factor to the volume fraction of matrix in the resin

$$k_{\text{theor}} = \left(\frac{1 + v_R}{1 - v_R}\right)^2 \qquad (2)$$

For the membrane used here v_R was 0.168, so that k_{theor} was 1.96, in fair agreement with that observed.

The self-diffusion of sodium and chloride ions in a Zeo-Karb 315 membrane has been studied by Meares,[10] who compared his observed diffusion coefficients with those calculated using equation 2. Interpreting his results in terms of tortuosity factors, the observed value of k was 7% less than calculated for chloride ions, and also for sodium ions when the membrane was in contact with concentrated solutions. Under such conditions sorption of electrolyte by the membrane was probably sufficient to screen the electrostatic drag between gegen and fixed ions.

In the derivation of equation 2 the diffusing particles were assumed to be of dimensions equal to the resin monomer units, whereas heavy water molecules and the hydrated ions discussed here are considerably smaller. It has been suggested by Kitchener and Lagos[11] that the tortuosity factor for small diffusing species may be less than for larger molecules. This might account for the fact that the observed k values are about 8% less than those calculated.

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KINETICS OF THE REACTIONS OF SODIUM CYANIDE WITH SOME ALKYL IODIDES

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The kinetics of the reactions between cyanide ions and methyl, ethyl and *n*-propyl iodides were studied between 11 and 43° in 50% aqueous ethanol; with methyl iodide the measurements were repeated for water solvent in the temperature range 11–58°. The reactions are kinetically of the first order with respect to either reagent. Observed differences in entropies of activation agree with the explanations for medium effects proposed by Hughes and Ingold and with the symmetry change arguments of Crowell and Hammett.

Introduction

Kinetic studies on the reactions in solution of simple alkyl iodides with cyanide ions are numerous but fragmentary,[1–3] except for an investigation of the cyanization of methyl iodide in water.[4] Such reactions as these, now well recognized as bimolecular nucleophilic substitutions,[5] seemed to us to be suitable for the study of carbon isotope fractionation in the formation of carbon–carbon bonds. As a desirable preliminary to such investigations, we have studied the kinetics of reactions between cyanide ions and methyl iodide (in water and aqueous ethanol), and ethyl and *n*-propyl iodides (in aqueous ethanol only), over 30 to 40° ranges of temperature.

Experimental

Reagents.—The alkyl iodide samples used were center cuts distilled from Eastman "White Label Grade" reagents the sodium cyanide was Fisher "Certified" reagent, and was used without further purification. Solvent water was deionized by passage through a mixed-bed resin ion exchanger. The solvent referred to below as "50% ethanol" was prepared by diluting with an equal volume of purified water U. S. Industrial Chemical Co.'s absolute ethanol. Reagents of analytical grade were employed in the analyses of reaction mixtures.

Kinetic Runs.—The solutions of cyanide and iodides ranged in concentration from 0.05 to 0.15 *M*. Five-ml. aliquots of freshly prepared reagent solutions were pipetted into Pyrex tubes which were sealed rapidly (flame sealing for water runs, tubes with ground glass stoppers being employed for aqueous ethanol runs) and immersed in the constant (±0.1°) temperature bath.[6] At pre-selected times reaction tubes were removed from the bath, the reaction quenched by their immersion in ice–water mixture, and samples prepared for analysis.

Analyses.—Both iodide ion production and cyanide ion consumption were measured, the former by titration with iodate,[7] the latter by titration with silver ion.

Results

In Table I are collected the results for the reaction of cyanide ion with methyl iodide in the two solvents. Four to ten kinetics runs were made at various concentration ratios at each temperature. The rate of reaction is strictly first order with respect to each reagent, and no deviation from overall second-order kinetics could be detected in runs which were allowed to proceed to as much as 70% reaction. It is important to note that the specific rate constants based on iodide ion production and cyanide ion disappearance are the same within the

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[5] See, for example, C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

[6] At the final concentrations used and over the temperature ranges of the experiments, no appreciable error attributable to reaction during warm-up of the vessels and their contents was expected nor was any observed.

[7] Cyanide does not interfere nor is there during the analysis detectable hydrolysis of either the alkyl iodide or the cyanide ion.

experimental scatter of replicate determinations of either kind; the same conclusion obtains for the experiments on ethyl iodide and *n*-propyl iodide (*vide infra*).

TABLE I

SPECIFIC RATE CONSTANTS FOR THE REACTION BETWEEN CYANIDE ION AND METHYL IODIDE

t, °C.	$(k_2 \pm$ av. devn., l. mole^{-1} sec.$^{-1}) \times 10^4$ from estimation of CN^-	I^-	Av.
	A. Solvent: water		
11.4	1.08 + 0.11		
19.5	3.04 ± 0.26		
31.0		10.5 ± 0.3	
45.8	40.3 ± 0.8		
58.3	137.1 ± 6.9		
	B. Solvent: 50% aqueous ethanol		
11.4	4.95 ± 0.05	4.89 ± 0.14	4.91 ± 0.14
31.0	38.4 ± 0.3	37.1 ± 0.4	37.8 ± 0.3
43.0	129.2 ± 5.6	125.5 ± 5.5	127.4 ± 5.7

The results obtained for the reaction of cyanide ion with ethyl and *n*-propyl iodides are summarized in Table II. The Arrhenius and Eyring equation parameters are collected in Table III.

TABLE II

SPECIFIC RATE CONSTANTS FOR THE REACTION BETWEEN CYANIDE ION AND ETHYL AND *n*-PROPYL IODIDES IN 50% AQUEOUS ETHANOL

t, °C.	$(k_2 \pm$ av. devn. l. mole^{-1} sec.$^{-1}) \times 10^4$ from estimation of CN^-	I^-	Av.
	A. Ethyl iodide		
11.4	1.12 ± 0.09	1.22 ± 0.09	1.17 ± 0.09
31.0	8.62 ± 0.28	9.13 ± .15	8.94 ± 0.26
43.2	50.4 ± 6.2	48.4 ± .8	49.2 ± 3.3
	B. *n*-Propyl iodide		
11.4	0.91 ± 0.06	0.91 ± 0.06	0.91 ± 0.06
31.0	7.10 ± 0.48	6.70 ± 0.35	6.90 ± 0.42
43.2	27.9 ± 2.4	27.9 ± 2.4	27.9 ± 2.4

TABLE III

PARAMETERS OF THE ARRHENIUS AND EYRING EQUATIONS FOR REACTION OF CYANIDE ION WITH ALKYL IODIDES

Iodide	Solvent	log A[8]	E_{exp}, kcal. mole^{-1}	$\Delta H^{\pm}$, kcal. mole^{-1}	$\Delta S^{\pm}_{298}$, e.u.
CH_3	W	10.8	19.2	18.6	−11.1
CH_3	Aq. EtOH	11.5	19.4	18.8	−7.5
C_2H_5	Aq. EtOH	11.7	20.4	19.8	−6.9
n-C_3H_7	Aq. EtOH	11.2	19.9	19.3	−9.3

Discussion

The values recorded in Table III are in general correspondence with activation parameters reported for similar ion–molecule reactions,[9-11] and in good agreement with the Arrhenius parameters reported recently by Marshall and Moelwyn-Hughes[12] for the methyl iodide cyanization in aqueous solution.

For methyl iodide cyanization the difference of about 3.5 e.u. in the entropies of activation in the two solvent systems is in the direction and of the magnitude which would be expected for a simple dielectric effect.[13,14] For a cyanide ion radius of 1.05 Å.,[15,16] and using values for the dielectric constants of water–ethanol mixtures interpolated from the data of Akerlof,[17] the effects of solvent on k_2, attributed solely to variation in the entropy of activation, correspond to a radius for the activated complex of approximately 4 Å., which seems quite reasonable.

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[8] Estimates of imprecision: log A, ±0.3; E_{exp} and $\Delta H^{\pm}$, ± 0.3 kcal. mole^{-1}; $\Delta S^{\pm}_{298}$, ±0.8 e.u.

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THE PREPARATION OF FINE POWDER HEXAGONAL Fe_2C AND ITS COERCIVE FORCE

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The relatively rare hexagonal form of Fe_2C has been prepared in fine powder form by the reaction of a gaseous mixture of H_2 and CO with Raney iron at 240°. The occurrence of the hexagonal form appears to require the exclusion of Fe_3O_4. If Fe_3O_4 is present, the carbide is found in the more common Hägg form. The coercive force of the fine powder hexagonal Fe_2C prepared by this method is approximately 800 oe.

Introduction

The compound Fe_2C is known to exist in two crystalline forms. The more common form is referred to as the Hägg carbide which may be indexed on either hexagonal or orthorhombic axes. The formula for this carbide has been given as both Fe_2C and $Fe_{20}C_9$.[1] The other form is relatively rare and is a distinctly different hexagonal structure in which the iron atoms are believed to be arranged in hexagonal close packing.[2] This form is referred to as the hexagonal carbide. The conditions for

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