graph was consistent with the proposed structures, since a linear relationship of the logarithmic retention time with molecular weight of **5**, **6**, and **7** was found. The infrared data of **7** are as follows: 2980 (m) and 2900 (m) (C–H st), 1422 (s), 1417 (m) (CH_2 def), 1274 (s), 998 (m), 966 (w), 947 (m), 905 (m), 877 (s), 842 (m) cm^{-1}. **7**'s mass spectrum had molecular ion 210, 0.1%; base peak, 76, 17.1%; 150, 0.5%; 146, 0.5%; 136, 4.1%; 60, 9.5%; 59, 8.3%; 45, 10.2%; 44, 3.4%; 41, 3.7%; and 32, 13.5%, all of Σ_{26}.

Registry No.—**1**, 13145-41-0; **2**, 10191-72-7; **3**, 10191-73-8; **4**, 10191-74-9; **4**·HCl, 10191-75-0; **5**, 180-97-2; **6**, 13145-46-5; **7**, 13145-47-6.

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The Kinetics of Cyanoethylation of Methanol in Mixed Methanol–Aprotic Solvents

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The kinetics of the cyanoethylation of methanol catalyzed by alkali metal methoxides was studied in solvent mixtures of methanol and the aprotic solvents dimethyl sulfoxide, dimethylformamide, dimethylformamide–dioxane (1:1), dioxane, tetrahydrofuran, and benzene. The rate of reaction was first order in acrylonitrile, first order in the alkali metal methoxide, and was proportional to $1/[CH_3OH]^n$, n being dependent on the aprotic solvent. It increased with increasing the concentration of the aprotic solvent in the solvent mixture, owing to its participation in the equilibrium reactions leading to desolvation of methanol-solvated methoxide ions. This enhancement was especially pronounced at low methanol concentrations. Depending on the aprotic solvent, the rate of reaction decreased in the order dimethyl sulfoxide > dimethylformamide ≫ tetrahydrofuran ≃ dioxane > benzene.

Rates of nucleophilic substitution reactions were highly accelerated when carried out in aprotic solvents such as dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) compared with the generally used protic solvents, such as alcohols. This effect of aprotic solvents was studied intensely recently[2–11] and applied synthetically, with great success, to various nucleophilic substitutions.[4–11] The role of aprotic solvents in the analogous base-catalyzed nucleophilic addition to activated carbon–carbon double bonds was very little investigated[12] although the Michael-type addition reaction is one of the most applicable organic reactions.[13] Rates of reaction involving nucleophilic attack on a carbonyl double bond, such as alkaline hydrolysis of esters, were enhanced[14] even to about 10^4 to 10^5 times[15] by substituting aprotic for hydroxylic solvents. Acid–base equilibria were strongly influenced by transfer from methanol to DMF.[16]

It was the purpose of the present work to study kinetically the influence of aprotic solvents on the methoxide-catalyzed cyanoethylation of methanol, the mechanism of which was previously derived when using methanol as sole solvent.[17] In addition, relatively detailed kinetic results were available for the cyanoethylation of hydroxylic compounds in protic solvents. The kinetics of the KOH-catalyzed cyanoethylation of ethanolamine in water[18] and that of the base-catalyzed cyanoethylation of water and mono- and polyhydric alcohols[19] were studied. It was found for all these systems that the nucleophilic attack on the double bond was the rate-determining step, the reaction being a second-order reaction, first order in each of the concentrations of the basic catalyst and acrylonitrile.

Results

The rate of the cyanoethylation of methanol in the mixed solvents was followed either dilatometrically or by titrimetric determination of the concentration of acrylonitrile.

The Order of Reaction in Acrylonitrile.—This was studied by measuring the rate of cyanoethylation of methanol in mixed solvents of methanol and each of the following aprotic solvents: DMSO, DMF, dioxane, tetrahydrofuran (THF), benzene, DMF–dioxane (1:1). The rate of reaction was first order in acrylonitrile for all types and compositions of the solvent systems used. This was evident from the straight lines obtained on plotting log $[AN]_0/[AN]_t$ or log $(A_t - A_\infty)$ *vs.* time (Figures 1 and 2) where $[AN]_0$ and $[AN]_t$ were the initial concentration and concentration at time t of acrylonitrile, respectively, and A_t and A_∞ were the readings of the dilatometer at time $t = t$ and at $t = \infty$. Pseudo-first-order rate constants, k_1, calculated from the slopes of the straight lines, and their dependence on the composition of the mixed solvents are summarized in Tables I–III.

The cyanoethylation in methanol–benzene mixed solvent gave straight lines on plotting log $(A_t - A_\infty)$

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TABLE I

CYANOETHYLATION OF METHANOL IN METHANOL–DMSO, IN METHANOL–DMF–DIOXANE (1:1), AND IN METHANOL–THF MIXED SOLVENTS[a]

Aprotic solvent, %	[Methanol], mole/l.	10^3k_1, min^{-1} DMSO[b]	DMF–dioxane[c]	THF[d]
65	8.45	6.24	...	...
70	7.23	8.38	50.02	15.48
75	5.96	17.99	94.43	19.21
80	4.80	42.70	152.80	...
85	3.64	111.35	274.00	27.27
90	2.40	393.62	697.90	61.95
93	1.66	...	816.75	105.70

[a] Experimental conditions: the rate of reaction was followed dilatometrically, $[AN]_0 = 0.508$ mole/l. [b] $[CH_3OK] = 1.65 \times 10^{-4}$ mole/l.; reaction temperature 25 ± 0.1°. [c] $[CH_3OK] = 6.76 \times 10^{-3}$ mole/l.; reaction temperature 20 ± 0.1°. [d] $[CH_3OK] = 6.78 \times 10^{-3}$ mole/l.; reaction temperature 20 ± 0.1°.

TABLE II

CYANOETHYLATION OF METHANOL IN METHANOL–DMF MIXED SOLVENTS[a]

DMF, %	[Methanol], mole/l.	10^3k_1, min^{-1} At 0°	At 15°	At 25°
50	12.07	...	...	1.33
65	8.45	...	1.80	3.69
75	5.95	...	4.16	11.46
80	4.80	1.84	9.47	21.86
85	3.64	4.61	19.39	61.41
90	2.40	10.80	64.40	153.03
93	1.66	50.83	164.29	...
95	1.16	109.01	...	...

[a] Experimental conditions: the rate of reaction was followed titrimetrically, $[AN]_0 = 0.508$ mole/l., $[CH_3OK] = 3.33 \times 10^{-4}$ mole/l.

TABLE III

CYANOETHYLATION OF METHANOL IN METHANOL–DIOXANE AND IN METHANOL–BENZENE MIXED SOLVENTS

Aprotic solvent %	[Methanol], mole/l.	10^3k_1, min^{-1} Dioxane[a] At 20°	Dioxane[a] At 30°	Benzene[b] At 20°	Benzene[b] At 30°
0	24.05	2.31	...	...	...
20.7	19.09	3.57	...	...	...
34.5	15.76	5.11	...	...	...
51.7	11.61	8.42	...	...	...
65	8.45	10.22	...	...	...
75	5.96	15.81	40.14 34.02	30.81	...
80	4.80	...	43.18	35.31 34.08	84.03
85	3.64	29.27	70.09 58.22	37.87	93.15
90	2.40	56.61	128.00	50.82	381.80
93	1.66	123.21	286.64 253.33	79.43 76.95	506.90
95	1.16	281.75	594.94 460.60	133.90	...

[a] Experimental conditions: the rate of reaction at 20° was followed titrimetrically, $[CH_3OK] = 6.72 \times 10^{-3}$ mole/l., while that at 30° was followed dilatometrically, $[CH_3OK] = 6.83 \times 10^{-3}$ mole/l.; $[AN]_0 = 0.50$ mole/l. [b] The rate of reaction was followed dilatometrically, $[AN]_0 = 0.508$ mole/l., $[CH_3OK] = 53.65 \times 10^{-3}$ mole/l.

vs. t, only up to about 40% conversion (Table III and Figure 2). In accordance, a log–log plot of initial rates *vs.* concentration of acrylonitrile gave a straight line with a slope $\alpha = 1$, corresponding to an order of one in acrylonitrile.

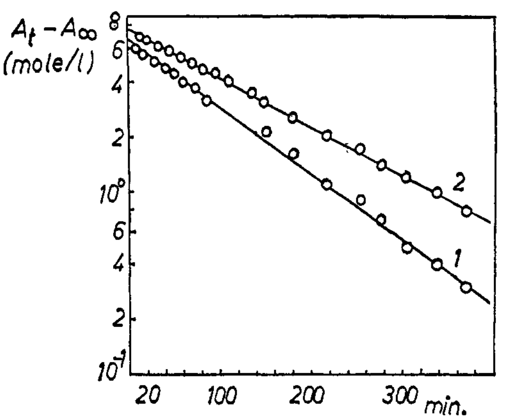

Figure 1.—First-order plots in acrylonitrile for the cyanoethylation in methanol-DMSO: 1, 70% DMSO; 2, 65% DMSO (Table I).

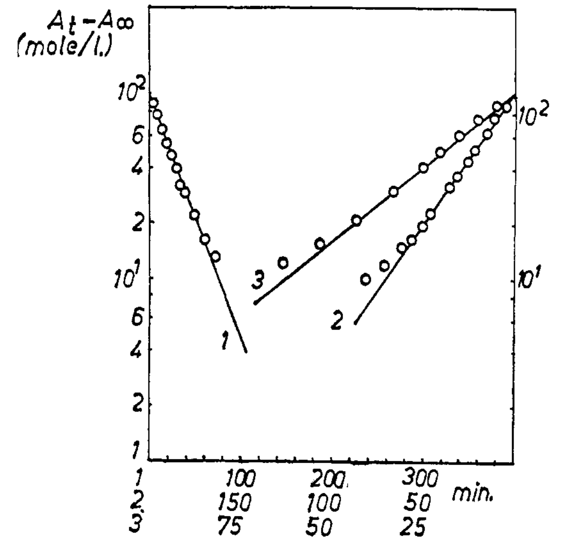

Figure 2.—First-order plots in acrylonitrile for the cyanoethylation in methanol–benzene: 1, 75% benzene; 2, 80% benzene; 3, 85% benzene (Table III).

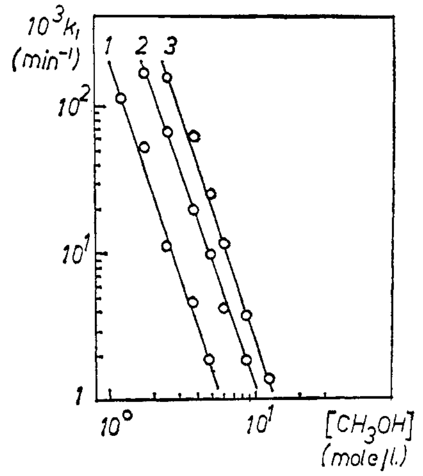

Figure 3.—Order of reaction in methanol for the cyanoethylation in methanol-DMF: 1, 0°; 2, 15°; 3, 25°.

The Order of Reaction in Methanol.—The pseudo-first-order rate constants k_1 presented in Tables I-III could be defined by

$$k_1 = k[CH_3OH]^b[CH_3O^-Me^+]^c \qquad (1)$$

where k, b, and c are the over-all rate constant, order of reaction in methanol, and order of reaction in the basic

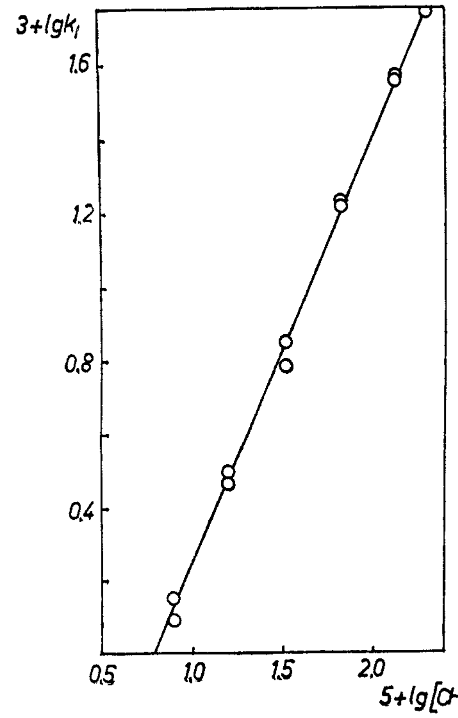

Figure 4.—Order of reaction in methoxide for the cyanoethylation in methanol-DMF (70% DMF) at 25°.

catalyst, respectively, and Me is alkali metal. By using the logarithmic form of the above equation, the order of reaction in methanol was calculated from the slopes of the straight lines obtained (Figure 3) on plotting log k_1 *vs.* log [CH_3OH].

The order of reaction in methanol was negative for all the solvent systems used. Relatively high negative values were obtained with the dipolar aprotic solvents DMSO and DMF (of high dielectric constants), as compared to the nonpolar solvents benzene, THF, and dioxane. The results obtained are summarized in Table IV.

TABLE IV

ORDER OF REACTION IN METHANOL FOR THE CYANOETHYLATION OF METHANOL IN MIXED METHANOL-APROTIC SOLVENTS

Aprotic solvent	Reaction temp, °C	Table no.	Order in methanol
Benzene	20	III	−0.55 ± 0.13
THF	20	I	−1.6 ± 0.2
Dioxane	20	III	−1.5 ± 0.1
	30	III	−1.5 ± 0.2
DMF-dioxane (1:1)	20	I	−2.8 ± 0.4
DMF	0	II	−2.9 ± 0.3
	15	II	−2.8 ± 0.1
	25	II	−2.9 ± 0.2
DMSO	25	I	−3.4 ± 0.2

The Order of Reaction in the Alkali Metal Methoxide.—This was investigated at different compositions of the mixed solvents and at various temperatures. The aprotic components of the solvent mixtures used were DMF, dioxane, THF, and benzene. The pseudo-first-order rate constants k_1 obtained with the different concentrations of the basic catalyst under the specified experimental conditions are presented in Table V. On plotting log k_1 against log [$CH_3O^-Me^+$], straight lines were obtained (Figure 4) in accordance with the logarithmic form of eq 1. It was found that the reaction was practically first order in the alkali methoxide, as was calculated from the slopes of these straight lines (Table V). The minor deviations from unity order observed might be attributed to dissociation factors. It should be mentioned here that the reaction was first order in the alkali methoxide when carried out in pure methanol.[17]

TABLE V

ORDER OF REACTION IN ALKALI METAL METHOXIDE FOR THE CYANOETHYLATION OF METHANOL IN MIXED METHANOL-APROTIC SOLVENTS[a]

10^4 [methoxide], mole/l.	10^3k_1, min^{-1}	Order in methoxide
	70% DMF, 25 ± 0.1°	
0.79	1.20, 1.40	1.15 ± 0.08
1.58	3.18, 2.93	
3.32	6.14, 7.04	
6.64	16.63, 17.04	
13.27	35.97, 36.42	
19.91	54.83	
	90% DMF, 15 ± 0.1°, CH_3OLi[b]	
0.83	8.75	0.93 ± 0.25
1.67	33.45	
3.33	82.80	
5.00	115.00	
6.67	163.09	
	75% Dioxane, 25 ± 0.1°	
16.67	3.31	0.96 ± 0.20
66.68	11.76, 12.21	
116.69	22.36, 20.15	
166.70	32.04, 32.48	
	90% Dioxane, 25 ± 0.1°	
17.07	9.50	1.05 ± 0.06
119.50	65.64, 83.25	
170.70	102.48	
	93% Dioxane, 25 ± 0.1°	
8.33	9.50	0.84 ± 0.14
26.66	33.81	
67.20	123.21	
	90% THF, 20 ± 0.1°	
0.17	14.52	
0.34	27.01	
0.68	61.95	
1.01	85.49	
	85% Benzene, 20 ± 0.1°	
0.67	4.11	1.05
1.34	8.05	
2.68	17.25	
5.36	37.87	

[a] Experimental conditions: the rate of reaction was followed dilatometrically, $[AN]_0$ = 0.508 mole/l., and potassium methoxide was used as basic catalyst. [b] The rate of reaction was followed by titration.

The Effect of the Alkali Metal on the Rate of Cyanoethylation.—The chemical reactivity of organometallic compounds is dependent on the type of the metallic ion and on the per cent ionic character of the carbon-metal bond. The rate of cyanoethylation of methanol in methanol as solvent was about the same on using lithium, sodium, or potassium methoxide as basic catalyst.[17] In order to evaluate the results of the kinetic measurments of the present work, the rates of cyanoethylation of methanol in mixed methanol-aprotic solvents, using the above-mentioned alkali metal

TABLE VI

EFFECT OF THE ALKALI METAL ON k_1

Aprotic solvent		Temp, °C	Li		Na		K		Ratios of rate constants Li:Na:K
Type	Vol. %[a]		$10^3[CH_3O^-]$, mole/l.	10^3k_1, min^{-1}	$10^3[CH_3O^-]$, mole/l.	10^3k_1, min^{-1}	$10^3[CH_3O^-]$, mole/l.	10^3k_1, min^{-1}	
DMSO	85	25	0.163	96.81	0.166	119.50	0.165	111.40	1.0:1.2:1.1
DMF	90	20	0.33	143.90	0.33	144.20	0.33	150.70	1.0:1.0:1.0
DMF	85	20	3.40	394.90	3.55	428.00	3.38	407.20	0.9:1.0:0.9
THF	90	20	6.71	10.51	6.67	44.79	6.78	61.95	1.0:4.3:5.9
Dioxane	90	20	6.72	3.22	6.89	29.60	6.72	56.61	1.0:9.2:17.6
Benzene	90	20	53.35	16.5	53.76	39.40	53.65	50.82	1.0:2.4:3.1
...	0	15	40.36	7.93	40.92	9.61	40.40	8.55	1.0:1.2:1.1

[a] Methanol was the second component of the mixed solvent.

methoxides, were compared. Results showing the dependence of the pseudo-first-order rate constant on the alkali metal used, under comparable conditions, are summarized in Table VI.

The Over-all Rate Constant k.—The over-all rate constant of the presently investigated cyanoethylation of methanol was calculated by using the equation

$$R_0 = k[AN]^a[CH_3OH]^b[CH_3O^-Me^+]^c \tag{2}$$

where R_0 is the initial rate of the reaction.

The reaction was first order in acrylonitrile in all the solvent systems used; $R_0 = k_1\ [AN]^1$, where k_1 is the pseudo-first-order rate constant. Consequently, k is given by

$$k = \frac{k_1}{[CH_3OH]^b[CH_3O^-Me^+]^c} \tag{3}$$

The order of reaction in the alkali methoxide was practically one (Table V). Values of b, the order of reaction in methanol, are given in Table IV. Accordingly, k values were calculated by using eq 3 and their average values are summarized in Table VII.

TABLE VII

OVER-ALL RATE CONSTANTS IN VARIOUS SOLVENTS[a,b]

Aprotic solvent	Table no.	Order in CH_3OH	Temp, °C	k (av), (mole/l.)$^{-(b+c)}$ min^{-1}
DMSO	I	−3.4	25	49,150 ± 5100
DMF	II	−3	0	570 ± 95
DMF	II	−3	15	2900 ± 230
DMF	II	−3	25	7600 ± 750
DMF–dioxane (1:1)	I	−2.8	20	1580 ± 400
Dioxane	III	−1.5	20	39 ± 9
Dioxane	III		30	79 ± 12
THF	I	−1.6	20	42 ± 10
Benzene	III	−0.55	20	1.5 ± 0.05

[a] Averaged from the results presented in the tables. [b] Values of activation energy, E_a, enthalpy of activation, ΔH^*, and activation entropy, ΔS^*, were calculated for the cyanoethylation of methanol in methanol–DMF mixed solvents at various temperatures (0, 15, and 25°) using values of the over-all rate constants. ΔS^* was calculated from the equation $\Delta S^* = 2.303R \log\left(\frac{kh}{KT}\right) + \left(\frac{\Delta H^*}{T}\right)$ where h is Planck's constant and K is Boltzman's constant. The data obtained were the following: E_a = 16,400 cal, ΔH^* = 15,800 cal, ΔS^* = 5.3 eu (calculated for T 288°K).

Discussion

The results of the kinetic rate measurements of the cyanoethylation of methanol in mixed methanol aprotic solvents might be summarized by the experimental rate equation (eq 4). The most important characteristic of this reaction system was the observed linear dependence of R on $1/[CH_3OH]$, which resulted in a large enhancement of the rate of cyanoethylation at low methanol concentrations.

$$R = k\,\frac{[\text{base}]\,[\text{acrylonitrile}]}{[CH_3OH]^n} \tag{4}$$

The prevailing mechanism of alkoxide-catalyzed cyanoethylation of alcohols[17] as well as of other cyanoethylations[18,19] and various Michael-type addition reactions[20] was that the rate-determining step was a nucleophilic attack on the double bond. Consequently, in the present case, increasing the reactivity of the alkoxide anion or increasing the concentration of the free alkoxide ions should increase the rate of cyanoethylation.

The nucleophilic attack of the methoxide anion on the neutral acrylonitrile molecule leads to dispersion of the negative charge. According to theory, reactions in which existing charge is dispersed should experience a rate increase going to less polar solvents.[21,22] It is obvious that explanations of the observed rate changes with varying solvent composition in terms of bulk dielectric constants break down if applied to the cyanoethylation in the dipolar aprotic solvents DMF (ϵ 37.6)[23] and DMSO (ϵ 46.4),[24] whose dielectric constants are higher than that of methanol (ϵ 34).[25] In addition, the increase of the rate of cyanoethylation observed in mixtures of methanol and aprotic solvents of low dielectric constant (THF, ϵ 7.6; dioxane, ϵ 2.2; benzene, ϵ 2.2) was too high to be attributed to lowering of dielectric constant only.[22]

Anions in protic solvents are solvated by the molecules of the solvent through hydrogen bonding.[3,6,15] The increased reactivity of anions in the presence of aprotic solvents was ascribed to a reduction of their degree of solvation by the protic solvent.[1,7,26–28]

In regard to the presently investigated cyanoethylation, it might be well assumed that the same nucleophile, the free methoxide anion, is participating in the rate-determining step when carrying out the reaction in either pure methanol or in mixed methanol–aprotic solvents. The methoxide anion is in equilibrium with

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$$
\begin{aligned}
&CH_3O^-\cdot nCH_3OH \rightleftarrows CH_3O^-\cdot(n-1)CH_3OH + CH_3OH\\
&CH_3O^-\cdot(n-1)CH_3OH \rightleftarrows\\
&\qquad CH_3O^-\cdot(n-2)CH_3OH + CH_3OH \quad (5)\\
&CH_3O^-\cdot CH_3OH \rightleftarrows CH_3O^- + CH_3OH
\end{aligned}
$$

its solvated forms as shown in eq 5. Consequently, the relatively high rates of cyanoethylation with low methanol concentrations in the mixed solvents might be due, at least in part, to an increased concentration of free CH_3O^- ions caused by a shift of the equilibrium system (eq 5) toward the formation of these ions. However, the incompatibility of the rate changes observed (Tables I–III) with the dielectric properties of the mixed solvents and the extraordinary rate enhancement exerted by DMSO and DMF (compared with THF, dioxane, and benzene) are strongly in favor of the existence of some specific effect of the aprotic solvent on the concentration of the methanol. This might be explained by the capability of the dipolar molecules of DMSO and DMF to be strongly associated with the alcohol, since these solvents are known as powerful hydrogen-bond acceptors.[29–32] Consequently, the effective concentration of free methanol is reduced, resulting in a shift of the equilibrium system (eq 5) toward the formation of free methoxide ions.

The relatively large enhancement of the rate of cyanoethylation observed at the range of low methanol concentrations with all types of aprotic solvents used was a result of the effective low concentration of free methanol and stemmed from the essential fact that the rate of cyanoethylation was directly proportional to $1/[CH_3OH]^n$. This was evident from the constancy of the order of reaction in methanol in the mixed solvents over the whole range of methanol concentrations used. A good example is provided by the methanol–dioxane system, for which a log–log plot of k_1 against $[CH_3OH]$ gave a straight line on using 0–95% by volume of dioxane.

It might be concluded that the rate of the presently investigated cyanoethylation was affected not only by the dilution effect of the aprotic solvent, but to a much greater extent by its mode of participation in a series of equilibrium reactions leading to the complete desolvation of the methanol-solvated methoxide ions. If its dilution effect were dominant, the rate of reaction should have been about the same with all the aprotic solvents used, under comparable experimental conditions.

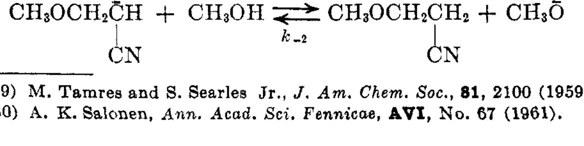
The experimentally found rate equation for the methoxide-catalyzed cyanoethylation of methanol in pure methanol as solvent is given by eq 6.[17] A rate equation

$$R = (k[\text{base}])(\text{total }[AN]) \qquad (6)$$

(eq 7) was derived[17] based on the steps of cyanoethylation

$$R = k[CH_3O^-][AN] \qquad (7)$$

tion given by eq 8. Participation of solvated methoxide



(8)

$$
\begin{aligned}
&CH_3O^- + \underset{CN}{CH_2{=}CH} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CH_3OCH_2\underset{CN}{\bar{C}H}\\
&CH_3OCH_2\underset{CN}{\bar{C}H} + CH_3OH \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} CH_3OCH_2\underset{CN}{CH_2} + CH_3\bar{O}
\end{aligned}
$$

ions ($CH_3O^-\cdot nCH_3OH$) in reaction 8 is also possible, but their contribution to the rate of reaction seems to be negligible, since the nucleophilic reactivity of CH_3O^- is expected to be much greater than that of any of its solvated[1] or ion-paired forms.[33]

On using a simplified form of eq 5, such as eq 9,

$$CH_3O^-\cdot nCH_3OH \overset{K}{\rightleftarrows} CH_3O^- + nCH_3OH \qquad (9)$$

$[CH_3O^-]$ can be expressed by

$$[CH_3O^-] = K\frac{[CH_3O^-\cdot nCH_3OH]}{[CH_3OH]^n} \qquad (10)$$

It should be noted that the concentration of unassociated methanol in eq 10 is practically the total concentration of methanol introduced, since concentration of the latter is much greater than that of methoxide.

Substitution of $[CH_3O^-]$ in eq 7 gives a rate equation

$$R = k'\frac{[CH_3O^-\cdot nCH_3OH][AN]}{[CH_3OH]^n} \qquad (11)$$

where k' is the product of the rate constant and the equilibrium constants. This equation is practically identical with the experimentally obtained rate equation (eq 4), assuming that $[CH_3O^-\cdot nCH_3OH] \simeq [\text{base}]$ total as enough methanol to solvate the methoxide ions was present. This treatment accounts only for the dilution effect of the aprotic solvent. That this was not its sole effect was evident from the different values of the order of reaction in methanol found with the aprotic solvents used.

Equation 11 indicates that the order of reaction in methanol is related to the extent of solvation of the methoxide ions by methanol. The different values of the order of reaction in methanol found might be due to the existence of different species of methanol-solvated methoxide ions in the various solvent systems investigated.

In solvent systems where ion pairing is present, the extent of solvation of the methoxide ion pairs by methanol may be expected to be different from that of free methoxide ions and therefore affect the kinetic order in methanol. It may be noted that the results of Table VI show that in the case of solvent mixtures containing DMSO and DMF no ion pairing exists, while in solvent mixtures containing dioxane, benzene, and THF ion pairing is present. The extent of ion pairing of $CH_3O^-K^+$ in the latter solvents, if it is present at all, is obviously smaller than that of sodium and lithium methoxides, owing to the relatively greater ionic character of organopotassium compounds.

The rate constants observed regarding the aprotic solvent used decreased in the following order: DMSO > DMF > THF > dioxane > benzene. This order is the same as that of the hydrogen-bonding "capacity" of these solvents. Therefore it is expected that, under the same conditions, the extent of the shift of the equilibrium (eq 5) toward the formation of "free methoxide ions" will follow the same order, thus leading to the above decreasing order of the rate constants.

On using lithium, sodium, or potassium methoxides, the same rates of cyanoethylation in a given solvent mixture were obtained in DMSO, DMF, and methanol

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(32) A. Allerhand and P. von Ragué Schleyer, *ibid.*, **85**, 1715 (1963).

(33) G. Gee, W. C. E. Higginson and G. T. Merrall, *J. Chem. Soc.*, 1345 (1959).

(Table VI). This indicated the absence of ion pairing in these solvents. With THF, dioxane, and benzene in the mixed solvents, the rates of reaction increased in the order K > Na > Li, indicating that dissociation of the alkali methoxides was incomplete, at least in the case of lithium and sodium methoxides. Solvation of metallic cations by aprotic solvents increases the rate of reactions involving organometallic compounds.[34] However, this could not be the reason for the rate increase in the presently investigated cyanoethylation, since the ionic dissociation of the alkali methoxide was already complete in pure methanol.[17]

Experimental Section

Materials.—Acrylonitrile (BDH) was purified according to the method of Bamford and Jenkins.[35] Absolute methanol (BDH) suitable for anhydrous titrations containing no more than 0.01% water was used. Dimethylformamide[36] was subjected to azeotropic distillation with benzene and fractionally distilled *in vacuo* under nitrogen; the fraction boiling at 65–66° (35 mm) was used. DMSO was purified as DMF was purified. The fraction boiling at 93° (30 mm) was collected, shaken for 48 hr over calcium oxide, filtered under anhydrous conditions, and fractionally distilled. The middle fraction was used. Dioxane and tetrahydrofuran were first refluxed over sodium and then over sodium benzophenone ketyl and distilled. Benzene was refluxed over sodium and distilled. All purification procedures were carried out under pure nitrogen and anhydrous conditions. Materials were kept under nitrogen in flasks fitted with self-sealing rubber caps. Methanolic methoxide solutions were prepared by dissolving the alkali metal in methanol under reflux. The concentration of the base was determined by titration with standard acid using phenolphthalein as indicator.

Procedure for Kinetic Measurements.—The apparatus and procedure for the titrimetric determination of the rate of cyanoethylation were the same as previously described.[17] When the reaction was follow dilatometrically a conventional dilatometer consisting of a calibrated capillary tube, ending in a bulb of 3–25-ml volume, was used. A solution of acrylonitrile dissolved in the solvent mixture was introduced into the same apparatus as that used for the volumetric rate measurements. At the required temperature, the catalyst solution was added in one portion. Time of reaction was recorded from this point. A portion of the homogeneous reaction mixture was transferred quickly to the dilatometer (which had already the required temperature) by a hypodermic syringe. Calculations were made by standard methods as described in Frost and Pearson.[22] Product studies have shown the presence of β-methoxypropionitrile.

Registry No.—Methanol, 67-56-1; DMSO, 67-68-5; DMF, 68-12-2; dioxane, 123-91-1; THF, 109-99-9; benzene, 71-43-2.

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[34] H. E. Zaugg, B. W. Horrom, and S. Borgwardt, *J. Am. Chem. Soc.* **82**, 2895 (1960).

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[36] A. B. Thomas and E. G. Rochow, *J. Am. Chem. Soc.*, **79**, 1843 (1957).

Oxidation of Olefins by Palladium(II). III. Oxidation of Olefins by a Combination of Palladium(II) Chloride and Copper(II) Chloride in Acetic Acid[1,2]

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A combination of Pd(II) and Cu(II) in acetic acid oxidizes olefins to products which neither Pd(II) nor Cu(II) alone will produce. Pd(II) is known to oxidize olefins to vinyl and allylic acetates and Cu(II) alone gives no oxidation, but, in a system containing both palladium(II) chloride and copper(II) chloride, acetate esters of glycol and chloro alcohols are formed. If ethylene is oxidized in reaction mixtures with high cupric ion concentrations, little vinyl acetate is produced but, rather, 2-chloroethyl acetate, ethylene glycol diacetate, and ethylene glycol monoacetate are formed. At 100°, propylene and 1-butene give mainly 1,2-di- and 1,2-chloro acetates with smaller amounts of 1,3 isomers. In addition, 1-butene gives traces of 1,4 and 2,3 isomers. *cis*- and *trans*-2-butene, on the other hand, give comparable quantities of both 2,3 and 1,3 isomers. These results are consistent with a mechanism involving oxypalladation adducts as intermediates. The oxypalladation adducts decompose by reaction with copper(II) chloride. The product distribution can be explained by isomerization of the oxypalladation adduct prior to reaction with Cu(II).

The oxidation of ethylene to vinyl acetate[3] and of

$$C_2H_4 + Pd^{+2} + 2OAc^- \longrightarrow C_2H_3OAc + HOAc + Pd^0 \tag{1}$$

other olefins to a mixture of vinyl and allylic acetates,[4] first reported by Russian workers,[3a] is the subject of several recent patents.[5] In several of the patents, Cu(II) is used as a redox system to make the reaction catalytic in Pd(II).

$$C_2H_4 + 2Cu(II) + OAc^- \xrightarrow[HOAc]{Pd(II)} C_2H_3OAc + 2Cu(I) + HOAc \tag{2}$$

However, in the presence of Cu(II), a side reaction takes place which can be made the predominant reaction under certain conditions. This new reaction, which requires the presence of both Pd(II) and Cu(II), is the formation of the acetate esters of chloro alcohols and glycols. Thus, with ethylene, the reaction is as shown in eq 3.

$$C_2H_4 + CuCl_2 + OAc^- \xrightarrow[HOAc + H_2O]{PdCl_2} \begin{matrix} AcOCH_2CH_2Cl \\ AcOCH_2CH_2OAc \\ AcOCH_2CH_2OH \end{matrix} + CuCl \tag{3}$$

While this work was in progress, two reports of this reaction have appeared. The first, in the patent literature,[6] does not disclose the acetate esters of the

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[1] Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966; Abstracts, p 37N.

[2] Paper II: P. M. Henry, *J. Am. Chem. Soc.*, **88**, 1595 (1966).

[3] (a) I. I. Moiseev, M. N. Vargaftik, and Ya. K. Sirkin, *Dokl. Akad. Nauk SSSR*, **133**, 377 (1960); (b) E. W. Stern and M. L. Spector, *Proc. Chem. Soc.*, 370 (1961).

[4] (a) M. N. Vargaftik, I. I. Moiseev, and Ya. K. Sirkin, *Izv. Akad. Nauk USSR, Otd. Khim. Nauk*, 930 (1962); (b) I. I. Moiseev, A. P. Belov, and Ya. K. Sirkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1527 (1963).

[5] For example, Imperial Chemical Industries, Belgian Patents 635,425, 635,426, and 638,268 (1964).

[6] D. Clark and P. Hayden, Canadian Patent 711,719 (1965).