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An Isotope Effect in a Simple Chemical Reaction

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By

Peter E. Yankwich and Melvin Calvin

July 13, 1948

Berkeley, California

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ABSTRACT

AN ISOTOPE EFFECT IN A SIMPLE CHEMICAL REACTION

By

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University of California, Berkeley, California*

July 13, 1948

ABSTRACT

It has been found that the carbon dioxide obtained from the decarboxylation of singly-carboxyl labeled malonic acid is impoverished in the C^{14} label and that the acetic acid formed is correspondingly enriched.

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* This paper is based upon work performed under Contract #W-7405-Eng-48 with the Atomic Energy Commission in connection with the Radiation Laboratory, University of California, Berkeley.

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AN ISOTOPE EFFECT IN A SIMPLE CHEMICAL REACTION

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July 13, 1948

The effect of isotope labeling on the course of simple chemical reactions is ordinarily presumed to be negligibly small except in the case of hydrogen and, perhaps, lithium. That appreciable isotope effects can be found in heavier elements is demonstrated by the exchange processes for the concentration of the heavy isotope of carbon, C^{13}. It must be emphasized from the start that we are not herein concerned with the physical effects of isotope labels, use of which is made in processes such as thermal diffusion concentration of isotopic species, except insofar as they exert influence upon the course of a chemical reaction. The exchange reactions, such as -

$$HC^{12}N(g) + C^{13}N^- = HC^{13}N(g) + C^{12}N^-$$

are on the borderline of such a classification. The effect of deuterium on the course of reactions involving hydrogen is now well known, and it is to be expected that chemical effects of labeling will make them-

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(1) This paper is based upon work performed under Contract #W-7405-Eng-48 with the Atomic Energy Commission in connection with the Radiation Laboratory, University of California, Berkeley, California.

selves known primarily through changes in reaction rate. If a non-exchange process is studied it is possible that the magnitude of the departure from normal behavior will be large compared with that observed in an exchange reaction. The equilibrium constant for the reaction written above is 1.012 at 25°, yet departures different by an order of magnitude have been observed in the electron bombardment of propane labeled with C^{13} in a terminal position.

In a study of the isomerization of propane, Beeck et. al. (2) noted that the peak heights on their mass spectrometer record were not those which one would have predicted on the basis of equal dissociation probabilities for the C^{12}-C^{12} and C^{12}-C^{13} bonds. Experiments, on a sample containing 54 atom percent excess C^{13} in the label, showed that the dissociation probability of the C^{12}-C^{12} bond was increased 7 percent and that of the C^{12}-C^{13} bond was decreased 12 percent from the C^{12}-C^{12} dissociation probability in unlabeled propane. These figures correspond to a value of 1.22 for the frequency of rupture ratio C^{12}-C^{12}/C^{12}-C^{13}. Unpublished experiments by the same authors yield a ratio of 1.08 for thermal cracking at about 500°. From these data it is possible to predict only the gross extent of similar differences involving C^{14} labeled compounds under different conditions.

Decarboxylation reactions can be made to take place at rather moderate temperatures, and for a given reaction the isotope effect observed should increase with decreasing temperature. Suppose that

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(2) Beeck, O., Otvos, J.W., Stevenson, D.P., and Wagner, C.D., J. Chem. Phys., 16, 255 (1948).

propionic acid labeled with C^{14} in the carboxyl group is decarboxylated, and the concentration of C^{14} in the carbon dioxide is determined from time to time. Assume that the rupture of the C^{12}-C^{14} bond is less likely than that of the C^{12}-C^{12} bond.At first, the concentration of C^{14} in the effluent carbon dioxide is less than the concentration in the in the original label, and as the course of the reaction procedes the acid remaining becomes enriched in C^{14}. As this enrichment process takes place the rate at which C^{14} is evolved will increase until, as the last molecules are decomposed, the concentration of C^{14} in the carbon dioxide being evolved is <u>greater</u> than that of the original label. The end result is to convert the whole label to a gaseous form and no net isotope concentration is observed if the decarboxylation is carried to completion, though at any instant up to that point, some, though decreasing, concentration will have been achieved.

If a symmetrical dicarboxylic acid, similarly singly labeled, is decomposed to form a monocarboxylic acid and carbon dioxide, the picture is somewhat different. The primary competetion to lose carbon dioxide is not so much between molecules as it is between the different functional groups in the same molecule. At first, the carbon dioxide would be impoverished in C^{14} and mono-acid produced would be slightly enriched in the label. The isotopic constitution of the remaining di-acid is not affected. As the reaction procedes the rates of rupture for the two C-C bonds remain the same and the enrichment of the remaining acid and impoverishment of the evolved carbon dioxide takes place at a constant rate; therefore, the isotopic concentrations of the label in these molecules remain the same throughout the reaction, though different from that in the original di-acid. Thus, symmetry can be used to "retire" part of the "chemically active" label, the result of which process is a level rate of isotope label enhancement with a constant net effect at any time.

Malonic acid was labeled in one carboxyl group by the reaction of radioactive sodium cyanide with inactive chloroacetic acid, after the procedure of Weiner (3). (The synthesis was carried out on a scale 1/50th as large as that suggested in reference 3.) The product malonic acid was carefully recrystallized from a mixture of diethyl ether and 60° petroleum ether. The recrystallized product melted at 135°, with decomposition,.

PROCEDURE FOR SMALL SAMPLES: -

A small amount of the solid was placed in the bottom of a 50 cc. pear shaped flask. A side arm admitted a capillary which led to the bottom of the flask and through which the sweep gas, nitrogen, was admitted. The flask was heated with an oil bath at 150-155°. The gas stream passed out of the flask into two small "cold-finger" traps in series; these traps were cooled with a mixture of dry ice and isopropyl alcohol. The first finger removed little acetic acid, but served to cool the gas stream so that the acid was completely held back by the second trap. The gas stream was then conducted through two spiral bubblers filled with 1 N sodium hydroxide. After approximately 40 minutes heating and sweeping the second trap was removed

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(3) Weiner, N., Organic Syntheses, Coll. Vol. II, John Wiley & Sons, Inc., New York, 1943, p. 376.

from the train and connected to a combustion furnace. The trap was then heated to about 90° with steam and the vapors of acetic acid were swept into the furnace with oxygen.

PROCEDURE FOR LARGE SAMPLES: -

The procedure employed with the larger samples was the same as that detailed above except that the second trap was removed from the train and warmed to room temperature after a small glass angle was attached to the input joint. As the crystals of acetic acid melted the liquid dripped from the cold finger into the carefully cleaned angle without contacting any other surface. The acid was removed from the angle with a micropipet and transferred to a porcelain boat before combustion.

The specific activities of the barium carbonate samples derived from the decarboxylation and combustion, and from combustion of a sample of original malonic acid, were determined by counting barium carbonate plates, prepared by methods described in detail elsewhere (4).

The first group of experiments involved the decarboxylation of four samples of malonic acid containing from 1.0 to 1.5 millimoles of compound. It was found that the failure to agree of the rupture ratios calculated on several bases was due to dilution of the acetic acid combustion product by carbon dioxide from small amounts of organic matter which had been ineffectually removed from the rapid oxygen

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(4) Yankwich, P. E., Report CC-3567.
Calvin, M., Heidelberger, C., Reid, J. C., Tolbert, B. M., and Yankwich, P. E., "Isotopic Carbon", John Wiley & Sons, Inc., New York, in press.

stream. The second group of experiments consisted of one decarboxylation of 6.0 mmoles and one of 10.0 mmoles. It was hoped that this scale-up would reduce the effects of slight contamination.

The results of all experiments are shown in Table I. The frequency of rupture ratios were obtained by pairing each of the specific activity figures in turn with those remaining, and the approach to identity of the three quotients thus obtained is a measure of the internal consistency of the experimentally derived data. The three bases noted are: A, carbon dioxide and malonic acid; B, acetic and malonic acids; C, carbon dioxide and acetic acid.

TABLE I

	F_{12-12}	F_{12-14}	F_{12-12}/F_{12-14} Bases A	B	C
Small scale experiments (4)	0.516 ± 0.005	0.452 ± 0.005	1.21 ± 0.017	1.066 ± 0.02	1.14 ± 0.013
Large scale experiments (2)	0.531 ± 0.016	0.474 ± 0.015	1.13 ± 0.03	1.11 ± 0.03	1.12 ± 0.03

The frequency ratios derived from the larger scale experiments correspond to a difference of approximately 96 cal/mole (34 cm^{-1}) in the activation energies of the two rupture processes.

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