and δ 92 cps due to D on β-, γ-, and insulated methylenes [CD-$(CH_2)_{n \geq 1}C{=}C$-], and are not resolved.

Registry No.—Methyl sorbate, 1515-80-6; 1,3-cyclohexadiene, 592-57-4; 1,4-cyclohexadiene, 628-41-1; methyl octadeca-10,12-dienoate, 1002-79-5; methyl *cis*-9,*trans*-11-octadecadienoate, 13058-52-1; methyl *trans*-9,*trans*-11-octadecadienoate, 13038-47-6; methyl benzoate–$Cr(CO)_3$, 12125-87-0; benzene–$Cr(CO)_3$, 12082-08-5; methyl linoleate, 112-63-0; methyl oleate, 112-62-9; methyl elaidate, 1937-62-8; **4,** 21899-41-2.

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The Effect of Dipolar Aprotic Solvents on the Nucleophilic Addition of Alcohols to Activated Olefins

B. A. FEIT[1] AND Z. BIGON

Department of Chemistry, Tel Aviv University, Tel Aviv, Israel

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The effect of dipolar aprotic solvents on the alkoxide-catalyzed addition of methanol and ethanol to methyl esters and nitriles of acrylic and methacrylic acid was investigated kinetically. The rate equation found was $R = (k_{\text{obsd}}\,[\text{olefin}][\text{alkoxide}])/[\text{ROH}]^n$. Rates of addition were relatively very high in solvent mixture poor in alcohol. The order of reaction in alcohol was dependent only on the type of the aprotic solvent used; its absolute value increased with increasing the hydrogen-bonding capability of the aprotic solvent. It is suggested that mainly one and the same nucleophile is involved in the addition reaction, in both pure alcohol and in alcohol dipolar aprotic solvent mixtures poor in alcohol.

The rates of reactions involving nucleophiles or bases have been found to be strongly accelerated in dipolar aprotic solvents as compared to protic solvents. This effect was recently investigated kinetically and synthetically[2-4] mainly with nucleophilic substitutions and with various base-catalyzed reactions such as eliminations,[5] H–D exchange[6] reactions, isomerizations,[7] oxidations,[8] etc. In only a few cases was this effect reported with regard to reactions involving unsaturated compounds. These include nucleophilic additions to olefins[9] and to carbonylic compounds such as esters,[10] ketones,[11] carbon dioxide,[12] and carbon disulfide.[13]

Gradual replacement of a protic solvent by a dipolar aprotic solvent in a mixed protic–dipolar aprotic solvent caused only a slight increase in the rate of nucleophilic substitutions,[14,15] alkaline hydrolysis of esters,[10a,b,d,e] base-catalyzed oxidations,[8] etc. However, in the range of low concentrations of the protic component, a dramatic rate enhancement was observed on further decreasing of its concentration. This behavior was ascribed to a large increase in the reactivity of the nucleophilic species.[2,14] The accepted opinion is that less reactive hydrogen-bonded solvated nucleophiles operate at relatively high concentrations of the protic component, whereas unsolvated and much more reactive nucleophiles operate at low concentrations. Desolvation of the nucleophiles is facilitated by the strong association of dipolar aprotic solvents with hydroxylic solvents.[16-19] According to others, the above-mentioned rate enhancement was due in some cases to a catalytic effect of the dipolar aprotic solvent.[14,15]

The base-catalyzed addition of methanol to acrylonitrile in mixed methanol–dipolar aprotic solvents was previously investigated.[9] The experimental rate equation was

$$R = k\frac{[\text{acrylonitrile}]\,[\text{CH}_3\text{O}^-]_{\text{total}}}{[\text{CH}_3\text{OH}]^n_{\text{total}}}$$

This equation accounted for the large rate enhancement which was observed in the presence of low concentration of methanol. The rate constant and the order of reaction in methanol were dependent on the aprotic solvent used.[9] These were higher with the dipolar aprotic solvents (DMF, DMSO) than with apolar aprotic solvents (THF, dioxane).

Negatively charged large transition states are poorly hydrogen bonded owing to dispersion of charge, as compared to small anions. Anions are in general poorly solvated in aprotic solvents, but negatively charged polarizable transition states are solvated by dipolar aprotic solvents to about the same extent as they are in protic solvents. Consequently, bimolecular reactions of anions which pass through large polarizable transition states containing these anions are much faster in dipolar–aprotic than in protic solvents.[20] Based on this assumption concerning the effect of the medium on

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(1) To whom correspondence should be addressed: Polymer Research Center, State University College of Forestry, Syracuse, N. Y. 13210.

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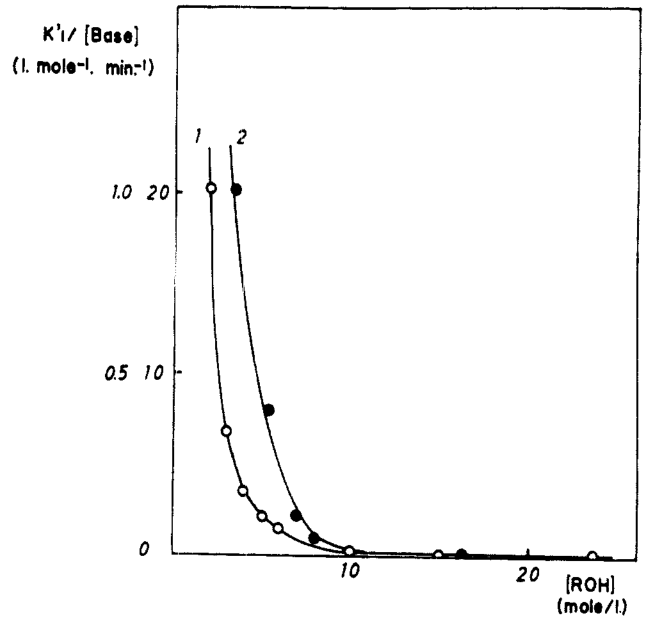

Figure 1.—Plot of the observed second-order rate constant k_1'/[base] against concentration of alcohol: (1) addition of methanol to methylmethacrylate (0.5 mol/l.) in methanol–DMF mixtures; (2) addition of ethanol to methacrylonitrile (0.5 mol/l.) in ethanol–DMF mixtures.

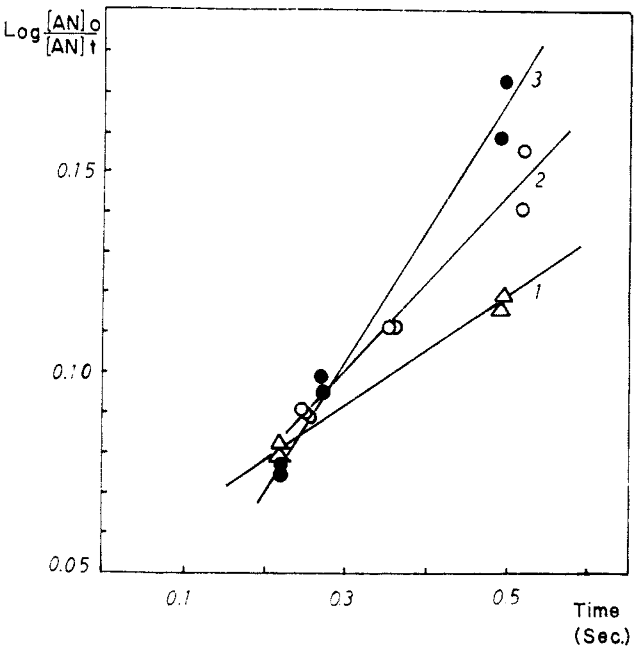

Figure 2.—First-order plots of log$[AN]_0/[AN]_t$ *vs.* t for the cyanoethylation of methanol in methanol–DMF mixed solvent (rates were measured in a flow system): (1) runs 60–63; (2) runs 28–35; (3) runs 54–59.

bimolecular nucleophilic reactions, and on the fact that the rate constant and the order of reaction in methanol for the nucleophilic addition of methanol to acrylonitrile were dependent[9] on the solvation properties of the aprotic component, it was expected that this order would be influenced by the type of the olefinic substrate. Different olefins would lead to different negatively charged transition states.

It was the purpose of the present work to determine the factors influencing the rate increase and the value of the order of reaction in alcohol, for nucleophilic additions in mixed alcohol–dipolar aprotic solvent. Kinetic rate measurements of the alkoxide-catalyzed addition of methanol and ethanol to methyl esters and nitriles of acrylic acid and methacrylic acid were carried out in mixed solvents of alcohol–DMF and alcohol–DMSO.

Results

The Order of Reaction in the Olefin.—The rates of the nucleophilic additions of methanol and ethanol to the activated olefins were followed dilatometrically. The rate measurements were carried out with the following systems, using the derived sodium alkoxide as basic catalyst: (a) solvent, DMF–methanol; olefins, acrylonitrile (AN), methacrylonitrile (MAN), methyl acrylate (MA), and methyl methacrylate (MMA); (b) solvent, DMF–ethanol; olefins, acrylonitrile and methacrylonitrile; (c) solvent, DMSO–methanol; olefins, methyl acrylate and methacrylonitrile. The reaction was first-order in olefin for all of these reaction systems, over the whole range of alcohol concentrations used. This was evident from the straight lines obtained on plotting log $(A_t - A_\infty)$ *vs.* t, where A_t and A_∞ were the readings of the dilatometer at time $t = t$ and $t = \infty$, respectively. Pseudo-first-order rate constants were calculated from the slopes of these lines. With all the kinetic measurements carried out dilatometrically, alcohol was in at least twofold excess of the olefin. As seen from the plots of the observed second-order rate constants k_1'/[base] *vs.* concentration of alcohol (Figure 1), these were relatively very high at the low alcohol concentrations; with a still lower alcohol/olefins ratio the reaction was too fast to be followed dilatometrically with sufficient accuracy, and anionic polymerizations could occur. Thus, a flow system[21] was used for the rate measurement of the methoxide-catalyzed cyanoethylation of methanol in DMF–CH_3OH mixed solvent using $[CH_3OH]/[AN] \leq 2$. The addition reaction was very fast and conversions were appreciable even in reaction periods of 0.2–0.5 sec. The cyanoethylation of methanol was faster than the anionic propagation, so that it was possible to quench the reaction mixture before any polymerization of acrylonitrile took place, even with $[CH_3OH]$/[acrylonitrile] <1. Unreacted acrylonitrile was then determined titrimetrically by the *n*-dodecyl mercaptan method.[22] The kinetic results of cyanoethylation of methanol under such conditions are summarized in Table I. The reaction was first order in acrylonitrile, as was evident from the plots of log $[AN]_0/[AN]_t$ *vs.* t, which were straight lines (Figure 2).

The Order of Reaction in Alcohol.—The pseudo-first-order rate constant k_1' could be defined by

$$k_1' = k[RO^-Na^+][ROH]^n$$

where k is the overall rate constant and n is the order of reaction in alcohol. Accordingly, plotting of log $(k_1'/[Ro^-Na^+])$ or of log k_1' *vs.* log [ROH] was used to derive the order of reaction in alcohol from the slopes of the straight lines, which were indeed obtained (Figure 3). This was done for all the above-mentioned nucleophilic additions over a wide range of alcohol concentrations (10–100%).

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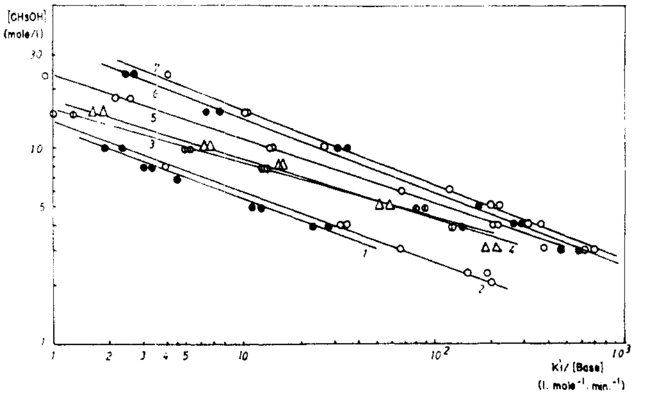

Figure 3.—Log–log plots of concentration of methanol *vs.* k_1'/[base]: (1) methacrylonitrile (1.5 mol/l.)–methanol–DMF, $n = -2.76$; (2) methacrylonitrile (0.5 mol/l.)–methanol–DMF, $n = -2.78$; (3) methacrylonitrile (0.5 mol/l.)–methanol–DMSO, $n = -3.60$; (4) methyl acrylate (0.5 mol/l.)–methanol–DMSO, $n = -3.65$; (5) acrylonitrile (0.71 mol/l.)–methanol–DMF, $n = -3.04$; (6) methyl acylate (0.5 mol/l.)–methanol–DMF, $n = -2.71$; (7) methyl methacrylate (0.5 mol/l.)–methanol–DMF, $n = -2.62$.

Table I

Addition of Methanol to Acrylonitrile in Methanol–DMF Mixed Solvent[a,b]

Run no.	[Acrylonitrile], mol/l.	$[CH_3OH]_0$, mol/l.	10^3 $[CH_3O^-Na^+]$, mol/l.	Reaction time, sec	Conversion, %	k_1'/[base], l. mol^{-1} sec^{-1}
28	0.901	1.281	13.04	0.244	19.0	
31	0.901	1.289		0.258	17.0	
34	0.897	1.295		0.248	18.6	40.49
33	0.899	1.295		0.355	22.3	
35	0.898	1.293		0.354	23.2	
30	0.919	1.260		0.517	27.6	
32	0.919	1.261		0.520	30.2	
55	0.922	1.904	32.70	0.222	15.6	
58	0.919	1.909		0.222	16.4	
56	0.929	1.887		0.268	20.4	
59	1.033	1.961		0.269	19.7	24.31
54	0.946	1.850		0.495	31.5	
57	0.940	1.864		0.491	30.6	
60	0.885	2.648	32.70	0.219	16.6	
61	0.886	2.644		0.220	17.2	
59	0.880	2.664		0.488	24.1	8.93
62	0.877	2.671		0.490	22.5	

[a] A flow system[21] was used for the rate measurements. Reaction temperature was 26 ± 0.2°. [b] A plot of log k_1'/[base] *vs.* log $[CH_3OH]_0$ gave a straight line with a slope of −2.1.

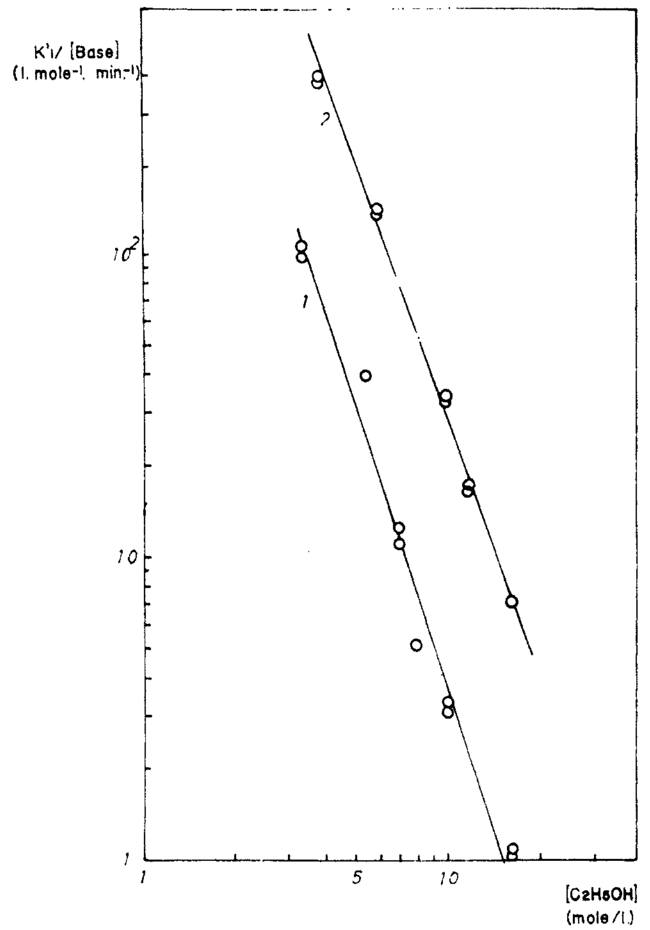

Figure 4.—Log–log plots of the observed second-order rate constants against concentration of ethanol: (1) addition of ethanol to methacrylonitrile in ethanol–DMF mixed solvent; (2) addition of ethanol to acrylonitrile in ethanol–DMF mixed solvent.

Table II

Rates of Nucleophilic Addition of Methanol to Activated Olefins in Methanol Solvent[a]

Olefin	Concn, mol/l.	$10^2[CH_3O^-Na^+]$, mol/l.	$10^2k_1'$, min^{-1}	k_2 av = k_1'/[base], l. mol^{-1} min^{-1}
Acrylonitrile	0.71	1.30	1.18, 1.15	0.90
Methyl acrylate	0.50	6.30	1.50, 1.62	0.25
Methyl methacrylate	0.50	75.30	0.305	0.041
Methacrylonitrile	1.50	21.62	0.15	0.070

[a] Experimental conditions: the rate of reaction was followed dilatometrically. Reaction temperature was 30 ± 0.1°.

The order of reaction in alcohol was negative with all of these reaction systems. It was independent of the type of olefin used and of its electrophilic reactivity. The relative electrophilic reactivity of the olefins acrylonitrile, methacrylonitrile, and methyl acrylate is presented quantitatively (Table II) by comparing the values of k_1' for the addition reaction of methanol to the olefin in pure methanol as solvent. The order of reaction in alcohol for these olefins (using olefin concentrations of 0.5 and 1.5 mol/l.) was in the range of about −2.5 to −3.0 in methanol–DMF mixtures (Table III, Figure 3).

Substitution of ethanol for methanol in the solvent mixture did not change the values of n (Table IV, Figure 4). However, the order of reaction in alcohol was dependent on the type of dipolar aprotic solvent used. Its absolute value in methanol–DMSO mixtures was higher (3.4–3.7; Table V) than in methanol–DMF mixtures. Such a dependence on the dipolar aprotic component and about the same values of n were previously found for the cyanoethylation of methanol in these solvent systems.[9]

It is important to emphasize in this connection that plots of log k'_1/[base] *vs.* log [ROH] gave straight lines over the whole range of alcohol concentrations used up to 100% alcohol (Figure 3).

In the case of the cyanoethylation of methanol carried out in the flow system, where methanol was in a relatively small excess of acrylonitrile, the value of n obtained was −2.1 (Table I). Since our kinetic experiments using the flow system were limited in number, it cannot be concluded that the absolute value of n changes downward in the presence of relatively very low concentrations of alcohol.

The Order of Reaction in the Sodium Alkoxide.—It has already been shown that the order of reaction in the alkoxide basic catalyst was one for the cyanoethylation

TABLE III
ADDITION OF METHANOL TO ACTIVATED OLEFINS IN METHANOL–DMF MIXED SOLVENTS

Olefin (mol/l.)	[CH_3OH], mol/l.	$10^3[CH_3O^-Na^+]$, mol/l.	$10^2k_1'$, min^{-1}	$k_2 = k_1'/[base]$, l. mol^{-1} min^{-1}	Order in methanol[a]
Acrylonitrile	2.00	0.43	47.70	1104.16	
(0.5)	3.00	0.43	16.70, 16.70	386.57	
	4.00	2.16	48.00, 46.30	222.22, 214.35	
	6.00	2.16	14.95, 15.10	69.29, 69.91	
	10.00	2.16	3.14, 3.08	14.54, 14.26	−3.04
	18.00	6.48	1.40, 1.69	2.16, 2.61	
	23.8	12.96	1.18, 1.15	0.91, 0.89	
Acrylonitrile	3.0	0.44	12.28	281.65	
(1.5)	4.0	1.09	20.60, 20.65	189.00, 189.40	
	5.0	1.24	12.01, 10.41	96.90, 83.95	
	6.0	2.06	14.15, 13.41	68.68, 65.10	−3.09
	8.0	2.06	4.88, 4.32	23.70, 20.97	
	15.0	4.36	1.50, 1.52	3.44, 3.49	
	22.5	17.44	2.13, 2.16	1.22, 1.24	
Methyl acrylate	2.0	1.06	15.34, 12.60	144.72, 118.68	
(0.5)	3.1	2.12	12.12, 9.66	57.17, 45.57	
	4.0	3.18	9.38, 8.57	29.50, 26.95	
	5.0	2.12	3.69, 3.71	17.41, 17.50	−2.71
	10.0	21.00	7.37, 6.67	3.51, 3.18	
	15.0	31.50	2.03, 2.40	0.64, 0.76	
	23.8	63.00	1.52, 1.62	0.24, 0.26	
Methyl acrylate	3.0		17.20, 17.20		
(1.5)	4.0	4.50	25.33, 23.72	56.29, 52.71	
	5.0	10.60	31.80, 31.62	30.00, 29.83	
	6.0	21.20	37.70	17.78	
	8.0	21.20	20.70, 22.30	9.76, 10.52	
	10.0	42.40	16.20, 16.60	3.82, 3.92	−2.95
	15.0	54.06	6.10, 5.81	1.13, 1.07	
	21.65	90.10	3.70, 5.31	0.41, 0.59	
Methyl methacrylate	2.0	43.72	8.85	2.02	
(0.5)	3.0	87.44	5.97, 5.37	0.68, 0.61	
	4.0	349.76	13.02, 11.56	0.37, 0.33	−2.62
	5.0	262.32	5.30, 5.97	0.20, 0.23	
	6.0	218.60	3.31, 2.68	0.15, 0.12	
	10.0	262.40	0.71	0.027	
	15.0	376.40	0.41, 0.40	0.011	
	23.75	753.00	0.31	0.004	
Methyl methacrylate	3.0	43.80	1.90, 2.12	0.43, 0.48	
(1.5)	5.0	131.20	1.63, 1.68	0.12, 0.13	
	8.0	146.30	0.64, 0.59	0.044, 0.040	−2.44
	10.0	146.40	0.40, 0.32	0.027, 0.022	
	15.0	226.00	0.26	0.012	
Methacrylonitrile	1.5	11.82	3.94, 2.63	3.33, 2.23	
(0.5)	2.0	26.10	5.23, 8.88	2.00, 3.40	
	2.25	11.82	2.28, 1.79	1.93, 1.51	−2.78
	3.0	11.82	0.79, 0.80	0.67	
	4.0	11.82	0.38, 0.42	0.32, 0.36	
	8.0	104.40	0.41	0.039	
	15.0	261.00	0.20, 0.27	0.008, 0.010	
Methacrylonitrile	3.0	20.60	3.68, 3.52	1.79, 1.71	
(1.5)	3.5	20.60	1.73, 1.69	0.84, 0.82	
	4.0	39.64	0.93, 0.91	0.23	−2.76
	5.0	52.20	0.65, 0.59	0.12, 0.11	
	7.0	72.80	0.33, 0.33	0.045	
	8.0	104.40	0.32, 0.35	0.031, 0.034	
	10.0	76.40	0.15, 0.18	0.020, 0.024	

[a] Calculated from the slopes of the straight lines in Figure 3.

of methanol in the mixture of DMF–CH_3OH and DMSO of various composition.[9] This was verified in the present work for methacrylonitrile and methyl acrylate in DMF–CH_3OH mixed solvents (Table VI).

Discussion

Any explanation of the experimental results and derivation of a rate equation for the presently investigated nucleophilic addition in mixed protic–aprotic solvents should be compatible with the observed rate equation

$$R = k\frac{[\text{olefin}][RO^-]_{\text{total}}}{[ROH]^n_{\text{total}}} \qquad (1)$$

and should also provide answers to some essential questions. (a) What is the reason for the rate increase with decreasing concentration of the alcoholic compo-

TABLE IV

ADDITION OF ETHANOL TO ACTIVATED OLEFINS IN ETHANOL–DMF MIXED SOLVENT

Olefin (mol/l.)	$[C_2H_5OH]$, mol/l.	$10^3[C_2H_5O^-Na^+]$, mol/l.	$10^2k_1'$, min^{-1}	$k_2 = k_1'/[\text{base}]$, l. mol^{-1} min^{-1}	Order in ethanol[a]
Acrylonitrile (0.71)	3.0	0.48	32.40, 32.40	675.00	
	3.96	0.95	37.90, 35.20	398.95, 370.53	
	6.0	0.95	13.32, 12.84	140.21, 135.16	
	10.0	1.90	6.38, 6.24	33.58, 32.84	−2.78
	12.0	2.86	4.79, 4.90	16.75, 17.13	
	16.3	4.29	3.03, 3.06	7.06, 7.13	
Methacrylonitrile (0.5)	3.4	42.00	4.05, 4.52	0.96, 1.08	
	5.46	63.00	2.48, 2.47	0.39	
	7.0	105.00	1.15, 1.29	0.11, 0.123	−3.16
	8.0	84.00	0.43	0.051	
	10.0	147.00	0.48, 0.45	0.033, 0.031	
	16.35	201.00	0.22, 0.21	0.011, 0.010	
Methacrylonitrile (1.5)	4.0	40.00	2.20, 2.20	0.55	
	5.0		1.25	0.31	
	5.87		0.60, 0.75	0.15, 0.19	−2.84
	8.0		0.49	0.12	
	10.0		0.17, 0.16	0.43, 0.040	

[a] Calculated from the slopes of the straight lines in Figure 4.

TABLE V

ADDITION OF METHANOL TO ACTIVATED OLEFINS IN METHANOL–DMSO MIXED SOLVENT

Olefin (mol/l.)	$[CH_3OH]$, mol/l.	$10^3[CH_3O^-Na^+]$, mol/l.	$10^2k_1'$, min^{-1}	$k_2 = k_1'/[\text{base}]$, l. mol^{-1} min^{-1}	Order in methanol[a]
Methyl acrylate (0.5)	3.0	9.55	18.00, 20.50	18.85, 21.47	
	5.0	19.10	11.95, 11.28	6.26, 5.91	
	8.0	25.65	3.97, 4.06	1.55, 1.58	−3.65
	10.0	38.10	2.45, 2.56	0.64, 0.67	
	15.0	51.30	0.96, 0.84	0.19, 0.16	
Methacrylonitrile (0.5)	4.0	38.20	5.52, 4.82	1.44, 1.26	
	5.0	57.30	4.71, 5.20	0.82, 0.91	
	8.0	76.40	1.04, 0.98	0.14, 0.13	−3.60
	10.0	95.50	0.48, 0.52	0.050, 0.053	
	15.0	152.80	0.20	0.013	
Acrylonitrile (0.508)	1.66–8.45	16.50			−3.40[b]

[a] Calculated from the slope of the corresponding straight line in Figure 3. [b] Result taken from previous work.[9] Basic catalyst $CH_3O^-K^+$, reaction temperature 25°.

TABLE VI

EFFECT OF BASE CONCENTRATION ON THE ADDITION OF METHANOL TO ACTIVATED OLEFINS IN METHANOL–DMF MIXED SOLVENT[a]

Olefin	$10^3[CH_3O^-Na^+]$, mol/l.	$10^2k_1'$, min^{-1}	Order in methoxide[b]
Methacrylonitrile	20.00	0.48, 0.49	
	40.00	1.25, 1.24	
	60.00	1.96, 2.18	1.18
	70.00	2.34	
Methyl acrylate	1.06	4.59, 4.54	
	2.12	7.35, 7.50	
	3.18	10.80, 13.45	0.84
	4.24	12.65, 12.10	
	4.55	25.33, 23.72	

[a] Concentration of olefin 1.5 mol/l., concentration of methanol 4 mol/l. [b] The order of reaction in the alkali alkoxide was calculated from the slopes of straight lines obtained on a log–log plotting of k_1' against concentration of sodium methoxide.

nent of the mixed solvent? (b) Why is this increase extremely high at low alcohol concentrations? (c) What is the reason for the different values of the order of reaction in alcohol obtained on using different aprotic solvents?

According to theory, a reaction in which an existing charge is dispersed should experience a rate decrease with increase in the dielectric constant of the solvent.[23] The observed rate increase with increasing concentrations of DMF (ϵ 37.6) and DMSO (ϵ 34) in the solvent mixtures with methanol (ϵ 34) cannot therefore be explained in terms of changes of dielectric constants as an important factor. In addition, the rate of reaction increases in the same manner on using aprotic solvents either of high or of low dielectric constant, such as dioxane and THF.[9]

The nucleophilic substitution of various halo nitrobenzenes[15] and benzyl chlorides[14] by methoxide anions in DMSO–CH_3OH mixtures was also associated with a large rate increase in methanol-poor mixtures. This was ascribed to a catalytic effect of the dipolar aprotic solvent DMSO. The kinetic results there were in accordance with the equation $\log (k_{\text{obsd}} - k_0) = r[\text{DMSO}] + \text{constant}$, where r is a measure of the sensitivity of a given system to DMSO catalysis and k_0 is the rate constant in pure methanol. In the present case, a catalytic effect of the dipolar aprotic solvent is rejected, since no straight lines were obtained on plotting $\log (k_{\text{obsd}} - k_0)$ *vs.* [DMF] for the addition reaction of methanol to acrylonitrile and to methyl acrylate.

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[23] C. K. Ingold, "Structure and Mechanism in Chemistry," Cornell University Press, Ithaca, N. Y., p 345.

It is well established that anions in dipolar aprotic solvents are poorly solvated and that rates of reactions involving these anions are very fast as compared to the same reactions in protic solvents.[2-8] It seems, however, that the accepted explanation for the rate enhancement of nucleophilic reactions in mixed protic–dipolar aprotic solvents, in terms of a complete desolvation of hydrogen-bonded anions at a certain concentration of the aprotic component resulting in increased reactivity of the anions,[2,20,24,25] does not hold in our case. Hydrogen bonding of anions might be regarded as an equilibrium system. With methoxide anions in methanol, for example, the following equilibrium system might be described.

$$\begin{aligned} &CH_3O^-\cdot xCH_3OH \overset{K_1}{\rightleftharpoons} CH_3O^-\cdot(x-1)CH_3OH + CH_3OH \\ &CH_3O^-\cdot(x-1)CH_3OH \overset{K_2}{\rightleftharpoons} CH_3O^-\cdot(x-2)CH_3OH + CH_3OH \qquad (2) \\ &CH_3O^-\cdot CH_3OH \overset{K_x}{\rightleftharpoons} CH_3O^- + CH_3OH \end{aligned}$$

Kinetic and spectroscopic studies also established that anions in mixed protic–dipolar aprotic solvents do not form specific 1:1 adducts with hydrogen donors.[26,27] As a result, one cannot exclude the possibility that free unsolvated anions, which are present in a very small equilibrium concentration, might be the active nucleophiles owing to their relatively very high nucleophilic reactivity as compared to hydrogen-bonded anions. Thus, the above-mentioned rate enhancement might be due to an increased concentration of unsolvated anions and not (only) to different nucleophilic species being active at different compositions of the mixed solvent. By using a simplified form of the equilibrium

$$CH_3O^-\cdot xCH_3OH \overset{K}{\rightleftharpoons} CH_3O^- + x\ CH_3OH \qquad (3)$$

the concentration of CH_3O^- is given by

$$[CH_3O^-] = \frac{K[CH_3O^-\cdot xCH_3OH]}{[CH_3OH]^x} \qquad (4)$$

The observed rate equation for nucleophilic additions of alcohols to acrylonitrile[28] and other olefins[29] catalyzed by the derived alkoxides was a second-order one.

$$R = k_{obsd}[\text{olefin}][RO^-]_{total} \qquad (5)$$

The derived rate equation, based on the assumption that the contribution of any solvated form of the alkoxides to the rate of addition might be neglected, was[28]

$$R = k_2[\text{olefin}][RO^-]_{free} \qquad (6)$$

Substitution of $[CH_3O^-]$ in eq 6 gives

$$R = k_2\cdot K[\text{olefin}]\cdot\frac{[CH_3O^-\cdot xCH_3OH]}{[CH_3OH]^x_{free}} \qquad (7)$$

It might be well assumed that most of the methoxide ions are solvated, which means that $[CH_3O^-\cdot xCH_3OH] \cong [CH_3O^-]_{total}$.

As the experimental conditions were such that $[RO^-]_{total} \ll [ROH]$, it follows that $[ROH]_{free} \cong [ROH]_{total}$. Equation 7 then becomes

$$R = \frac{k_2K}{[CH_3OH]^x_{total}}[\text{olefin}][RO^-]_{total} \qquad (8)$$

In pure alcohol the concentration of olefin was much smaller than the concentration of alcohol, so that the concentration of the latter might be regarded as constant. In this case, eq 6 and 8 therefore become identical with the experimental rate eq 5. Equation 8 is also identical with the experimentally found rate equation for the additions in mixed solvents, which was

$$R = k_{obsd}\frac{[\text{olefin}][RO^-]_{total}}{[ROH]^n_{total}} \qquad (1)$$

This rate equation accounts for the observed linear dependence of R on $1/[ROH]^n_{total}$. Such a dependence of R on [ROH] might be (with $|n| > 1$) the reason for the dramatic increase of the reaction rate at a certain range of alcohol concentration in the mixed solvent (Figure 1). If this were the only reason for the enhanced rates, the order of reaction in alcohol should be independent of the type of aprotic component. The results of the present (Tables III–V) and previous[9] work (VII) showed this order to be clearly dependent on the type of the aprotic component in the mixed solvent. More clearly, the absolute value of the order of reaction in alcohol increased with increasing hydrogen-bonding capability of the aprotic solvent. It is therefore obvious that, besides the dilution effect of the aprotic component on the rate enhancement, it has some other specific effect which should be considered. Dipolar aprotic solvents interact with protic solvents, forming associates through hydrogen bonding.[16-19] An equilibrium reaction similar to eq 2 might be described for this association (eq 9)

TABLE VII

Aprotic solvent	DMSO	DMF	Dioxane	BHF
Order[a] in alcohol[b]	−3.4 ± 0.2	−2.9 ± 0.2	−1.5 ± 0.1	−1.6 ± 0.2
Order in alcohol (Tables I–III)	−3.60 to 3.65[c]	−2.44 to −3.09[d]		

[a] Reference 9. [b] Olefin, acrylonitrile, and alcohol–methanol. [c] Olefins, methyl acrylate and methacrylonitrile (Table III). [d] Olefins, acrylonitrile, methacrylonitrile, methyl acrylate, and methyl methacrylate.

$$APS + m\ CH_3OH \overset{K'}{\rightleftharpoons} APS\cdot mCH_3OH \qquad (9)$$

where APS is aprotic solvent. From the ratio $K/K' = K''$, an expression for $[CH_3O^-]_{free}$ in the mixed protic–aprotic solvent is obtained (eq 10). Substitution

$$[CH_3O^-] = \frac{K''[CH_3O^-\cdot xCH_3OH][APS\cdot mCH_3OH]}{[CH_3OH]^{x+m}_{free}[APS]_{unassociated}} \qquad (10)$$

in eq 6 gives

$$R = \frac{K''k_2[\text{olefin}][RO^-]_{total}}{[ROH]^{x+m}_{free}}\cdot\frac{[APS\cdot mCH_3OH]}{[APS]_{unassociated}} \qquad (11)$$

where RO^- stands for methoxide anion.

The next step is to show the identity between this equation and the experimentally observed rate equation (1). The mathematical treatment of this problem is difficult, and for the present we must content ourselves with this stage (eq 11) and with the experimental results. Nevertheless, eq 11 might offer an explanation

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to the physical meaning of n; it indicates that the order of reaction in alcohol in mixed alcoholic–aprotic solvent is a sum of two entities. One of them, x, is constant, related only to the composition of the solvate $RO^- \cdot xROH$. The other, m, is variable arising from the composition of the adduct $APS \cdot mROH$, which in turn is dependent on the capability of the aprotic solvent to form hydrogen bonding with the alcohol. Various kinds of methoxide ions are present in the reaction mixture. It might therefore be argued that various nucleophilic species are contributing to the measured rate of reaction. However, the kinetic behavior of the investigated reaction system was the same over the whole range of alcohol concentrations used, from about 24 mol/l. (pure methanol) down to 2 mol/l. This was evident from the fact that plots of log $k_1'/[RO^-]$ *vs.* log [ROH] gave straight lines over this range of alcohol concentrations. It follows that mainly *one* nucleophile (whatever it is) contributes to the measured rate of reaction. In addition, it might be also concluded that the same nucleophile attacks the double bond in a rate-determining step, in mixed alcohol–dipolar aprotic solvents as well as in the alcohol itself used as solvent. We assume that this one nucleophile is the most reactive nucleophile present, namely, the unsolvated methoxide ion. However, no experimental evidence is presented to indicate that this and not any other (*one*) type of methoxide ion present is the active nucleophile. It might well be *one* of the less solvated methoxide ions, if, for example, the lifetime of the unsolvated methoxide ion is relatively very small. The enhanced rates of addition observed in mixtures poor in alcohol are due to increased concentration of this nucleophile.

Experimental Section

Materials.—Acrylonitrile was purified according to the method of Bamford and Jenkins.[30] It was treated with dilute acid (5%), dilute sodium carbonate (5%), and distilled water, and then dried over calcium chloride. The fraction boiling at 78° was used. Methacrylonitrile was treated with sodium hydroxide solution (1%) and distilled water and dried over calcium chloride. The fraction boiling at 88–89° was used. Methyl acrylate was dried over sodium sulfate and then fractionally distilled. A middle fraction was used. Methyl methacrylate was treated with sodium hydroxide solution (1%) and distilled water, dried over sodium sulfate, and then fractionally distilled. A middle fraction was used.

Methanol and ethanol were dried over magnesium according to Vogel.[31] All distillations were carried out under purified nitrogen.

Dimethylformamide (Fluka, AR) was subjected to azeotropic distillation with benzene (10% by volume) and fractionally distilled *in vacuo* under nitrogen.[32] The fraction boiling at 65–66° (30 mm) was used. Dimethyl sulfoxide was purified in the same manner.

The alcoholic sodium alkoxide solutions were prepared by dissolving the sodium in the alcohol under reflux.

All liquid materials, olefins, solvents, and alcoholic sodium alkoxide solutions were kept under dry, pure nitrogen in flasks fitted with self-sealing rubber caps. Aliquot portions were removed from these with syringes by applying positive nitrogen pressure.

Procedure for Kinetic Measurements.—Olefin, solvent, and alcohol were introduced into dried flasks under nitrogen fitted with self-sealing rubber caps by the use of syringes. The solution was thermostated to the required temperature. The alkoxide solution was then added in one portion with shaking of the flask, and the time was recorded. A portion of the homogeneous reaction mixture was then quickly removed to a dilatometer by the use of a hypodermic syringe. The dilatometer consisted of two vertical calibrated capillaries terminating in a bulb of 5–40-ml volume. Calculations were made by standard methods.[33] Product studies by vpc showed that the only product was that of the addition of the alcohol to the olefin. Yields at the end of the kinetic runs were determined by vpc using an inner reference. In general, yields of 40–90% were observed.

The capillary flow technique, as described in detail by Szwarc and coworker,[21] was used for the rate measurements of the relatively very fast cyanoethylations of methanol in methanol–DMF mixed solvent. The addition reaction was stopped by quenching the reaction mixture with a solution of hydrochloric acid in 2-propanol. Conversions of olefin were then determined titrimetrically by the n-dodecyl mercaptan method.[22]

Registry No.—Methanol, 67-56-1; ethanol, 64-17-5; acrylonitrile, 107-13-1; methyl acrylate, 96-33-3; methyl methacrylate, 80-62-6; methacrylonitrile, 126-98-7.

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