[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

# Fractionation of the Carbon Isotopes in Decarboxylation Reactions. V. The Mechanism of the Pyrolysis of Barium Adipate[1]

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A study of the fractionation of the carbon isotopes in the pyrolysis of barium adipate to form barium carbonate and cyclopentanone has been made. At 350° the fractionation factor is less than a few tenths of a per cent. In the pyrolysis of a mixture of barium adipate and radioactive barium carbonate all the C$^{14}$ remains in the BaCO$_3$. These results are interpreted in terms of a mechanism which involves a rapid, reversible proton removal from an alpha carbon in the adipate ion, followed by a concerted decarboxylation and ring closure reaction.

Two different approaches have been employed in the use of isotopes to elucidate the mechanisms of chemical reactions. The most frequent approach involves the tracing of an isotope through the course of a reaction. The other method is the investigation of the effect of isotopic substitution on the rate of the reaction. The latter type of investigation is at present limited to the light elements where the isotope effects on rates are measurable by present techniques. These two approaches are not necessarily mutually exclusive. In the case of most of the first row elements in the Periodic Table, the relative rates of reaction of the isotopic species can be determined by measuring the change in the natural isotopic abundance occurring during the course of the reaction. Tagged atom studies necessarily require abnormal isotopic compositions.

In recent years there has been considerable experimental and theoretical work on the carbon isotope effect in decarboxylation reactions. These researches have been reviewed recently by Bigeleisen.[2] The agreement between theory and experiment is sufficiently good to allow one to proceed with some confidence to use the isotopic fractionation technique as a tool in the study of the mechanisms of some decarboxylation reactions. Such an approach is valuable in cases where conventional kinetic techniques are difficult to apply.

The decarboxylation of the aliphatic dicarboxylic acids cannot be put into any simple general scheme. Brown[3] has recently reviewed the chemical and kinetic evidence and attempted a classification of decarboxylation reactions in terms of $S_E1$ and $S_E2$ type mechanisms. Even after such a classification is made, more detailed knowledge of possible intermediates and the transition state are desirable.

In the case of the pyrolysis of barium adipate, decarboxylation is coupled with cyclization to produce cyclopentanone. That the presence of an $\alpha$-hydrogen atom is necessary for this reaction has been established by Farmer and Kracovski[4] who showed that $\alpha,\alpha,\alpha',\alpha'$-tetramethylbarium adipate is neither cyclized nor decarboxylated under more drastic conditions than is customary in pyrolysis of barium adipate. Neunhoeffer and Paschke[5] suggested a mechanism for the reaction involving preliminary removal of a proton from an $\alpha$-carbon, cyclization to a $\beta$-keto acid or salt, and subsequent elimination of carbon dioxide. Their suggestion is made entirely on the basis of investigation of the products of specific chemical reactions. It is not known whether the $\alpha$-hydrogen which is removed to form the postulated intermediate salt of the $\beta$-keto acid results from an inter- or intramolecular rearrangement.

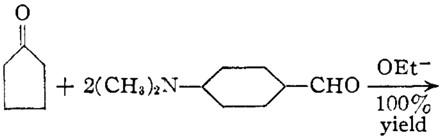
Subsequently Wiberg[6] showed that in the pyrolysis of mixtures of barium butyrate and barium butyrate-$\alpha$-$d_2$ there is complete exchange of the deuterium in the undecomposed salt after 25% decarboxylation. This is in accord with the Neunhoeffer–Paschke mechanism.

In a study of the nitrogen isotope effect in the thermal deammonation of phthalamide it has been shown that the isotope fractionation technique is particularly powerful in determining whether or not bond rupture and ring formation occur simultaneously.[7] A similar study of the fractionation of the carbon isotopes in the pyrolysis of barium adipate has been carried out with the hope of learning something about the mechanism.

## Experimental

Barium adipate was prepared by adding a stoichiometric amount of carbonate-free Ba(OH)$_2$ solution to a weighed amount of dissolved adipic acid (Eastman Kodak Co.), which had previously been twice recrystallized from water. The solution was cooled and barium adipate precipitated by the addition of ethanol. The sample was filtered and then vacuum-dried at 110°. A portion of the barium adipate was converted to CO$_2$ for isotopic assay by wet combustion.[8]

A one-gram sample of barium adipate was then sealed in an evacuated Carius tube. One end of the tube was heated in a micro-furnace to 350° for six hours. The cyclopentanone formed from the cyclization condensed in the cool portion of the tube. The tube was carefully opened and the cyclopentanone separated from the barium carbonate. CO$_2$ was generated from the BaCO$_3$ by treatment with concentrated H$_2$SO$_4$ and was assayed mass spectrometrically for C$^{13}$. The cyclopentanone was assayed for C$^{13}$ in two ways. In the first assay a portion of the cyclopentanone was completely oxidized to CO$_2$ to check on the C$^{13}$ material balance. In another experiment an attempt was made to isolate the carbonyl carbon specifically: CO$_2$ from the carbonyl carbon was obtained by the sequence of reactions



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[1] Research carried out at the Brookhaven National Laboratory under the auspices of the U. S. Atomic Energy Commission. The material in this paper was presented at the Brookhaven Conference on the "Use of Tracers in Organic Reaction Mechanism Studies," January 19, 1950.

[2] J. Bigeleisen, *J. Phys. Chem.*, **56**, 823 (1952).

[3] B. R. Brown, *Quart. Rev. Chem. Soc. (London)*, **5**, 131 (1951).

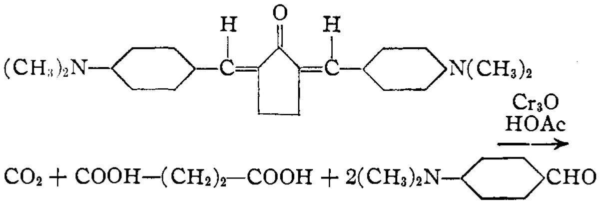
[4] E. H. Farmer and J. Kracovski, *J. Chem. Soc.*, 680 (1927).

[5] O. Neunhoeffer and P. Paschke, *Ber.*, **72**, 919 (1939).

[6] K. B. Wiberg, THIS JOURNAL, **74**, 4381 (1952).

[7] J. Bigeleisen, *Can. J. Chem.*, **30**, 443 (1952).

[8] R. C. Anderson, Y. Delabarre and A. A. Bothner-By, *Anal. Chem.*, **24**, 1298 (1952).



Unfortunately the yield of $CO_2$ from the $\alpha,\alpha'$-bis-($p$-dimethylaminobenzal)-cyclopentanone is but 60% and therefore the $C^{13}$ assay on the $CO_2$ from the carbonyl carbon cannot be used as a reliable determination of the $C^{13}$ content of the carbonyl carbon in the cyclopentanone. All mass spectrometer analyses were carried out with a Consolidated-Nier isotope ratio instrument.

Neunhoeffer and Paschke found a small amount of adipic acid formed from a mixture of cyclopentanone, sodium bicarbonate and acetic acid heated to 330°. To determine whether or not the decarboxylation of the barium salt might be in part reversible, a tracer experiment was carried out with $BaC^{14}O_3$. Twenty milligrams of the latter containing about 20 $\mu$curies of $C^{14}$ was admixed with a sample of barium adipate and pyrolyzed completely. No activity could be detected in the cyclopentanone formed. Under these conditions the pyrolysis is therefore irreversible.

## Results and Discussion

The results of the isotopic analyses are given in Table I.

TABLE I

$C^{13}$ ANALYSES OF PRODUCTS FROM THE PYROLYSIS OF BARIUM ADIPATE

| Sample | $C^{13}O_2/C^{12}O_2 \times 10^4$ |
|---|---|
| Starting, barium adipate—total C | 107.00 ± 0.05 |
| Product, $BaCO_3$ | 107.13 ± .05 |
| Product, cyclopentanone—total C | 106.94 ± .04 |
| Product, cyclopentanone—carbonyl C | 106.62 ± .14 |
| Tank $CO_2$—reference | 106.97 ± .07 |

It is seen from the results in Table I that the barium adipate is of normal isotopic composition with respect to carbon and that there is no fractionation during the pyrolysis. The slight depletion (0.4%) in the carbonyl carbon sample probably arises from the incomplete conversion of the cyclopentanone to $CO_2$ and succinic acid.

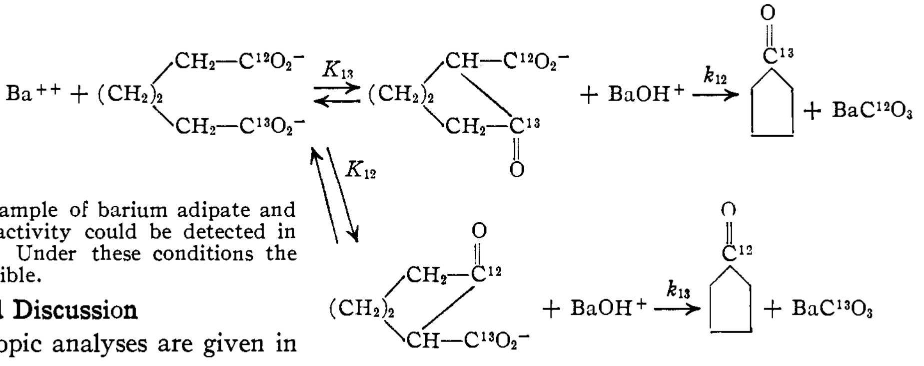
Any mechanism for the pyrolysis should be consistent with the following facts: (1) a mobile $\alpha$-hydrogen is necessary, (2) there is no exchange of carbon in the course of the reaction with admixed $BaCO_3$, (3) there is no isotopic fractionation during the reaction.

Wiberg's deuterium exchange study[6] supports a rapid reversible removal of a proton from an $\alpha$-hydrogen in the pyrolysis of barium butyrate. If we reason by analogy in the case of the adipate pyrolysis, we may eliminate mechanisms which start with a slow irreversible removal of a hydrogen from the $\alpha$-carbon atom. The condition of no exchange eliminates one reaction mechanism suggested by Neunhoeffer and Paschke, where there is an equilibrium between barium adipate and the salt of the $\beta$-keto acid which in turn is in equilibrium with cyclopentanone and barium carbonate. There are two types of mechanisms which conform to the first two conditions above. One is a reversible equilibrium between the barium adipate and the salt of the $\beta$-keto acid, followed by an irreversible decarboxylation (A). The second is a reversible dissociation of a proton from an $\alpha$-carbon followed by a concerted reaction to give the enolate anion of cyclopentanone and barium carbonate (B). We shall examine these for possible isotope fractionation.

From mechanism A the isotopic composition of the barium carbonate at complete reaction is related to the natural abundance by the equation[9]

$$(C^{13}O_3^{=}/C^{12}O_3^{=})/(\alpha/1 - \alpha) = 2k_3/(k_3 + k_4) \quad (1)$$

where $\alpha$ is the natural abundance of $C^{13}$ in the barium adipate, $k_3 = k_{13}K_{12}$, and $k_4 = k_{12}K_{13}$. The quantities $k_{12}$, $k_{13}$, $K_{12}$ and $K_{13}$ are defined by the reactions

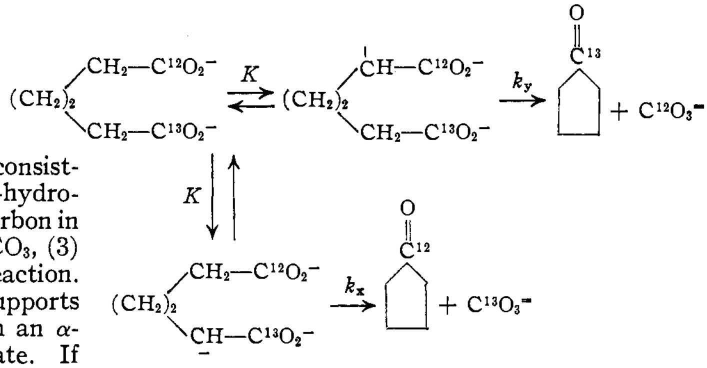


From equation (1), the definitions of the $k$'s and $K$'s and the data in Table I one finds for mechanism A

$$(k_{12}/k_{13})(K_{13}/K_{12}) = 1.00 \quad (2)$$

The ratio $k_{12}/k_{13}$ can be calculated[2] to be 1.027 while the ratio of equilibrium constants, $K_{13}/K_{12}$, does not differ from unity by more than a few tenths of a per cent. at 350°. These calculations cast doubt on the mechanism.

Under mechanism B the ratio of $BaC^{13}O_3$ to $BaC^{12}O_3$ is given by equation (1) where $k_3 = Kk_x$ and $k_4 = Kk_y$, which are defined by the reactions



No effect of the isotopic composition of the carbon in the carbonyl group on $K$ is to be expected. In the reaction which leads to $C^{13}O_3^{=}$ one $C^{12}$–$C^{12}$ and one $C^{13}$–$O^{16}$ bond are formed while one $C^{12}$–$C^{13}$ and one $C^{12}$–$O^{16}$ are ruptured. In the reaction which produces $C^{12}O_3^{=}$ the bonds formed are $C^{12}$–$C^{13}$ and $C^{12}$–$O^{16}$ while a $C^{12}$–$C^{12}$ and a $C^{13}$–$O^{16}$ bond are ruptured. In the calculation of the ratio

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(9) For a derivation of this equation see J. Bigeleisen, *Science*, **110**, 14 (1949); and J. Bigeleisen and L. Friedman, *J. Chem. Phys.*, **17**, 998 (1949).

$k_x/k_y$ the contribution from the zero point energy effect will be less than 1% for processes of the type involved in this reaction at 350°. It has been shown that the reduced mass effect is unity if similar bonds are made and ruptured in the transition state.[7] Therefore there will be no reduced mass contribution to the ratio $k_x/k_y$ and as a result its value should be unity within less than 1%. Thus an analysis of mechanism B predicts no fractionation of carbon isotopes during the pyrolysis, which is in agreement with experiment. Almost any concerted reaction mechanism for the pyrolysis will lead to this same result.

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[CONTRIBUTION FROM CHEMICAL AND PHYSICAL RESEARCH LABORATORIES, THE FIRESTONE TIRE AND RUBBER COMPANY]

# The Effect of Comonomer on the Microstructure of Butadiene Copolymers

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The microstructure of butadiene–styrene copolymers having a wide range of styrene contents has been determined by infrared absorption. The results demonstrate that the percentage of *trans*-1,4-addition increases, the 1,2-addition decreases and the *cis*-1,4-addition decreases as the styrene content is increased. Similar measurements on five other butadiene copolymer systems indicate that all of these vinyl monomers, acrylonitrile, methacrylonitrile, methyl vinyl ketone, vinylpyridine and α-methylstyrene, change the microstructure in the same direction as styrene, differing only in the magnitude of their effect. A theoretical explanation, consistent with the experimental results obtained, is given for the change in microstructure with comonomer content.

It is well-known that butadiene polymerizes by 1,2-addition to produce side vinyl (—CH=CH$_2$) groups and by 1,4-addition to produce double bonds in the polymer chain with *cis* and *trans* configurations. With butadiene–vinyl copolymers the diene portion of the copolymer chain may also have any or all of the three microstructures mentioned above. It is known[1] that, in general, increasing the temperature of polymerization, for both types of polymers, increases the amount of *cis*-1,4-addition and decreases the amount of *trans*-1,4-addition. It is also known that a variation in the mechanism of polymerization causes a change in the microstructure of butadiene polymers; thus, 1,2-addition predominates in sodium-catalyzed butadiene polymers.

Little or nothing is known about the effect of the kind or concentration of the vinyl comonomer on the microstructure of the diene polymer. Thus early workers[2] by ozonolysis concluded that copolymers of butadiene with methyl methacrylate and methacrylonitrile probably contained more 1,4-addition than polybutadiene. Early infrared work[3] indicated that butadiene–styrene or butadiene–acrylonitrile copolymers had smaller amounts of 1,2-addition than polybutadiene. However, Kolthoff, Lee and Mairs,[4] using the perbenzoic acid method, reported that the amount of 1,2-addition did not vary with kind or concentration of the comonomer in butadiene copolymers. Hart and Meyer[5] on the basis of infrared measurements, concluded that the amount of styrene had no effect on the amounts of 1,2- and 1,4-addition in the butadiene portion of butadiene–styrene copolymers. However, their data show a slight increase of *trans*-1,4-addition with a corresponding decrease of *cis*-1,4-addition as the styrene concentration was increased from 0 to 23%.

With many of the butadiene copolymers reported above the range of concentration of the comonomer was small and the experimental uncertainties too large to show small trends. Therefore, the effect of kind and concentration of the comonomer in butadiene–vinyl copolymers was investigated, in the present work, using large concentration ranges. Because of the dependence of microstructure on temperature and polymerization mechanism, all of the polymers reported here were prepared at the same temperature using free radical catalysis.

## Experimental

All vinyl monomers were purified by distillation before use. Monomers were tested for the absence of polymer before use. Physical constants found for the monomers were: acrylonitrile, $n^{20}_{\mathrm{D}}$ 1.3916; methacrylonitrile, $n^{20}_{\mathrm{D}}$ 1.4005; α-methylstyrene, $n^{20}_{\mathrm{D}}$ 1.5386, methyl vinyl ketone, $n^{20}_{\mathrm{D}}$ 1.4117; 2-vinylpyridine, $n^{20}_{\mathrm{D}}$ 1.5482 and styrene, $n^{20}_{\mathrm{D}}$ 1.5468.

Butadiene, supplied by Koppers Company and meeting Rubber Reserve standards of purity, was merely condensed before use.

All copolymerizations were conducted at 50° using the following recipe

| | |
|---|---|
| Water | 180 |
| Monomers | 100 |
| S F Flakes | 5 |
| Potassium persulfate | 0.3 |
| Dodecanethiol | 0.75 |

Conversions were varied from low to complete conversion.

Copolymers were coagulated with methanol and washed several times with water and with methanol. Final purification was accomplished by extracting the copolymers under gentle reflux with ethanol–toluene azeotrope (70–30 by volume). Three changes of solvent were used, each extraction lasting an hour. The copolymers were then extracted three times with acetone and dried under vacuum. It was necessary to substitute methanol for acetone in the final extractions of the acrylonitrile copolymers, methacrylonitrile copolymers and the high styrene copolymers in

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(4) I. M. Kolthoff, T. S. Lee and M. A. Mairs, *J. Polymer Sci.*, **2**, 220 (1947).

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