *The Rate Equations*



The scheme shows the reactions taking place in the system. D_i and D_i^* represent "normal" and reactive molecules, respectively, containing i deuterium atoms, their fractions being denoted by d_i and d_i^*; thus in addition and analogous to Eq. (1) we also have

$$\sum_{i=0}^{N} d_i^* = 1$$

If the fraction, ϵ, of molecules in the starred state is constant, $k_1 = k_{-1}\epsilon$ and the rate equations for the d_i^* and the d_i can be written as

$$\begin{aligned}(d/dt)d_i^* &= k_{-1}(d_i - d_i^*) \\ &\quad + [(N-i+1)/N]k_2 d^*_{i-1}s \\ &\quad -(i/N)k_2 d_i^* r - [(N-i)/N]k_2 d_i^* s \\ &\qquad + [(i+1)/N]k_2 d^*_{i+1} r \\ (d/dt)d_i &= -k_{-1}\epsilon(d_i - d_i^*) \end{aligned} \tag{41}$$

If we introduce $k_2/Nk_{-1} = \beta/N = \gamma$ and a new time-scale defined by $d\tau = k_1 dt = \epsilon k_{-1} dt$, $\tau = 0$ for $t = 0$, and we use the same matrix notation as in Section I [Eq. (10)], the Eqs. (41) become:

$$\begin{aligned}\epsilon(d/d\tau)\mathbf{d}^* &= \gamma\mathbf{F}\mathbf{d}^* + (\mathbf{d} - \mathbf{d}^*) \\ (d/d\tau)\mathbf{d} &= \mathbf{d}^* - \mathbf{d}\end{aligned} \tag{42}$$

The quantities $\mathbf{d}$ in Eq. (42) are observable, while the $\mathbf{d}^*$, which refer to a very small portion of the system ($\epsilon \ll 1$) are not. So we are interested in calculating the $\mathbf{d}$ only. As $\epsilon \ll 1$ it seems reasonable to neglect in (42) the one term containing ϵ. We can then eliminate $\mathbf{d}^*$ from the equations and solve for $\mathbf{d}$.

This approximation must be justified. It is not sufficient for ϵ to be small; we must also show the impossibility of very large $(d/d\tau)\mathbf{d}^*$, at least after a short period in the τ scale. This can indeed be proven. For the case that $s = 1$ the system (42) can be solved exactly and the consequences of the "steady state" approximation (Bodenstein) can be seen from the exact solution (*15*).

Thus, assuming $\epsilon(d/d\tau)\mathbf{d}^* = 0$, we add the second equation of (42), premultiplied by $\mathbf{I} - \gamma\mathbf{F}$, to the first equation, and find the equation for $\mathbf{d}$

$$(\mathbf{I} - \gamma\mathbf{F})(d/d\tau)\mathbf{d} = \gamma\mathbf{F}\mathbf{d} \tag{43}$$

where $\mathbf{I}$ denotes the unit matrix: $\mathbf{I}_{i,j} = 1$ for $i = j$ and $= 0$ for $i \neq j$.

Note that in the particular case $\gamma \ll 1 (k_{-1} \gg k_2)$ Eq. (43) reduces to

$$(d/d\tau)\mathbf{d} = \gamma\mathbf{F}\mathbf{d}$$

which has the same form as the Eq. (9) for the stepwise process.

Although Eqs. (43) are more complicated than Eqs. (9), the same method of solution can be applied. It is then again found that the most desirable transformation of variables, viz. that leading to a separate equation for each variable, is only possible when the isotopic purity, s, of the deuterating agent is constant during the reaction, whereas the $\mathbf{P}$ transformation as defined by (15) leads to a solution also for variable s. It turns out, however, that in the latter case the solution contains expressions that become virtually intractable for values of N higher than 3 or 4.

In our experimental work we have often made use of the formulas obtained for constant s. This requires, of course, that experimental conditions must be chosen so that s does not vary too much. In many cases this is quite feasible; sometimes it is really difficult, e.g., in exchange reactions on a solid catalyst.

We shall now first sketch the general solution, with time-dependent s (II,1.1), and then treat in some detail the case of constant s (II,1.2).

1.1. General Solution of the Rate Equations

Applying to Eq. (43) the transformation $\mathbf{d} = \mathbf{P}\mathbf{u}$, with $\mathbf{P}$ defined by (15), we obtain

$$(\mathbf{I} - \gamma\mathbf{G})(d/d\tau)\mathbf{u} = \gamma\mathbf{G}\mathbf{u} \tag{44}$$

which, as the matrix $\mathbf{G}$ is given by (22), can be written as

$$\begin{aligned}&(1 + i\gamma)(d/d\tau)u_i + i\gamma u_i \\ &= -\gamma(N - i + 1)s[(d/d\tau)u_{i-1} + u_{i-1}]\end{aligned} \tag{45}$$

Since $u_0 = \Sigma d_i = 1$, we obtain for $i = 1$

$$(1 + \gamma)(d/d\tau)u_1 + \gamma u_1 = -\gamma N s \tag{46}$$

As $u_1 = -N\sigma$ and (3) gives the relation between s and σ this equation can be integrated to yield expressions for s and σ

$$\begin{aligned}s - s(\infty) &= [s(0) - s(\infty)] \\ &\qquad \exp[-(1 + a)m_1\tau] \\ \sigma - \sigma(\infty) &= [\sigma(0) - \sigma(\infty)] \\ &\qquad \exp[-(1 + a)m_1\tau]\end{aligned} \tag{47}$$

where m_1 is defined by (58). It gives the average degree of deuteration as a function of τ.

If ϵ, k_1 and k_2 are constant, $m_1\tau$ is proportional to t and Eq. (47) represents the well-known rate law for exchange. It differs from the one for stepwise exchange [Eq. (28)] only by the factor m_1. It should be pointed out that for the present, multiple, case this simple result is only obtained after introducing the steady state approximation.

To obtain information on the distribution of deuterium over the various isotopic species, we can substitute the result for u_1 in the next equation of (45), ($i = 2$), which can then be integrated. In this way we proceed through the whole set of equations. From the set of solutions for u_i, the solution for d_i can be obtained.

There is no difficulty in carrying out this program, except that the explicit formulae for the solution become very involved, and cannot be presented in a surveyable form (neither for u_i nor for d_i).

1.2. The Solution for Constant s

The problem is considerably simplified when s is constant. Since in that case $a = 0$, Eq. (47) for the change of the average degree of deuteration σ reads

$$\sigma - \sigma(\infty) = [\sigma(o) - \sigma(\infty)] \exp(-m_1\tau) \tag{48}$$

In the case of constant s, complete separation of variables is possible by means of a new transformation. The procedure is demonstrated in Section II,1.2,a; the reader not interested in the derivation is referred to II,1.2,b, where we discuss the resulting solution.

***a.* Transformation and integration of the rate equations.** Returning to Eqs. (43) we can state our problem as follows. We wish to find a transformation

$$\mathbf{d} = \mathbf{R}\mathbf{v} \tag{49}$$

leading to

$$(\mathbf{I} - \gamma\mathbf{L})(d/d\tau)\mathbf{v} = \gamma\mathbf{L}\mathbf{v} \tag{50}$$

with

$$\mathbf{L} = \mathbf{R}^{-1}\mathbf{F}\mathbf{R} \tag{51}$$

where **L** has a diagonal form.

In order to express the latter requirement in terms of **R** we consider:

(a) The statement: "**L** has a diagonal form" is equivalent with "the columns of the unit matrix **I** are eigenvectors of **L**," with $\mathbf{L}_{j,j}$ as the eigenvalue corresponding to column j of **I** ($j = 0,1,\ldots,N$).

(b) The eigenvectors and eigenvalues have the following invariance property: If $\mathbf{d} = \mathbf{f}$ (which means, **f** considered as a particular vector of the **d** space) is an eigenvector of **F**, then the corresponding **g** of the **v** space, given by $\mathbf{f} = \mathbf{R}\mathbf{g}$, is an eigenvector of **L**, and conversely. This proposition is expressed by the equivalence of the equations $\mathbf{F}\mathbf{f} = \mathbf{f}\lambda$ and $\mathbf{L}\mathbf{g} = \mathbf{g}\lambda$, when $\mathbf{f} = \mathbf{R}\mathbf{g}$ (**R** is supposed to be nonsingular).

Combination of (a) and (b) leads to the conclusion that the necessary and sufficient condition for **L** to have a diagonal form is: Each column j of **R** is an eigenvector of **F** (the corresponding eigenvalue is $\mathbf{L}_{j,j}$). We can see this by observing that the vectors **g** mentioned in statement (b) are the columns of **I**, and their corresponding **f** are the columns of **R**.

In the actual calculation we prefer to proceed from equations (44) instead of (43), thus making use of the simplification obtained by the transformation $\mathbf{d} = \mathbf{P}\mathbf{u}$. We then apply the transformation $\mathbf{u} = \mathbf{Q}\mathbf{v}$ which has to give the matrix

$$\mathbf{L} = \mathbf{R}^{-1}\mathbf{F}\mathbf{R} = \mathbf{Q}^{-1}\mathbf{G}\mathbf{Q} \tag{51}$$

(where $\mathbf{R} = \mathbf{P}\mathbf{Q}$) its diagonal form.

We know that the columns of **Q** must be eigenvectors of **G**. We remark in advance that if they can be found they are not uniquely determined, since each of them may be multiplied freely by a constant number.

The eigenvalues of **G** are easily obtained: The determinant $(\mathbf{G} - \lambda\mathbf{I})$ consists of the diagonal term only, and we see that the roots of $\det(\mathbf{G} - \lambda\mathbf{I}) = 0$ are $\lambda = 0, -1, \ldots, -N$.

For finding the eigenvector **q** corresponding to the eigenvalue $-k (0 \leqq k \leqq N)$ we have to solve $\mathbf{G}\mathbf{q} = -\mathbf{q}k$, which in terms of the components q_j can be written: $(k - j)q_j = (N - j + 1)sq_{j-1}$ with $j = 0,1,\ldots,N$. For $j = k$ we find $q_{j-1} = 0$ and consequently all components with $j < k$ are zero.

Now we may *choose* q_k. Taking $q_k = 1$ we find

$$q_j = \binom{N-k}{j-k}(-s)^{j-k}$$

This $\mathbf{q}$ becomes column k in the matrix $\mathbf{Q}$, so we have

$$Q_{j,k} = \binom{N-k}{j-k}(-s)^{j-k} \tag{52}$$

For further calculations we express (52) in the form of a characterizing relation

$$(1, x, \ldots, x^N)\mathbf{Q}\mathbf{e}_j = x^j(1 - sx)^{N-j} \tag{53}$$

We also need the inverse, $\mathbf{Q}^{-1}$, of $\mathbf{Q}$. A characterizing relation is obtained from (53) if we take $x/(1 - sx) = y$ or $x = y/(1 + sy)$ and then write (53) in terms of y

$$(1, y, \ldots, y^N)\mathbf{Q}^{-1}\mathbf{e}_j = y^j(1 + sy)^{N-j} \tag{54}$$

Now the transformations $\mathbf{d} = \mathbf{Pu}$, $\mathbf{u} = \mathbf{Qv}$ result in $\mathbf{d} = \mathbf{Rv}$, with $\mathbf{R} = \mathbf{PQ}$ and $\mathbf{R}^{-1} = \mathbf{Q}^{-1}\mathbf{P}^{-1}$.

Combining this with the characterizing relations for $\mathbf{P}$ and $\mathbf{Q}$ and their inverses we find $\mathbf{R}$ and $\mathbf{R}^{-1}$ to be characterized by:

$$(1, x, \ldots, x^N)\mathbf{R}\mathbf{e}_j = (1 - x)^j(r + sx)^{N-j} \tag{55}$$

$$(1, y, \ldots, y^N)\mathbf{R}^{-1}\mathbf{e}_j = (1 - ry)^j(1 + sy)^{N-j} \tag{56}$$

We have now carried out the program described by (49), (50), and (51) and $\mathbf{L}$ has the diagonal form. We also know the diagonal elements. Since according to (51) $\mathbf{L} = \mathbf{Q}^{-1}\mathbf{GQ}$ and $\mathbf{Q}$ satisfies the relation

$$\mathbf{GQe}_j = -\mathbf{Qe}_j \cdot j$$

we can write

$$\begin{aligned} L_{i,j} = \mathbf{e}'_i\mathbf{L}\mathbf{e}_j &= \mathbf{e}'_i\mathbf{Q}^{-1}\mathbf{GQ}\mathbf{e}_j \\ &= -\mathbf{e}'_i\mathbf{Q}^{-1}\mathbf{Q}\mathbf{e}_j \cdot j = -\mathbf{e}'_i\mathbf{e}_j \cdot j \end{aligned}$$

(the prime denotes transposition, i.e. interchange of rows with columns), or

$$L_{i,j} = -jI_{i,j} \tag{57}$$

We can now write the equations of (50) separately:

$$(1 + i\gamma)(d/d\tau)v_i = -i\gamma v_i$$

or, with

$$\begin{aligned} m_i &= i\gamma/(1 + i\gamma) \\ (d/d\tau)v_i &= -m_i v_i \end{aligned} \tag{58}$$

The solution is:

$$v_i(\tau)/v_i(0) = \exp(-m_i\tau)$$

or, in more condensed form:

$$\mathbf{v}(\tau) = \mathbf{M}(\tau)\mathbf{v}(\mathrm{o}) \tag{59}$$

where $\mathbf{M}(\tau)$ is the matrix defined by:

$$M_{i,j}(\tau) = \begin{cases} \exp(-m_i\tau) & \text{for } j = i \\ 0 & \text{for } j \neq i \end{cases} \tag{60}$$

The solution in terms of $\mathbf{u}$ is obtained from (59) by using $\mathbf{v} = \mathbf{Q}^{-1}\mathbf{u}$, which leads to

$$\mathbf{u} = \mathbf{QMQ}^{-1}\mathbf{u}(\mathrm{o}) \tag{61}$$

***b.* Solution for arbitrary initial conditions.** The expression for $\mathbf{d}$ as a function of its initial values, $\mathbf{d}(\mathrm{o})$, and of the time, τ, is easily obtained from Eqs. (59), using $\mathbf{v} = \mathbf{R}^{-1}\mathbf{d}$

$$\mathbf{d} = \mathbf{RMR}^{-1}\mathbf{d}(\mathrm{o}) \tag{62}$$

where the matrices $\mathbf{R}$, $\mathbf{R}^{-1}$, and $\mathbf{M}$ are defined by Eqs. (55), (56), and (60), respectively.

It is possible to write the solution in a form which differs from (62) in that it uses only one matrix, $\mathbf{A}$, instead of $\mathbf{R}$ and $\mathbf{R}^{-1}$

$$\mathbf{d} = r^{-N}\mathbf{AMAd}(\mathrm{o}) \tag{63}$$

A proof of the equivalence of Eqs. (62) and (63), and simple rules for the construction of matrices $\mathbf{R}$, $\mathbf{R}^{-1}$, and $\mathbf{A}$ are given in the Appendix.

***c.* Solution for special initial conditions.** In many cases we have special initial conditions, which lead to a considerable simplification of Eqs. (62) and (63). This holds notably for the frequently occurring case that we start the reaction with undeuterated compound: $d_0(\mathrm{o}) = 1$ or, in vector formulation: $\mathbf{d}(\mathrm{o}) = \mathbf{e}_0$.

From (56) we obtain:

$$(1, y, \ldots, y^N)\mathbf{R}^{-1}\mathbf{e}_0 = (1 + sy)^N$$

and from (55), using $y = 1 - x$

$$(1,x,\ldots,x^N)\mathbf{RM}(\mathbf{R}^{-1}\mathbf{e}_0) = \sum_j y^j(1-sy)^{N-j}M_{j,j}\binom{N}{j}s^j$$

Since

$$y^j(1-sy)^{N-j} = \sum_k (-1)^k s^k\binom{N-j}{k}y^{j+k} = \sum_k (-1)^k\binom{N-j}{k}s^k(1-x)^{j+k}$$

$$(1,x,\ldots,x^N)\mathbf{RM}(\mathbf{R}^{-1}\mathbf{e}_0) = \sum_j M_{j,j}\binom{N}{j}s^j\sum_k(-1)^k\binom{N-j}{k}s^k \sum_i(-1)^i\binom{k+j}{i}x^i$$

$$= \sum_j M_{j,j}\binom{N}{j}\sum_{k,i}(-1)^{i+k}\binom{N-j}{k}\binom{k+j}{i}s^{k+j}x^i$$

$$= \sum_j M_{j,j}\binom{N}{j}\sum_{h,i}(-1)^{i+h+j}\binom{N-j}{h-j}\binom{h}{i}s^h x^i$$

when we introduce $h = k + j$. The coefficient of x^i in this expression gives d_i, so

$$d_i = \binom{N}{i}\sum_j M_{j,j}\sum_h(-1)^{i+j+h}\binom{N-i}{N-h}\binom{h}{j}s^h \qquad (64)$$

2. *Transition Probabilities*

A different approach to the problem, which only applies when $s = 1$ and $d_0(0) = 1$, can be based on the calculus of probabilities. Of course, this method gives nothing new, but it has some merit since it deals only with the d_i and in all its stages seems more closely related to the chemical processes taking place than the solving of differential equations with its change of variables. For example, the exponents in the solution will prove to be closely connected with certain transition probabilities.

For reasons of simplicity we shall discuss a molecule containing four exchangeable hydrogen atoms, reacting according to the mechanism shown in Section II,1; extension to the case of N exchangeable atoms and to other mechanisms is fairly obvious.

Consider an undeuterated molecule in the starred state. It can undergo exchange or return to the normal state, the ratio of the chances of the two processes being equal to β.

In scheme (65) the sum of the two probabilities has been taken to be equal to 1, which means that no molecule can remain

$$\begin{tikzcd} \mathrm{D}_0^* \arrow[r, "\beta/1+\beta"] \arrow[d, "1/1+\beta"] & \mathrm{D}_1^* \\ \mathrm{D}_0 & \end{tikzcd} \qquad (65)$$

in the starred state indefinitely. This seems to be the equivalent of the steady state approximation in the solving of the differential equations: If the molecules in the starred state form a very small part of the total, a measurable quantity of reaction products is only obtained if the population of the starred state is renewed a great many times.

When $i \neq 0$ we have to take into account that the exchange reaction of D_i^* leads to the formation of D^*_{i+1} only in $4 - i$ cases out of 4; there is a chance $\frac{1}{4}i$ that D is exchanged for D and so a fraction $\frac{1}{4}i[\beta/(1+\beta)]$ of the D_i^* molecules remains unaltered. This fraction has again a chance $1/(1+\beta)$ to become a normal molecule D_i, a chance $\frac{1}{4}(4-i)[\beta/(1+\beta)]$ to become D^*_{i+1} and a chance $\frac{1}{4}i[\beta/(1+\beta)]$ to remain D_i^*.

Repeating this process one easily calculates that a fraction 1 of D_i^* gives ultimately a fraction

$$\frac{1}{1+\beta}+\frac{i}{4}\frac{\beta}{1+\beta}\frac{1}{1+\beta}+\left(\frac{i}{4}\frac{\beta}{1+\beta}\right)^2\frac{1}{1+\beta}+\cdots\cdots = \frac{4}{4+(4-i)\beta}$$

of D_i and a fraction $(4-i)\beta/[4+(4-i)\beta]$ of D^*_{i+1}.

Thus we obtain the following scheme of transition probabilities:

$$\begin{tikzcd}
D_0^* \arrow[r, "\frac{4\beta}{4+4\beta}"] \arrow[d, "\frac{4}{4+4\beta}"'] & D_1^* \arrow[r, "\frac{3\beta}{4+3\beta}"] \arrow[d, "\frac{4}{4+3\beta}"'] & D_2^* \arrow[r, "\frac{2\beta}{4+2\beta}"] \arrow[d, "\frac{4}{4+2\beta}"'] & D_3^* \arrow[r, "\frac{\beta}{4+\beta}"] \arrow[d, "\frac{4}{4+\beta}"'] & D_4^* \arrow[d, "1"] \\
D_0 & D_1 & D_2 & D_3 & D_4
\end{tikzcd} \qquad (66)$$

Using this scheme we can calculate the probability, p_{ji}, that D_i is obtained from D_j^* ($i \geqq j$) by multiplying the probabilities along the reaction path

$$p_{ji} = \frac{4}{4 + (4 - i)\beta} \prod_{k=4-i}^{4-j} \frac{k\beta}{4 + k\beta} \qquad (67)$$

If we start the reaction with only D_0^*, the fractions of reaction products are given by the p_{0i}

$$\begin{aligned}
d_0 &= \frac{4}{4 + 4\beta} \\
d_1 &= \frac{16\beta}{(4 + 4\beta)(4 + 3\beta)} \\
d_2 &= \frac{48\beta^2}{(4 + 4\beta)(4 + 3\beta)(4 + 2\beta)} \\
d_3 &= \frac{96\beta^3}{(4 + 4\beta)(4 + 3\beta)(4 + 2\beta)(4 + \beta)} \\
d_4 &= \frac{24\beta^4}{(4 + 4\beta)(4 + 3\beta)(4 + 2\beta)(4 + \beta)}
\end{aligned} \qquad (68)$$

Similar results have been derived earlier, in a somewhat different way, by Anderson and Kemball (*16*). They used the formulas to discuss the composition of the initial products of certain exchange reactions.

Equation (*68*) gives us the distribution of deuterium among the molecules that have reacted once (to react means to pass from normal to starred state, followed by possible H–D exchange and return to the normal state). To obtain the isotope distribution over the molecules that have reacted twice, we calculate with (67) the reaction products of a mixture of D_j^* ($j = 0,1, \ldots, 4$), having the composition given by (68). By repeating the calculation we determine the isotope distribution, d_i^m, for the molecules that have reacted m times ($i = 0,1, \ldots, 4$).

Now we calculate the fractions, Φ_m, of the molecules which have reacted m times. Suppose that in a time Δt a fraction $k_1\Delta t$ reacts and a fraction $1 - k_1\Delta t$ does not react. Then, in a time $n\Delta t$, we have fractions, Φ_m, which have reacted m times ($m = 0,1, \ldots, n$), given by

$$\Phi_m = \binom{n}{m} (k_1\Delta t)^m (1 - k_1\Delta t)^{n-m}$$

By multiplying the d_i^m by the corresponding Φ_m, summation over m and taking the limiting value for $\Delta t \to 0$ we obtain the d_i as a function of time.

The result (of the lengthy calculation) is

$$\begin{aligned}
d_0 &= [1 \left[\exp\left(-\frac{4\beta}{4 + 4\beta} k_1 t\right)\right] \\
d_1 &= 4 \left[-\exp\left(-\frac{4\beta}{4 + 4\beta} k_1 t\right) + \exp\left(-\frac{3\beta}{4 + 3\beta} k_1 t\right)\right] \\
d_2 &= 6 \left[\exp\left(-\frac{4\beta}{4 + 4\beta} k_1 t\right) - 2\exp\left(-\frac{3\beta}{4 + 3\beta} k_1 t\right) + \exp\left(-\frac{2\beta}{4 + 2\beta} k_1 t\right)\right] \\
d_3 &= 4 \left[-\exp\left(-\frac{4\beta}{4 + 4\beta} k_1 t\right) + 3\exp\left(-\frac{3\beta}{4 + 3\beta} k_1 t\right) - 3\exp\left(-\frac{2\beta}{4 + 2\beta} k_1 t\right) + \exp\left(-\frac{\beta}{4 + \beta} k_1 t\right)\right] \\
d_4 &= 1 \left[\exp\left(-\frac{4\beta}{4 + 4\beta} k_1 t\right) - 4\exp\left(-\frac{3\beta}{4 + 3\beta} k_1 t\right) + 6\exp\left(-\frac{2\beta}{4 + 2\beta} k_1 t\right) - 4\exp\left(-\frac{\beta}{4 + \beta} k_1 t\right) + 1\right]
\end{aligned} \qquad (69)$$

or, in general formulation:

$$d_i = \binom{4}{i} \sum_{j=0}^{i} (-1)^{i+j} \binom{i}{j} \exp\left(-\frac{(4-j)\beta}{4+(4-j)\beta} k_1 t\right)$$

The expressions are identical with the solution of the differential equations (64) if we substitute in the latter $s = 1$ and $N = 4$.

On comparing the expressions (69) with the scheme of transition probabilities (66) we observe that the exponents of the new exponential terms appearing in the equations are equal to $-q_i k_1 t$, where $1 - q_i$ is the chance that, when D_i reacts, D_i is formed again.

3. *Discussion*

In this section (II) a multiple exchange process was considered. The molecules in the "privileged" state contained, like the normal molecules, N equivalent exchangeable hydrogen atoms. Isotope effects were ignored. Provided the steady state approximation is introduced, the general case can be solved. The average degree of deuteration changes exponentially [Eq. (47)]. The expressions for the individual d_i are obtained in a surveyable form only when s is constant, i.e. for an infinite reservoir of deuterating reagent. For arbitrary initial conditions, the d_i as a function of time is given by Eq. (62) or (63).

For the frequently occurring case that $d_0(\mathrm{o}) = 1$, the time-dependence of the fractions of various isotopic species is given by Eq. (64). By means of Eq. (48), τ can be eliminated from Eq. (64) and, recalling that $\sigma(\mathrm{o}) = 0$ and s is constant, one obtains

$$d_i = \binom{N}{i} \sum_j \left(1 - \frac{\sigma}{s}\right)^{j(N+\beta)/(N+j\beta)} \sum_h (-1)^{i+j+h} \binom{N-i}{N-h} \binom{h}{j} s^h \qquad (70)$$

This equation shows how the distribution is determined by two parameters: the average degree of deuteration σ, and β, which is a ratio of rate constants. A least-squares calculation will give values for these two parameters. The time-dependence of σ wil yield a rate constant.

Two extreme values for β can be considered. If $\beta \rightarrow 0$, it can be shown that Eq. (70) reduces to the binomial distribution [Eq. (39)]. This result is expected from the definition of stepwise exchange and the meaning of β. If $\beta \rightarrow \infty$, Eq. (70) transforms into

$$\begin{aligned} d_0 &= (\sigma/s)(1-s)^N + [1 - (\sigma/s)] \\ d_{i(\neq 0)} &= \frac{\sigma}{s}\binom{N}{i} s^i (1-s)^{N-i} \end{aligned} \qquad (71)$$

This result expresses what one intuitively (*17*) expects for this case: A fraction $[1 - (\sigma/s)]$ has not reacted (d_0), and the fraction σ/s that has reacted shows a binomial distribution with an average degree of deuteration s, the isotopic purity of the deuterating agent.

The present result [Eq. (70)] enables one to find β, which provides information about the reactivity of the "privileged" molecules. Presumably, most reliable data for β in a multiple exchange process will be obtained when one is sufficiently far removed from the two extremes.

III. Isotope Distribution for Various Mechanisms of the Multiple Exchange Reaction

The discussion of the multiple exchange process in Section II has been limited to one particular model for the starred state. The question arises whether a different model for the starred state leads to the same formulae for the isotope distribution. If it does, an experimental distribution will only give a value for β, i.e. the reactivity of the starred state. If it does not, it is possible to get additional information about the nature of the starred state.

That the second supposition holds is readily seen by considering limiting cases. Take, e.g., $s = 1$ and $\beta = 0$. The reaction treated in Section II will then lead to a binomial distribution of deuterium. In the case, however, that the starred state is formed from the normal molecule by loss of two hydrogen atoms (dissociative adsorption) which are replaced by deuterium from the catalyst when the molecule returns to the normal state, the first product formed will be D_2 and D_1 will never be formed. Hence, the distribution cannot be binomial and β, if not equal to zero, must occur in the formulas in a different way.

We shall discuss the results obtained for various models. They apply to the case that $N = 4$. In picturing the starred state we shall make use of ethylene as adsorbed on a solid surface. Not only is this a case actually investigated *(14)*, but ethylene has the additional advantage that unsymmetrical starred states can be visualized. Whether every model is physically meaningful is immaterial.

The results reported in Table 1 were without exception arrived at in two ways, viz. by solving the differential equations (II,1) and by calculus of probabilities (II,2).

Since in most cases minor or greater complications arise which necessitate the introduction of extra variables, the method for one mechanism (K) is explicitly given in Section III,2 to illustrate how such problems are solved.

The reader not interested in the integration procedures might nevertheless wish to find the solution for other mechanisms than those discussed here. He is referred to Section III,3, where we describe a simple procedure for obtaining the solution for any mechanism of the exchange reaction. As for all results in this section, the procedure is valid only for the case that s is constant and the hydrocarbon is undeuterated in the initial state.

1. *Results*

We have found that complete information on the mechanism of the exchange reaction will be contained in the expressions for the q_i as defined in Section II,2. In other words only the exponential terms in the expressions for the d_i [Eqs. (69)] depend upon the mechanism; the coefficients are the same for all mechanisms. It follows that the isotope distribution is completely given by the expression for d_4.

As argued in Section II,3 we prefer to write this equation in a slightly different form by eliminating the time t from it by means of*

$$p = 1 - \sigma = 1 - \frac{1}{4}\sum_{i=1}^{4} id_i = \exp\left(-\frac{\beta}{4+\beta}k_1t\right) \quad (72)$$

The expression for d_4 in (69) then becomes

$$d_4 = p^{4[(4+\beta)/(4+4\beta)]} - 4p^{3[(4+\beta)/(4+3\beta)]} + 6p^{2[(4+\beta)/(4+2\beta)]} - 4p + 1 \quad (73)$$

The table shows these expressions for a number of mechanisms, together with the formula for p [in the form of $(-1/k_1t)\ln p$] and the reaction products in extreme cases ($\beta = 0$ and $\beta = \infty$).

The following mechanisms have been considered.

A. The molecule is adsorbed as such (e.g. as a π complex); the molecule in the starred state contains four equivalent hydrogen atoms. This is the model discussed in Section II. The distribution for $\beta = 0$ is called "apparently binomial" since for $\beta \to 0$, $p \to 1$ which means that no deuteration occurs.

B. The molecule is adsorbed with loss of one hydrogen atom; on desorption a hydrogen atom from the deuterating agent is added. The three hydrogen atoms in the starred species are equivalent. The isotope distribution is identical with that of case A, as can be verified by substituting $\beta_B = \frac{3}{4}\beta_A$. Note that for $\beta = 0$ the binomial distribution now has a physical meaning.

C. The molecule is adsorbed with loss of two hydrogen atoms; on desorption two hydrogen atoms from the deuterating agent are added. The two hydrogen atoms in the starred species are equivalent.

D. The molecule is adsorbed with loss of three hydrogen atoms; on desorption three hydrogen atoms of the deuterating agent are added.

E. The adsorption takes place through one hydrogen atom, which is not exchanged.

F. On adsorption a hydrogen atom from the deuterating agent is added to the molecule. The starred species (ethyl) has five equivalent exchangeable hydrogen atoms, one of which is lost on desorption. The distribution is identical with that of case A when we substitute $\beta_F = \frac{5}{4}\beta_A$.

G. The molecule is adsorbed in an asym-

---

* We use p here for $1 - \sigma$ and not ρ since in the case that $s \neq 1$ the expression becomes: $p = 1 - (\sigma/s)$.

TABLE 1

ISOTOPE DISTRIBUTION FOR VARIOUS REACTION MECHANISMS, FOR $s = 1$

Mechanism	d_4	$-\frac{1}{k_1 t}\ln p$	Reaction products when $\beta = \infty$	Distribution when $\beta = 0$
A	$p^{4\frac{(4+\beta)}{(4+4\beta)}} - 4p^{3\frac{(4+\beta)}{(4+3\beta)}} + 6p^{2\frac{(4+\beta)}{(4+2\beta)}} - 4p + 1$	$\frac{\beta}{4+\beta}$	D_0, D_4	Apparently binomial
B	$p^{4\frac{(3+\beta)}{(3+4\beta)}} - 4p^{3\frac{(3+\beta)}{(3+3\beta)}} + 6p^{2\frac{(3+\beta)}{(3+2\beta)}} - 4p + 1$	$\frac{3+4\beta}{4(3+\beta)}$	D_0, D_4	Binomial
C	$p^{\frac{(2+\beta)}{(1+\beta)}} - 4p^{\frac{(2+\beta)}{(1+\beta)}} + 6p^{\frac{(2+\beta)(5/6+\beta)}{(1+\beta)(1+\beta)}} - 4p + 1$	$\frac{1+\beta}{2+\beta}$	D_0, D_4	Nonbinomial
D	$p^{4\frac{(1+\beta)}{(3+4\beta)}} - 4p^{4\frac{(1+\beta)}{(3+4\beta)}} + 6p^{4\frac{(1+\beta)}{(3+4\beta)}} - 4p + 1$	$\frac{3+4\beta}{4(1+\beta)}$	D_0, D_4	Nonbinomial
E	$p^{\frac{4(3+\beta)}{3(1+\beta)}} - 4p^{\frac{(3+\beta)(9+8\beta)}{3(3+2\beta)(1+\beta)}} + 6p^{\frac{2(9+4\beta)}{3(3+2\beta)}} - 4p + 1$	$\frac{3\beta}{4(1+\beta)}$	D_0, D_3, D_4	Apparently binomial
F	$p^{4\frac{(5+\beta)}{(5+4\beta)}} - 4p^{3\frac{(5+\beta)}{(5+3\beta)}} + 6p^{2\frac{(5+\beta)}{(5+2\beta)}} - 4p + 1$	$\frac{1+\beta}{5+\beta}$	D_0, D_4	Binomial
G	$p^{\frac{(4+2\beta)}{(1+\beta)}} - 4p^{\frac{(3+2\beta)}{(1+\beta)}} + 6\left(\frac{1}{3}p^{\frac{(2+\beta)}{(1+\beta)}} + \frac{2}{3}p^2\right) - 4p + 1$	$\frac{\beta}{2(2+\beta)}$	D_0, D_2, D_4	Binomial
H	$p^{4\frac{(3+\beta)}{(3+2\beta)}} - 4p^{\frac{(9+4\beta)}{(3+2\beta)}} + 6\left(\frac{1}{3}p^{2\frac{(3+\beta)}{(3+2\beta)}} + \frac{2}{3}p^2\right) - 4p + 1$	$\frac{1+\beta}{2(3+\beta)}$	D_0, D_2, D_4	Binomial
K	$p^{\frac{(2+\beta)}{(1+\beta)}} - 4p^{\frac{(2+\beta)}{(1+\beta)}} + 6\left(\frac{1}{3}p^{\frac{(2+\beta)(1+2\beta)}{2(1+\beta)(1+\beta)}} + \frac{2}{3}p^{\frac{(2+\beta)}{(1+\beta)}}\right) - 4p + 1$	$\frac{1+\beta}{2+\beta}$	D_0, D_4	d_0, d_2, d_4

metric manner, viz. by formation of a bond at one of the carbon atoms, with only the two hydrogen atoms of one of the CH_2 groups exchangeable. One may suspect that this mechanism can be described by saying that two groups of two hydrogen atoms each independently react according to mechanism A. For each group the deuterium distribution would be given by (cf. A)

$$\Delta_0 = p^{(2+\beta)/(1+\beta)};$$
$$\Delta_1 = 2(-p^{(2+\beta)/(1+\beta)} + p);$$
$$\Delta_2 = p^{(2+\beta)/(1+\beta)} - 2p + 1$$

By means of the relations: $d_0 = \Delta_0^2$; $d_1 = 2\Delta_0\Delta_1$; $d_2 = \Delta_1^2 + 2\Delta_0\Delta_2$; $d_3 = 2\Delta_1\Delta_2$; $d_4 = \Delta_2^2$, the distribution over the whole molecule can be calculated. As expected, the formula given in Table 1 is obtained.

H. On adsorption a hydrogen atom from the deuterating agent is added to the molecule. Contrary to case F, now only the three hydrogen atoms of the methyl group are exchangeable. One of these is lost on desorption. In analogy with the relation of case G to A, the present case can be considered as consisting of two groups of two hydrogen atoms each, which react according to F.

K. The molecule is adsorbed with loss of two *cis* hydrogen atoms. The remaining two atoms are exchangeable. Desorption occurs by *cis* addition of two hydrogen atoms of the deuterating agent.

Some remarks may be added. In cases C, D, and K some of the exponential terms are equal and could have been taken together. This has not been done in order to preserve the regularity of the coefficient matrix.

The results in Table 1 hold for $s = 1$. For $s \neq 1$ the coefficient matrix is

for

$$\begin{array}{llllll}
d_0 & s^4 & 4s^3 - 4s^4 & 6s^2 - 12s^3 + 6s^4 & 4s - 12s^2 + 12s^3 - 4s^4 & 1 - 4s + 6s^2 - 4s^3 + s^4 \\
d_1 & -4s^4 & -12s^3 + 16s^4 & -12s^2 + 36s^3 - 24s^4 & -4s + 24s^2 - 36s^3 + 16s^4 & 4s - 12s^2 + 12s^3 - 4s^4 \\
d_2 & 6s^4 & 12s^3 - 24s^4 & 6s^2 - 36s^3 + 36s^4 & -12s^2 + 36s^3 - 24s^4 & 6s^2 - 12s^3 + 6s^4 \\
d_3 & -4s^4 & -4s^3 + 16s^4 & 12s^3 - 24s^4 & -12s^3 + 16s^4 & 4s^3 - 4s^4 \\
d_4 & s^4 & -4s^4 & 6s^4 & -4s^4 & +s^4
\end{array} \qquad (74)$$

It is easily seen that for $s = 1$ the coefficient matrix of (69) is obtained.

2. Solution for Mechanism K

We shall now derive the solution for mechanism K, first for $s = 1$ by means of the procedure of Section II,2, then for s = constant, by solving the differential equations.

The complication in mechanism K is the behavior of the D_2 molecules in the reaction. On the one hand, we have *cis*-1,2-dideuteroethylene D_{2a} which loses either 0 or 2 D atoms on adsorption; on the other hand, 1,1-dideuteroethylene and *trans*-1,2-dideuteroethylene (taken together as D_{2b}) always lose one deuterium atom on adsorption.

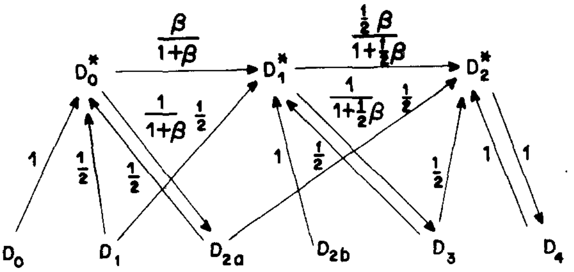
2.1. Solution from Transition Probabilities

The scheme (75) shows the reaction probabilities of each of the species present, in the case that $s = 1$. Note that when $s = 1$ D_1 and D_{2b} will never be formed.

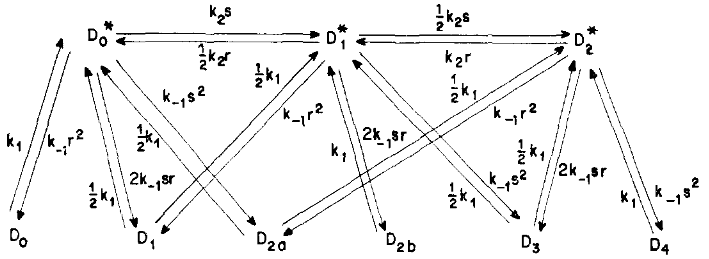
By using the procedure outlined in II,2 we obtain the following solution

$$\begin{aligned}
d_0 &= p^{(2+\beta)/(1+\beta)} \\
d_1 &= 0 \\
d_{2a} &= -2p^{(2+\beta)/(1+\beta)} \\
&\qquad + 2p^{(2+\beta)(1+2\beta)/2(1+\beta)(1+\beta)} \\
d_{2b} &= 0 \qquad\qquad (76) \\
d_3 &= -4p^{(2+\beta)(1+2\beta)/2(1+\beta)(1+\beta)} + 4p \\
d_4 &= p^{(2+\beta)/(1+\beta)} + 2p^{(2+\beta)(1+2\beta)/2(1+\beta)(1+\beta)} \\
&\qquad - 4p + 1
\end{aligned}$$

where $p = 1 - \sigma = \exp[-(1 + \beta)/(2 + \beta)] k_1 t.$



(75)



(77)

2.2. *Solution of the Rate Equations*

The rate equations can be written down from the scheme (77) in the following way, if we apply the usual substitutions:

$$
\begin{aligned}
d\tau &= k_{-1}\epsilon dt\\
k_{-1}\epsilon &= k_1\\
k_2/k_{-1} &= \beta
\end{aligned}
$$

They read as follows:

$$
\begin{aligned}
(d/d\tau)d_0 &= -d_0 + r^2d_0^*\\
(d/d\tau)d_1 &= -d_1 + 2srd_0^* + r^2d_1^*\\
(d/d\tau)d_{2a} &= -d_{2a} + s^2d_0^* + r^2d_2^*\\
(d/d\tau)d_{2b} &= -d_{2b} + 2srd_1^*\\
(d/d\tau)d_3 &= -d_3 + s^2d_1^* + 2srd_2^*\\
(d/d\tau)d_4 &= -d_4 + s^2d_2^*\\
\epsilon(d/d\tau)d_0^* &= d_0 + \tfrac{1}{2}d_1 + \tfrac{1}{2}d_{2a} - d_0^*\\
&\quad + \beta(-sd_0^* + \tfrac{1}{2}rd_1^*)\\
\epsilon(d/d\tau)d_1^* &= \tfrac{1}{2}d_1 + d_{2b} + \tfrac{1}{2}d_3 - d_1^*\\
&\quad + \beta(sd_0^* - \tfrac{1}{2}d_1^* + rd_2^*)\\
\epsilon(d/d\tau)d_2^* &= \tfrac{1}{2}d_{2a} + \tfrac{1}{2}d_3 + d_4 - d_2^*\\
&\quad + \beta(\tfrac{1}{2}sd_1^* - rd_2^*) \qquad (78)
\end{aligned}
$$

We now introduce new variables in the usual way:

$$
\begin{aligned}
u_0 &= d_0 + d_1 + d_2 + d_3 + d_4 = 1\\
u_1 &= \quad - d_1 - 2d_2 - 3d_3 - 4d_4\\
u_2 &= \quad d_2 + 3d_3 + 6d_4\\
u_3 &= \quad - d_3 - 4d_4\\
u_4 &= \quad d_4
\end{aligned}
$$

and

$$
\begin{aligned}
u_0^* &= d_0^* + d_1^* + d_2^* = 1\\
u_1^* &= \quad - d_1^* - 2d_2^*\\
u_2^* &= \quad d_2^*
\end{aligned}
$$

If we now try to obtain expressions for the $(d/d\tau)u_i$ and $(d/d\tau)u_i^*$, by suitable combination of the **d** and **d*** equations, we find that not all the d_i can be eliminated. This is to be expected since, having five independent d_i, we also want five variables u_i for a complete description of the system. We have some freedom in choosing this new variable, u, but care must be taken that d_{2a} and d_{2b} have different coefficients in u (u should tell us something new about the composition of d_2). We may, e.g. simply take $u = d_{2a}$. A choice which follows naturally from the process of transforming the **d** equations, is $u = d_{2a} + d_3 + 2d_4$ [it can for example be seen that $\tfrac{1}{2}u$ occurs in the right-hand side of the equation for d_2^* in (78)].

We can now obtain the following complete system of equations

$$
\begin{aligned}
(d/d\tau)u_0 + u_0 &= u_0^*\\
(d/d\tau)u_1 + u_1 &= -2su_0^* + u_1^*\\
(d/d\tau)u_2 + u_2 &= s^2u_0^* - 2su_1^* + u_2^*
\end{aligned}
$$

$$
\begin{aligned}
(d/d\tau)u_3 + u_3 &= && s^2u_1{}^* - 2su_2{}^* \\
(d/d\tau)u_4 + u_4 &= && s^2u_2{}^* \\
(d/d\tau)u + u &= s^2u_0 && + u_2{}^* \\
\epsilon(d/d\tau)u_0{}^* &= u_0 - u_0{}^* = 0 \\
\epsilon(d/d\tau)u_1{}^* &= \tfrac{1}{2}u_1 - \beta su_0{}^* - (1 + \tfrac{1}{2}\beta)u_1{}^* \\
\epsilon(d/d\tau)u_2{}^* &= \tfrac{1}{2}u - \tfrac{1}{2}\beta su_1{}^* - (1 + \beta)u_2{}^*
\end{aligned}
\tag{79}
$$

By making the approximation $\epsilon(d/d\tau)u_i{}^* = 0$ we can express the $u_i{}^*$ in the u_i and substitute the result in the **u** equations of (79). These can now be integrated in the order $u_0, u_1, u, u_2, u_3, u_4$; $u_0 = 1$ is already known; the equation for u_1 contains only u_1, after substitution of $u_0{}^*$ and $u_1{}^*$, and can be integrated. The u equation can now be integrated, since $u_1{}^*$ is a known function of time, etc.

The result of the integration is:

$$
\begin{aligned}
u_0 &= 1 \\
u_1 &= -4s\left[1 - \exp\left(-\frac{1+\beta}{2+\beta}\tau\right)\right] \\
u_2 &= 6s^2\left\{1 - 2\exp\left(-\frac{1+\beta}{2+\beta}\tau\right) + \frac{1}{3}\exp\left[-\frac{1+2\beta}{2(1+\beta)}\tau\right] + \frac{2}{3}\exp(-\tau)\right\} \\
u_3 &= -4s^3\left\{1 - 3\exp\left(-\frac{1+\beta}{2+\beta}\tau\right) + \exp\left[-\frac{1+2\beta}{2(1+\beta)}\tau\right] + \exp(-\tau)\right\} \\
u_4 &= s^4\left\{1 - 4\exp\left(-\frac{1+\beta}{2+\beta}\tau\right) + 2\exp\left[-\frac{1+2\beta}{2(1+\beta)}\tau\right] + \exp(-\tau)\right\} \\
u &= s^2\left\{1 - 2\exp\left(-\frac{1+\beta}{2+\beta}\tau\right) + \exp\left[-\frac{1+2\beta}{2(1+\beta)}\tau\right]\right\}
\end{aligned}
\tag{80}
$$

From the equations defining u and the u_i we can calculate the d_i. If we introduce $p = 1 - (\sigma/s) = \exp[-\{(1+\beta)/(2+\beta)\}k_1t]$ we obtain:

$$
\begin{aligned}
d_0 &= (4s^2 - 4s^3 + s^4)p^{\frac{2+\beta}{1+\beta}} + (2s^2 - 4s^3 + 2s^4)p^{\frac{(2+\beta)(1+2\beta)}{2(1+\beta)(1+\beta)}} \\
&\quad + (4s - 12s^2 + 12s^3 - 4s^4)p + (1 - 4s + 6s^2 - 4s^3 + s^4) \\
d_1 &= 4s\left[(-2s + 3s^2 - s^3)p^{\frac{2+\beta}{1+\beta}} + (-s + 3s^2 - 2s^3)p^{\frac{(2+\beta)(1+2\beta)}{2(1+\beta)(1+\beta)}}\right. \\
&\quad \left. + (-1 + 6s - 9s^2 + 4s^3)p + (1 - 3s + 3s^2 - s^3)\right] \\
d_2 &= 6s^2\left[(\tfrac{2}{3} - 2s + s^2)p^{\frac{2+\beta}{1+\beta}} + (\tfrac{1}{3} - 2s + 2s^2)\,p^{\frac{(2+\beta)(1+2\beta)}{2(1+\beta)(1+\beta)}}\right. \\
&\quad \left. + (-2 + 6s - 4s^2)p + (1 - 2s + s^2)\right] \\
d_{2a} &= 6s^2\left[(-\tfrac{2}{3}s + \tfrac{1}{3}s^2)p^{\frac{2+\beta}{1+\beta}} + (\tfrac{1}{3} - \tfrac{2}{3}s + \tfrac{2}{3}s^2)\,p^{\frac{(2+\beta)(1+2\beta)}{2(1+\beta)(1+\beta)}}\right. \\
&\quad \left. + (-\tfrac{2}{3} + 2s - \tfrac{4}{3}s^2)p + (\tfrac{1}{3} - \tfrac{2}{3}s + \tfrac{1}{3}s^2)\right] \\
d_{2b} &= 6s^2\left[(\tfrac{2}{3} - \tfrac{4}{3}s + \tfrac{2}{3}s^2)p^{\frac{2+\beta}{1+\beta}} + (-\tfrac{4}{3}s + \tfrac{4}{3}s^2)\,p^{\frac{(2+\beta)(1+2\beta)}{2(1+\beta)(1+\beta)}}\right. \\
&\quad \left. + (-\tfrac{4}{3} + 4s - \tfrac{8}{3}s^2)p + (\tfrac{2}{3} - \tfrac{4}{3}s + \tfrac{2}{3}s^2)\right]
\end{aligned}
\tag{81}
$$

$$d_3 = 4s^3\left[(1-s)p^{\frac{2+\beta}{1+\beta}} + (1-2s)\,p^{\frac{(2+\beta)(1+2\beta)}{2(1+\beta)(1+\beta)}} + (-3+4s)p + (1-s)\right]$$

$$d_4 = s^4\left[p^{\frac{2+\beta}{1+\beta}} + 2p^{\frac{(2+\beta)(1+2\beta)}{2(1+\beta)(1+\beta)}} - 4p + 1\right]$$

3. Recipe for Obtaining the Solution for Any Mechanism if $d_0(\mathrm{o}) = 1$ and s = constant

At first sight, the solutions (76) and (81) for the mechanism K impress one as irregular. Their pattern is clearly different from the very regular one of mechanism A and some other mechanisms. It proves possible, however, to write such "irregular" solutions in the regular form determined by the coefficient matrix (74); the apparent irregularity arises if one takes together terms with—accidentally—equal exponents. In Table 1 all expressions have been written in the regular form.

By analyzing the expressions it also becomes clear that the observation made at the end of Section II,2 is a general one: For all mechanisms of the exchange reaction which we have studied so far, the exponential terms in the expressions for the d_i are related to the transition probabilities in the way mentioned.

This provides us with a very simple procedure for obtaining the isotopic distribution for any exchange reaction in the case that *the reaction starts with undeuterated material* and *s is constant during the reaction:*

(a) Draw up the scheme of transition probabilities for the mechanism concerned.

(b) Derive from it the exponential terms $Q_j = \exp(-q_j k_1 t)$, where $1 - q_j$ is the chance that, when D_j reacts, D_j is formed back.

(c) Write down the quantities

$$u_h = \binom{N}{h} s^h \sum_j (-1)^{h+j}\binom{h}{j} Q_{N-j}$$

(d) Obtain the d_i from the u_h by means of the transformation $\mathbf{d} = \mathbf{Pu}$, where $P_{i,h} = (-1)^i\binom{h}{i}$.

It is easily verified that this procedure leads to the following result

$$d_i = (-1)^i \sum_h \binom{h}{i}\binom{N}{h} s^h \sum_j (-1)^{h+j}\binom{h}{j} Q_{N-j}$$

or

$$d_i = \binom{N}{i} \sum_j Q_{N-j} \sum_h (-1)^{i+j+h} \binom{N-i}{N-h}\binom{h}{j} s^h$$

which is identical with Eq. (64) if $Q_{N-j} = M_{j,j}$. It follows from (60) and the definition of Q_{N-j} that this is true.

We have not found a rigid proof for the correctness of this procedure, but it does give the correct solutions, not only for the cases mentioned above, but also for more complicated cases.

4. Discussion

In this section (III), formulas were derived for the distributions in a multiple exchange reaction for various mechanisms. Since different mechanisms may lead to different distribution patterns, evaluation of experimental data (as outlined in II,3) enables one to narrow down the number of possible mechanisms.

Information of this type can only be obtained when the formulas for d_i in terms of p [cf. Eq. (73)] contain more than one exponent. For $N = 2$ composite terms (as found for G, H, and K in Table 1) will not arise, the reason being that isomers for D_0, D_1, and D_2 are nonexistent. Thus for $N = 2$ there is always one exponent. Hence, information about the mechanism of a multiple exchange reaction can only be obtained from the distribution pattern when $N > 2$.

IV. Redistribution Reactions

In exchange reactions, as discussed in Sections I, II, and III, a net transport of isotopes between chemically different species occurs. In a redistribution or equilibration reaction, on the other hand, the average degree of deuteration of the hydrocarbon does not change. At $t = 0$ the distribution of deuterium among the hydrocarbon molecules is different from the one in equilibrium (binomial); thus the reaction consists of a redistribution of deuterium over the hydrocarbon molecules.

Redistribution experiments have repeatedly been performed (*18*), but a sound general method of evaluation of the data is lacking. For only a few specific cases (*19*) has the solution come to our attention: The stepwise (in present terminology $\beta = 0$) redistribution for $N = 4$ with the initial conditions (a): $d_0(\mathrm{o}) = d_4(\mathrm{o}) = 0.5$ and (b): $d_2(\mathrm{o}) = 1$. It is interesting to note that the solution for case (a) has been given earlier in connection with the redistribution of alkyl groups in metal-organic compounds (tetra-alkyllead) (*20*).

Redistribution can occur in two ways: either by direct interchange between the chemically identical species involved or through the intermediary of a chemically different species, e.g. a catalyst or a radical. Redistribution in the latter case is formally an exchange reaction and in this section we offer the solution of its kinetics. The, presumably rare, former case shows different kinetics and has not been investigated further. It is possible that the mathematical method outlined in Section II may also be helpful here.

1. Kinetics and Distribution

Redistribution by way of exchange with a chemically different species implies the additional condition $\sigma = s =$ constant. Confining ourselves for the present to the type of multiple process outlined in Section II, of which the stepwise process (Section I) is a limiting case ($\beta = 0$), then all information concerning this type of reaction is contained in Eqs. (62) or (63), in which we must introduce

$$s = \sigma = \sigma(\mathrm{o}) = \frac{1}{N} \sum_{i=1}^{N} i d_i$$

The resulting formulae describe the time-dependence of each individual d_i in a redistribution reaction.

As described in II,3 the distribution in an exchange reaction is obtained by eliminating τ by means of Eq. (48), which is the general rate law for exchange. To see whether analogous possibilities exist in a redistribution reaction, we will consider the variables $\mathbf{u}$ instead of $\mathbf{d}$. The expressions for the first four variables read [Eq. (61)] (for $N = 4$, cf. the Appendix)

$$\begin{aligned}
u_0 &= +1 \\
u_1 &= -\binom{N}{1} s + \left[\binom{N}{1} s + u_1(\mathrm{o})\right] M_1 \\
u_2 &= +\binom{N}{2} s^2 - \binom{N-1}{1} s \left[\binom{N}{1} s + u_1(\mathrm{o})\right] M_1 + \\
&\qquad \left[\binom{N}{2} s^2 + \binom{N-1}{1} s u_1(\mathrm{o}) + u_2(\mathrm{o})\right] M_2 \qquad (82) \\
u_3 &= -\binom{N}{3} s^3 + \binom{N-2}{2} s^2 \left[\binom{N}{1} s + u_1(\mathrm{o})\right] M_1 - \\
&\qquad \binom{N-2}{1} s \left[\binom{N}{2} s^2 + \binom{N-1}{1} s u_1(\mathrm{o}) + u_2(\mathrm{o})\right] M_2 \\
&\qquad + \left[\binom{N}{3} s^3 + \binom{N-1}{2} s^2 u_1(\mathrm{o}) + \binom{N-2}{1} s u_2(\mathrm{o}) + u_3(\mathrm{o})\right] M_3
\end{aligned}$$

where M_i is identical with $M_{i,i}$ as defined by (60): $M_i = \exp(-m_i\tau)$; and $\mathbf{u} = \mathbf{Pd}$ with $\mathbf{P}$ the matrix as defined by (15).

Since $-(1/N)u_1(\infty) = \sigma(\infty) = s$, the second equation of (82) can be written

$$u_1 = u_1(\infty) + [-u_1(\infty) + u_1(\text{o})]M_1$$

or

$$u_1 - u_1(\infty) = [u_1(\text{o}) - u_1(\infty)] \exp(-m_1\tau) \tag{83}$$

This equation is the same as Eq. (48) and is the rate law for exchange. Note that it holds for any mechanism: The mechanism determines the form of m_1 (see Section III).

In a redistribution reaction $u_1(\text{o}) = -N\sigma = -Ns$ which causes the M_1 term in the Eqs. (82) to vanish; thus Eq. (83) is meaningless. However, the third equation of (82) now becomes:

$$u_2 = \binom{N}{2}s^2 + \left[\binom{N}{2}s^2 + \binom{N-1}{1}s(-Ns) + u_2(\text{o})\right]M_2$$

or, since

$$u_2(\infty) = \binom{N}{2}s^2$$

then

$$u_2 - u_2(\infty) = [u_2(\text{o}) - u_2(\infty)] \exp(-m_2\tau) \tag{84}$$

This result is the rate law for redistribution: The variable u_2 changes exponentially with time. Before discussing it further, we note that by means of Eq. (84) time can be eliminated from the distribution [Eq. (62) or (63)]. As was found for exchange reactions (I,4 and II,3), the distribution in a redistribution reaction is completely determined by one parameter, u_2, for a stepwise process, whereas for a multiple process the additional parameter β (contained in m_i) appears in the expressions.

2. *The Rate Law for Redistribution*

The ratio of m_2 of a redistribution to m_1 of the corresponding exchange reaction depends upon the value of β and may depend upon the mechanism, as can be seen from Sections II and III. For a stepwise exchange process the ratio m_2/m_1 will always be equal to 2.

Returning to the rate law for redistribution we note that like the law for exchange it supposes the absence of isotope effects. It is, however, not as general as the latter: It may be affected both by the mechanism of the reaction and by the initial conditions. Thus, the rate law (84) holds for the stepwise mechanism (Section I) and the mechanisms A through F of Section III, but not for G, H, and K. The reason for this is easily seen from Table 1. For mechanisms G, H, and K, M_2 is not a single exponential function, but a sum of two, which makes it impossible to write the rate law for u_2 as a simple exponential expression. From the recipe given in III,3 it can readily be seen when this will occur in a multiple process: M_2 is determined by the chance that when D_{N-2} reacts, D_{N-2} is formed back. Evidently M_2 will be a single function if either there is only one isotopic species D_{N-2}, e.g. CH_2D_2, or when there are different isotopic species D_{N-2}, but all of them have the same chance to be formed back when reacting. If not all of them have the same chance, as 1,1-, *cis*-1,2-, and *trans*-1,2-$C_2H_2D_2$ in mechanism K (III,2), the rate law (84) for redistribution breaks down.

To eliminate time in order to obtain the formulas for the distribution we must have a variable that changes exponentially with time. If this does not hold for u_2 [Eq. (84)] such a variable can be arrived at in two ways.

Firstly, for arbitrary initial conditions, there is a u [but not a u_i as defined by Eq. (23)] that changes exponentially. There is no unique way for finding this variable. For mechanism K, discussed in III,2 the extra variable $u = d_{2a} + d_3 + 2d_4$ serves the purpose. For this approach one needs experimental information on the isomeric composition of D_{N-2}, an evident conclusion since this yields information about the separate terms of the composite M_2.

Secondly, one can choose initial conditions so that

$$u_2(\text{o}) = \binom{N}{2}s^2$$

Then the coefficient of M_2 in Eq. (82) vanishes. The fourth equation of (82) now takes a simple form and it is the variable u_3 that changes exponentially, provided M_3 is a single expression. If this is not so, one can put further restrictions on the initial conditions and proceed to the next u_i. There will always be a u_i that changes exponentially.

3. Discussion

The simplest case where a redistribution can be observed by analysis is for $N = 2$. No information can then be obtained about β. When $N = 2$, it follows from Eq. (84) that d_2 ($= u_2$) follows exponential kinetics and the same is true for d_0 and d_1, since they are linearly related by the material balance.

For $N = 2$, the case most often studied (*18*, *21*, *22*) is the redistribution

$$H_2 + D_2 \rightleftarrows 2HD$$

The exponential kinetics of this reaction are common knowledge. (It may be remarked that the kinetics do not seem to be severely disturbed by the fact that distribution in equilibrium in the temperature range usually investigated differs appreciably from the binomial distribution.) For the rationalization of these simple kinetics one usually refers to the kinetics of exchange reactions (*23*). This, however, is not justified, since these kinetics are not observed for the individual D_i when $N > 2$ (special cases excepted; see below). In some publications (*13*) on the catalytic equilibration of $H_2 + D_2$ one finds the equation (*23*)

$$[HD] - [HD]_\infty = \{[HD]_0 - [HD]_\infty\}e^{-2kt} \tag{85}$$

used. In view of what has been said about the ratio of m_2 and m_1, it follows from the introduction of the factor 2 that one has already (unwittingly) decided in favor of a stepwise mechanism [in this particular case the so-called Eley-Rideal mechanism; the Bonhoeffer-Farkas mechanism would give a ratio of 1 (*22*)].

Another example for $N = 2$ is the redistribution in acetylene

$$C_2H_2 + C_2D_2 \rightleftarrows 2C_2HD$$

which also shows exponential kinetics for the individual species (*24*). However, this should not be considered as a proof for any proposed mechanism (*25*), since all mechanisms lead to these kinetics.

When $N > 2$, simple exponential kinetics will in general not hold for the individual isotopic species. Only if $\beta = \infty$ and all exchangeable hydrogen atoms are equally reactive in the reactive intermediate will this be true for any set of initial conditions, since then all m_i (except of course m_0) are equal. In this particular case the isotopic species leaving the reactive state have equilibrium composition. If β is not infinitely large, then for $N > 2$, simple kinetics for all or some of the isotopic species will only be observed for special initial conditions. If, e.g. for $N = 3$ the initial composition is

$$d_1(o) = 1; \quad d_0(o) = d_2(o) = d_3(o) = 0$$

only d_2 obeys exponential kinetics for any value of β. On the other hand, for $N = 3$ with

$$d_0(o) = d_3(o) = 0.5; \quad d_1(o) = d_2(o) = 0$$

or for $N = 4$ with

$$d_0(o) = d_4(o) = 0.125; \quad d_1(o) = d_3(o) = 0; \quad d_2(o) = 0.75$$

all isotopic species follow exponential kinetics for any value of β. In these cases β cannot be obtained from the redistribution experiment, nor can it be decided whether the process is stepwise or multiple. In the past there has been a tendency to start with symmetrical initial compositions. As shown by one of the illustrations given, this is not always advisable, since in doing so one may lose information.

In the last example (for $N = 4$) we have $\sigma = s = \frac{1}{2}$; $u_1(o) = -2$; $u_2(o) = 3/2$; $u_3(o) = -\frac{1}{2}$; $u_4(o) = 1/8$ and thus $u_2 = u_2(o) = u_2(\infty)$ and also $u_3 = u_3(o) = u_3(\infty)$. As a consequence of the choice of initial conditions only m_4 can be obtained from the experiment.

We conclude from the above analysis of redistribution reactions that they can provide information of the same nature as exchange reactions. We have only lost one degree of freedom.

Redistribution reactions may be particularly helpful in those cases where the practical condition for a multiple exchange experiment, viz. s = constant, implying an infinite excess of deuterating agent, cannot be realized. This might apply for solid–hydrocarbon systems.

Conclusion

Isotope interchange of a hydrocarbon with N equivalent hydrogen atoms yields values for $d_0, d_1, \ldots, d_N$, the sum of which is unity and hence N data are available.

In exchange reactions with $N = 1$ the only information obtainable is the rate constant of the exchange, which is obtained from the exponential kinetics of the (average) degree of deuteration σ.

With $N = 2$, the distribution yields further information. When the distribution is binomial during the reaction (starting from a nondeuterated compound) exchange occurs stepwise, involving only one rate constant. Nonbinomial distributions arise from a multiple process. The distribution yields a value for β which is the reactivity of the intermediate occurring in any postulated mechanism.

From $N = 3$ onwards, distribution data afford the possibility of narrowing down the number of possible mechanisms.

Beyond $N = 2$ or 3 the mathematical complexity of the more general case of variable s limits the extraction of information to systems with a large excess of deuterating reagent (constant s).

When this condition cannot be experimentally realized, redistribution reactions open new possibilities. In this case σ is constant and one degree of freedom is lost. Thus, redistribution can only be observed for $N \geqq 2$. The rate constant for redistribution can be obtained from the exponential kinetics of a function of the d_i, which will often be

$$u_2 = \sum \binom{i}{2} d_i$$

Only for $N \geqq 3$ can one distinguish between a stepwise or a multiple mechanism for the redistribution.

Thus, in systems where the condition for exchange reactions of constant s cannot be met experimentally, a redistribution experiment may yield equally valuable information.

APPENDIX

Matrices

1. Construction of the Matrices $\mathbf{R}$, $\mathbf{R}^{-1}$, *and* $\mathbf{A}$

For the case of constant s, the general solution of the rate equations for the multiple exchange reaction is given by Eq. (62)

$$\mathbf{d} = \mathbf{RMR}^{-1}\mathbf{d}(o)$$

together with the Eqs. (55), (56), and (61), which define $\mathbf{R}$, $\mathbf{R}^{-1}$, and $\mathbf{M}$, respectively.

This solution is not easy to handle, since the expressions for $R_{i,j}$ and $R_{i,j}^{-1}$ which can be obtained from (55) and (56) are fairly complicated. We have found, however, a simple procedure for constructing the elements of these matrices, which is also of great value in numerical calculations.

We first note that the "boundary" elements of, e.g., $\mathbf{R}$ are quite simple

$$\begin{aligned} R_{0,j} &= r^{N-j} \\ R_{N,j} &= (-1)^j s^{N-j} \\ R_{i,0} &= \binom{N}{i} s^i r^{N-i} \\ R_{i,N} &= (-1)^i \binom{N}{i} \end{aligned}$$

If we now find a relation between elements $R_{i,j}$, $R_{i,j+1}$, $R_{i+1,j}$ and $R_{i+1,j+1}$ we can obtain successively all the elements of $\mathbf{R}$ by working from the boundary to the center.

For that purpose we now write these elements, and the expressions in which they are the coefficients of x^{i+1}, employing (55)

$$\begin{aligned} R_{i,j} &: x(1 - x)^j (r + sx)^{N-j} \\ R_{i,j+1} &: x(1 - x)^{j+1} (r + sx)^{N-j-1} \\ R_{i+1,j} &: \ (1 - x)^j (r + sx)^{N-j} \\ R_{i+1,j+1} &: \ (1 + x)^{j+1} (r + sx)^{N-j-1} \end{aligned}$$

After dividing these expressions by the common factor $(1 - x)^j (r + sx)^{N-j-1}$ we obtain

$$\begin{array}{c} x(r + sx) \\ x(1 - x) \\ r + sx \\ 1 - x \end{array} \quad \text{or} \quad \begin{array}{r} rx + sx^2 \\ x - x^2 \\ r + sx \\ 1 - x \end{array}$$

$$\text{or} \quad \begin{pmatrix} 0 & r & s \\ 0 & 1 & -1 \\ r & s & 0 \\ 1 & -1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ x \\ x^2 \end{pmatrix}$$

It is easily seen that a linear relation exists between the four expressions. The solution is essentially unique, viz. $(1,s,-1,r)$. Thus:

$$R_{i,j} + sR_{i,j+1} - R_{i+1,j} + rR_{i+1,j+1} = 0$$

In the same way we derive from (56):

$$rR^{-1}{}_{i,j} + sR^{-1}{}_{i,j+1} - R^{-1}{}_{i+1,j} + R^{-1}{}_{i+1,j+1} = 0$$

with

$$\begin{aligned} R^{-1}{}_{0,j} &= 1 \\ R^{-1}{}_{N,j} &= (-1)^j r^j s^{N-j} \\ R^{-1}{}_{i,0} &= \binom{N}{i} s^i \\ R^{-1}{}_{i,N} &= (-1)^i r^i \end{aligned}$$

As observed in Section II,1.2,b an even simpler calculation is possible, which involves the use of only one auxiliary matrix $\mathbf{A}$ instead of $\mathbf{R}$ and $\mathbf{R}^{-1}$. The solution is then given by (63), with $A_{i,j} = r^j R_{i,j}$.

Proof: By substituting x for rx in (55) we can obtain

$$(1,rx, \ldots, (rx)^N \mathbf{R}\mathbf{e}_j r^j = (1 - rx)^j (r + srx)^{N-j} r^j$$

From (56) it follows that

$$(1,x, \ldots, x^N)\mathbf{R}^{-1}\mathbf{e}_j r^N = (1 - rx)^j (1 + sx)^{N-j} r^N$$

and hence:

$$(1,x, \ldots, x^N)\mathbf{R}^{-1}\mathbf{e}_j r^N = (1,rx, \ldots, (rx)^N)\mathbf{R}\mathbf{e}_j r^j \quad (86)$$

Introduce now the diagonal matrix $\mathbf{J}$ ($J_{i,i} = r^i$). Then

$$1,rx, \ldots, (rx)^N = (1,x, \ldots, x^N)\mathbf{J} \quad \text{and} \quad \mathbf{e}_j r^j = \mathbf{J}\mathbf{e}_j$$

We can now write (86) as

$$(1,x, \ldots, x^N)\mathbf{R}^{-1}\mathbf{e}_j r^N = (1,x, \ldots, x^N)\mathbf{J}\mathbf{R}\mathbf{J}\mathbf{e}_j$$

or

$$\mathbf{R}^{-1} r^N = \mathbf{J}\mathbf{R}\mathbf{J} \quad \text{or} \quad \mathbf{J}^{-1}\mathbf{R}^{-1} r^N = \mathbf{R}\mathbf{J}$$

We now return to (62). Since $\mathbf{M}$ and $\mathbf{J}$ are diagonal matrices

$\mathbf{M} = \mathbf{J}\mathbf{M}\mathbf{J}^{-1}$ and hence

$$\mathbf{R}\mathbf{J}\mathbf{M}\mathbf{J}^{-1}\mathbf{R}^{-1} = r^{-N}(\mathbf{R}\mathbf{J})\mathbf{M}(\mathbf{R}\mathbf{J})$$

With $\mathbf{A} = \mathbf{R}\mathbf{J}$ ($A_{i,j} = R_{i,j} r^j$) we find $\mathbf{d} = r^{-N}\mathbf{A}\mathbf{M}\mathbf{A}\mathbf{d}(0)$. (63)

The rules for the construction of $\mathbf{A}$ can be derived from those for $\mathbf{R}$. We find

$$A_{i,j} + \frac{s}{r} A_{i,j+1} - A_{i+1,j} + A_{i+1,j+1} = 0$$

with

$$A_{0,j} = r^N \quad A_{N,j} = (-1)^j r^j s^{N-j}$$

$$A_{i,0} = \binom{N}{i} s^i r^{N-i} \quad A_{i,N} = (-1)^i \binom{N}{i} r^N$$

2. Explicit Expressions for Some Matrices

As an aid to the reader and also to show symmetry and regularity we give now the explicit expressions for a number of frequently used matrices. We have chosen $N = 4$; extrapolation to other values of N is not difficult.

$$\mathbf{F} = \begin{pmatrix} -4s & +r & 0 & 0 & 0 \\ +4s & -3s - r & +2r & 0 & 0 \\ 0 & +3s & -2s - 2r & +3r & 0 \\ 0 & 0 & +2s & -s - 3r & +4r \\ 0 & 0 & 0 & +s & -4r \end{pmatrix} \quad \mathbf{P} = \mathbf{P}^{-1} = \begin{pmatrix} +1 & +1 & +1 & +1 & +1 \\ 0 & -1 & -2 & -3 & -4 \\ 0 & 0 & +1 & +3 & +6 \\ 0 & 0 & 0 & -1 & -4 \\ 0 & 0 & 0 & 0 & +1 \end{pmatrix}$$

$$\mathbf{G} = \mathbf{P}^{-1}\mathbf{F}\mathbf{P} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ -4s & -1 & 0 & 0 & 0 \\ 0 & -3s & -2 & 0 & 0 \\ 0 & 0 & -2s & -3 & 0 \\ 0 & 0 & 0 & -s & -4 \end{pmatrix} \quad \mathbf{Q} = \begin{pmatrix} +1 & 0 & 0 & 0 & 0 \\ -4s & +1 & 0 & 0 & 0 \\ +6s^2 & -3s & +1 & 0 & 0 \\ -4s^3 & +3s^2 & -2s & +1 & 0 \\ +\ s^4 & -\ s^3 & +\ s^2 & -s & +1 \end{pmatrix}$$

$$\mathbf{Q}^{-1} = \begin{pmatrix} +1 & 0 & 0 & 0 & 0 \\ +4s & +1 & 0 & 0 & 0 \\ +6s^2 & +3s & +1 & 0 & 0 \\ +4s^3 & +3s^2 & +2s & +1 & 0 \\ +\ s^4 & +\ s^3 & +\ s^2 & +s & +1 \end{pmatrix} \quad \mathbf{GQ} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 \\ 0 & +3s & -2 & 0 & 0 \\ 0 & -3s^2 & +4s & -3 & 0 \\ 0 & +\ s^3 & -2s^2 & +3s & -4 \end{pmatrix}$$

$$\mathbf{L} = \mathbf{Q}^{-1}\mathbf{GQ} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & -2 & 0 & 0 \\ 0 & 0 & 0 & -3 & 0 \\ 0 & 0 & 0 & 0 & -4 \end{pmatrix}$$

$$\mathbf{R} = \mathbf{PQ} =$$

$$\begin{pmatrix} +1 - 4s + 6s^2 - 4s^3 + s^4 & +1 - 3s + 3s^2 - s^3 & +1 - 2s + s^2 & +1 - s & +1 \\ +4s - 12s^2 + 12s^3 - 4s^4 & -1 + 6s - 9s^2 + 4s^3 & -2 + 6s - 4s^2 & -3 + 4s & -4 \\ +6s^2 - 12s^3 + 6s^4 & -3s + 9s^2 - 6s^3 & +1 - 6s + 6s^2 & +3 - 6s & +6 \\ +4s^3 - 4s^4 & -3s^2 + 4s^3 & +2s - 4s^2 & -1 + 4s & -4 \\ +s^4 & -s^3 & +s^2 & -s & +1 \end{pmatrix}$$

$$\equiv \begin{pmatrix} r^4 & r^3 & r^2 & r & 1 \\ 4sr^3 & -r^3 + 3sr^2 & -2r^2 + 2sr & -3r + s & -4 \\ 6s^2r^2 & -3sr^2 + 3s^2r & r^2 - 4sr + s^2 & 3r - 3s & 6 \\ 4s^3r & -3s^2r + s^3 & 2sr - 2s^2 & -r + 3s & -4 \\ s^4 & -\ s^3 & s^2 & -s & 1 \end{pmatrix}$$

$$\mathbf{R}^{-1} =$$

$$\begin{pmatrix} +1 & +1 & +1 & +1 & +1 \\ +4s & -1 + 4s & -2 + 4s & -3 + 4s & -4 + 4s \\ +6s^2 & -3s + 6s^2 & +1 - 6s + 6s^2 & +3 - 9s + 6s^2 & +6 - 12s + 6s^2 \\ +4s^3 & -3s^2 + 4s^3 & +2s - 6s^2 + 4s^3 & -1 + 6s - 9s^2 + 4s^3 & -4 + 12s - 12s^2 + 4s^3 \\ +\ s^4 & -\ s^3 + s^4 & +s^2 - 2s^3 + s^4 & -s + 3s^2 - 3s^3 + s^4 & +1 - 4s + 6s^2 - 4s^3 + s^4 \end{pmatrix}$$

$$\mathbf{A} =$$

$$\begin{pmatrix} +r^4 & +r^4 & +r^4 & +r^4 & +r^4 \\ +4sr^3 & -r^4 + 3sr^3 & -2r^4 + 2sr^3 & -3r^4 + sr^3 & -4r^4 \\ +6s^2r^2 & -3sr^3 + 3s^2r^2 & +r^4 - 4sr^3 + s^2r^2 & +3r^4 - 3sr^3 & +6r^4 \\ +4s^3r & -3s^2r^2 + s^3r & +2sr^3 - 2s^2r^2 & -r^4 + 3sr^3 & -4r^4 \\ +s^4 & -s^3r & +s^2r^2 & -sr^3 & +r^4 \end{pmatrix}$$

3. Solution in Terms of the Variables **u** *for Arbitrary Initial Conditions with* $N = 4$ *and* $s =$ *Constant [Eq. (61)]*

$$u_0 = u_0(o)M_0$$

$$u_1 = -4su_0(o)M_0 + \{4su_0(o) + u_1(o)\}M_1$$

$$u_2 = 6s^2u_0(o)M_0 - 3s\,\{4su_0(o) + u_1(o)\}M_1 + \{6s^2u_0(o) + 3su_1(o) + u_2(o)\}M_2$$

$$u_3 = -4s^3u_0(o)M_0 + 3s^2\{4su_0(o) + u_1(o)\}M_1 - 2s\{6s^2u_0(o) + 3su_1(o) + u_2(o)\}M_2 + \{4s^3u_0(o) + 3s^2u_1(o) + 2su_2(o) + u_3(o)\}M_3$$

$$u_4 = s^4u_0(o)M_0 - s^3\{4su_0(o) + u_1(o)\}M_1 + s^2\{6s^2u_0(o) + 3su_1(o) + u_2(o)\}M_2 - s\{4s^3u_0(o) + 3s^2u_1(o) + 2su_2(o) + u_3(o)\}M_3 + \{s^4u_0(o) + s^3u_1(o) + s^2u_2(o) + su_3(o) + u_4(o)\}M_4$$

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