ISOTOPIC EFFECT IN THE KINETICS OF BIMOLECULAR HYDROGEN-EXCHANGE REACTIONS

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A study has been made of the isotopic effect in the kinetics of bimolecular hydrogen-exchange reactions. It is shown that, even for exponential kinetics, the time-independent exchange rate must be calculated with an account of corrections which are functions of the equilibrium constants, the concentration ratio, and the initial label content in one of the components. Various methods for calculating the kinetic curves for isotopic hydrogen exchange are compared for the case of an alcohol–mercaptan system.

The kinetics of hydrogen-exchange reactions must often be studied through the use of deuterium- or tritium-labeled compounds, and in this case the experimental rate determined is the rate r ($\sec^{-1}$) at which an equilibrium label distribution is established. This value is used to calculate the rate Q of the hydrogen-exchange reaction, which is independent of the time [1]; Q is always determined with an accuracy to within a constant factor (Q/g) [2]. If the isotope is distributed uniformly, the establishment of the equilibrium is an exponential process, and Q/g can be calculated very simply. The more complicated case of a nonuniform isotope distribution was analyzed in detail in [3-5]. A general equation was derived in [3, 4] for the kinetics of such reactions, and conditions under which the process is pseudomonomolecular were formulated.

In the spectroscopic studies of the kinetics of exchange reactions

$$\mathrm{XH} + \mathrm{YH}^* \rightarrow \mathrm{XH}^* + \mathrm{YH}$$

in which groups capable of forming hydrogen bonds both as proton donors and as proton acceptors participate [6-9], large deviations from an exponential dependence are generally not observed, even for systems in which the equilibrium constant differs significantly from unity. In this case, however, it becomes necessary to analyze the relation between the experimental rate r at which the system approaches equilibrium and the value Q/g. We restrict the discussion to the uncomplicated case of a homogeneous bimolecular reaction

$$\mathrm{XH} + \mathrm{YD} \rightleftarrows \mathrm{XD} + \mathrm{YH} \tag{1}$$

We introduce the notation, a = [YD] + [YH], b = [XD] + [XH], c = [YD] for t = 0, d = [XD] for t = 0 (there is no loss in generality here by assuming d = 0, since it is this case which is usually studied experimentally), and $x(t) = \Delta[\mathrm{XD}] = -\Delta[\mathrm{YD}]$. The equilibrium constant for reaction (1) is

$$K = \frac{[\mathrm{YH}]_\infty [\mathrm{XD}]_\infty}{[\mathrm{YD}]_\infty [\mathrm{XH}]_\infty} = \frac{g}{f}, \tag{2}$$

where g and f are the isotopic corrections to the expressions for the partial rates of the processes in the system [2]. Assuming $K \neq 1$, i.e., $g \neq f$, we find

$$\frac{dx}{dt} = \frac{Q}{gab}\{x^2(K-1) - x[K(b+c) + (a-c)] + Kcb\}, \tag{3}$$

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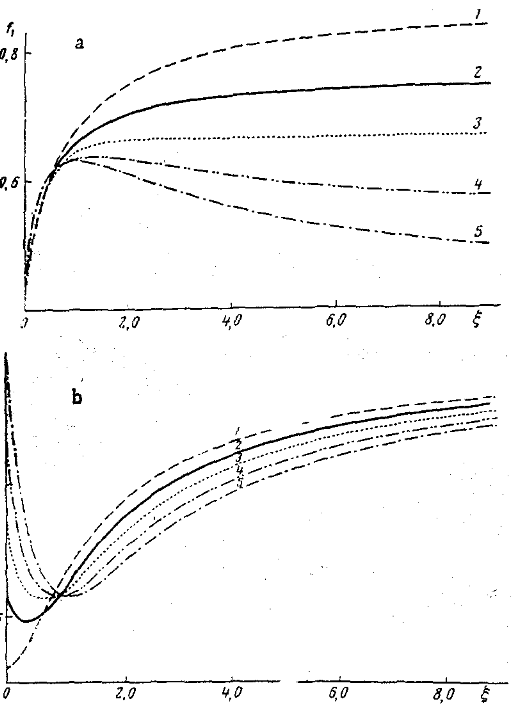

Fig. 1

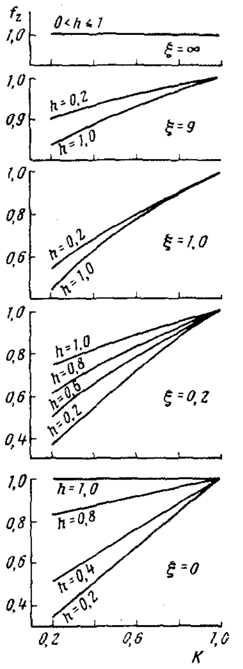

Fig. 2

Fig. 1. Dependence of f_1 for the "forward" process (a) and f_2 for the "reverse" process (b) on the concentration ratio for various initial deuterium contents in one of the components: 1) h = 0.2; 2) 0.4; 3) 0.6; 4) 0.8; 5) 1.0 (K = 0.4).

Fig. 2. Dependence of f_2 on the equilibrium constant for various concentration ratios and for various initial deuterium contents.

where Q is the rate at which hydrogen is exchanged between molecules XH and YH in a system having component concentrations of a and b in the absence of a label. Integration of Eq. (3) with an account of the condition x = 0 at t = 0 yields

$$\ln \frac{1 - x/x_{\infty_1}}{1 - x/l} = -\frac{Q}{\xi b g}\mu t = -r_1 t, \tag{4}$$

where $\xi = a/b$; $h_1 = c/a = c/\xi b$; $\mu = \sqrt{\nu^2 - 4K(K-1)\xi h_1}$, $\nu = K(\xi h_1 + 1) + \xi(1 - h_1)$; $x_{\infty_1} = \frac{\nu - \mu}{2(K-1)} b$ is the equilibrium [XD] value (i.e., $x_{\infty_1} \equiv [\mathrm{XD}]_\infty$), and $l = \frac{\nu + \mu}{2(K-1)} b$.

For practical purposes it is convenient to also examine the kinetics of the "reverse" process, which has the initial condition c = 0, d = [XD] at t = 0. The equilibrium constant for this process is evidently K' = 1/K (with this in mind, we will carry out the further analysis for the case K < 1). For this process. and with the same notation, we find

$$\ln \frac{1 - x/x_{\infty_2}}{1 - x/p} = -\frac{Q}{\xi b g}\eta t = -r_2 t \tag{5}$$

where $h_2 = d/b$; $\eta = \sqrt{\omega^2 - 4(1-K)\xi h_2}$; $\omega = K(1 - h_2) + (\xi + h_2)$; $x_{\infty_2} = \frac{\omega - \eta}{2(1-K)} b$ is the equilibrium [YD] value (i.e., $x_{\infty_2} \equiv [\mathrm{YD}]_\infty$) and $p = \frac{\omega + \eta}{2(1-K)} b$. Equations (4) and (5) agree with the equation found in [3].

In the case g = f; i.e., K = 1, the kinetic equation becomes

$$\ln(1 - x/x_\infty) = -\frac{Q}{\xi b g}(1 + \xi)t = -rt, \tag{6}$$

where

$$x_\infty = \frac{\xi h}{1 + \xi} b.$$

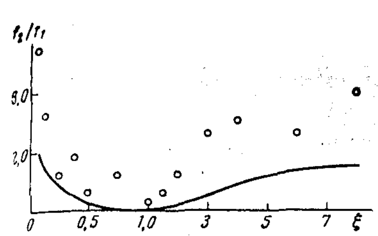

Fig. 3. Dependence of the ratio f_2/f_1 on the concentration ratio for the system $CH_3OH + C_{12}H_{25}SH$. Points) experimental; curves) calculated.

Equation (6) is usually used to analyze experimental data.

In studying the kinetics of processes for which $K \neq 1$, it is important to find the systematic error incorporated in the experimental Q/g value because approximation (6) is used instead of exact equation (4) or (5).

Equation (4) shows that, first, the experimental points do not conform to a straight line when plotted as $\ln(1-x/x_{\infty 1})$ vs t, and the deviation from the line is due to the time dependence of the term $\ln(1-x/l)$ Since we have $l > x_{\infty 1}$, the denominator on the left side of (4) changes very slowly at large t, and the experimental t dependence of $\ln(1-x/x_{\infty 1})$ is approximated well by a straight line which generally does not pass through the origin.

The slope of this line is equal to that of the line $\ln(1-x/x_{\infty 1}) - \ln(1-x/l) = \varphi(t)$. A more detailed analysis shows that the deviation $x_{\infty 1}/l$ reaches a maximum magnitude at the point $\xi = K/[h(K-1)+1]$. When completely deuterated compounds are used, with h = 1, the greatest deviations from the exponential dependence arise at a ratio $\xi = 1$ of the component concentrations.

Second, even when the deviations from an exponential nature are small, the hydrogen-exchange rate Q/g should be determined from the experimental line slope, through the use of

$$\frac{Q}{g} = r\frac{\xi b}{\mu}. \tag{7}$$

Let us analyze the systematic error introduced into Q/g through the use of simple Eq. (6) instead of the more complicated Eq. (7), which leads to the same accurate information about K and h. These errors can be characterized by the functions

$$f_1 = \frac{\mu}{\xi+1} = \frac{\sqrt{\nu^2 - 4K(K-1)\xi h_1}}{\xi+1} \tag{8}$$

$$f_2 = \frac{\eta}{\xi+1} = \frac{\sqrt{\omega^2 - 4(1-K)\xi h_2}}{\xi+1}, \tag{9}$$

which depend on the variables K, H, and ξ. While K is governed only by the molecular nature of the reaction components, h and ξ depend on the experimental conditions. The dependence of f_1 and f_2 on ξ are particularly important, since we must study the concentration dependence of the exchange rate in order to determine the reaction order. Analysis shows that

$$\left.\begin{aligned} &f_1 \to K \\ &f_2 \to h_2(1-K)+K \end{aligned}\right\} \text{ as } \xi \to 0$$

$$\left.\begin{aligned} &f_1 \to h_1(K-1)+1 \\ &f_2 \to 1 \end{aligned}\right\}, \text{ as } \xi \to \infty;$$

f_1 and f_2 have extrema at, respectively,

$$\xi_1 = \frac{K(h_1+1)}{h_1^2(K-1)+h_1(K+2)-1} \text{ (a minimum).} \tag{10}$$

$$\xi_2 = \frac{h_2^2(1-K)+h_2(1+2K)-K}{1+h_2} \text{ (a maximum),} \tag{11}$$

As h_1 decreases, the f_1 maximum shifts toward larger ξ and becomes infinite at the h_1 value at which the denominator in (10) vanishes. The f_2 minimum undergoes an analogous displacement toward smaller ξ. At the f_1 maximum, the systematic error in the determination of Q/g is minimal, and that at the f_2 minimum is maximal. In the limiting case h = 1, the f_1 and f_2 extrema coincide, $f_1 = f_2 = \sqrt{K}$, and both are at the point $\xi = 1$. The dependences of f_1 and f_2 on ξ were calculated on a computer for various h and K for $0 < h < 1$, $0 < \xi < 10$, $0.2 < K < 1$. For the particular case K = 0.4 (see below), the ξ dependences of f_1 and f_2 are shown for various h in Fig. 1. The effect of the equilibrium constant can be followed in Fig. 2, which shows the dependence of f_2 on K for various h and ξ.

The systematic error in the determination of Q/g through the use of Eq. (6) thus turns out to be quite large in many cases – of the order of 10-50%; this circumstance significantly increases the random experimental error. We emphasize that these relations refer to the case of a bimolecular reaction, so that their use requires previous knowledge of the mechanism for the process. *Since, strictly speaking, the concentration dependences* of f_1 and f_2 cannot be studied separately in an experiment, even in this case we can obtain additional information about the mechanism for the process by studying it in the forward and reverse directions. By comparing the dependence of the function f_2/f_1 with the concentration dependence of the ratio of the rates found for these processes by analyzing results on the basis of Eq. (6), we can conclude whether there is a bimolecular mechanism.

TABLE 1

Method	α	β	$k \cdot 10^2$
I	1,4±0,2	0,8±0,2	7,5±0,8
II	1,3±0,2	0,9±0,2	14±2
III	1,5±0,1	0,9±0,1	20±1
IV	1,5±0,1	0,9±0,1	15±1

In a study of the kinetics of hydrogen exchange between hydroxyl and thiohydrol groups [7, 8], we analyzed these corrections. According to [4], the distribution coefficient for the distribution of deuterium between the hydrides of oxygen and sulfur is approximately a factor of two away from unity, so in these systems we can expect noticeable kinetic isotopic effects. The equilibrium constant for the reaction

$$CH_3OD + CH_3SH \rightleftarrows CH_3OH + CH_3SD$$

was determined experimentally and calculated from spectroscopic data. The experiments were carried out in the gas phase at component pressures in the range 20-80 torr at room temperature on the basis of the νOH and νOD methanol bands in the IR absorption spectrum. The average value calculated from the results of twenty experiments is K = 0.38 ± 0.06. The calculation was carried out on the basis of the harmonic-oscillator model (the set of mercaptan frequencies was taken from [10], and the set of alcohol frequencies was taken from [11]) and the rigid-rotator model (the moments inertia were taken from [12, 23]). The internal rotation was taken into account by the procedure of [14]; a value of K = 0.47 was found. Study of the isotopic-exchange kinetics in this gas-phase system has shown [6] that the mechanism is trimolecular. In a CCl_4 solution, on the other hand, the kinetics of hydrogen exchange between methanol and butylmercaptan (and also $C_{12}H_{25}SH$) is approximately bimolecular [7]. Accordingly, the use of Eqs. (4) and (5) is more valid for an alcohol–mercaptan system in a CCl_4 solution, in which the equilibrium constant is, according to our measurements, also equal to 0.4 ± 0.1.

The forward and reverse reactions in the system of CH_3OH and $C_{12}H_{25}SH$ in CCl_4 were studied in the concentration range 0.05-0.8 M on the basis of the νOH and νOD bands and, in certain cases, the νSH band in the IR absorption spectrum. The experimental results were analyzed on the basis of Eq. (6), and the ratio of experimental r values was constructed for the forward and reverse reactions: $f_2/f_1 = \eta/\mu$. Figure 3 shows the experimental f_2/f_1 values and those calculated from Eqs. (4) and (5) for K = 0.4. The dependence of f_2/f_1 on ξ is in qualitative agreement with that calculated. Analogous results were obtained for the CH_3OH + i-C_4H_9SH system. We note, in addition, that the effect of these isotopic effects can be followed by measuring the reaction rate at various h values (corresponding to the label content in one of the components). Figure 1 shows that for the forward reaction this effect is maximal at large ξ, while for the reverse reaction it is maximal at small ξ. This dependence is qualitatively the same as that found experimentally.

In conclusion we consider the results found from an analysis of a series of 19 kinetic experiments for the system CH_3OH + iso-C_4H_9SH in CCl_4 in various approximations. The accompanying table shows the reaction orders with respect to alcohol α and mercaptan β and the rate constants k found through the use of Eq. (6) (method I) and Eq. (7) (method II), i.e., without an account of the nonexponential nature, but with an account of the correction in the exponent. Here r is the slope of the line drawn through the experimental points over the entire time interval. These values are also calculated from Eq. (7), but the r value was determined from the asymptotic slope of the experimental t dependence of $(1-x/x_\infty)$ at large times (method III). The experimental curves were found to essentially coincide with their asymptotic values, beginning at values 1.0-1.5. Unfortunately, the experimental error in the measurement of this function is quite large at these times, so we cannot recommend this method for an accurate determination of the exchange rate. Finally, Table 1 shows the results of the most rigorous solution found for the problem, on the basis of Eq. (5) (method IV). The α, β, and k values for all the cases were obtained by solving a system of 19 equations by the method of least squares. Comparison of method I with methods II-IV, which give approximately the same results, shows that in this case an account of the nonexponential nature of the process is less important than the corrections in the exponent.

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