# Exchange of Tritium Between Tritiated Water and the Alpha-Hydrogen Atoms of Malonic Acid

ERNEST M. HODNETT and WILLIAM R. ANDREWS, Department of Chemistry, Oklahoma State University, Stillwater

Isotopic exchange studies of organic compounds require molecules of different isotopic composition and a mechanism by which the isotopes may be interchanged. Without the second istotope there would be no observable chemical reaction. Such a reaction generally involves an equilibrium. Equations for the rate of approach to equilibrium (Harris, 1951) and for the position of equilibrium (Urey, 1947) have been developed.

The reaction studied in this investigation was

$$H_2C(CO_2H)_2 + HTO \rightleftharpoons HTC(CO_2H)_2 + H_2O$$
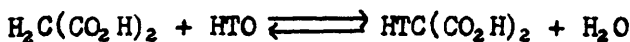
This isotopic exchange was chosen because of (1) the relatively simple structures of the molecules, (2) the convenient rate of exchange, and (3) the physical properties of malonic acid. The rate of exchange and the position of equilibrium was investigated at 30° and theoretical calculations were made of the latter.

Experimental Details

The general procedure in each case was to weigh carefully the malonic acid, water-t, water and standardized sodium hydroxide solution needed as shown in Table I for Runs 10 and 11. The pH of the solution was determined with a glass electrode. The solution was divided into several vials and placed in a constant temperature bath. At measured intervals a vial was withdrawn for assay of its tritium content. A solution

TABLE I

Composition of Typical Reaction Mixtures

	Run 10	Run 11
Malonic Acid, g.	0.9383	0.9173
Water-t, g.	1.0254	1.0254
Water, g.	2.8841	2.8252
Sodium Hydroxide (6.45 N), g.	3.9909	4.0717
pH	7.0	7.0

of barium hydroxide was added, and the precipitated barium salt was quickly filtered and washed with water. The sample was then dried and assayed on a vibrating-reed electrometer (Wilzbach, Kaplan and Brown, 1953; Wilzbach, Van Dyken and Kaplan, 1954). Results of Run 10 are given in Table II. Each radio-activity measurement represents an average of at least three assays.

Results

The rate of approach to equilibrium in an exchange is given (Friedlander and Kennedy, 1955) by the equation

$$\ln(1-F) = -(a+b)Rt/ab$$

In this case F is the ratio of the activity of the malonic acid at time t

TABLE II

Data for Run 10

Sample No.	Time, hr.	Radioactivity of Acid, microcuries/mmole	Extent of Reaction
1	12	1.30	0.438
2	17	1.71	0.576
3	24	1.27	0.428
4	36	1.94	0.653
5	48	2.26	0.761
6	72	2.59	0.872
7	7,360*	2.97	1.000

*The radioactivity of the water at this time was 4.03 microcuries/mmole

to that at equilibrium, a is the concentration of malonic acid and b that of water, and R is the rate of the reaction. When the data for Runs 6, 10, and 11 are plotted with log $(1-F)$ on the ordinate and time on the abscissa reasonably straight lines are obtained. The half time of the reaction under these conditions is approximately 25 hours. Samples of Runs 10 and 11 were assayed for tritium after more than 250 half times of reaction. These mixtures were undoubtedly at equilibrium.

The equilibrium constant for the reaction studied is calculated from the following mass-law equation:

$$K = [HTC(CO_2H)_2] \ [H_2O]/[H_2C(CO_2H)_2] \ [HTO]$$

or

$$K = \text{Molar activity of malonic acid/Molar activity of water}$$

Values of K for Runs 10 and 11 are 0.737 and 0.703, or an average of 0.720.

Urey (1947) has shown that in the equilibrium reaction

$$aA + bB^* \rightleftharpoons aA^* + bB$$

$$K = (Q_A^*/Q_A)^a / (Q_B^*/Q_B)^b$$

and that

$$\frac{Q^*}{Q} = \frac{J}{J^*} \prod \frac{u^* \exp(-u^*/2) \ (1 - \exp(-u))}{u \ \exp(-u/2) \ (1 - \exp(-u^*))}$$

where Q is a partition function for each molecule, J is the symmetry number, u is hcv/kT (in which h is Planck's constant, c the speed of light, v a frequency of vibration of the molecule, k Boltzmann's constant and T the absolute temperature).

The vibrational frequencies in wave numbers (cm^{-1}) used in calculating the equilibrium constant are given in Table III. The first frequency listed for malonic acid is the carbon-hydrogen stretching frequency. This was calculated for the tritiated compound from the known stretching frequency of ordinary malonic acid by use of the equation:

$$W_2 = W_1 \ (m_1/m_2)^{\frac{1}{2}} \tag{1}$$

where W_t is the frequency of the tritiated acid, W_t the frequency of the ordinary acid, m_t the reduced carbon-hydrogen mass, and m_t the reduced carbon-tritium mass. The second frequency given for each acid is a CH_2 bending frequency which is calculated for the tritiated acid from the value for the ordinary acid by equation (1); in this case m_t is the hydrogen-hydrogen reduced mass and m_t is the hydrogen-tritium reduced mass. The other frequencies are for CH_2 wagging and CH_2 rocking respectively. The values for the tritiated compound are calculated with equation (1) using the formula weight of CH_2 for m_t and that of CHT for m_r. From these data the value of K is calculated to be 0.474.

TABLE III

Frequencies of Compounds (in cm^{-1})

Water (Urey, 1947)		Malonic Acid	
H^2O	HTO	$H^2C(CO_2H)$ (Schmelz et al., 1959)	$HTC(CO_2H)$
3825	2365	2980	1848
1654	1374	1418	1158
3936	3883	1219	1140
		933	872

Qualitatively the rate of the exchange was found to be greater in both acid and basic solution. At a pH of 2.3 and a temperature of 50° equilibrium was reached in less than 18 hours. Results of varying the pH and the temperature will be studied further.

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