amalgam. As was anticipated, the results of these experiments are difficult to interpret, and details will be reported in a subsequent paper.

The effect of the *adsorption* of halide ions on the reduction wave of persulfate was studied by Kalish and Frumkin[15,17] using much greater concentrations of halide (0.01 to 1 M) than used in our experiments. They found, for example, that the half-wave potential of the persulfate wave is about 0.6 v. more negative in 1 M potassium bromide than in 1 N sodium sulfate but made no mention of the effect of halide films such as we observed in the presence of small concentrations of iodide. From the results in Fig. 9 it is clear that 10^{-5} M iodide (curve 2) suppresses the extremely pronounced maximum (curve 1) observed in our supporting electrolyte. However, just at the potential (− 0.4 v.) where the adsorption film disappears, a slight maximum still did occur. The waves observed in the presence of larger concentrations of iodide have a very abnormal appearance. Starting at the most positive potentials the current starts to rise and reaches a maximum which is considerably below the diffusion current. It appears that in this range the iodide does not affect the electrode process. The reason is clear from curve 2 in Fig. 3 which indicates that the film of mercurous iodide breaks down at potentials more positive than + 0.3 volt. Considering the persulfate wave in 10^{-4} M iodide (curve 3, Fig. 9), the monomolecular layer of mercurous iodide is being formed after the current attains a maximum value at about +0.4 v. This film interferes with the reduction of persulfate and the current decreases to a minimum value at −0.1 v. When the potential is being made more negative, the film is being dissolved and the current increases and attains the value of the diffusion current at −0.4 v. From the results at higher iodide concentrations (curves 5 and 6 in Fig. 9) it appears that multimolecular layers of mercurous iodide can entirely prevent the reduction of persulfate until potentials are attained where the film becomes less than monomolecular.

The first oxygen wave is made more irreversible by a film of mercurous iodide. Bagozkaya[13,14] found that the adsorption of halide ions increases the overvoltage in the reduction of oxygen. Mancy and Okum[19] also found that anionic organic surface-active substances make the oxygen wave more irreversible. Thus the effect of the adsorbed mercurous iodide film on the reduction of oxygen appears to be of the same nature as that of adsorbed anions.

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Cyanide Carbon Isotope Fractionation in the Reaction of Cyanide Ion and Methyl Iodide. Carbon Isotope Effect in the Hydrolysis of Methyl Iodide

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The C^{13} isotope effects for isotopy at the cyanide carbon in the cyanization of methyl iodide and that in the hydrolysis of methyl iodide have been investigated for water solvent over the temperature range 11.4 to 58°. The results for hydrolysis are somewhat smaller than expected from the single value reported by Bender and Hoeg for the C^{14} effect, being at the 3.5% level; the cyanide carbon isotope effect in the cyanization is only about 1.0%. The results are examined in terms of a Bigeleisen–Wolfsberg–Slater three-particle model for the reacting system, special attention being paid to the choice between "atomic" and "molecular fragment" masses in the calculation of the temperature-independent factor in the isotopic rate constant ratios. The data do not permit a clear choice to be made between these bases for the computations.

Introduction

The reaction of cyanide ions with an alkyl halide offers a particularly simple example of a carbon–carbon bond forming process. The kinetics of several such substitutions have been studied,[1-3] and their mechanisms are known to be S_N2 in character. The cyanizations of the methyl halides in particular seem to be sufficiently devoid of complexity to permit a reasonably straightforward comparison of experimental and theoretical carbon isotope effects.[4] In this paper we report the results of experiments on the fractionation of C^{13} contained in cyanide ions during the cyanization of methyl iodide. Since methyl iodide is hydrolyzed very slowly under the conditions of the reaction,[5] data on the C^{13} fractionation in the hydrolysis and its temperature dependence were obtained also. (The C^{14} isotope effect in the methyl iodide hydrolysis in 50% aqueous dioxane, at 25° only, has been measured by Bender and Hoeg.[6]) The effect of this hydrolysis can be ignored in an ordinary kinetics study[2]; preliminary experiments on the methyl iodide cyanization in water solution[7] indicated that the isotope fractionation in the cyanide carbon was small with respect to that occurring in the methyl carbon during hydrolysis, but correction for the latter effect need not be entertained though the the results in the former case depend upon accurate knowledge of the isotopic constitution of

[1] M. F. Hawthorne, G. S. Hammond and B. M. Graybill, THIS JOURNAL, **77**, 486 (1955).

[2] B. W. Marshall and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 2640 (1959).

[3] K. R. Lynn and P. E. Yankwich, *J. Phys. Chem.*, **64**, 1719 (1960).

[4] A Pope, *Essay on Man*, I, 95.

[5] E. A. Moelwyn-Hughes, *Proc. Roy. Soc.* (*London*), **164A**, 295 (1938); **196A**, 540 (1949); **220A**, 386 (1953).

[6] M. L. Bender and D. F. Hoeg, THIS JOURNAL, **79**, 5649 (1957).

[7] K. R. Lynn and P. E. Yankwich, *Chem. and Ind.* (*London*), 117 (1960).

the methyl carbon in the methyl nitrile product (*vide infra*).

Let isotopic rate constants for cyanization be defined as

$$C^{12}H_3I + C^{12}N^- \xrightarrow{k_1} C^{12}H_3C^{12}N + I^- \quad (1)$$

$$C^{13}H_3I + C^{12}N^- \xrightarrow{k_2} C^{13}H_3C^{12}N + I^- \quad (2)$$

$$C^{12}H_3I + C^{13}N^- \xrightarrow{k_3} C^{12}H_3C^{13}N + I^- \quad (3)$$

$$C^{13}H_3I + C^{13}N^- \xrightarrow{k_4} C^{13}H_3C^{13}N + I^- \quad (4)$$

At any given degree of completion, the isotopic constitution of methyl nitrile product formed from originally equimolar concentrations of cyanide and methyl iodide will be a complicated function of the degree of reaction and of the several isotopic rate constant ratios. Evaluation of the rate constant ratios from the results of such experiments is not possible unless the isotope content of each product carbon is obtained. A technique based upon accurate knowledge of the isotopic constitution of one of the carbon atoms of the product nitrile would permit evaluation of one of the ratios (k_1/k_2) or (k_1/k_3) from the over-all C^{13} content of the product; similarly, the other ratio could be obtained from the results of experiments in which one input datum was the C^{13} content of the other carbon atom in the nitrile.

The cyanization of methyl iodide can be driven essentially to completion in terms of one reagent by having the other reagent present in large excess and waiting. Since the minor reagent is converted completely to one carbon atom of the product, the isotopic constitution of that carbon atom is the same as that of the original minor reagent. Isotope fractionation occurs in the reagent present in excess, and the isotopic rate constant ratio for such fractionation is obtained from isotope analysis either of the residual major reagent or the product. Thus, one can obtain values for (k_1/k_2) by the reaction of a small concentration of cyanide with a large excess of methyl iodide and values for (k_1/k_3) from reactions of a small concentration of methyl iodide with a large excess of cyanide. The advantage of such an approach to the problem of C^{13} fractionation during the formation of a carbon–carbon bond is that one need not degrade the product nitrile in order to learn the details of the distribution of C^{13} between its carbon atoms. (This high concentration-ratio technique obviously is capable of extension to systems in which one reagent contains many carbon atoms; under suitable conditions it may be applicable to reactions in which both reagents contain several carbon atoms.[7])

Moelwyn-Hughes[5] has shown that the predominant reaction in the hydrolysis of methyl iodide involves hydroxyl ions. The isotopic reactions investigated in this research are

$$C^{12}H_3I + OH^- \xrightarrow{k_5} C^{12}H_3OH + I^- \quad (5)$$

$$C^{13}H_3I + OH^- \xrightarrow{k_6} C^{13}H_3OH + I^- \quad (6)$$

It is important to note that, under the conditions employed in this investigation there is no appreciable exchange of methyl nitrile carbon with methyl iodide or methanol,[8,9] nor is there similar exchange between methanol and methyl iodide.[10]

Experimental

Reagents.—Fisher "Certified" sodium cyanide and Mallinckrodt "Analytical Reagent" sodium hydroxide were used without further purification; the methyl iodide samples were center cuts distilled from Eastman "White Label Grade" material. Solvent water was de-ionized by passage through a mixed-bed resin ion exchanger. Reagents of analytical grade were employed in the analyses of reactants and products.

Cyanization Runs.—Reactions were carried out at two different concentration levels: (a) 5 ml. of 1.00 *M* sodium cyanide and 5 ml. of 0.03 *M* methyl iodide were mixed; or (b) 90 ml. of 0.05 *M* sodium cyanide and 10 ml. of 0.015 *M* methyl iodide were mixed. The isotope ratios of carbon dioxide samples obtained from combustion of the product nitrile were independent of the concentration level, and results from both types of experiment were combined. In either case, aliquots of sodium cyanide solution and freshly prepared methyl iodide solution were brought to the reaction temperature (± 0.1°), then mixed in glass-stoppered vessels of appropriate volume. Reaction was allowed to proceed for not less than fifteen (and as much as fifty) times the calculated *half-time;* then the vessel was attached to a vacuum manifold and the product, with some solvent, distilled into a trap cooled to liquid nitrogen temperature. Two succeeding similar distillations further separated the products from the solvent. (It was established by blank experiments that no isotope fractionation of the product was effected by these distillations.)

Final isolation of the methyl nitrile was achieved by vapor phase chromatography. A 0.5 cm i.d. coiled Pyrex column of 5 meters tube length, packed with washed firebrick (Johns-Manville "Sil-O-Cel," C-22, 40–60 mesh) coated with 20% by weight of tri-cresyl phosphate (Pittsburgh Plasticizer Co.), maintained at 43° and swept with purified helium at a flow rate of 55 ml. min.$^{-1}$, separated methyl cyanide (retention time 24 min.) from methyl iodide (r.t. 8 min., but only traces were observed in the cyanization experiments) and methanol (r.t. 14 min.). The length of the water "band" was such that the methyl cyanide was collected along with an approximately equal amount of water. The methyl nitrile, collected in a cold trap upon elution from the chromatographic column, was distilled into a vacuum manifold and there burned to carbon dioxide by repeated distillation through a bed of copper oxide wire at *ca.* 700° Oxides of nitrogen produced during the combustion were reduced to nitrogen by passage over elemental copper foil at about 450°. The carbon dioxide was further purified and prepared for mass spectrometric analysis by procedures described in previous publications from this Laboratory.[11-14]

Carbon dioxide for mass spectrometric analysis was obtained similarly from samples of the reactants by combustion over copper oxide in a conventional Pregl apparatus. Sodium cyanide was mixed intimately with finely powdered vanadium pentoxide before ignition; as above, the oxides of nitrogen were reduced over copper. Iodine was removed from the combustion products of methyl iodide by distillation through a tube packed with small silver pellets. The concentrations of methyl iodide solutions employed in the investigation were determined by iodate titrimetry of iodide ion upon complete hydrolysis or cyanization of samples.

Hydrolysis Runs.—Reactions were carried out at only one concentration level, but at two volume levels: (a) 1 ml. of 0.50 *M* sodium hydroxide and 10 ml. of 0.05 *M* methyl iodide were mixed; or (b) 10 ml. of base and 100 ml. of halide

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[8] R. G. Pearson and R. L. Dillon, THIS JOURNAL, **75**, 2439 (1953).

[9] L. Tsai and M. Kamen, *J. Chem. Phys.*, **17**, 585 (1949).

[10] I. Roberts, *J. Chem. Phys.*, **6**, 294 (1938).

[11] P. E. Yankwich and R. L. Belford, THIS JOURNAL, **75**, 4178 (1953).

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

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

[14] To make sure that inappreciable isotope fractionation of the methyl cyanide occurred during the chromatography, $(C^{13}O_2/C^{12}O_2)$ ratios of carbon dioxide from combustions of purified reagent nitrile and the same material after chromatography were compared: $R_{CO_2} \times 10^6 = 10695 \pm 3$ (before), 10687 ± 3 (after).

were mixed. Results from the two types of experiment were insensitive to the volume level and were combined. In either case, aliquots of sodium hydroxide solution and freshly prepared methyl iodide solution were brought to the reaction temperature (± 0.1°) then mixed in glass-stoppered vessels of appropriate volume fitted with suitable vacuum connections. After passage of pre-selected time intervals, the hydrolysis was stopped by vacuum distillation of the nitrile and residual iodide (with some solvent) from the reaction mixture. Reproducible yields of methanol were not obtained from application of the analytical scheme described above; a number of obvious variations also were unsuccessful. As a consequence, the isotope fractionation in the hydrolysis was calculated from the C^{13} content of the residual methyl iodide, that of the original reagent, and the measured degree of reaction.[15]

In both the cyanization and hydrolysis experiments the sequence of individual runs as regards temperature was selected with the aid of a table of random numbers.

Results

Hydrolysis.—Had the methanol yields been reproducible, it would have been possible to calculate the carbon isotope effect in the hydrolysis of methyl iodide from the relation

$$(k_5/k_6) = (R_I)^0/(R_A)_0 \qquad (7)$$

where $(R_I)^0$ is the ratio $(C^{13}O_2/C^{12}O_2)$ obtained for carbon dioxide from the combustion of the original methyl iodide reagent, and $(R_A)_0$ is the corresponding ratio for methanol product collected at low degree of reaction, usually less than 5%. However, it was necessary to base the calculation of (k_5/k_6) on $(X_I)^0$ and $(X_I)_f$,[16] the latter being the atom fraction of C^{13} in unreacted methyl iodide after reaction fraction f (as always, the isotope measurements are carried out on carbon dioxide obtained by combustion).

The results of forty-one hydrolysis experiments are collected in Table I. Because of the large number of runs, the primary data are shown only for one temperature, 11.4°; they are typical. A convenient representation of such isotopic rate constant results is a plot of $L(k_5/k_6)$ *versus* $(1000/T)$[17]; the equation of the least-squares fitted line through this plot is

$$L(k_5/k_6) = (0.12 \pm 0.04)(1000/T) + (2.86 \pm 0.72) \qquad (8)$$

the average deviation of experimental points from the line being ± 0.70.

TABLE I

C^{13} ISOTOPE EFFECTS IN THE HYDROLYSIS OF METHYL IODIDE: $(X_I)^0 \times 10^6 = 9845 \pm 2$

Temp., °C.	f	$(X_I)_f \times 10^6$	(k_5/k_6)	Average (k_5/k_6)
11.4	0.44	10075	1.0278	
	.44	10075	1.0278	
	.21	10012	1.0417	
	.43	10127	1.0326	
	.43	10153	1.0427	
	.29	10058	1.0420	
	.43	10159	1.0441	
	.32	10067	1.0397	
	.42	10079	1.0301	
	.42	10062	1.0268	1.0355 ± 0.0065
31.0		11 expts.		1.0348 ± .0059
43.2		5 expts.		1.0267 ± .0009
58.0		5 expts.		1.0385 ± .0098

Cyanization.—Complete reaction of the methyl iodide in the presence of an approximately thirty-fold excess of cyanide ions is equivalent to about 3% reaction of the latter. Under these conditions the isotopic constitution of the cyanide is not altered significantly during the reaction. Let X_N be the atom fraction of C^{13} in the carbon dioxide obtained by combustion of methyl cyanide product, $(C^{12}H_3I)$ and $(C^{13}H_3I)$ the initial concentrations of the isotopic methyl iodides, f^{12} and f^{13} the fractions of $C^{12}H_3I$ and $C^{13}H_3I$ which react with $C^{13}N^-$, and R_C the ratio $(C^{13}N^-/C^{12}N^-)$ of the cyanide reagent material. Then

$$X_N = \frac{(C^{13}H_3I) + f^{12}(C^{12}H_3I) + f^{13}(C^{13}H_3I)}{2(C^{12}H_3I) + 2(C^{13}H_3I)} \qquad (9)$$

where

$$f^{12} = \frac{k_3(C^{13}N^-)}{k_3(C^{13}N^-) + k_1(C^{12}N^-)} = \frac{k_3R_C}{k_3R_C + k_1} \qquad (10)$$

and

$$f^{13} = \frac{k_4(C^{1}\ N^-)}{k_4(C^{13}N^-) + k_2(C^{12}N^-)} = \frac{k_4R_C}{k_4R_C + k_2} \qquad (11)$$

Preliminary experiments showed that isotope fractionation at the cyanide carbon is much smaller than that at the methyl carbon in the cyanization. Thus (k_1/k_2) and (k_3/k_4), which are the isotopic rate constant ratios for fractionation of methyl carbon reacting with different cyanides, are, to a high degree of approximation, equal. Exchanging the means, we write

$$(k_1/k_3) = (k_2/k_4) \qquad (12)$$

which implies that

$$f^{12} = f^{13} = F \qquad (13)$$

In terms of the new symbol F, (9) becomes

$$X_N = \frac{(X_I)^0 + F}{2} \qquad (14)$$

substitution of (10) and (12) in (14) yields[18]

$$(k_1/k_3) = R_C\,\frac{1 - 2X_N + (X_I)^0}{2X_N - (X_I)^0} \qquad (15)$$

Average values of (k_1/k_3) obtained from forty-eight cyanization experiments are summarized in Table II. Because of the large number of runs, the primary data are shown only for one temperature, 11.4°. The equation of the least-squares fitted line through the plot of $L(k_1/k_3)$ *versus* $(1000/T)$ is

$$L(k_1/k_3) = (0.99 \pm 0.58)(1000/T) - (2.20 \pm 2.46) \qquad (17)$$

the average deviation of the experimental points from the calculated line being ± 0.55.

Discussion

The values of (k_5/k_6) shown in Table I are somewhat smaller than one would have expected from the result at 25° reported for C^{14} fractionation by

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[15] J. Y.-P. Tong and P. E. Yankwich, *J. Phys. Chem.*, **61**, 540 (1957).

[16] These are C^{13} atom-fractions, $X = R/(1 + R)$.

[17] $L(x) = 100 \ln (x)$.

[18] Results calculated by application of Eq. 15 are relatively insensitive to the approximation $(k_1/k_2) = (k_3/k_4)$. This was tested by applying the rigorous relation $(k_1/k_2) = P\cdot(k_3/k_4)$, where P is a proportionality constant. In these terms, $f^{12} = f^{13}/(P - f^{13}[P - 1])$. The difference between f^{12} and f^{13} is found to be without significant effect upon the results calculated for (k_1/k_3) for reasonable ranges of values of P and (k_3/k_4). For example, with $(0.9 < k_3/k_4 < 1.1)$ and $(0.6 < P < 1.4)$ the calculated values of (k_1/k_3) are shifted by less than the effect of the average deviations in the experimental isotope ratios. Indeed, for the range of (k_3/k_4) indicated, P must deviate from unity by more than 0.1 to affect the calculated value of k_1/k_3 in the *fifth* significant figure.

TABLE II

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

$(X_I)^0 \times 10^6 = 9845 \pm 2$; $R_C \times 10^6 = 10779 \pm 5$

Temp., °C.	$X_N \times 10^6$	(k_1/k_3) eq. 15	Average (k_1/k_3)
11.4	10172	1.0159	
	10159	1.0184	
	10178	1.0147	
	10195	1.0110	
	10168	1.0167	
	10171	1.0161	
	10175	1.0153	
	10195	1.0110	1.0149 ± 0.0020
31.0	18 expts.		1.0091 ± .0069
43.2	12 expts.		1.0122 ± .0061
58.0	10 expts.		1.0089 ± .0058

Bender and Hoeg[6]; however, the discrepancy lies within the combined experimental errors of the two sets of determinations. At temperatures other than 43.2°, the average deviations are about eight to twelve times as large as those observed in studies involving simpler analytical procedures, and it is our belief that it is primarily the complex analytical method employed in this experimentation which is responsible for the large scatter of the data. We have, however, no evidence for either "memory" or "overlap" effects in the chromatography.

The isotopic rate constant ratio (k_5/k_6) is the product of two factors, one temperature independent (TIF), the other temperature dependent (TDF).[19-20] The reaction coördinate motion alone determines TIF.[19,21] Employing the semiempirical method described in two earlier publications,[22,23] one obtains as an estimate of TIF in (k_5/k_6): 1.031 ± 0.007, consonant with the small observed temperature dependence shown in Table I and in general agreement with the value 1.026 calculated for a pure S$_N$2 mechanism by Bender and Hoeg[6] using the Bigeleisen–Wolfsberg–Slater[20,24] three-particle reaction coördinate.

Bigeleisen and Wolfsberg derived an expression for TIF in a three-center system A–B–C, in which a bond between particles B and C is broken and a bond between particles A and B is formed. TIF is a function of the particle mass numbers, the angle ABC, and a parameter p which, for this situation, is the square of (amount of bond formation, between A and B)/(amount of bond extension between B and C). For the pure S$_N$1 mechanism $p = 0$; while for S$_N$2, $p = 1$. Originally, the particles A, B and C were taken, after Slater, to be the atoms involved in the changes in chemical bonding; however, in a later discussion of the problem, Bigeleisen and Wolfsberg proposed[25] that the mass numbers of molecular fragments be substituted for atomic mass numbers in making calculations for a "simple decomposition process." In Table III are collected some values for TIF calculated on the two different mass bases for three reactions of interest in the present discussion: the hydrolysis of methyl iodide and the two isotope effects in the cyanization of methyl iodide. We consider first the hydrolysis results, (k_5/k_6).

TABLE III

TIF CALCULATIONS FOR THE BIGELEISEN–WOLFSBERG–SLATER THREE-PARTICLE REACTION COÖRDINATE: COMPARISON OF USE OF "ATOMIC" AND "MOLECULAR FRAGMENT" MASSES

(The asterisk indicates the atom which is C^{12} or C^{13})

A	B	C	TIF for p = 0	1	∞
O	C*	I	1.0371	1.0335	1.0194
HO	C^*H_3	I	1.0292	1.0260	1.0170
C	C*	I	1.0371	1.0316	1.0198
NC	C^*H_3	I	1.0292	1.0278	1.0207
C*	C	I	1.0000	1.0076	1.0198
NC*	CH_3	I	1.0000	1.0023	1.0069

The range of value for p for a given prototype mechanism must be rather limited; the problem has not received detailed study. In both the hydrolysis and the cyanization reaction of methyl iodide the reaction kinetics conform to the S$_N$2 classification which, strictly interpreted, should require that p be unity. In actuality, unity is probably an approximate upper limit to p for an S$_N$2 reaction. It is our guess that a reasonable lower limit would be approximately 0.7. Comparison of the first two lines of Table III shows that TIF calculated on either mass basis is relatively insensitive to p in the region near $p = 1$. For purposes of discussion, then, we take 1.026 as a lower bound to TIF and 1.034 as an upper bound.

If one accepts the least-squares equation 8 and errors as representative of the data, then the mean value of TDF for these experiments is 1.007 ± 0.007 if TIF = 1.026. Over the temperature span of the hydrolysis runs, such a TDF would change by 0.002–0.004; this variation is well within the experimental error. A TDF of this magnitude is smaller than one would calculate for simple C–I bond rupture; but, if p is to be near unity, one must include the effect of partial C–C bond formation, which would tend to reduce TDF, perhaps to a value as low as that indicated.[26] If one assumes that TIF = 1.034, then the mean value of TDF for the hydrolysis experiments is in the range 1.000–1.007, the low end of the range being the most probable value. A TIF of 1.034 in a simple decomposition reaction would have associated with it in this temperature range a TDF approximately equal to 1.020.[6] Clearly the scatter of (k_5/k_6) values is not sufficiently great to mask such a TDF. Rather, if one accepts the high value of 1.034 for TIF, it is necessary to seek mechanisms whereby

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[19] J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949), *J. Phys. Chem.*, **56**, 823 (1952).

[20] J. Bigeleisen and M. Wolfsberg, *J. Chem. Phys.*, **21**, 1972 (1953), **22**, 1264 (1954).

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

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

[23] P. E. Yankwich and R. M. Ikeda, *ibid.*, **81**, 1532 (1959).

[24] N. B. Slater, *Proc. Roy. Soc.* (*London*), **194A**, 113 (1948).

[25] J. Bigeleisen and M. Wolfsberg, *Advances in Chemical Physics*, **I**, 30 (1958).

[26] It should be noted that in a three-particle TIF calculation for this reaction based either on the skeleton O–C–I or on the one consisting of molecular fragments containing these atoms, one throws away the effects of hybridization changes in the C–H bonds. Such changes are sometimes responsible for large contributions to TDF because of the related alterations in bending mode frequencies.

the TDF could be reduced to near unity. Comparison of the TIF values for $p = 0, 1$ and ∞ shows that TIF is, for central particle isotope substitution, more sensitive to the component of bond formation than it is to bond rupture.[27] In this three-particle system, then, one would expect the effect on TDF of A–B bond formation to override those of B–C bond rupture at some value of p less than unity. The mechanism for an unusually small TDF is thus at hand; the question which cannot be answered at the moment is whether the critical value for p will lie in the range descriptive of an SN2 reaction. It is for this reason that the data on the hydrolytic isotope effect do not permit a clear choice to be made between "atomic" and molecular fragment mass bases for TIF calculations.

The role of solvation isotope effects in decomposition reactions seems quite uniformly to be such as to result in an over-all isotope fractionation greater than that attributable to the kinetic effect.[19b,28] In the two reactions considered in this paper, it seems quite likely that solvation isotope effects would lie in the same direction, since both incoming groups are negative ions and these are but weakly solvated in water; changes in solvation state upon activation, therefore, will, if they occur at all, be confined largely to the methyl iodide "region" and would be expected to enhance the observed fractionation. Such positive effects cannot be invoked to explain an unusually low TDF.

The temperature dependence of the cyanization isotope effect (k_1/k_3) as given by eq. 17 corresponds to TDF = 1.022 ± 0.010 (at $1000/T = 3.25$) and TIF = 0.988 ± 0.010.[23] We have no reason to expect a value of TIF smaller than unity in this reaction; indeed, it is difficult to see how this situation can arise, though there is good evidence for it from experiments whose results are of higher reliability than those reported here.[12,28] The value of (k_1/k_3) at the mean temperature is 1.010 ± 0.006. If TIF has the value 1.0023, TDF at this temperature is 1.008 ± 0.006; while this is within the range of the experimental value, we are faced with a situation where the isotope effect from the reaction coördinate motion (TIF − 1) is only about a third as large (or even smaller) as the isotope effect from the aggregate changes in genuine vibrations upon activation (TDF − 1). Consistent calculations for TIF and TDF made on simple models seem quite uniformly, in this temperature range, to predict TIF > TDF, so we could regard this low value of TIF as definitely suspect. The "molecular fragment" value for TIF, 1.0078, requires that TDF be 1.002 ± 0.006, which seems to be appropriate in magnitude relative to TIF; however, this indicated value of TDF seems to be well outside the range of the experimental value, 1.022 ± 0.009. This kind of impasse occurs whenever an isotopic rate constant ratio has a temperature dependence larger than would be expected from its magnitude; in the present situation it means that we have no valid basis for choosing between the "atomic" and "molecular fragment" models for the calculation of TIF.

There is available[7] a preliminary value for (k_1/k_2) at 11.4°: 1.074 ± 0.005. The value of p applicable to isotope fractionation at the methyl carbon is, of course, the same as that applicable to the cyanide carbon isotope effect (provided the reaction is viewed in terms of the same three particles in both instances). In the SN2 range, one has for the "atomic" mass basis TIF = 1.032 − 1.034 and for the "molecular fragment" basis TIF = 1.028; these correspond to TDF values, respectively, of 1.040 ± 0.005 and 1.045 ± 0.005. The ratios of contributions to the over-all isotope effect (TDF/TIF) are 1.2 ± 0.2 on the "atomic" basis and 1.6 ± 0.2 on the "molecular fragment" basis. While one could be led to prefer the atomic mass calculation for TIF for this reason, there is actually much less stringency here than in the case of (k_1/k_3), and the choice must be made on other grounds. Finally, it must be noted that the difference between the magnitudes of (k_1/k_2) and (k_5/k_6) cannot be accounted for in terms of three-particle models for the two substitution reactions; if this fact is to be accorded prime significance, then the speculations above on the choice between the "atomic" and "molecular fragment" versions of the TIF calculation are idle. However, this seems to be an over-critical conclusion in view of the success with which three-particle models have been applied to the estimation of various isotope effects.[25] Certainly both OH^- and CN^- are sufficiently "stiff" diatoms that if any polyatomic fragments can be treated as single particles they can.

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[27] This is just because the B–C, two-particle, TIF ($p = 0$) differs from the A–B–C, SN2, TIF ($p = 1$) by *less* than does the A–B, two-particle, TIF ($p = \infty$).

[28] P. E. Yankwich and R. M. Ikeda, THIS JOURNAL, **82**, 1891 (1960).