

For reactions involving primary deuterium isotope effects, we show how the zero point energy of the hydrogen may be conserved in the transition state, either because of asymmetry about the hydrogen or because of strong hydrogen bonding in proton transfers between electronegative atoms.

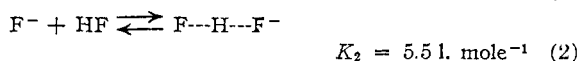
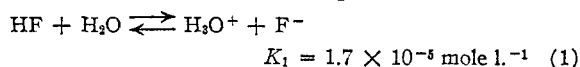
Reaction rate theory requires that any transition state for a solution reaction be in solvation equilibrium. Therefore if this theory is accepted it must be concluded that isotope effects, like any kinetic method, cannot provide proof of the existence of any equilibrium involving solvent molecules preceding the formation of the transition state.<sup>23</sup> The fact that an observed isotope effect may be explained in terms of a pre-equilibrium proton transfer should not lead us to accept this formulation if it is not conveniently consistent with other chemical behavior. However, postulation of conjugate acids and bases as intermediates in equilibrium with reactants, provides a very useful basis for discussion and classification when chemical species which are structurally analogous to these intermediates are well-known.

### Appendix

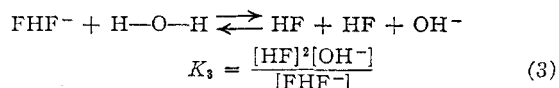
**Justification of Free Proton Model.**—In the "free-proton" model we assume that the strengths of H-bonds to the bases, which in the transition state share the proton, are the same as in the absence of the proton. Our working hypothesis is therefore that the basicities of these atoms are

(23) L. Melander and P. C. Myhre, *Arkiv. Kemi.*, **13**, 507 (1959).

not influenced markedly by the presence of the proton shared between them in the transition state. Some justification for this view can be drawn from a consideration of the basicity of  $\text{HF}_2^-$  compared to  $\text{F}^-$ . The equilibria involved are



The basicity of  $\text{FHF}^-$  is measured by the equilibrium constant of reaction 3. This constant



can be evaluated from  $K_w$ ,  $K_1$  and  $K_2$ .

$$K_3 = \frac{K_w}{K_1 K_2} = \frac{[\text{H}_3\text{O}^+][\text{OH}^-][\text{HF}][\text{F}^-]}{[\text{FHF}^-][\text{H}_3\text{O}^+][\text{F}^-]} = \frac{10^{-14}}{1.7 \times 10^{-5} \times 5.5} = 1.1 \times 10^{-10}$$

The basicity of the fluoride ion is  $K_w/K_1 = 5.9 \times 10^{-10}$ . Thus the basicity of fluoride ion in  $\text{HF}_2^-$  is not largely affected by the proton which is shared apparently equally between it and another fluoride. The transition states for proton transfers will generally not be bound by any H-bonds nearly so strong as the one in  $\text{HF}_2^-$ , and the bases involved should therefore show essentially the same basicity as they do in the absence of the proton.

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

## Isotope Fractionation at the Methyl Carbon in the Reactions of Cyanide Ion with Methyl Chloride and Methyl Bromide

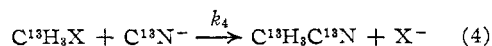
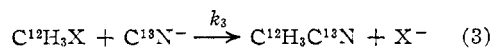
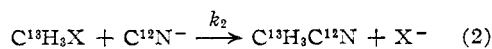
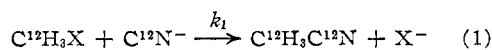
BY K. R. LYNN AND PETER E. YANKWICH\*

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The  $\text{C}^{13}$  isotope effect for isotopy at the methyl carbon atom has been measured in the cyanizations of methyl chloride and methyl bromide in water solution between 11.4 and 55.5°. In contrast with results previously reported for the iodide reaction, the chloride and bromide systems exhibit relatively large temperature dependence, indicative of the greater importance of bond rupture than bond forming in the reaction coordinate motion. Simple three particle models for the reaction seem incapable of reproducing the experimental values of both the temperature-dependent and temperature-independent factors in the isotopic rate constant ratios. The situation with respect to the latter is especially grievous. Some improvement in calculation of the temperature-dependent factors is available in the consideration of the changes which occur upon activation in the configuration of the methyl hydrogens. The possibility of significantly different reaction coordinate motions in the three cases is considered but does not seem particularly fruitful.

### Introduction

Four isotopic reactions occur when cyanide ions react with a methyl halide



In recent publications from this Laboratory results have been reported for isotope fractionation at the

cyanide carbon<sup>1</sup> and at the methyl carbon<sup>2</sup> in the reaction of cyanide ion with methyl iodide; the data were obtained from experiments in which the reagents were present at very different concentrations (complete reaction of the minor reagent corresponding to approximately 3% reaction of the major)<sup>3</sup> and checked through experiments in which they were present at the same concentration.<sup>2</sup> The present extension of these investigations to isotope fractionation at the methyl carbon in the reactions of methyl chloride and bromide with cyanide ion was in-

(1) K. R. Lynn and P. E. Yankwich, *J. Am. Chem. Soc.*, **83**, 53 (1961).

(2) K. R. Lynn and P. E. Yankwich, *ibid.*, **83**, 790 (1961).

(3) K. R. Lynn and P. E. Yankwich, *Chemistry and Industry*, 117 (1960).

\* National Science Foundation Senior Postdoctoral Fellow, 1960-1961, California Institute of Technology, Pasadena, California.

tended (i) to furnish information concerning the effects of the nature (particularly the mass) of the "leaving group," and (ii) to establish whether or not the rather large experimental imprecision associated with the results obtained earlier by the high concentration-ratio technique<sup>1,2</sup> was a characteristic of the iodide system.

### Experimental

**Reagents.**—Fisher "Certified" sodium cyanide was used without further purification; the methyl halide samples were distilled from stock of Matheson Co. "99.5% pure" materials but were not otherwise purified. Solvent water was deionized by passage through a mixed-bed resin ion exchanger. Reagents of analytical grade were employed in the analyses of reactants and products.

**Procedure.**—Aliquots of sodium cyanide solutions (10 ml., 0.015 *M*) were measured into reaction vessels which were cooled, evacuated and sealed. Five millimoles of methyl halide (manometric measurement) then was distilled into a side arm on each vessel. After temperature equilibration in baths maintained at constant ( $\pm 0.1^\circ$ ) temperature, the reactants were mixed and the reaction allowed to proceed for at least 15 times the calculated half-time of reaction under the conditions employed.<sup>4</sup> The reaction was stopped by distilling to a cold trap the product, residual major reagent and some solvent. Following further distillations, the product was isolated by vapor phase chromatography, combusted to carbon dioxide and its isotopic composition determined using procedures described in earlier publications.<sup>1,2</sup> In the reaction vessels employed, much of the alkyl halide was present in the vapor phase; that equilibrium between the liquid and the vapor was maintained was evidenced by the lack of reflection in the isotopic constitution of the product of variations in the free volume of the vessels from 25 to 135 ml. The reactions were studied at four temperatures between 11.4 and 55.5°.

**Calculations.**—The isotopic rate constant ratio descriptive of carbon isotope fractionation at the methyl position is  $(k_1/k_2)_x$ , given by the relation

$$(k_1/k_2)_x = R_x \times \frac{1 - 2X_N + X_C}{2X_N - X_C} \quad (5)$$

where  $R_x$  is the ratio ( $C^{13}H_2X/C^{12}H_2X$ ) for the original methyl halide reactant (equivalent to the corresponding ratio of isotopic carbon dioxides obtained by combustion of the reagent material),  $X_C$  the corresponding  $C^{13}$  atom fraction ( $X = R/[1+R]$ ) of  $C^{13}$  in the reagent cyanide and  $X_N$  that in the carbon dioxide obtained by combustion of methyl nitrile product.<sup>5</sup>

### Results

Average values of  $(k_1/k_2)_{Cl}$  obtained from thirty-two experiments are given in Table I; those of  $(k_1/k_2)_{Br}$  from twenty-four experiments are recorded in Table II. Because of the large number of runs, the primary data are shown only for one temperature, 11.4°. A convenient representation of results such as these is a plot of  $L(k_1/k_2)_x$  versus  $(1000/T)^6$ ; the equations of the least squares fitted lines through these plots are

$$L(k_1/k_2)_{Cl} = (2.50 \pm 0.89)(1000/T) - (1.32 \pm 2.88) \quad (6)$$

the average deviation of the experimental points from the calculated line being 0.70

$$L(k_1/k_2)_{Br} = (2.12 \pm 0.91)(1000/T) + (0.70 \pm 3.10) \quad (7)$$

(4) K. R. Lynn and P. E. Yankwich, unpublished experiments.

(5) The details of the derivation of eq. 5 are given in the first two references cited above and will not be repeated here. It is estimated that the imprecision in  $(k_1/k_2)_x$  inherent in the approximations involved in the derivation is, at the reagent concentration-ratio employed in these experiments, less than  $\pm 0.0005$ .

(6)  $L(x) = 100 \times \ln(x)$ . Throughout this paper the errors appended are average deviations.

TABLE I

$C^{13}$  ISOTOPE EFFECTS IN THE CYANIZATION OF METHYL CHLORIDE

Temp., °C.	$X_N \times 10^6$	$X_C \times 10^6 = 10664 \pm 5$ ; $R_{Cl} \times 10^6 = 10543 \pm 5$		
		$(k_1/k_2)_{Cl}$ eq. 5	Av. $(k_1/k_2)_{Cl}$	
11.4	10136	1.0868		
	10139	1.0861		
	10235	1.0650		
	10149	1.0884		
	10195	1.0735		
	10175	1.0779		
	10216	1.0685	1.0780 $\pm$ 0.0076	
	31.0	9 expts.		1.0711 $\pm$ .0078
	43.2	7 expts.		1.0666 $\pm$ .0092
	55.5	9 expts.		1.0657 $\pm$ .0069

TABLE II

$C^{13}$  ISOTOPE EFFECTS IN THE CYANIZATION OF METHYL BROMIDE

Temp., °C.	$X_N \times 10^6$	$X_C \times 10^6 = 10664 \pm 5$ ; $R_{Br} \times 10^6 = 10535 \pm 2$		
		$(k_1/k_2)_{Br}$ eq. 5	Av. $(k_1/k_2)_{Br}$	
11.4	10180	1.0760		
	10157	1.0812		
	10186	1.0747		
	10186	1.0747		
	10147	1.0835		
	10150	1.0828		
	10187	1.0745	1.0782 $\pm$ 0.0036	
	31.0	5 expts.		1.0815 $\pm$ .0068
	43.2	7 expts.		1.0750 $\pm$ .0064
	55.5	5 expts.		1.0698 $\pm$ .0058

average deviation 0.71; and, from an earlier publication<sup>2</sup>

$$L(k_1/k_2)_I = (0.56 \pm 0.56)(1000/T) + (4.95 \pm 1.52) \quad (8)$$

average deviation 0.49.

### Discussion

The experimental scatter reflected in the data recorded in Tables I and II is similar to that reported for the methyl carbon isotope effect in the cyanization of methyl iodide. In these systems, then, there is a consistent pattern of irreproducibility of results when the high concentration-ratio technique is employed. In studying the chloride and bromide reactions, checks were made of the more obvious possible sources of variation in the results, as was done for the iodide system, but there were no positive findings. The quality of the data makes it necessary to limit discussion of the results to consideration in terms of the simplest models for the reactions.

An isotopic rate constant ratio such as  $(k_1/k_2)$  is the product of a temperature independent factor (TIF, the high temperature limit of the ratio and the contribution of the reaction coordinate motion to the over-all isotopic effect, difficult to calculate) and a temperature dependent factor (TDF, the contribution to the isotope effect of isotopic frequency shifts in the genuine vibrations of the normal molecules and activated complexes, relatively easy to calculate—but agreement with experiment produced often with models which are

chemically or physically unreasonable<sup>7-10</sup>). From equations such as (6), (7) and (8), "experimental" values of TIF (and therefrom of TDF at any temperature in the experimental range) can be obtained by a semi-empirical method<sup>11,12</sup>; such values are collected in Table III, TDF being calculated for  $1000/T = 3.25$  (approximately 35°, the mid-temperature of the experimental range).

TABLE III

Reagent	TEMPERATURE-INDEPENDENT AND TEMPERATURE-DEPENDENT FACTORS OF ( $k_1/k_2$ )	
	TIF	TDF at 1000/T = 3.25
CH <sub>3</sub> Cl	1.007 ± 0.013	1.063 ± 0.013
CH <sub>3</sub> Br	1.025 ± .013	1.052 ± .013
CH <sub>3</sub> I	1.057 ± .010	1.012 ± .010

With due respect for the appended errors, it will be noted that there is a consistent trend with increasing halogen atom mass of both TDF and TIF. If the reaction coördinate motions are identical in the three reactions, one would expect the bromide and iodide system values to be close together rather than the bromide and chloride as is observed. Qualitatively, the trend of the TIF values is that expected from consideration of simple models of these S<sub>N</sub>2 reactions. In Table IV are collected the calculated TIF's for the Bigeleisen-Wolfsberg-Slater<sup>9,13</sup> three-particle representation of the cyanization, the masses of the molecular fragments<sup>14</sup> being employed. (Strictly speaking, molecular fragment masses can be used in these calculations instead of atomic masses only where the reaction coördinate motion is the rupture of an isolated bond,<sup>15</sup> as in the S<sub>N</sub>1 mechanism; such substitution, however, is warranted here because of the stiffness of the C-H and C-N vibrations.) Quantitatively, there is no agreement with experiment for any consistent value of the parameter  $p$ ,<sup>16</sup> but for values of  $p$  less than 1 the experimental and calculated TIF's are similarly affected by changes in halogen atom mass. Note, however, that the change from methyl chloride to methyl iodide in the experimental value of (TIF-1) is about eight times the chloride value. No simple model is capable of yielding such variation for a constant reaction coördinate motion in the three cases; the largest such effect is found for simple rupture of the C-X bond, and even there (TIF-1) for the iodide case is only about 25% larger than for the chloride.

The value of (TDF-1) for methyl chloride cyanization is apparently about five times as large as that for the reaction of the iodide. As in the

(7) J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).(8) J. Bigeleisen, *J. Phys. Chem.*, **56**, 823 (1952).(9) J. Bigeleisen and M. Wolfsberg, *J. Chem. Phys.*, **21**, 1927 (1953); **22**, 1264 (1954).(10) H. S. Johnston, W. A. Bonner and D. J. Wilson, *ibid.*, **26**, 1002 (1957).(11) P. E. Yankwich and H. S. Weber, *J. Am. Chem. Soc.*, **78**, 564 (1956).(12) P. E. Yankwich and R. M. Ikeda, *ibid.*, **81**, 1532 (1959).(13) N. B. Slater, *Proc. Roy. Soc. (London)*, **194A**, 113 (1948).(14) J. Bigeleisen and M. Wolfsberg, *Advances in Chem. Phys.*, **1**, 30 (1958).

(15) J. Bigeleisen and M. Wolfsberg, private communication.

(16) For the model A-B-C,  $p$  is the square of (amount of bond formation between A and B)/(amount of bond extension between B and C).

TABLE IV

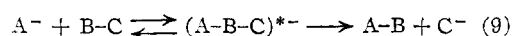
TIF CALCULATIONS FOR THE BIGELEISEN-WOLFSBERG-SLATER LINEAR THREE-PARTICLE MODEL EMPLOYING MOLECULAR FRAGMENT MASSES

(The asterisk indicates the atom which is C<sup>12</sup> or C<sup>13</sup>)

A	B	C	0	TIF for $p =$	
				1	∞
C <sup>12</sup> N	C*H <sub>3</sub>	Cl	1.0237	1.0248	1.0207
C <sup>12</sup> N	C*H <sub>3</sub>	Br	1.0274	1.0273	1.0207
C <sup>12</sup> N	C*H <sub>3</sub>	I	1.0292	1.0278	1.0207

case of TIF, no simple model seems capable of reproducing this variation for a consistent reaction coördinate motion, though a factor of two might be achieved by making assignments of force constants for activated complexes, which, though imaginative, are not unreasonable.

We can gain additional insight into the results by considering the reactions in terms of motions asymmetric with respect to B in the linear three-particle model



where A = CN, B = CH<sub>3</sub> and C = Cl, Br or I. The asymmetric stretching vibration,  $\omega_3$ , of A-B-C is a logical choice for the reaction coördinate motion; TIF is then the corresponding  $\omega_{12}/\omega_{13}$ , which is approximately 1.025 and insensitive to halogen atom mass.<sup>17,18</sup> The model thus fails in explanation of the observed values of TIF.

There are three contributions to TDF, a positive one from the B-C stretching vibration and negative ones from the bending and symmetric stretching vibrations of A-B-C. For the chloride, bromide and iodide, respectively, the B-C stretching frequencies (and the ratios of  $\omega_{12}/\omega_{13}$ ) are: 732 cm.<sup>-1</sup> (1.030), 611 cm.<sup>-1</sup> (1.035) and 533 cm.<sup>-1</sup> (1.037); the trends of these two sets of parameters are not compensatory, so the positive contribution to TDF will be moderate and will depend upon the halogen atom mass. Similar situations obtain for the genuine frequencies of the activated complex, except that the isotopic frequency ratios for the symmetric stretching vibrations are only 1.008-1.014 (chloride-iodide), while the frequencies themselves (for stretching force constants of approximately "half-bond" magnitude) are somewhat smaller than those of B-C. The TDF's yielded by these models, then, are greater than unity (in a bond forming reaction TDF can, in principle, be less than unity), have normal temperature dependence, decrease with increasing halogen atom mass and approximate 1.016 at  $1000/T = 3.25$ . Only for the reaction of methyl iodide is the calculated TDF even approximately the size indicated by the experimental results.

Since the C-N linkage is but little altered during the course of these reactions, further complication of the model would involve consideration of changes in the configuration of the hydrogen atoms bound to carbon and of the isotopic shifts in the several vibrational modes involving hydrogen. We have not attempted a detailed analysis of this more sophisticated model. Preliminary consideration, however, leads us to the following tentative

(17) F. Lechner, *Monatsh. Chem.*, **61**, 385 (1932).(18) A. Adel, *Phys. Rev.*, **45**, 56 (1934).

conclusions: first, the increments to TDF from this additional complexity of the model would be small (of the order of 0.004); second, the increments would, however, be more strongly dependent on halogen atom mass than the three genuine vibrations considered above; third, in aggregate, the additional complexities would not account for the degree of sensitivity to halogen atom mass indicated experimentally for either TIF or TDF.

For a consistent reaction coordinate motion, then, the obvious models fail to reproduce the experimental results. What of the possibility that each of the reactions actually involves a somewhat different reaction coordinate motion? If one insists upon linear or nearly linear transition states, one's freedom in calculation is limited mostly to the juggling of force constants and bond distances, differences in reaction coordinate motion being described essentially as differences in applicable values of a parameter such as the  $p$  of the Bigeleisen-

Wolfsberg treatment. Comparison of Table IV and the first column of Table III leads us to conclude that one might by this means bring the calculations for the methyl chloride and methyl bromide reactions into reasonable consonance, but TIF for the cyanization of methyl iodide is just too large to fit into such a picture. Departures from linearity in the configurations of the activated complexes result in lowering the calculated values of TIF; but, the shifts are moderate even for  $\text{CN}^-$  attack at  $90^\circ$ , and no better correspondence between calculated and apparent experimental values of TIF can be achieved by the assumption of halogen dependence of the single ABC. The rather large scatter in the data furnishes no refuge from these conclusions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, INDIANA]

## The Thermodynamic Properties of High Temperature Aqueous Solutions. I. Standard Partial Molal Heat Capacities of Sodium Chloride and Barium Chloride from 0 to $100^\circ$ <sup>1</sup>

BY CECIL M. CRISS<sup>2</sup> AND J. W. COBBLE

RECEIVED FEBRUARY 22, 1961

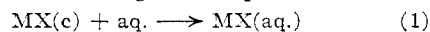
A sensitive submarine type solution calorimeter using electronic amplification and automatic recording has been constructed to measure heats of solution up to  $100^\circ$ . Nearly 300 integral heats of solution of sodium chloride and barium chloride have been determined at various concentrations from near 0 to  $95^\circ$ . From the extrapolated values of the heats at infinite dilution, values of  $\bar{C}_{p_2}^0$  as a function of temperature have been calculated for these salts. The observed heat capacities show maxima between  $50$  and  $70^\circ$  and then decrease as the temperature is further increased.

### Introduction

Within the past several years there has been an increasing interest in the thermodynamic properties of aqueous solutions at higher temperatures, both from a practical and theoretical point of view. One of the best methods of obtaining these properties at higher temperatures is to extend the known thermodynamic functions at  $25^\circ$  by use of partial molal heat capacities over the desired temperature range. Usually, it is the standard state functions (*i.e.*, at infinite dilution) that are desired; therefore, it is the partial molal heat capacity at infinite dilution and a function of temperature which is of real interest. Unfortunately, only a few reliable values have been reported at temperatures much above  $25^\circ$ .<sup>3-6</sup> Furthermore, what values are available were obtained from extrapolations derived from specific heat measurements of concentrated solutions. The reliability of extrapolations from such concentrations to infinite dilution is subject to question. Indeed, even the

theoretical limiting slope for  $\Phi_{\text{CP}}$  at  $25^\circ$  is uncertain by 25% for a 1:1 electrolyte.<sup>7</sup> Gucker<sup>8</sup> has suggested that more reliable values of  $\Phi_{\text{CP}}^0$  can be obtained by combining the temperature coefficients of the relative apparent molal heat contents,  $\Phi_{\text{L}}$ , with apparent molal heat capacities of more concentrated solutions. Harned and Owen<sup>9</sup> have suggested that the use of the temperature coefficient of the relative heat content can lead to better values for  $\bar{C}_{p_2}^0$ . Gulbransen and Robinson<sup>10</sup> in still another method have combined the heats of dilution,  $-\Phi_{\text{L}}$ , at two temperatures with the integral heats of solution at the same two temperatures to calculate  $\bar{C}_{p_2}^0$  for  $\text{NaCl}(\text{aq.})$  at  $22.5^\circ$ .

The approach used in this investigation is a slight variation on the latter method and will hereafter be referred to as the "integral heat method." It involves only heat-of-solution measurements. The amount of heat released when a solute is dissolved in water according to the equation



(1) Supported in part by a grant from the National Science Foundation.

(2) From the Ph.D. Thesis of Cecil M. Criss, Purdue University, 1961.

(3) M. Eigen and E. Wicke, *Z. Elektrochem.*, **55**, 354 (1951).

(4) E. Wicke, M. Eigen and Th. Ackermann, *Z. physik. Chem. NF*, **1**, 340 (1954).

(5) Th. Ackermann, *Disc. Faraday Soc.*, **24**, 180 (1957).

(6) Th. Ackermann, *Z. Elektrochem.*, **62**, 411 (1958).

(7) E. A. Guggenheim and J. E. Prue, *Trans. Faraday Soc.*, **50**, 710 (1954).

(8) F. T. Gucker, Jr., *Ann. N. Y. Acad. Sci.*, **51**, 680 (1949).

(9) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1958, p. 352.

(10) E. A. Gulbransen and A. L. Robinson, *J. Am. Chem. Soc.*, **56**, 2637 (1934).