

## An Effect of Isotopic Mass on the Rate of a Reaction Involving the Carbon Carbon Bond

Peter E. Yankwich and Melvin Calvin

Citation: *The Journal of Chemical Physics* **17**, 109 (1949); doi: 10.1063/1.1747046

View online: <http://dx.doi.org/10.1063/1.1747046>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/17/1?ver=pdfcov>

Published by the AIP Publishing

---

### Articles you may be interested in

[Carbon-carbon bond forming reactions on Cu\(110\) surfaces](#)

J. Vac. Sci. Technol. A **10**, 2185 (1992); 10.1116/1.578002

[Isotope Size Effect in Van der Waals Radii and the Barrier to Rotation around the CarbonCarbon Single Bond](#)

J. Chem. Phys. **35**, 1527 (1961); 10.1063/1.1732100

[Rotational Isomerism Involving the 2-3 CarbonCarbon Bond of the 1Alkenes](#)

J. Chem. Phys. **33**, 298 (1960); 10.1063/1.1731105

[Carbon Isotope Effect on Reaction Rates](#)

J. Chem. Phys. **17**, 1341 (1949); 10.1063/1.1747175

[Isotope Effect in the Rupture of CarbonCarbon Bonds in Propane-1C13](#)

J. Chem. Phys. **17**, 344 (1949); 10.1063/1.1747250

---



TABLE I. Distances between neighboring absorption bands in A.

Solvent	Distance between adjacent bands								
	A-B	B-C	C-D	D-E	E-F	F-G	G-H	H-I	I-J
Iso-octane	223	78	114	161	62	80	66	83	78
Ethyl alcohol	232	65	124	155	67	80	65	82	79
Chloroform	212	78	123	135	74	76	71	82	79
Benzene	—	—	125	—	—	85	71	84	81

tively smaller distances from their long wave-length neighbors.

Of some interest is also the *percentage* change in absorption intensity on passing from iso-octane to one of the other three solvents. All three give rise to an increase in absorption intensity at the long wave-length end of the spectrum (Table II), and only ethyl alcohol seems to weaken the absorption at the short wave-length end.

TABLE II. Percentage change of absorption intensity in the ultra-violet spectrum of phenanthrene in various solvents both below and above 3000A as compared to phenanthrene in iso-octane.

Solvent	Maximum percentage change of absorption	
	below 3000A	above 3000A
Ethyl alcohol	-6 to -20	+3.5 to +17
Chloroform	-3.5 to +15.5	+9.1 to +40.4
Benzene	+9.5 to +10.1	+32.3 to +45

<sup>1</sup> B. Vodar and S. Robin, J. Chem. Phys. 16, 996 (1948).

<sup>2</sup> R. Schnurmann and S. Whincup, Petroleum 8, 122 (1945).

<sup>3</sup> We are indebted to Dr. M. Sulzbacher of the Grosvenor Laboratory, London, for the synthesis of this particular sample of phenanthrene.

<sup>4</sup> A detailed account of this work will be published elsewhere.

<sup>5</sup> The phenanthrene bands are here lettered alphabetically beginning with A at the short wave-length end of the spectrum.

## An Effect of Isotopic Mass on the Rate of a Reaction Involving the Carbon-Carbon Bond\*

PETER E. YANKWICH\*\* AND MELVIN CALVIN

Department of Chemistry and Radiation Laboratory, University of California, Berkeley, California\*\*\*

November 12, 1948

INVESTIGATION on the effect of the difference in mass between isotopes upon the rate of a chemical transformation has been limited entirely to the very lightest of the elements, especially hydrogen, although the effect of isotopic mass upon the rate of many physical processes has been extended throughout the periodic table.<sup>1</sup> The effect of isotopic mass on certain chemical equilibria has been used to separate the isotopes of carbon and nitrogen. Recently, the isotope effect on the rate of a chemical reaction has been observed by Beeck<sup>2</sup> who demonstrated in the course of a study of the isomerization of propane that the dissociation probability of the C<sup>12</sup>-C<sup>12</sup> bond was increased 77 percent, and that of the C<sup>13</sup>-C<sup>12</sup> bond decreased 12 percent from the dissociation probability of the C<sup>12</sup>-C<sup>12</sup> bond in unlabeled propane. Further experiments<sup>3</sup> by the same authors yield a C<sup>12</sup>-C<sup>12</sup>/C<sup>13</sup>-C<sup>12</sup> rupture ratio of 1.08 for thermal cracking at 500°, contrasted with 1.22 for electron impact rupture.

Decarboxylation reactions can be made to take place at moderate temperatures, and for a given reaction the isotope effect should increase with decreasing temperature. If a symmetrical dicarboxylic acid, labeled in only one carboxyl group, is decomposed to form a monocarboxylic acid and carbon dioxide, the primary competition for reaction is between the different functional groups in the same molecule. Assuming the same type of bond strengthening and weakening noted above, the carbon dioxide evolved would be impoverished in the label, while the mono-acid produced would be similarly enriched in label. Since the isotopic constitution of the remaining di-acid is unaffected, this result of symmetry can be used to "retire" part of the "chemically active" label and produce a level rate of isotope label enhancement with a constant net effect at any stage of the decarboxylation process.

Singly labeled malonic acid was prepared from chloroacetic acid and active cyanide after the procedure of Weiner.<sup>4</sup> The product was recrystallized from diethyl ether-60° petroleum ether mixtures; m.p. 135°. A part of this acid was treated with bromine in moist ether, and the bromomalonic acid formed recrystallized from acetone and benzene. (The bromomalonic acid finally employed was not of great purity.)

A few hundred mg of acid was placed in the bottom of a pear-shaped flask, which could be swept throughout with nitrogen. The flask was heated in an oil bath ~10° above the decomposition temperature of the acid; carbon dioxide was swept through dry-ice-acetone traps (which served to collect much of the product mono-acid) into sodium hydroxide-filled absorption bubblers. After apparent completion of the reaction, the mono-acid was transferred to a combustion train. Two malonic acid experiments were performed, using 6 and 10 moles, respectively; one 2.1 mole bromomalonic acid decarboxylation was carried out.

The results of the experiments are shown in Table I. The frequency of rupture ratios was obtained by pairing each of the specific activity figures 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 di-acid; B, mono-acid and di-acid; C, carbon dioxide and mono-acid.

It is to be noted that the above ratios, that is 1.12 for malonic acid and 1.4 for the bromomalonic, are considerably larger than any isotope effects that have been observed in chemical equilibria. It is, of course, to be expected that the effect of the zero-point energy difference on a chemical rate process should be larger than its effect on an

TABLE I.

Compound	$F_{12-12}$ basis B	$F_{12-14}$ basis A	$F_{12-12}/F_{12-14}$ basis	
			B	C
Malonic acid	0.531 ± 0.016	0.474 ± 0.015	1.13 ± 0.03	1.12 ± 0.03
Bromo-malonic acid	0.61 ± 0.04	0.44 ± 0.03	1.30 ± 0.11	1.57 ± 0.15
				1.41 ± 0.08

equilibrium, because the zero-point energy differences are also found in the product of an equilibrium as well as in the reactants while in a rate process presumably only the zero-point energy difference of the reactants is effective. However, if one tries to attribute the above-observed ratios entirely to differences in activation energy for the splitting off of the two different carboxyl groups, one arrives at a value of 96 calories for the difference in malonic acid and 250 for the difference in bromomalonic acid. These differences are rather larger than can be accounted for in terms of the effect of mass on the carbon-carbon stretching vibration (approximately 1000 wave numbers), and it is evident that the situation is more complex than that.

The assistance of Mr. Wilbur Melbye in the bromomalonic acid experiment is gratefully acknowledged.

\* This paper is based on work performed under Contract No. W-7405-Eng-48 with the Atomic Energy Commission in connection with the Radiation Laboratory, University of California, Berkeley, California.

\*\* Present address: Department of Chemistry, University of Illinois, Urbana, Illinois.

\*\*\* This paper has been presented at the 113th National Meeting of the American Chemical Society, Chicago, Illinois, April, 1948 and at the meeting of the Pacific Intersectional Group of American Chemical Society Sections of the Pacific Division of the American Association for the Advancement of Science, Berkeley, California, June, 1948.

<sup>1</sup> H. C. Urey, *Record Chem. Progress* **9**, 69 (1948).

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

<sup>3</sup> D. P. Stevenson, C. D. Wagner, O. Beeck, and J. W. Otvos, *J. Chem. Phys.* **16**, 993 (1948).

<sup>4</sup> N. Weiner, *Organic Synthesis* (John Wiley and Sons, Inc., New York, 1943), Coll. Vol. II, p. 376.

### Errata: "Raman Spectrum of Tetraethyl Orthosilicate" and "Raman Spectrum of Trimethyl Silicon Chloride"

[*J. Chem. Phys.* **16**, 1006, 1009 (1948)]

JULES DUCHESNE, A. MONFILO, AND CLAUDE ANSPACH  
*Faculty of Science of the University, Brussels, Belgium*

THE names and addresses of the authors of these papers were incorrectly given. They should have appeared as "Raman spectrum of tetraethyl orthosilicate" by Jules Duchesne and A. Monfillo, Faculty of Science of the University, Brussels, Belgium, and "Raman spectrum of trimethyl silicon chloride" by Claude Anspach and Jules Duchesne, Faculty of Science of the University, Brussels, Belgium.

The following note should have appeared with both articles.

"One of us (Jules Duchesne\*) wishes to express his sincere thanks to the University of Brussels for its kind hospitality during the tenure of his professorship there."

\* Present address: Department of Chemical Physics of the University of Liege, Belgium.