Intramolecular Kinetic Carbon Isotope Effect in the Gas Phase

Decomposition of Deuteriooxalic Acid

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The intramolecular C¹³ kinetic isotope effect has been measured between 127 and 180° in the decomposition to carbon dioxide and formic acid of oxalic acid- d_2 vapor at an initial pressure of 0.8 mm. This isotope effect is small, 0.5% maximum, but has a temperature dependence so large that it inverts within the experimental range. It is shown that ordinary isotope effect theory and assumptions of low pressure effects, such as described by Rabinovitch and his co-workers, are inadequate to explain the results or would not come into play, respectively. It is postulated that multiple reaction paths are responsible for the phenomena observed.

Introduction

Recently, we reported results on the kinetics of the decompositions of oxalic $\operatorname{acid}^{2\mathfrak{a}}$ and of $\operatorname{oxalic} \operatorname{acid}^{d_2^{2\mathfrak{b}}}$ in the gas phase at pressures near 1 mm. Comparison of the two sets of rate constants for the temperature range $127-156^{\circ}$ revealed a small deuterium isotope effect normal in direction, $k_{\rm H} > k_{\rm D}$, at low temperatures, which disappears near 145°, and is *inverted*, $k_{\rm D} > k_{\rm H}$, at higher temperatures.

In an attempt to explain this unusual phenomenon, we showed that: the size of the temperature dependence of $k_{\rm H}/k_{\rm D}$ could be accounted for by combination of kinetic, equilibrium (e.g., between cyclic and noncyclic structures arising through intramolecular intercarboxyl hydrogen bonding), and tunneling isotope effects; the observed magnitude of $(k_{\rm H}/k_{\rm D}-1)$ is reasonable if there were impressed on the above combination a virtually temperature-independent inverse isotope effect such as that described and observed by Rabinovitch and his co-workers.³⁻⁷

Since the Rabinovitch effect should appear only in the low-pressure region of a gaseous unimolecular decomposition, and since we have no information on the rate of the oxalic acid pyrolysis as a function of pressure, it seemed possible that study of the temperature dependence of C^{13} kinetic isotope effects might reveal additional information about the reaction mechanism. Under the experimental conditions accessible to us.^{2a} only the *intramolecular* carbon isotope effect (that arising in the bifunctionality of the reagent and determined from measurements on the isotopic constitution of the products) could be studied conveniently.

We expected the intramolecular carbon kinetic isotope effect to be small (of the order of 1%) because there is but one C-C bond in the oxalic acid molecule, and it must always be broken during the pyrolysis to carbon dioxide and formic acid; this isotope effect depends only upon the structural and related energetic differences between isotopically isomeric forms of activated molecules.

Consider now a possible statistical inverse intramolecular carbon isotope effect in this decomposition. A number of factors operate to ensure its smallness: first, the reduced mass effect is only about 5% of that for hydrogen isotopy in the same molecule; second, the

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differences between the quantum statistical densities of energy states which contribute to the isotopically *isomeric* decomposition modes (characteristic of the *intra*molecular isotope effect) are much smaller than the corresponding differences which contribute to the isotopic decomposition modes characteristic of the *inter*molecular isotope effect; third, a consideration similar to the second operates through the isotopic and isotopically isomeric critical energies, $(E_0)_i$.

We expected, therefore, that in the decomposition of oxalic acid- d_2 the above factors and the additional suppression of nonclassical effects because of the substitution of D for H should serve to eliminate or to reduce to marginal observability a statistical inverse intramolecular carbon isotope effect; these considerations operate whether the actual decomposition is homogeneous or heterogeneous (the latter possibility having been mentioned but not explored in the earlier work on the rate of the reaction²). Were such an expectation sound, and in the absence of an as yet unsuspected mechanism for inversion of primary kinetic isotope effects, any isotope fractionation observed could be attributed to an ordinary kinetic origin; though small, such an isotope effect should be a monotonic function of temperature and should not invert.

Experimental Section

Reagent. Fisher Analytical grade oxalic acid was purified by vacuum sublimation at 110° , and labeled to at least 99.3 atom % D in both carboxyl groups by repeated evaporation to dryness from solution in 99.5% deuterium oxide. The material was dried *in vacuo* and stored over magnesium perchlorate until used.

Apparatus and Procedure. The apparatus and procedures were identical with those employed in the kinetics studies^{2a} with two exceptions: (1) because the intramolecular isotope effect is determined from measurements on the final products, run times were extended so that the decomposition was 99.9% or more; (2) all samples of carbon dioxide were equilibrated with standard water to reduce to *nil* the variation in the correction applied for the presence of O¹⁷.

Because the reaction was taken essentially to completion, higher temperatures could be employed than in the kinetics studies, and experiments were carried out between 127 and 180°. At 180°, $k_{\rm D}$ is about 4.6 × 10^{-3} sec⁻¹, but thermal equilibration is so rapid under the conditions employed that there is inappreciable reaction during warm-up even at this temperature. There is, however, a total of $1.3 \pm 0.4\%$ reaction during the sublimation and injection steps, which occur, effectively, at a temperature of 130°. Correction for this effect proved too small to have significant in fluence on the results reported below.

Isotope Analyses. The procedures employed have been detailed in earlier publications from this laboratory.⁸⁻¹⁰ Because preliminary experiments showed the carbon isotope effects to be very small, extra precision was achieved by replacing the dc amplifiers of the original mass spectrometer with a slaved pair of vibrating-reed electrometers (Applied Physics Corp., Pasadena, Calif.).

Notation and Calculations. The isotopic rate constant ratio sought was $(k_2/k_3)_D$ in the notation of Lindsay, McElcheran, and Thode¹¹

$$C^{13}OOD \xrightarrow{(k_2)_D} C^{13}O_2 + DC^{12}OOD \qquad (1)$$

$$C^{12}OOD \xrightarrow{(k_3)D_1} C^{12}O_2 + DC^{13}OOD$$
 (2)

Let $(X_{\rm C})_t$ be the mole fraction of ${\rm C}^{13}{\rm O}_2$ in carbon dioxide product collected up to any time t, and $(X_{\rm F})_t$ be the corresponding mole fraction of DC¹³OOD derived from measurements on carbon dioxide obtained by combustion (in a Pregl-like apparatus) of the formic acid product. Then

$$\frac{(X_{\rm C})_{\iota}}{(X_{\rm F})_{\iota}} = (k_2/k_3)_{\rm D}$$
(3)

that is, this ratio of isotopic rate constants results from the indicated quotient of mole fractions for any time t, whether it corresponds to partial or complete decomposition.

Results

The results obtained at seven temperatures are collected in Table I and plotted as the open points in Figure 1. Bands representing the results obtained for the intermolecular hydrogen isotope effect are shown for comparison. The line through the intramolecular carbon isotope effect results is a least-squares fit to all of the data except those for 180°; its equation is

$$L(k_2/k_3)_{\rm D} = (3.20 \pm 0.14)\theta - (7.61 \pm 0.34) \quad (4)$$

where $L(x) = 100 \ln x$, and $\theta = 10^3/T(^{\circ}K)$; the average scatter of the experimental results from the least-squares line is ± 0.06 in $\ln x$, equivalent to ± 0.0006 in $(k_2/k_3)_{\rm D}$. Like the deuterium isotope effect observed earlier,² this carbon isotope effect is relatively small, apparently normal in sense¹¹ at low

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Figure 1. Temperature dependence of the intramolecular carbon isotope effect, $L(k_2/k_3)_{\rm D}$, in the decomposition of oxalic acid- $d_2({\rm g})$. The vertical rectangles encompass average deviations from the mean; horizontal bars indicate maximum and minimum results observed. Solid line is least-squares fitted to all data except those for 180°. The bands represent smoothed average results for the intermolecular rate constant ratio $(k_{\rm H}/k_{\rm D})$;² their vertical widths encompass average deviations from the mean results at all temperatures. The upper band (horizontal shading) is least-squares fit to the original data; the lower band (vertical shading) is based on corrected results for $(k_{\rm H})_{\rm av}$ at 134.1°. Estimated inversion temperatures are $(k_2/k_3)_{\rm D}$, 147 \pm 5°; $k_{\rm H}/k_{\rm D}$, upper band, 145 \pm 13°, lower band, 139 \pm 9°.

temperatures, but inverted at higher temperatures. The inversion temperatures are similar for the two isotopic rate constant ratios.

Discussion

Although isotope effect inversion is uncommon, it can be brought about, for reaction along a single chemical path, in a number of ways: by equilibria precedent to the rate-determining step, by equilibriumrelated structural changes upon activation, by an appropriate isotope shift pattern in the vibrational modes of the normal and activated molecules,¹² or through a statistical phenomenon such as that described by Rabinovitch and his co-workers.³⁻⁷ In a gaseous reaction, the C¹³ intramolecular isotope effect should not be affected by the first two, and we believe that our use of deuteriooxalic acid has removed or reduced drastically the possibility of occurrence of the last. The temperature dependence of an ordinary kinetic isotope effect is due to the vibrational isotope shifts and bears an almost uniform relation to the *magnitude* of the effect.¹³⁻¹⁵ The temperature dependence ob-

Table I: Intramolecular Isotope Effect in (COOD)₂(g) Decomposition

Run		
°C	$(k_2/k_3)_{\mathrm{D}}$	Av $(k_2/k_3)_{\rm D}$
126.6	$\begin{array}{c} 1.00492\\ 1.00340\\ 1.00422\\ 1.00427\\ 1.00470\\ 1.00392\\ 1.00379\end{array}$	1.00417 ± 0.00040
134.1	1.00258 1.00068 1.00236 1.00212	1.00194 ± 0.00063
146.4	1.00118 0.99916 0.99938 0.99880 1.00129	0.99996 ± 0.00102
155.6	$\begin{array}{c} 0.99941 \\ 0.99836 \\ 0.99788 \\ 0.99809 \\ 0.99751 \end{array}$	0.99825 ± 0.00051
160.0	$\begin{array}{c} 0.99749\\ 0.99789\\ 0.99765\\ 0.99823\\ 0.99784 \end{array}$	0.99782 ± 0.00020
170.0	$\begin{array}{c} 0.99606 \\ 0.99659 \\ 0.99574 \\ 0.99674 \\ 0.99692 \end{array}$	0.99641 ± 0.00041
180.0	$\begin{array}{c} 0.99666\\ 0.99728\\ 0.99674\\ 0.99601\\ 0.99648\\ 0.99694 \end{array}$	0.9966a ± 0.0003a

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served in these experiments is enormous even when compared with the largest fractionation observed, that at the lowest temperature. Neither ordinary isotope effect theory nor assumption of an effect related to the possibility that 1 mm is well into the *low-pressure* region for the decomposition can explain this extreme relative temperature dependence. Since chemical reactions on surfaces and in the gas phase have the fundamental similarity that both require the modification of extant molecular force fields upon activation, one does not expect new *kinds* of isotope fractionation effects to arise where the reaction proceeds along a single chemical path involving a surface; therefore, the above conclusions concerning isotope effect inversion are valid equally for homogeneous and heterogeneous reactions.

We believe that this unusual isotope effect is due to accessibility to the reaction of at least two decomposition paths; that is, at least two pairs of isotopically isomeric activated molecules yield products in this decarboxylation. If this notion is correct, the deviant result at 180° may actually be due to the final predominance of one path over the other(s) as the temperature is increased; the different decomposition paths may involve activated molecules similar or drastically different in structure. In our first paper on this reaction,^{2a} it was pointed out that there might be a heterogeneous component to the observed reaction rate; a combination of heterogeneous and homogeneous mechanisms provide one kind of decomposition-path duality which could explain the inverting intramolecular isotope effect. In the same place, we indicated (for an assumed unimolecular mechanism) our preference for a reaction coordinate in which there was intramolecular hydrogen atom transfer from one carboxyl group to the carbonyl oxygen of the other; another kind of decomposition-path duality would be provided were reaction to occur simultaneously via a reaction coordinate we did not favor at that time, viz., direct intramolecular hydrogen transfer to carbon.

Though the quality of these data is high, the temperature range of the experiments covers only one region of the isotope effect spectrum anticipated for the reaction model mentioned above, and no detailed treatment is possible. Similarly, the linear form assumed for representation of the temperature dependence as in eq 4, though customary and adequate for our limited purposes here, may be incorrect; a graph with very slight upward curvature would improve the fit at 127 and 170°, but would not affect the deviant character of the observations at 180°.

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