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Temperature Dependence of the Carbon Isotope Effect in the Dehydration of Formic Acid by Concentrated Sulfuric Acid

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The C^{13} kinetic isotope fractionation in the dehydration of formic acid by concentrated sulfuric acid has been studied over the range −30.0 to 0.0°. The observed temperature dependence was examined by the "gamma-bar" method of Bigeleisen and Wolfsberg (both with and without consideration of the effects of loss of bending frequencies) and by the "semi-empirical" method of Yankwich, Weber and Ikeda. Calculated values of the temperature-independent factor in the isotopic rate constant ratio lie within 1% of unity; the calculated sums of the differences upon activation of the diagonal cartesian force constants correspond especially well with the value expected for C–O bond rupture when bending frequency losses are taken into account, being near 7 md.Å.$^{-1}$.

Introduction

A number of investigations of the influence of temperature on kinetic isotope effects have produced results for the appropriate ratios of the isotopic specific rate constants which exhibit abnormally large temperature dependence.[2-5] In such cases the apparent value of the temperature independent factor (TIF) in the isotopic rate constant ratio is smaller than unity (*i.e.*, the *lighter* molecule has the *lower* imaginary frequency associated with its reaction coordinate motion). The unlikelihood of such a situation was detailed first by Bigeleisen[6] and has been the subject of comprehensive review in a later publication by Bigeleisen and Wolfsberg.[7]

The kinetic isotope effect in the dehydration of formic acid-C^{14} in concentrated sulfuric acid[2] appears to have a temperature coefficient about twice as large as one would expect from simple models for the reaction[8]; however, the experiments reported by Ropp and his co-workers were not designed to yield high precision in the temperature coefficient.

Because of the theoretical importance of the kinetic isotope effect in the dehydration of formic acid, we have carried out an investigation of this reaction employing C^{13} at the natural abundance level.

Experimental

Reagents.—The formic acid azeotrope used in these experiments was obtained by distillation of a mixture of reagent grade formic acid and distilled water until the azeotrope was obtained at 107° under a pressure of 747.4 mm.; titration with standard base showed it to be 77.4% formic acid by weight. Reagent grade sulfuric acid, 95.6% acid by weight, was used.

Apparatus and Procedure.—Except in the runs at −26.0° and −30.0°, approximately 2 g. of the formic acid azeotrope, sealed and weighed in a small thin-walled glass bulb, was added, by breaking the bulb, to 350 g. of sulfuric acid contained in a flask of about 225 cc. volume which had been pre-cooled to the reaction temperature in a refrigerated thermostat. A sweep of carbon dioxide-free helium (maintained during the pre-cooling period of 2 hr.) conveyed the carbon monoxide product to a gas handling train consisting of the following, in sequence: a trap filled with magnesium perchlorate, for removal of all but traces of entrained water; a combustion furnace at 700° packed with copper oxide wire; collection traps cooled in liquid nitrogen (three were arranged in parallel so that successive samples of the combusted product gases could be collected); a protective trap packed with magnesium perchlorate and Ascarite.

The rate of the dehydration is so slow at the lowest temperatures employed that a static collection system was used instead of the flow system described above. The reaction vessel (whose contents were stirred vigorously) was connected to an evacuated 2 l. ballast bulb, from which it could be isolated by a stopcock and which was connected to a train consisting of: a small McLeod gage; a trap packed with magnesium perchlorate; a combustion furnace at 130–150° filled with iodine pentoxide; a trap containing magnesium perchlorate and sodium thiosulfate; collection traps cooled in liquid nitrogen. The train was evacuated continuously while the sample was collected in the ballast bulb; combustion was effected by diffusion after the ballast was isolated from the reaction vessel and the train from the vacuum system. Check experiments using the static apparatus were carried out at 0°; no difference in isotope effect from that obtained with the sweep system was observed (for example, run No. 40b).

The samples of carbon dioxide obtained by combustion of carbon monoxide product were passed several times between traps at −78° and −196° (their volumes were determined in a calibrated manometer), and finally distilled into mass spectrometer sample bulbs for later isotope analysis. Routinely, the first (or *a*) sample from all runs carried out in the sweep apparatus was rejected to avoid the possibilities of error attributable to the momentary increase in temperature which occurs when the reagents are mixed and to the small amount of air entrapped in the bulb containing the formic acid.

Product collection was never carried beyond 2.3% reaction, so that the "zero-time approximation"[9-11] could be employed in the calculation of results. Collection times were estimated from rate constants obtained by extrapolation of kinetics results for slightly higher temperatures than those employed in these experiments.[2,12-15] One percent reaction times varied from 3 min. at 0° to approximately 260 min. at −30°.

Isotope Analyses.—The procedures employed have been described in detail in earlier publications.[3,16]

Notation and Calculations.—The isotopic rate constant ratio measured was (k_{12}/k_{13}) in the following notation

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[1] This paper is based on experimental results obtained at the University of Illinois by RHH and PEY; the theoretical analysis by JB, MW and PEY was undertaken at Brookhaven National Laboratory.

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[13] E. R. Schierz and H. T. Ward, *ibid.*, **50**, 3240 (1928).

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[15] A. I. Gel'bshtein, G. G. Shcheglova and M. I. Temkin, *Zhur. Fiz. Khim.*, **30**, 2267 (1956).

[16] P. E. Yankwich and J. L. Copeland, *J. Am. Chem. Soc.*, **79**, 2081 (1957).

$$HC^{12}OOH \xrightarrow{k_{12}} C^{12}O + H_2O \quad (1)$$

$$HC^{13}OOH \xrightarrow{k_{13}} C^{13}O + H_2O \quad (2)$$

Here

$$(k_{12}/k_{13})_{\text{obsd}} = (R_F/R_C) \quad (3)$$

where R_F is the ratio ($HC^{13}OOH/HC^{12}OOH$) derived from measurements on carbon dioxide obtained by combustion (in a standard Pregl apparatus) of samples of the original formic acid azeotrope,[17] and R_C is the ratio ($C^{13}O/C^{12}O$) from measurements on carbon dioxide obtained from combustion of the samples of product carbon monoxide; for the formic acid used in these experiments, $R_F \times 10^6 = 10923 \pm 2$.

Results

The corrected[3,16] carbon isotope ratio for each sample is given in Table I, along with the value of (k_{12}/k_{13}) to which it corresponds; the appended errors in the last column are average deviations. The mean precision of the individual (k_{12}/k_{13}) values is estimated to be ± 0.0003. The values of $L(k_{12}/k_{13}) = 100 \ln (k_{12}/k_{13})$ calculated from the last column of Table I are plotted *versus* $(1000/T)$ in Fig. 1; the vertical rectangles encompass the average deviations. The data of Ropp, Weinberger and Neville,[2] calculated as C^{13} isotope effects, are shown also in Fig. 1, for comparison; for those data the small horizontal bars encompass the average deviations. The reduction of C^{14} kinetic isotope effects to the corresponding C^{13} effects involves a small degree of arbitrariness. The ratio of the two isotope effects, expressed as $[(k_{12}/k_{14}) - 1]/[(k_{12}/k_{13}) - 1]$, and assuming that the reaction coordinate motion involves C–O bond rupture, lies between 1.86[7] and 1.95; the exact value of the ratio depends on the relative magnitudes of TIF and the temperature dependent factor (TDF) in the isotopic specific rate constant ratios. For both sets of experiments summarized in Fig. 1 the temperature dependence is so large that TIF must lie near unity; hence, the value 1.86 was employed for the C^{14}/C^{13} isotope effects ratio in reducing the data of Ropp and his co-workers to the C^{13} base. Least-squares fitting of the results recorded in Table I yields the equations

$$L(k_{12}/k_{13}) = 2.793(10^3/T) - 3.827 \quad (4)$$

$$= 0.391(10^6/T^2) + 1.125 \quad (5)$$

the average deviation of experimental points from the least-squares curve being ± 0.09 in both cases A line corresponding to equation 4 is drawn through the plot of results in Fig. 1.

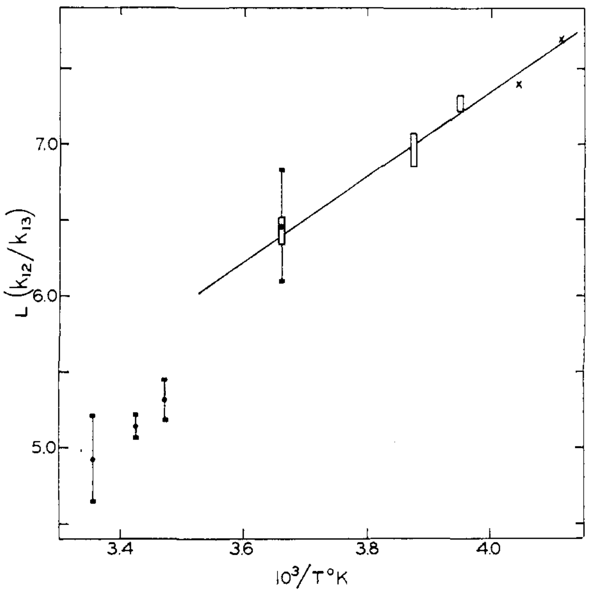

Fig. 1.—Influence of temperature on the intermolecular isotope effect: ———, open rectangles: this research (the X's indicate single experiments): filled circles: results of Ropp, Weinberger and Neville for $HC^{14}OOH$ reduced to the $HC^{13}OOH$ basis.

Table I

Corrected Isotope Ratios of Experimental Samples; Calculated Intermolecular Isotope Effects

Temp., °C.	Sample	De-hydr., %	$R_C \times 10^6$	$(k_{12}/k_{13})_{\text{obsd.}}$	Av. $(k_{12}/k_{13})_{\text{obsd.}}$
−30.0	35a	0.0–1.5	10115	1.0799	. . .
−26.0	36a	.0–1.1	10146	1.0767	. . .
−20.0	25b	.8–1.5	10170	1.0744	
	26b	.6–1.2	10153	1.0758	
	26c	1.2–2.0	10160	1.0751	
	27c	1.4–2.3	10148	1.0764	
	28b	0.6–1.5	10157	1.0754	
	32b	0.6–1.4	10155	1.0756	
	32c	1.4–2.2	10163	1.0748	
	33b	0.8–1.5	10163	1.0748	
	34b	0.8–1.5	10155	1.0756	
	34c	1.5–2.3	10165	1.0747	1.0753 ± 0.0005
−15.0	14b	0.6–1.3	10201	1.0708	
	14c	1.3–1.9	10232	1.0675	
	15b	0.6–1.3	10197	1.0712	
	16b	0.6–1.3	10175	1.0735	
	16c	1.3–1.9	10175	1.0735	
	17b	0.6–1.3	10185	1.0725	
	18b	.6–1.3	10194	1.0715	
	19b	.6–1.3	10162	1.0749	
	19c	1.3–1.9	10183	1.0726	
	21b	0.6–1.3	10188	1.0721	
	21c	1.3–1.9	10182	1.0728	
	22b	0.6–1.3	10195	1.0714	
	22c	1.3–1.9	10191	1.0718	
	23c	1.3–1.9	10191	1.0718	1.0720 ± 0.0011
0.0	9b	0.7–1.3	10251	1.0656	
	9c	1.3–2.0	10243	1.0664	
	10c	1.3–2.0	10222	1.0686	
	11b	0.7–1.3	10231	1.0676	
	12c	1.3–2.0	10252	1.0655	
	13b	0.7–1.3	10254	1.0652	
	13c	1.3–2.0	10247	1.0660	
	40b	0.7–2.3	10242	1.0665	1.0664 ± 0.0009

Discussion

The results of the present experiments confirm the magnitude of those obtained with formic acid-C^{14} by Ropp, *et al.*, and provide a basis for interpretation of the temperature coefficient of the kinetic isotope effect. The temperature dependence of a kinetic isotope effect arises in the mass dependence of the vibrational frequencies of the normal and activated molecules. A theoretical analysis of

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(17) Because they contained originally large amounts of water, these samples of carbon dioxide were purified by several distillations between traps at −150° and −196°.

TABLE II

"EXPERIMENTAL" VALUES OF TIF; APPARENT CHANGES IN FORCE CONSTANT SUMS

Assumed critical frequency, cm.$^{-1}$	Values of $\bar{\gamma}$				$\Sigma(a_{jj} - a^{\neq}_{jj})$ md. Å.$^{-1}$		TIF			
	258.2°K.		273.2°K.							
	(*A*)	(*B*)^a	(*A*)	(*B*)	(*A*)	(*B*)	Calcd. eq. (6) and (7)	Lower lim. eq. (4)	Upper lim. eq. (5)	Semi-empir.
1000	0.699	0.744	0.718	0.761	7.0	6.6	1.003	0.962	1.011	0.991
1200	0.631	0.684	0.652	0.702	8.3	7.7	0.999			

^{a} $\nu_{\text{stretch}} = 3\nu_{\text{bend}}$.

the temperature dependence of small isotope effects can be made without detailed knowledge of the vibrations of the isotopic normal molecules and the transition states by the "gamma-bar" method of Bigeleisen and Wolfsberg.[7] It is to such a test that we will subject the experimental results.

According to the "gamma-bar" method, the natural logarithm of TDF is given by the relation

$$\ln(\text{TDF}) = 0.1464(10^6/T^2)\bar{\gamma} \sum_{j}^{3n}\left(\frac{1}{m_{ij}} - \frac{1}{m_{2j}}\right)(a_{jj} - a_{jj}{\mp}) \quad (6)$$

where n is the number of atoms in the molecule, m is the mass of an atom in a.m.u., the subscripts 1 and 2 refer, respectively, to the light and heavy isotopic species, and the a_{jj} are diagonal cartesian force constants in md. Å.$^{-1}$; $\bar{\gamma}$ is a suitably weighted average value, for the particular reaction under discussion, of the function $12G(u_i)/u_i$, where $u_i = hc\omega_i/kT$, and $G(u_i)$ is the function of Bigeleisen and Mayer.[18] The value of $\bar{\gamma}$ to be employed in a particular calculation is estimated from an approximate knowledge of the frequencies of the normal and activated molecules. If it can be assumed that the principal change in vibration frequencies upon activation is associated with that normal mode which becomes the reaction coordinate motion, then the most important component of $\bar{\gamma}$ arises in that single frequency.

Gel'bshtein, Shcheglova and Temkin[15] have recorded evidence in support of the acid-catalyzed carbonium ion mechanism for the decarbonylation of formic acid in concentrated sulfuric and phosphoric acids; the rate determining step is C–O bond rupture in a species such as $HCOOH_2^+$. In the present case, then, a reasonable simple view of the reaction is that activation consists in loss of the C–O stretching vibration. *At each temperature* $\bar{\gamma}$ will be the value of $12G(u_i)/u_i$ appropriate for a frequency of about 1000–1200 cm.$^{-1}$, and the related sum of the differences $(a_{jj}\text{-}a^{\neq}_{jj})$ should be nearly the force constant f_{C-O}, or 5–6 md. Å.$^{-1}$. Further, if we recall that

$$(k_{12}/k_{13}) = (\text{TIF})(\text{TDF}) \quad (7)$$

the diagonal force constant sum can be eliminated between a pair of expressions like eq. 7 to yield an "experimental" value for TIF. In the remainder of this Discussion, this single frequency representation will be denoted by (*A*). A similar but slightly more accurate view of the reaction would consist in the addition to the effect of the loss of the C–O stretching vibration that of the loss of the related bending vibrations; this representation will be denoted by (*B*). The values of $\bar{\gamma}$ calculated for (*B*) will be somewhat larger than those for (*A*) because of the inclusion in the former of the lower bending frequencies; a suitable weighting procedure is embodied in the relation for (*B*)

$$\bar{\gamma} = \gamma_{\text{stretch}} \cdot \frac{a_{\text{stretch}}}{a_{\text{stretch}} + 2a_{\text{bend}}} + \gamma_{\text{bend}} \cdot \frac{2a_{\text{bend}}}{a_{\text{stretch}} + 2a_{\text{bend}}} \quad (8)$$

For the situation (*B*), then, the calculated sum of the differences $(a_{jj}\text{-}a^{\neq}_{jj})$ should lie in the range 6–7 md.Å.$^{-1}$.

At high temperatures, eq. 6 approaches linear dependence on $(1/T^2)$, while at low temperatures it is linear in $(1/T)$. This situation means that the intercepts of equations like (4) and (5) are, respectively, lower and upper limits for L(TIF).[19] Still another "experimental" estimate of TIF can be obtained by employing the semi-empirical method described in two earlier publications.[20,21] The semi-empirical method is based on the fact that a plot of $[L(\text{TDF})_{T_2} + L(\text{TDF})_{T_1}]$ *versus* $[L(\text{TDF})_{T_2} - L(\text{TDF})_{T_1}]$ for a moderate temperature interval is nearly linear and has slope and intercept but very slightly dependent upon the complexities of the models employed in *calculation* of L(TDF).[21] In this sense, there is some correspondence between the semi-empirical method and the "gamma-bar" method. In Table II, we have collected the values of these several estimates of TIF, as well as the calculated sums of the differences $(a_{jj}\text{-}a^{\neq}_{jj})$ for situations *A* and *B*.

The values of the changes in force constant sums calculated from the results in Table I are very close to the expected range, especially in situation *B*. The TIF values calculated by the semi-empirical and "gamma-bar" methods are in good agreement with each other and are sufficiently close to unity as to do no violence to our expectation that TIF should be unity or slightly larger. It is interesting to note that the value of TIF calculated for a 2-center molecular fragment model,[7] (HCO)(OH) or $(HCO)(OH_2^+)$, is 1.006, which agrees, within the limits of their accuracy, with all the calculated (as opposed to extrapolated) values of TIF recorded for this research in Table II; whereas, the value of TIF calculated for an atomic fragment model, (C)(O), following Slater,[22] is 1.023 and far from correspondence with the values shown in Table II.

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(19) This statement is strictly correct if the $G(u)\Delta u$ formalism is applicable and if the corresponding γ_i's span a narrow range. If the zero-point energy isotope effect tends to an inverse isotope effect, then lower and upper above are interchanged.

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