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THE ISOTOPE EFFECT IN THE DECARBONYLATION OF BENZOYLFORMIC ACID

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### Authors

Fingerman, Bernice  
Lemmon, Richard M.

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*Ernest O. Lawrence*

*Radiation  
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ABSTRACT

The  $C^{14}/C^{12}$  isotope effect has been measured for the acid-catalyzed thermal decarbonylation of benzoylformic acid. The decarbonylation, which involves the breaking of a C-O bond in the rate-determining step, was found to have a value for  $k_{C^{14}}/k_{C^{12}}$  of 0.977.

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Most investigations of  $C^{14}/C^{12}$  and  $C^{13}/C^{12}$  isotope effects in chemical reactions have involved the separation of  $CO_2$  as a product; however, such an isotope effect have been measured in a decarbonylation reaction (separation of CO). Frey<sup>1</sup> described an attempt to measure an isotope effect involved in the thermal decomposition of ethyl and butyl pyruvates. However, no isotope effect due solely to decarbonylation could be measured, since large amounts of  $CO_2$  were obtained along with the evolved CO. Recently Elliot and Hammick<sup>2</sup> and Banholzer and Schmid<sup>3</sup> described the nearly quantitative decarbonylation of benzoylformic acid; only traces of  $CO_2$  were evolved. In this report, the  $C^{14}/C^{12}$  isotope effect was determined in the acid-catalyzed thermal decarbonylation of labeled benzoylformic acid,  $C_6H_5COC^{14}O_2H$ . The  $C^{13}/C^{12}$  isotope effect was also observed in the decarbonylation of the unlabeled compound.

Experimental Procedure

Preparation of Carboxyl-Labeled Benzoylformic Acid

A synthesis of  $C_6H_5COC^{14}O_2H$  was carried out following the procedure of Banholzer and Schmid.<sup>3</sup> Labeled potassium cyanide was prepared from

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1. H. M. Frey, Thermal Decomposition of Pyruvic Acid and its Esters Leading to  $CO_2$ , UCRL-3358, April 1956.
  2. W. W. Elliot and D. Hammick, J. Chem. Soc. 3402, (1951).
  3. K. Banholzer and H. Schmid, Helv. Chim. Acta 39, 548 (1956).

metallic K,  $\text{BaC}^{14}\text{O}_3$ , and  $\text{NH}_4\text{Cl}$ , according to the method of Sixma et al.<sup>4</sup> The  $\text{KC}^{14}\text{N}$  was converted to  $\text{Cu}_2(\text{C}^{14}\text{N})_2$  which, in turn, was reacted with benzoyl chloride to give  $\text{C}_6\text{H}_5\text{COC}^{14}\text{N}$ . The labeled benzoyl formic acid was then prepared by hydrolysis of the nitrile with concentrated HCl. The product had a specific activity of 0.012  $\mu\text{C}/\text{mg}$  or 1.802  $\mu\text{C}/\text{mmole}$ . To facilitate radioactivity determinations in an ionization chamber, the acid was diluted with unlabeled material, similarly prepared. The final specific activity of the benzoylformic acid was 0.366  $\mu\text{C}/\text{mmole}$ , as determined by combustion followed by ionization chamber assay.

#### Decarbonylation Experiments

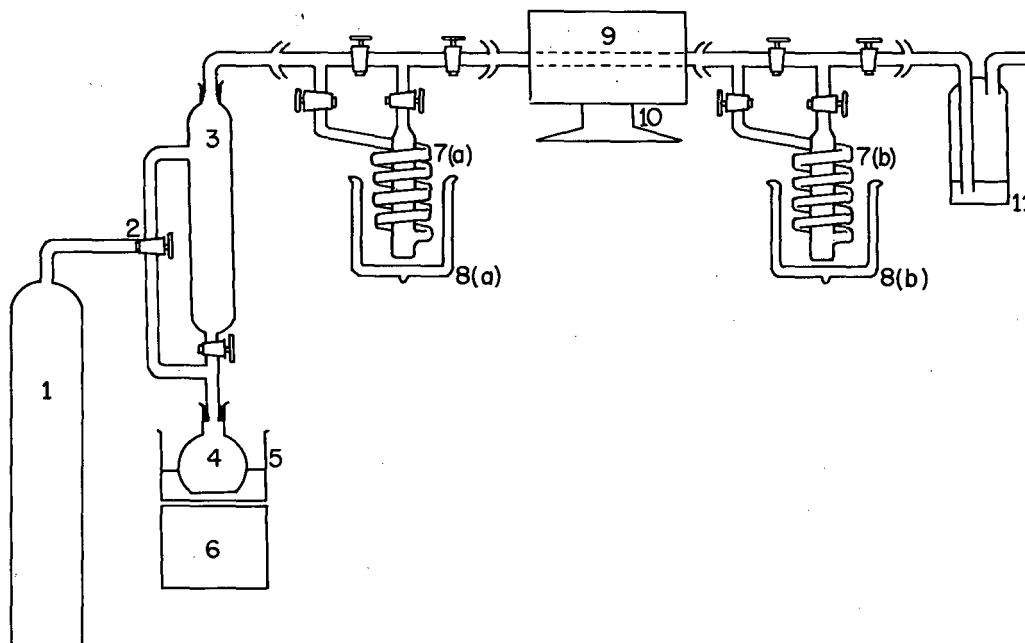
The decarbonylation was carried out in an oil bath at 35° by the addition of 15 ml of 97%  $\text{H}_2\text{SO}_4$  to about 1 mmole (the specific amount being known each time) of the benzoylformic acid. The apparatus shown in Fig. 1 was used for the decarbonylation. During the reaction, constant stirring was maintained; a stream of helium at the rate of 65 cc/min was used to sweep the evolved carbon oxides through the system immediately as they were produced. Any evolved  $\text{CO}_2$  was condensed in the first trap. The remaining gases then passed over CuO heated to 600° in a furnace. Carbon monoxide converted to  $\text{CO}_2$  was condensed in the second trap. This trap was removed and the amount of  $\text{CO}_2$  was measured by allowing the gas to expand into a known volume on a vacuum line. The apparatus was calibrated by passing known amounts of  $\text{CO}_2$  of known specific activity through the decarbonylation train (omitting the first trap) into the manometer system, and finally into the ionization chamber. This procedure gave reproducible results (four experiments) with a maximum spread of 1%.

The specific activity of the  $\text{CO}_2$  was determined by transference into an ionization chamber. The "rate-of-charge method" was used. These techniques were described earlier.<sup>5</sup>

4. Sixma, Hendricks, Helle, Hollstein, and Van Ling, *Rec. trav. chim.* 73, 161 (1954).

5. B. M. Tolbert, "Ionization Chamber Assay of Radioactive Gases," UCRL-3499, March 1956.





MU-14272

Fig. 1. Apparatus for the decarbonylation of benzoylformic acid.

1. Helium tank
2. Three-way stopcock
3. Pressure-compensated dropping funnel
4. 100-ml decarbonylation flask
5. Oil bath with heating coil
6. Magnetic stirrer
7. Spiral traps
8. Liquid nitrogen baths
9. Tube of CuO
10. Combustion furnace (600°)
11. Sulfuric acid bubbler

A  $C^{13}/C^{12}$  isotope effect was also observed in the decarbonylation of benzoylformic acid. We used the natural level of  $C^{13}$  present in unlabeled benzoylformic acid synthesized in our laboratory from benzoyl chloride and freshly prepared cuprous cyanide. The analyses for  $C^{13}$  were performed on a Consolidated Engineering Corporation Model 21-103A mass spectrometer. To determine the level of  $C^{13}$  in the carboxyl carbon of the benzoylformic acid the compound was nearly completely (98.5%) decarbonylated as described above, and the level of  $C^{13}$  in the resulting  $CO_2$  determined.

### Results and Discussion

About 1% of the gas evolved during the reaction appeared as  $CO_2$ ; and from 95% to 99% as CO. We have employed the method of collecting successive fractions of product CO (as  $CO_2$ ) and observing their specific activities. Comparison with the initial specific activity of the benzoylformic acid shows a "positive" or "normal" isotope effect, i. e., in the rate-determining step, bonds involving  $C^{12}$  of carboxyl group are breaking more easily than bonds involving  $C^{14}$  in that group. As might be anticipated for such an effect, successive fractions of  $CO_2$  consistently showed increasing specific activities. However, for quantitative determination of the isotope effect for this reaction, we have used an expression similar to that of Bothner-By and Bigeleisen.<sup>6</sup> The expression is derived from integration of an equation involving the ratio of rate equations for reaction of the  $C^{14}$ -labeled compound and the  $C^{12}$ -labeled compound:

$$\log \left( \frac{1}{1-\lambda} \right) = \beta/\alpha \log \left( \frac{1}{1-\gamma} \right),$$

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6. A. Bothner-By and J. Bigeleisen, J. Chem. Phys. 19, 755 (1951).

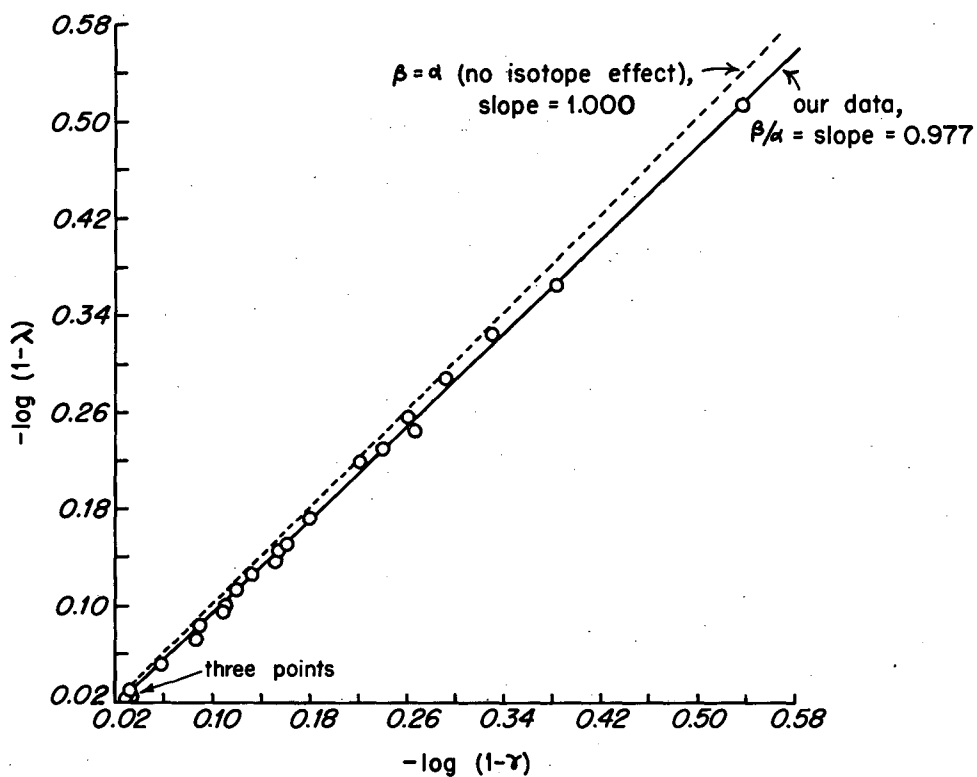
where  $\beta$  = rate constant for reaction of labeled reactant molecules,  
 $\alpha$  = rate constant for reaction of unlabeled reactant molecules,  
 $\lambda$  = fraction of the initial total activity found in the cumulative product,  
 $\gamma$  = fraction of complete reaction.

The only assumption in the derivation is that the labeled compound exists in very low concentrations. By plotting  $\log\left(\frac{1}{1-\lambda}\right)$  vs  $\log\left(\frac{1}{1-\gamma}\right)$ , one should have a straight line whose slope is  $\beta/\alpha$ , the ratio of the two rate constants.

The data from eight separate decarbonylation experiments, with a total of 22 fractions, are plotted in Fig. 2. The straight line shown on the graph was obtained by the method of least squares, which gives the slope of the line,  $\beta/\alpha$ . We have used data out to 65% reaction and have found a slope  $\beta/\alpha = 0.977$ . Thus,  $k_{C^{14}}/k_{C^{12}} = 0.977$ , or our isotope effect is 2.3%. In principle, any single point in the plot in Fig. 2 may be used to measure an isotope effect. There are 22 points plotted in the figure; the individual values for  $\beta/\alpha$  range from 0.822 to 0.996. The average for these values is 0.941 and the mean deviation is 0.040. However, the data are not equally valid for varying fractions of decarbonylation, and we have therefore chosen the least-squares method in order to evaluate our data.

In the  $C^{13}$  experiment the reaction was carried to 10% completion and this first 10% of CO collected as  $CO_2$ . The starting benzoylformic acid contained  $1.157 \pm 0.003\%$   $C^{13}$  in the carboxyl position, whereas the first 10% of the product contained  $1.087 \pm 0.003\%$   $C^{13}$ . Thus a normal or "positive" isotope effect was again observed. However, a quantitative determination of the  $C^{13}/C^{12}$  isotope effect could not be made from this single experiment.

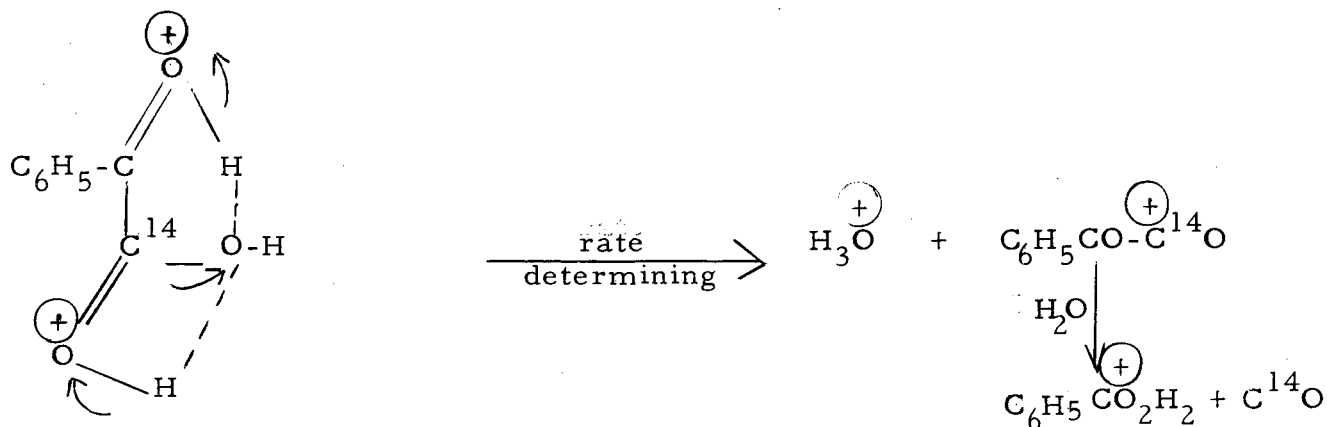
Elliot and Hammick<sup>2</sup> had shown that the  $H_2SO_4$ -catalyzed decarbonylation of the benzoylformic acid was first-order in the organic acid, and that the



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Fig. 2. Isotope effect in the decarboxylation of benzoylformic acid.

rate-determining step was the decomposition of a di-protonated species,  $\left[ \text{C}_6\text{H}_5-\overset{\oplus}{\text{C}}\text{OH}-\overset{\oplus}{\text{C}}\text{O}_2\text{H}_2 \right]$ . In addition, Schmid's work, which we were able to repeat, showed that all the CO comes from the carboxyl group. The resultant mechanism for the reaction is therefore



Significantly, it is the breaking of a C-O bond at the labeled site in the rate-determining step which must account for the observed isotope effect, whereas most  $\text{C}^{14}/\text{C}^{12}$  isotope effect studies (both theoretical and experimental) have involved the breaking of a C-C bond. It thus appears that the isotope effect for the breaking of a C-C bond is of a magnitude comparable to that for the breaking of a C-O bond.

#### Acknowledgment

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