TABLE VI

MOLAR EXTINCTION COEFFICIENTS IN LITER MOLE^{-1} CM.$^{-1}$

λ, mμ	e(FeiCy)	e(FeoCy)	$e(\mathrm{I}_2)$	$e(\mathrm{I}_3^-)$	$e(\mathrm{I}^-)$
470	18	0	530	623	0
420	1010	0	390	2.90×10^3	0
350	318	184	170	2.43×10^4	0

TABLE VII

THE EQUILIBRIUM CONSTANT FOR $2\mathrm{Fe(CN)_6}^{-4} + \mathrm{I_2} = 2\mathrm{Fe(CN)_6}^{-3} + 2\mathrm{I}^-$; 24°, $\mu = 0.10$

pH	$[\mathrm{FeOCy}]_0 \times 10^5$, M	$[\mathrm{I_2}]_0 \times 10^5$, M	$K_c \times 10^3$	$K_a \times 10^3$	K_c'	K_a'
4.78	10.5	5.22	11	1.3	9100	1000
	10.5	5.22	10	1.2	8300	950
	19.8	4.96	0.91	0.10	760	86
	44.4	22.2	2.1	0.24	1700	200
	88.9	22.2	0	0	0	0
1.48	11.8	5.86	8.4	0.95	0.75	0.085
	3.85	1.92	22.6	2.6	2.0	0.23

the acid media used and this concentration value for $\mathrm{Fe(CN)_6}^{-4}$ employed in the calculation of K, the primed constants were obtained. The value of K_a was most nearly constant in the range $1 \times 10^2 \leqslant K_a \leqslant 2.6 \times 10^3$ liter/mole except for one experiment. However, K_a appeared to increase with decreasing initial concentrations of FeoCy and $\mathrm{I_2}$ at a constant value of $[\mathrm{FeoCy}]_0/[\mathrm{I_2}]_0$ and to decrease with decrease in the ratio $[\mathrm{FeoCy}]_0/[\mathrm{I_2}]_0$. K_a' varied greatly with conditions. It should be noted that if the equilibrium involved some ferrocyanide species (*e.g.*, $\mathrm{HFe(CN)_6}^{-3}$) other than $\mathrm{Fe(CN)_6}^{-4}$ then K_a would not be equal to the true equilibrium constant but would be proportional to it at a given pH; the proportionality constant would be independent of the initial concentrations of the reactants but would vary with the pH of the medium.

Since considerable $\mathrm{I_2}$ remained when "equilibrium" was attained (within a few minutes) in systems containing initially equivalent concentrations of FeoCy and $\mathrm{I_2}$, then considerable $\mathrm{I_2}$ should be formed when excess I^- is added to a solution of FeiCy. In one experiment with $[\mathrm{FeiCy}]_0 = 2.38 \times 10^{-4}\ M$ and $[\mathrm{I}^-]_0 = 4.76 \times 10^{-4}\ M$ the amounts of $\mathrm{I_3}^-$ and $\mathrm{I_2}$ formed were so small as to make their determination unreliable even after 1 hr. Thus it is clear that the same positions of "equilibrium" were not attained from FeiCy + I^- and from FeoCy + $\mathrm{I_2}$ unless much longer times were allowed. Hydrolysis of the complex cyanides obscures the events which may happen when longer times are allowed, however.

From the reported facts it was concluded that equilibrium was not obtained between $\mathrm{Fe(CN)_6}^{-4}$, $\mathrm{Fe(CN)_6}^{-3}$, $\mathrm{I_2}$ (or $\mathrm{I_3}^-$) and I^- in the various systems described and that this could account for the negative values obtained for k_4 in many experiments.

MINNEAPOLIS 14, MINN.

[CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Temperature Dependence of the Carbon Isotope Effect in the Acid Hydrolysis of Urea

BY PETER E. YANKWICH AND AUDREY E. VEAZIE

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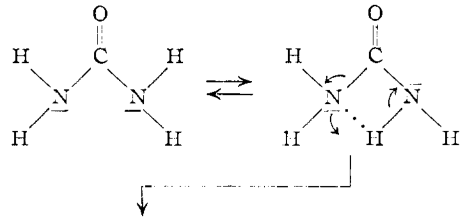
The carbon isotope effect in the hydrolysis of urea has been measured over the temperature range 60–96°. While theoretical calculations based on a number of models reproduce the temperature dependence observed, no model up to three centers with internally consistent properties was found to yield the experimentally observed temperature-independent factor in the isotopic rate constant ratio.

Introduction

In two recent papers, Shaw and his co-workers have presented the results of studies on the effects of salt and hydrogen-ion concentration on the rates of decomposition of aqueous urea[1] and thiourea.[2] The absence of a large primary salt effect, the activation energy of nearly 33 kcal. per mole, the modest entropy of activation (*ca.* 6 e.u.), and the absence of hydrogen-ion catalysis are compatible with the scheme



$$\mathrm{NH_3 + HNCO} \rightleftarrows \mathrm{NH_4^+ + NCO^-} \quad (1)$$

In acidic solutions cyanate is hydrolyzed rapidly[3]

$$2\mathrm{H^+ + NCO^- + H_2O = NH_4^+ + CO_2} \quad (2)$$

Schmitt and Daniels[4] have recorded only two experiments on the carbon isotope effects; the hydrolyses were carried out at 100° in a phosphate buffer system at pH 5.0. With C^{13} their result for k_1/k_2 (*vide infra*) was 1.055 ± 0.003, somewhat larger than the figure calculated from the exact Eyring equation[5] on the assumption of simple C–N bond rupture.

In this paper we report a study of the C^{13} isotope effect in the decomposition of urea in dilute aqueous acid over the temperature range 60–96° and comparison of the results with the predictions of theoretical models of various degrees of complexity.

Experimental

Materials.—J. T. Baker "Analyzed" reagent urea was used without further purification. The solvent was 0.05 M sulfuric acid prepared by dilution of the du Pont 96% C.P. re-

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[1] W. H. R. Shaw and J. J. Bordeaux, THIS JOURNAL, **77**, 4729 (1955). This paper contains a convenient summary of earlier investigations of the mechanism of urea hydrolysis.

[2] W. H. R. Shaw and D. G. Walker, *ibid.*, **78**, 5769 (1956).

[3] A. R. Amell, *ibid.*, **78**, 6234 (1956).

[4] J. A. Schmitt and F. Daniels, *ibid.*, **75**, 3564 (1953).

[5] H. Eyring and F. W. Cagle, *J. Phys. Chem.*, **56**, 889 (1952).

agent. As indicated by the study of Shaw and Bordeaux,[1] this concentration of acid is sufficient to suppress the reverse reaction.

Apparatus and Procedure.—At 96° the decomposition of urea in acidic solution is sufficiently rapid (1% in 8 min.) that a sweep collection system could be employed; the apparatus and general procedure have been described in a previous publication from this Laboratory.[6]

The runs at 60, 70 and 80° were carried out in sealed bulbs containing approximately 100 ml. of 0.05 *M* sulfuric acid to which was added about 0.6 g. of urea, weighed carefully. The bulb was evacuated several times to remove dissolved gases, then sealed off under vacuum. The sample was then immersed in a constant temperature bath (temperatures given are accurate to ±0.2°; the bath was regulated to ±0.05°) until the desired degree of decomposition had been achieved, then removed and chilled in ice-water. After the reaction had been stopped, the sample bulb was attached to the vacuum system and immersed in liquid nitrogen to freeze the contents; a break-off seal fitted to the bulb was broken and any traces of permanent gases removed and carbon dioxide distilled from the solution and purified by conventional high vacuum techniques.

In the runs at 89° a reaction vessel was used which permitted thermal equilibrium to be established before the urea was dissolved. A side arm was attached to the sample bulb and a sealed thin glass bulb containing the urea placed therein on the end of a piece of heavy glass rod to which was attached a glass-covered bar magnet. The reaction was started by removal of an external retaining magnet; this permitted the rod with attached sample to drop to the bottom of the reactor where the thin-walled sample bulb broke.

Isotope Analyses.—The procedures and calculation methods used for the carbon isotope ratio determinations have been detailed in previous publications from this Laboratory.[7-9] The isotope ratio of the original urea carbon was obtained from measurements on carbon dioxide from combustion of urea over copper oxide wire at 600°.

Calculations.—The ratio of the specific rate constants k_1/k_2 for the hydrolysis of C^{12}-urea and C^{13}-urea, respectively, is given by the relation $(k_1/k_2) = (X_D/X_C)$, where X_C is the corrected mole fraction of C^{13} in product carbon dioxide and X_D is that in original urea; the error intrinsic in the use of this equation is small compared with other experimental errors provided that the per cent. of reaction is kept smaller than 4 or 5.[10]

Results

The corrected C^{13} mole fraction for each experimental sample is given in Table I along with the value of $(k_1/k_2)_{obsd}$ computed therefrom. The uncertainty in any X is ±2 in the last digit, or less; the errors appended are average deviations. Let the operator L be defined so that $L(x) = 100 \ln(x)$. The values of $L(k_1/k_2)_{obsd}$ obtained from the last column of Table I yield the least-squares fitted line eq. 3

$$L(k_1/k_2)_{obsd} = (1.55 \pm 0.10)(1000/T) + (0.19 \pm 0.04) \quad (3)$$

TABLE I

A. Results of hydrolyses

Temp., °C.	Reaction, %	$X_C \times 10^6$	k_1/k_2	Av. k_1/k_2
60	2.7	10106	1.0496	
	2.5	10101	1.0501	
	2.7	10111	1.0490	
	1.2	10095	1.0506	1.0498 ± 0.0005
70	2.0	10116	1.0485	
	1.5	10124	1.0477	
	2.0	10121	1.0480	
	2.0	10115	1.0486	
	1.1	10123	1.0478	
	1.0	10121	1.0480	1.0481 ± .0003
80	2.0	10132	1.0469	
	2.0	10130	1.0471	
	2.0	10130	1.0471	1.0470 ± .0001
89	1.0	10141	1.0460	
	1.0	10146	1.0455	
	1.0	10138	1.0463	
	1.0	10143	1.0457	1.0459 ± .0003
96	0.0–1.0	10147	1.0454	
	1.0–2.0	10160	1.0440	
	2.0–3.0	10148	1.0453	1.0449 ± .0006

B. Results of combustions

$X_D \times 10^6$
10608
10606

Discussion

A ratio of isotopic rate constants is the product of two factors, one temperature independent, one temperature dependent.[11-14] In the present situation we can write

$$L(k_1/k_2) = L(\text{TIF}) + L(\text{TDF})$$

It is possible to obtain a value of TIF from isotopic rate constant ratio data taken over a sufficiently wide range of temperatures.[15] If we assume the validity of the Redlich–Teller product rule for activated complexes as well as for normal molecules, then, for the temperature range $1000/T = 2.75 - 3.00$, and virtually independent of the models assumed for the calculation, the change in L(TDF) and its mean value are found to be related as

$$L(\text{TDF})_{mean} = 8.48\,\Delta L(\text{TDF}) - 0.208 \quad (4)$$

From eq. 3, $\Delta L(\text{TDF}) = 0.388$ for this temperature range, and $L(k_1/k_2)_{mean} = 4.65$; from eq. 4, $L(\text{TDF})_{mean} = 3.08$, whence $L(\text{TIF}) = 1.57$, or TIF = 1.0158 ± 0.0021.

Two-center Model.—Following a suggestion of Slater[16] concerning the effective mass in the rupture of an isolated single bond, Bigeleisen[12] has obtained good agreement with a number of experimental results on the basis of two-center models. The Raman spectrum of urea in water has been observed by Otvos and Edsall[17] and the frequencies assigned and force constants calculated by Kellner[18] following the method of Lechner.[19] The input data for the calculation of k_1/k_2 are: C^{12}–N stretching vibration, $\omega_1 = 1008$ cm.$^{-1}$; ratio of isotopic frequencies, $\omega_1/\omega_2 = 1.02138$ = TIF. The result of this computation is shown as the last line of Table IIB. $L(k_1/k_2)_{calc}$ is 0.18 low at $1000/T = 2.75$ and 0.23 low at $1000/T = 3.00$; neither TIF nor TDF is satisfactory.

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(6) P. E. Yankwich, R. L. Belford and G. Fraenkel, THIS JOURNAL, **75**, 832 (1953).

(7) P. E. Yankwich and R. L. Belford, *ibid.*, **75**, 4178 (1953).

(8) P. E. Yankwich and R. L. Belford, *ibid.*, **76**, 3067 (1954).

(9) P. E. Yankwich and J. L. Copeland, *ibid.*, **79**, 2081 (1957).

(10) J. Y. Tong and P. E. Yankwich, *J. Phys. Chem.*, **61**, 540 (1957).

(11) J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).

(12) J. Bigeleisen, *J. Phys. Chem.*, **56**, 823 (1952).

(13) J. Bigeleisen and M. Wolfsberg, *J. Chem. Phys.*, **21**, 1972 (1953).

(14) J. Bigeleisen and M. Wolfsberg, *ibid.*, **22**, 1264 (1954).

(15) P. E. Yankwich and H. S. Weber, THIS JOURNAL, **78**, 564 (1956).

(16) N. B. Slater, *Proc. Roy. Soc.* (*London*), **A194**, 113 (1948).

(17) J. W. Otvos and J. T. Edsall, *J. Chem. Phys.*, **7**, 632 (1939).

(18) L. Kellner, *Proc. Roy. Soc.* (*London*), **A177**, 456 (1941).

(19) F. Lechner, *Sitzber. Akad. Wiss. Wien.*, *Math. naturw. Kl.*, *Abt IIa*, **141**, 291 (1932); *Monatsh. Chem.*, **61**, 385 (1932).

Alternate Single Frequency Models.—Two calculations employing a single vibration frequency and utilizing the experimental value of the temperature independent factor were suggested in an earlier paper from this Laboratory.[9] First, we set both TIF and ω_1/ω_2 equal to 1.0158; calculation shows that the least-squares fitted line in eq. 3 is matched for $\omega_1 = 1500$ cm.$^{-1}$. This frequency is closely that of the N–C–N asymmetric stretching vibration,[18] which would be a convenient decomposition coördinate; however, the probable value of ω_1/ω_2 for this mode is somewhat higher, 1.020–1.025. Second, we approximate the urea molecule with a three point-mass model—NH_2 = 16, $C^{12}O$ = 14—[20] follow Kellner and Lechner (*vide infra*), and calculate the following normal frequencies (and isotopic frequency ratios), in cm.$^{-1}$: 1104 (1.0153), 375 (1.0086), and 1359 (1.0213).[21] Selecting the asymmetric stretching vibration as the reaction coördinate, ω_1/ω_2 = 1.0213, we can match the experimental results with ω_1 = 1200 cm.$^{-1}$ for TIF = 1.0158, and with ω_1 = 1050 cm.$^{-1}$ for TIF = ω_1/ω_2; both these calculated frequencies are too low for the asymmetric stretching mode and (apart from the internal inconsistencies in the two) generate little confidence in our choice of the asymmetric vibration as the reaction coördinate. A similar and even less satisfactory situation results if the computation is based on the symmetric stretching vibration. We conclude then that these alternate models are too complex to give fortuitous agreement with experiment and too simple to reflect accurately the effect of activation on the vibrations not associated with the reaction coördinate.

Polyatomic Models.—In general, where isotopic substitution does not affect the relative symmetry of the molecule and activated complex, or the transmission coefficient, and where the product rule is applied to the activated complexes as well as to the normal molecules

$$(k_1/k_2) = (\nu_{1i}/\nu_{2i}) \times \frac{\prod\limits_{k=1}^{3n-6} \frac{\sinh(u_{1k}/2)}{\sinh(u_{2k}/2)} \times \frac{u_{2k}}{u_{1k}}}{\prod\limits_{k=1}^{3n-7} \frac{\sinh(u_1{}^{\ddagger}{}_k/2)}{\sinh(u_2{}^{\ddagger}{}_k/2)} \times \frac{u_2{}^{\ddagger}{}_k}{u_1{}^{\ddagger}{}_k}} \qquad (5)$$

where $u = hc\omega/kT$, $\ddagger$ refers to the activated complex, and ν_1 is the imaginary frequency obtained from the solution of the secular equation (usually after setting one force constant equal to zero and reducing).[5,11,22] The first factor on the right is TIF and is given by the relation

$$(\nu_{1i}/\nu_{2i}) = \frac{\prod\limits_{k=1}^{3n-6} (\omega_1/\omega_2)_k}{\prod\limits_{k=1}^{3n-7} (\omega_1{}^{\ddagger}/\omega_2{}^{\ddagger})_k} \qquad (6)$$

which is subject to the restriction that here all the ω values are computed for the configuration of the activated complexes and will be different from some used in the second factor on the right of eq. 5 if the normal molecules and activated complexes have different configurations.

In Table II are collected the results of some calculations on a three-center approximation to the urea molecule. The stretching force constants for the normal molecule (*N*) are taken from Kellner,[18] but the bending force constant is estimated and is probably a little low; the geometric parameters are taken from Wyckoff and Corey.[23] The vibration frequencies were calculated by Lechner's method.[19] The constants chosen for the three activated complex models were selected as follows: A, to imitate the rupture of an isolated bond (a three-center approach to the two-center model); B, to imitate a decomposition coördinate involving asymmetric motion of the NH_2 groups with respect to the carbon atom; C, to fit the experimental results for TDF.

Clearly, the parameters required to produce agreement with the experimental temperature dependence are not extraordinary. If the bending force constant is reduced to a low value in the model for the activated complex (a physically reasonable situation), the fit for models A and B is improved. The most significant feature of the results in Table IIB is that the isotope effect on TIF is barely half the experimental value. Experience with many such calculations indicates the span of computed TIF values to be 1.007–1.011, and these extremes require rather imaginative selection of a configuration for the activated complex, TIF for a given configuration being insensitive to the values chosen for the force constants.[24]

TABLE II

CALCULATED ISOTOPE EFFECTS FOR THREE-CENTER MODELS

A. Calculation of vibration frequencies

$m_1 = m_3 = 16$; $m_2 = 14$, $m'_2 = 15$; $\alpha = 115°$; $f_\alpha = 0.35 \times 10^5$ dynes cm.$^{-1}$. Units: ω (cm.$^{-1}$), d(Å.), f(10^5 dynes cm.$^{-1}$)

Model	*N*	A	B	C
d_{12}	1.37	1.37	1.65	1.37
d_{23}	1.37	1.37	1.25	1.37
f_{12}	6.6	0	0	0
f_{23}	6.6	6.6	6.2	5.3
ω_{11}	1102.2	....	....	....
ω_{21}	1085.6	....	....	....
ω_{12}	375.1	417.5	430.4	416.6
ω_{22}	1356.9	1233.5	1195.0	1107.6
ω_{23}	1328.5	1210.9	1173.2	1087.1

B. Calculated rate constant ratio factors

	(ν_{1i}/ν_{2i}) = TIF	L(TDF) at $1000/T$ = 2.75	3.00
Exptl.	1.0158	2.89	3.27
N → A	1.00870	2.476	2.816
N → B	1.00784	2.576	2.924
N → C	1.00870	2.889	3.275
2-center (CN)	1.02138	2.173	2.501

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[20] The C=O bond is not too stiff and the small correction Δm_c = +2 for the presence of the oxygen is sufficient; an adjusted force constant could have been used instead.

[21] The corresponding observed frequencies[17] are: 1008, 534(?), and 1478 cm.$^{-1}$. The uncertainty of the bending frequency assignment (534 cm.$^{-1}$) is relatively unimportant; total neglect of this mode in a complete 5-frequency calculation introduces an error of only 0.003 in k_1/k_2.

[22] H. S. Johnston, W. A. Bonner and D. J. Wilson, *J. Chem. Phys.*, **26**, 1002 (1957).

[23] R. W. G. Wyckoff and R. B. Corey, *Z. Krist.*, **89**, 462 (1934).

[24] A similar situation (though one involving reversal of the relation between calculated and experimental values for TIF) is to be found in the analysis by Johnston, Bonner and Wilson[22] of their results for the reaction $CO + NO_2 = CO_2 + NO$. Their detailed calcu-

Basically, TIF is the contribution to the isotope effect of the reaction coördinate,[11] and it is to be expected that a selection for that motion different from a normal mode may result in better agreement with experiment; this is the problem examined for three-center systems by Bigeleisen and Wolfsberg.[13,14,25] For the grouping at hand, N–C–N, TIF = 1.02138 for zero and infinite values of the Bigeleisen–Wolfsberg parameter p. If the motion of the N atoms is symmetric about the C atom, TIF falls gradually to near 1.0156 at $p = 1$, then rises; if this motion is asymmetric, TIF rises quickly and reaches 1.02541 at $p = 1$, then falls, slowly at first, to its original value as $p = \infty$ is approached. A Bigeleisen–Wolfsberg three-center model is thus required by the experimental value obtained for TIF to involve symmetric motion about the central atom as the reaction coördinate and nearly equal extensions of the C–N bonds; this is not a very satisfying picture.

It seems to us that there is implicit in the notion of Bigeleisen and Wolfsberg a statement of the most fruitful approach to the analysis of isotope effect data; whereas the temperature dependent factor usually can be fitted by a simple model, a rather complex reaction coordinate motion may have to be assumed in order to secure agreement with the experimental temperature independent factor. Thus, in the three-center models elaborated above, neither a normal mode of the activated complex, nor a three-center reaction coördinate motion formulated after Bigeleisen and Wolfsberg seems to be an adequate representation of the actual reaction coördinate motion. For urea hydrolysis a four-atom or more complex model is required if detailed correspondence of calculated and experimental TDF and TIF values is sought.

In general, the temperature independent part of a kinetic isotope effect provides information concerning the uncompensated changes in binding about the site of labeling which occur as a consequence of activation. The temperature dependent part includes the effects of these changes and also of any equilibrium process which affects the relative concentrations of the isotopic species which actually are activated. Kinetic isotope effects thus afford access to certain details of reaction mechanisms. In employing kinetic isotope effects to distinguish among likely reaction mechanisms it is necessary to perform calculations based on assumed models of the activated complexes involved. If each of several likely activated complexes differs from the others in the distribution of energy over available degrees of vibrational freedom (*i.e.*, has a unique decomposition mode), comparison of calculated and experimental values for the temperature independent part of the kinetic isotope effect will be useful in selecting probable mechanisms. No such selection is possible among mechanisms which are all similar in predicted decomposition mode. Of course, to make a definitive study of any reaction system one would have to employ models of such complexity as to reproduce all significant features of the real system; this seldom is possible. In most cases theoretical analysis is based upon a succession of progressively more complicated models; when the model reproduces the results of experiment without the introduction of spurious features due to the approximations involved, the analysis is stopped. In studies such as that reported, here, a satisfactory model would not do violence to the known kinetics of the system, and would yield satisfactory values for the temperature dependent and temperature independent factors of the isotopic rate constant ratio. The use of models here, then, is no different than in any other study where representations more simple than actuality must be employed.

Acknowledgment.—We are indebted to Mrs. Eula Ihnen for the mass spectrometric determinations, and to Dr. R. H. Haschemeyer for stimulating discussion. Mr. Richard M. Ikeda, with the assistance of the staff of the University of Illinois Digital Computer Laboratory, programmed and carried out many calculations upon which our discussion is based. This research was sponsored by the U. S. Atomic Energy Commission.

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lations on a five-atom model yield values for the isotopic rate constant ratio in fair agreement with experiment. However, the best model does not show a high enough temperature dependence, the discrepancy over the temperature range covered being about 15%. A value (ν_{1i}/ν_{2i}) = 1.0095 is yielded by the model, but the experimental value is close to 1.0081. If the latter is employed, a uniform reduction of just 5% in the best group of force constants will reproduce the experimental data accurately.

(25) There seems to be a discrepancy between the formulation of the reaction coördinate x_L for application to TIF computation[13] and its acceptable definition[14]; in the former case the only critical motion is in the reaction coördinate, in the latter—no motion.