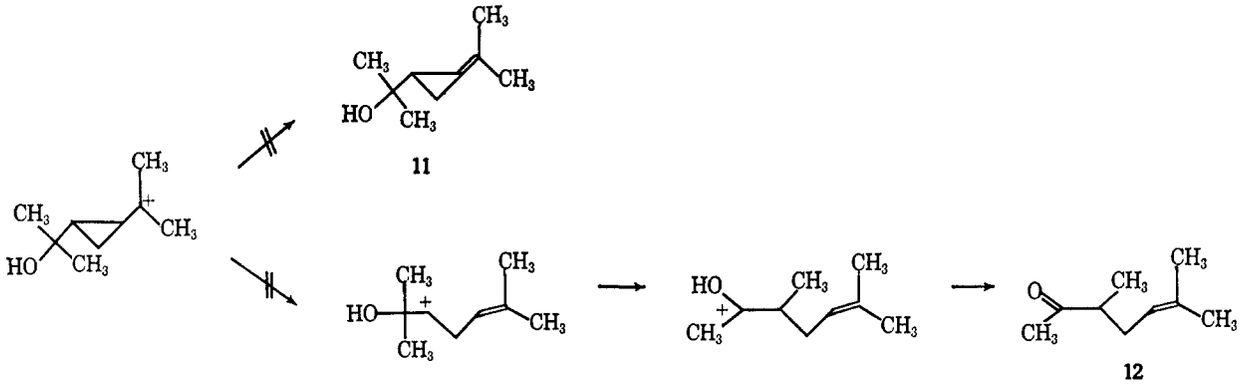
SCHEME II



The molar ratios of the catalyst to **1** or **2** were 1 and 0.1. The reaction was followed by vapor phase chromatographic analysis on a 2-m Silicon DC 550 column at 120°. Two of the results are shown in Figures 1 and 2.

Separation and Identification of the Products. A. Compound 4.—A solution of 10 g (0.063 mole) of **1** and 2.18 g (0.013 mole) of *p*-toluenesulfonic acid in 40 g of anhydrous dioxane was allowed to stand at room temperature for 7 days. After the reaction mixture was neutralized with sodium bicarbonate, it was distilled to give 1 g of **4** (11.4%): bp 61–62° at 39 mm; nmr data τ 8.77 (C_6 protons, singlet), 8.3 (C_1, singlet with small coupling), 7.85–8.42 (C_4 and C_5, multiplet), 5.63 (C_3, triplet), and 4.99 and 5.21 (C_2, doublet); infrared spectrum 1650, 900 (C=CH_2), 1370, 1390 [C(—CH_3)CH_3], and 1060–1080 (COH).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.89; H, 11.36.

B. Compound 5.—A solution of 6.32 g (0.04 mole) of **1** and 6.88 g (0.04 mole) of *p*-toluenesulfonic acid in 28 ml of dioxane was allowed to stand at room temperature for 5 hr. The reaction mixture was neutralized with sodium bicarbonate, dried, and distilled to yield 1.7 g of **5** (30%): bp 91° at 23 mm; nmr data τ 8.32 (C_1 protons, singlet), 8.4 (C_5, singlet), 7.82 (C_3, triplet), 6.46 (OH, singlet), 6.05 (C_4, triplet), 5.15 and 5.27 (C_6, doublet), and 4.9 (C_2, triplet); infrared spectrum 3360, 1020–1040 (COH), 1650, 890 (C=CH_2), and 830 (CH=C).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.97; H, 11.54.

C. Compound 9.—A solution of 5.6 g (0.04 mole) of **2**, 3.44 g (0.02 mole) of *p*-toluenesulfonic acid, and 0.72 g (0.04 mole) of water in 28 g of dioxane was allowed to stand at 20° for 30 min. After the reaction mixture was neutralized with sodium bicarbonate, **9** was separated by preparative vapor phase chromatograph (column, Apiezon L): nmr data τ 8.9 (C_1 protons, doublet), 8.25 (C_5, singlet), 7.2–7.8 (C_2, multiplet), 6.91 (C_3, doublet), and 4.65 (C_4, triplet). The 2,4-dinitrophenylhydrazone of **9** melted at 113–115°.

Anal. Calcd for $C_{15}H_{20}N_4O_4$: C, 56.24; H, 6.09. Found: C, 56.48; H, 5.96.

D. Compound 7 was synthesized by the method reported earlier[5] and identified by vapor phase chromatographic analysis.

Registry No.—**1**, 7731-99-9; methyl *trans*-2-(1-hydroxyisopropyl)cyclopropanecarboxylate, 7732-00-5; methyl *trans*-2-isopropenylcyclopropanecarboxylate, 7732-01-6; **2**, 7732-02-7; **4**, 7771-20-2; **5**, 7775-88-4; **9**, 5782-75-2; 2,4-dinitrophenylhydrazone of **9**, 7771-21-3.

Kinetics of the Addition of Alcohols to Activated Vinyl Compounds

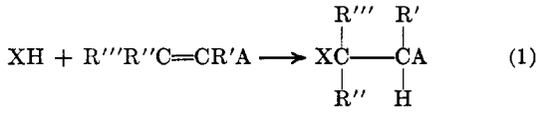
RICHARD N. RING, GIULIANA C. TESORO, AND DONALD R. MOORE

J. P. Stevens and Company, Inc., Central Research Laboratory, Garfield, New Jersey

Received July 1, 1966

The kinetics of the base-catalyzed addition of alcohols to 29 compounds containing activated carbon–carbon double bonds of the type R'''R''C=CR'A, where A is a strongly electron-attracting group, have been investigated. The effects of varying the activating group A and the groups R', R'', and R''' were explored. The rate-enhancing effect of the activating group was found to increase in the order CONHR < $CONH_2$ < $CONR_2$ < CO_2R < SO_2NR_2 < CN < SO_2R < COR ≤ $^+PR_3$, where R is the same lower alkyl group. A methyl group on either vinyl carbon lowers the rate compared with that of the unsubstituted activated vinyl compound, with α substitution producing the greater effect. Two β substituents produce a greater rate reduction than monosubstitution in either position.

The addition of nucleophiles to carbon–carbon double bonds activated by an adjacent electron-attracting group (A) is widely recognized and utilized in preparative organic chemistry. Kinetic studies of the Michael reaction and the activated vinyl reaction[1] have been reported, primarily for reaction with active hydrogen compounds other than alcohols.[2] Ogato, *et al.*,[2c] were the first to carry out a kinetic study of the base-catalyzed addition of an alcohol to an activated vinyl compound. These authors studied the kinetics of



(1)

(1) In accordance with present custom, the authors restrict the term Michael reaction to those additions involving carbon nucleophiles where a new carbon–carbon bond is formed, and prefer the term activated vinyl reaction (or addition) for noncarbon nucleophiles, *e.g.*, alcohols, amines, thiols.

(2) (a) W. J. Jones, *J. Chem. Soc.*, **105**, 1547 (1914); (b) M. J. Kamlet and D. J. Glover, *J. Am. Chem. Soc.*, **78**, 4556 (1956); (c) Y. Ogato, M. Okano, Y. Furuya, and I. Tabushi, *ibid.*, **78**, 5426 (1956); (d) R. Oda and T. Shono, *Nippon Kagaku Zasshi*, **78**, 1683 (1957); (e) V. G. Ostroverkhov, *Ukr. Khim. Zh.*, **23**, 474 (1957); *Chem. Abstr.*, **52**, 6196 (1958); (f) J. F. Bunnett and J. J. Randall, *J. Am. Chem. Soc.*, **80**, 6020 (1958); (g) U. Schmidt and H. Kubitzek, *Chem. Ber.*, **93**, 866 (1960); (h) J. Hine and L. A. Kaplan, *J. Am. Chem. Soc.*, **82**, 2915 (1960); (i) T. I. Crowell and A. W. Francis, Jr., *ibid.*, **83**, 591 (1961); (j) N. Ferry and F. J. McQuillin, *J. Chem. Soc.*, 103 (1962); (k) M. L. Bender and K. A. Connors, *J. Am. Chem. Soc.*, **84**, 1980 (1962); (l) T. O. Crowell, G. C. Helsley, R. E. Lutz, and W. L. Scott, *ibid.*, **85**, 443 (1963); (m) M. Friedman and J. S. Wall, *J. Org. Chem.*, **31**, 2888 (1966).

cyanoethylation for a group of compounds, including methanol, and found that the reaction was first order with respect to both acrylonitrile and methoxide anion. More recently, the kinetics and mechanism of the alkali metal alkoxide catalyzed nucleophilic addition of alcohols to acrylonitrile in alcoholic solvents have been studied extensively.[3] The rate of reaction was found to be independent of the alkali metal cation and to increase with increasing basic strength of the alkoxide anion.

Ferry and McQuillin[2i] have studied the alkoxide-catalyzed addition of methanol, ethanol, and 2-propanol to methyl vinyl ketone. They found that the rate of addition decreased in the order *i*-PrOH > EtOH > MeOH, and that the reaction was first order in the concentrations of both methyl vinyl ketone and the catalytic alkoxide ion.

Information on the relative reactivity of activated vinyl compounds is scant and, for the most part, only qualitative. Based on yield data, it has been reported that an unsaturated ketone is generally more reactive than the corresponding ester and the latter more reactive than the nitrile.[4] Substitution on the α- or β-carbon atoms of the activated vinyl system was observed to decrease the vinyl reactivity if the substituent was alkyl, aryl, carbethoxyl, or acyl.

A later report[5] states that the order of reactivity for addition to α,β-unsaturated compounds is ketones > nitriles > esters > sulfones. A comparison of these two sets of observations shows that they lead to conflicting conclusions regarding the relative reactivities of nitriles and esters.

The importance of compounds containing activated vinyl groups as reactants for the modification of cellulose aroused interest in our laboratory in establishing criteria for selecting chemical structures suitable for this purpose. Kinetic studies of the alkoxide-catalyzed addition of methanol and 2-propanol to 29 activated vinyl compounds were carried out to afford a measure of the relative electrophilicity of the active vinyl compounds toward alkoxide anions and to guide the selection of chemical structures suitable for cellulose modification.[6]

Experimental Section

Materials.—Laboratory preparations were carried out for the following activated vinyl compounds: tributylvinylphosphonium bromide,[7a] ethyl vinyl ketone,[7b] methyl propenyl ketone,[7c] N-methylacrylamide,[7d] 1-acryloylpiperidine,[7e] 1,3,5-triacryloylhexahydro-*s*-triazine,[7f] 2-methoxyethyl vinyl sulfone,[7g] vinyl sulfonamide,[7h] N,N-dimethyl and N,N-diethylvinyl sulfonamide,[7i] and fumaronitrile.[7j] 1,4-Diacryloylpiperazine[8] was prepared by the reaction of acryloyl chloride with piperazine in the presence of triethylamine. The other activated compounds were obtained from commercial sources. All the activated vinyl compounds used in this study were of purity greater than 95% as measured by the *n*-dodecyl mercaptan method[9] for vinyl analysis. Reagent methanol and 2-propanol and spectroscopic grade dimethylformamide were used as solvents. Sodium methoxide was used as a 25% solution in methanol, and potassium isopropoxide was freshly prepared using potassium metal. The concentration of stock catalyst solutions was determined by potentiometric titration with standard acid.

Kinetic Measurements.—The kinetic runs were carried out essentially by the procedure of Feit and Zilkha[3a] on 0.5 *N* alcoholic solutions of the activated vinyl compounds at 24°. Catalyst concentrations were determined by titration of an aliquot of the reaction mixture with standard acid and were 0.03 *N* sodium methoxide in methanol or 0.3 *N* potassium isopropoxide in 2-propanol unless otherwise stated. In all reactions, aliquots of the reaction mixture were titrated for residual vinyl content, using a modification of the *n*-dodecyl mercaptan method[9] in which analysis reaction time was varied as required for each vinyl compound. The time required for complete reaction with dodecyl mercaptan was established for each compound prior to the kinetic measurements. For all the activated vinyl compounds except ketones, the aliquots were conveniently quenched by addition to excess 1 *N* hydrochloric acid in 2-propanol; for ketones, it was found preferable to add the aliquots directly to alkaline *n*-dodecyl mercaptan in 2-propanol to avoid acid-catalyzed alcohol addition.

Competitive Reaction of Methanol and 2-Propanol with Activated Vinyl Compounds.—Sodium (0.003 g-atom) was dissolved in 100 ml of an equimolar mixture of methanol and 2-propanol and 0.05 mole of the active vinyl compound was then added. Samples were removed at intervals, neutralized with 1 *N* HCl in 2-propanol, and analyzed by gas–liquid partition chromatography. Samples were taken until no further reaction could be detected. The final product compositions observed for three activated vinyl compounds are listed in Table I.

TABLE I

Vinyl compd	Product compn, wt % Methyl ether	Isopropyl ether
CH_2=CHCN	98	2
CH_2=$CHCOCH_3$	78	22
CH_2=$CHSO_2C_2H_5$	98	2

Results and Discussion

In the addition of alcohols to activated vinyl compounds, two reactions (2 and 3) occur where A is a

$$RO^- + R'''R''C{=}CR'A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RO\overset{R'''}{\underset{R''}{C}}\!\!-\!\!\overset{\bar{}}{C}\overset{}{\underset{R'}{A}} \qquad (2)$$

$$RO\overset{R'''}{\underset{R''}{C}}\!\!-\!\!\overset{\bar{}}{C}\overset{}{\underset{R'}{A}} + ROH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} RO^- + RO\overset{R'''}{\underset{R''}{C}}\!\!-\!\!C\overset{R'}{\underset{H}{A}} \qquad (3)$$

strongly electron-attracting group. Reaction 2, the rate-determining step, is conveniently followed by measurement of the disappearance of the activated vinyl compound. Assuming the base concentration to remain constant throughout, the raw data can be used to calculate the values of the pseudo-first-order rate constants and, therefrom, the second-order rate constants (k) in the rate equation (4). Linear kinetic

$$\text{rate} = k[R'''R''C{=}CR'A][RO^-] \qquad (4)$$

plots were obtained for most reactions, confirming that the reactions are first order with respect to the activated

(3) (a) B. A. Feit and A. Zilkha, *J. Org. Chem.*, **28**, 406 (1963); (b) B. A. Feit, J. Sinnreich, and A. Zilkha, *ibid.*, **28**, 3245 (1963).

(4) R. Connor and W. R. McClellan, *ibid.*, **3**, 570 (1939).

(5) E. D. Bergman, D. Ginsburg, and R. Pappo, *Org. Reactions*, **10**, 179 (1959).

(6) G. C. Tesoro, *Am. Dyestuff Reptr.*, **32**, 1022 (1963).

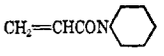
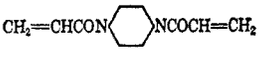
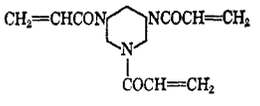
(7) (a) R. Rabinowitz, A. C. Henry, and R. Marcus, *J. Polymer Sci.*, **A3**, 2055 (1965); (b) R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler, and W. M. McLamore, *J. Am. Chem. Soc.*, **74**, 4223 (1952); (c) N. Jones and H. T. Taylor, *J. Chem. Soc.*, 1345 (1961); (d) P. F. Wiley, U. S. Patent 2,683,741 (July 13, 1954); (e) J. Parrod and J. Elles, *Compt. Rend.*, **243**, 1040 (1956); (f) W. D. Emmons, H. A. Rolewicz, W. N. Cannon, and R. M. Ross, *J. Am. Chem. Soc.*, **74**, 5524 (1952); (g) G. C. Tesoro and A. Oroszlan, *Textile Res. J.*, **33**, 93 (1963); (h) Badische Anilin and Soda Fabrik A. G., German Patent 1,168,891 (April 30, 1964); (i) K. A. Petrov and A. A. Neimysheva, *Zh. Obshch. Khim.*, **29**, 1494 (1959); *Chem. Abstr.*, **54**, 8621 (1960); (j) D. T. Mowry and J. M. Butler, *Org. Syn.*, **30**, 46 (1950).

(8) Details of this preparation will be described in a later publication.

(9) "The Chemistry of Acrylonitrile," 2nd ed, American Cyanamid Co., New York, N. Y., 1959, pp 61–63.

TABLE II

SECOND-ORDER RATE CONSTANTS (L. MOLE^{-1} MIN^{-1}) FOR REACTION OF ACTIVATED VINYL COMPOUNDS WITH ALCOHOLS AT 24°

		Reactant-solvent system[a]			
No.	Compd	M	M-D	I	I-D
1	$[(C_4H_9)_3{}^+PCH{=}CH_2]Br^-$	14.9			
2	$CH_3COCH{=}CH_2$	26.4[b]			
3	$CH_3CH_2COCH{=}CH_2$	14.1			
4	$CH_3COCH{=}CHCH_3$	3.23			
5	$CH_3COC(CH_3){=}CH_2$	0.482[c]		1.57[c]	
6	$CH_3COCH{=}C(CH_3)_2$			0	
7	$C_2H_5SO_2CH{=}CH_2$	2.46[d]	12.75		
		2.73[e]			
8	$CH_3OCH_2CH_2SO_2CH{=}CH_2$	2.35[d]			
9	$CH_2{=}CHSO_2CH{=}CH_2$ (1st vinyl)	11.38[d]			
		10.87[e]			
9	$CH_2{=}CHSO_2CH{=}CH_2$ (2nd vinyl)	2.90[d]			
		2.58[e]			
10	$CH_2{=}CHCN$	0.732		17.249[f]	
11	$CH_3CH{=}CHCN$			0.050	
12	$CH_2{=}C(CH_3)CN$			0.0115	
13	NCCH=CHCN (*trans*)	5.96[c,d]			
14	$CH_2{=}CHSO_2N(CH_3)_2$	0.235		*g*	
15	$CH_2{=}CHSO_2N(C_2H_5)_2$	0		2.67	
16	$CH_2{=}CHCO_2CH_3$	0.21[d]			
17	$CH_2{=}CHCONH_2$	0		0.019	0.0294
18	$CH_2{=}CHCONHCH_3$			0.0021	
19	$CH_2{=}CHCONHCH(CH_3)_2$			0.0021[c]	
20	$CH_2{=}CHCONHC(CH_3)_3$			0	
21	$CH_2{=}CHCONHC_6H_5$			0.00301[h]	0.00601
22	$CH_2{=}CHCONHC_{10}H_7$ (2-naphthyl)				0.00613
23	$(CH_2{=}CHCONH)_2CH_2$				0.0165
24	$CH_2{=}CHCON(CH_3)_2$			0.0700	
25	$CH_2{=}CHCON(C_2H_5)_2$			0.0351	
26				0.0301	
27				0.499	0.888
28		0.140[i]	0.815		>8.8
29	$CH_2{=}C(CH_3)CONH_2$			0	

[a] M = methanol–0.03 *N* sodium methoxide, M-D = 50% methanol in N,N-dimethylformamide–0.03 *N* sodium methoxide, I = 2-propanol–0.3 *N* potassium isopropoxide, I-D = 50% 2-propanol in N,N-dimethylformamide–0.3 *N* potassium isopropoxide. [b] Lit.[2i] values: 22.5 (18.6°) and 21.1, 24.2 (19°). [c] Constant for initial rate; rate decreases significantly with time. [d] Base consumed during reaction. [e] 0.004 *N* sodium methoxide used as catalyst. [f] Literature value[3a] obtained using 0.006667 *N* potassium isopropoxide. [g] Too fast to measure. [h] Constant for initial rate; rate increases significantly with time. [i] Compound dissolved hot and remained in solution when cooled. Much precipitated when catalyst was added, but it redissolved as reaction proceeded.

vinyl compounds. Those few casesw here deviation from linearity was observed are indicated, and here the initial slope of the plot was used to calculate the initial rate constant. For all the addition reactions studied, infrared spectra of the neutralized reaction mixtures confirmed that the expected products were obtained predominantly even for reactions producing curved rate plots. All data obtained are consistent with a general mechanism involving a slow, rate-determining addition of alkoxide anion to the activated vinyl compound (reaction 2), followed by a rapid abstraction of a proton from the solvent by the carbanion intermediate (reaction 3).

The rate constants obtained are shown in Table II. Solubility limitations and differences in reactivity of several orders of magnitude between compounds made it inconvenient to use a single reaction system (alcohol, solvent, catalyst) for all compounds investigated, and it was necessary to vary the conditions of the experiments in order to obtain a better comparison of results. 2-Propanol was used in place of methanol with vinyl compounds of lower reactivity, and N,N-dimethylformamide was used as a diluent when required by the low solubility of the vinyl compound. Analysis of the data obtained provides generalizations regarding effects of variations in the reaction medium and in the structure of the activated vinyl compound.

Variations in the Reaction Medium.—The effect of catalyst concentration was studied with compounds **7** and **9**, employing 0.004 *N* and 0.03 *N* sodium methoxide. The rate constants differ by no more than 10%, furnishing further evidence that the rate-determining reaction is first order with respect to alkoxide concentration, as previously reported for the addition of alcohols to acrylonitrile.[3a]

The observation reported for acrylonitrile[3a] that 2-propanol reacts more rapidly than methanol has been confirmed for other activated vinyl compounds investigated (**5**, **14**, **15**, **17**), but the magnitude of the effect varies over a considerable range. This order of

reactivity is expected, based on the apparent mechanism of the reaction and the relative nucleophilicity of the respective alkoxide anions. The results might lead one to expect that in competitive reaction of an activated vinyl compound with a mixture of methanol and 2-propanol, the reaction product with 2-propanol would predominate. This is not the case; such competitive reactions have been carried out with each of several activated vinyl compounds (acrylonitrile, methyl vinyl ketone, and ethyl vinyl sulfone), using equimolar mixtures of methanol and 2-propanol, and gave over 75% of the methoxy derivative in each case. In the competitive addition of two alcohols to activated vinyl compounds, the alkoxide equilibrium is indicated to be more important than the relative rates of independent addition. The product composition is controlled by the alkoxide equilibrium and favors the product derived by addition of the anion of the more acidic alcohol.

The addition of N,N-dimethylformamide (DMF) was required to dissolve some of the vinyl compounds. Rates were compared with and without the addition of this solvent for other selected compounds so that the effect of the addition of DMF could be independently determined. With both alcohols studied, a rate enhancement was observed. The enhancement in methanol was 5.2–5.8-fold (**7** and **28**) and, in 2-propanol, 1.6–2.0-fold (**17**, **21**, and **27**). These observations are in agreement with the work of Feit, *et al.*,[3b] on the effect of solvent composition on the kinetics of the cyanoethylation of methanol. They found that dilution of methanol with DMF or dioxane produced a rate enhancement which became greater as the proportion of methanol was decreased. This effect was attributed to the greater reactivity of less solvated alkoxide anions in aprotic solvent mixtures.

Variations in the Structure of the Activated Vinyl Compound.—The rate-enhancing effect of the activating group (A) has been found to increase in the order $CONHR < CONH_2 < CONR_2 < CO_2R < SO_2NR_2 < CN < SO_2R < COR \leq {}^+PR_3$. The most effective activating group imparts a rate constant approximately ten thousand times that of the least effective for the same vinyl structure. This order differs in part from the mutually contradictory orders of reactivity based on yield data which were discussed earlier.[4,5]

The substituent R in the activating groups listed above was found to have an appreciable effect on the rate constant. For a keto substituent (COR), changing R from ethyl to methyl almost doubles the rate. Alkyl substituents higher than ethyl in the activating group would be expected to exert no appreciable rate effect[10] except insofar as a steric effect is produced on the reaction site.

For amides, monosubstitution (CONHR) produced a rate-depressing effect of considerable magnitude (six- to ninefold) when R was methyl **18**, isopropyl **19**, phenyl **21**, or 2-naphthyl **22**. Some effect of steric contribution is indicated by the fact that no rate could be observed for the *t*-butyl derivative **20**. Unexpectedly, disubstitution ($CONR_2$) was found to have a rate-enhancing effect (**24**–**26**).

Alkyl substitution on the vinyl carbon atoms results in a considerable decrease in reactivity, with α substitution showing the greater effect. The proportion of unsubstituted/α substituted/β substituted for ketones was found to be 26.4:0.482:3.23 (**2**, **5**, **4**) and, for nitriles, 17.2:0.0115:0.050 (**10**, **12**, **11**). In the ketone series, the presence of a second β substituent (**6**) reduces the reactivity to the extent that the rate was no longer measurable. Interestingly, in the nitrile series, the presence of a second activating group on the β carbon has a marked rate-enhancing effect (**13**).

The presence of multiple activated vinyl groups in the molecule produces a rate enhancement with sulfones and amides. The results obtained for the sodium methoxide catalyzed reaction of divinyl sulfone (**9**) with methanol are noteworthy. At catalyst concentrations of both 0.004 *N* and 0.03 *N* a change in the slope of the rate plot occurs. If the initial and later slopes are extended, they intersect at the point of 55% reaction. This is believed to indicate that the initial slope is produced by the reaction of the first vinyl. As the concentration of the first vinyl is reduced, the reaction of the second vinyl becomes increasingly important until the final constant slope is due to the reaction of the second vinyl only. The rate constants indicated by these two slopes are those included in the table as first and second vinyl rate constants. The rate constant for the reaction of the first vinyl is approximately four times that of the second.

For cyclic amides with multiple functionality, a significant rate enhancement is noted. N,N′-Diacryloylpiperazine (**27**) shows 16 times the rate of N-acryloylpiperidine (**26**) with 2-propanol, while the reaction rate for the trifunctional compound, 1,3,5-triacryloylhexahydro-*s*-triazine (**28**), is at least ten times greater than that of N,N-diacryloylpiperazine in the mixed solvent system 50% 2-propanol–dimethylformamide. The fact that the nitrogen substituents are involved in a ring does not of itself produce a rate enhancement, since the rates for N,N-diethylacrylamide (**25**) and N-acryloylpiperidine are essentially equal.

Registry No.—**1**, 1883-19-8; **2**, 78-94-4; **3**, 1629-58-9; **4**, 625-33-2; **5**, 814-78-8; **7**, 1889-59-4; **8**, 7700-06-3; **9**, 77-77-0; **10**, 107-13-1; **11**, 627-26-9; **12**, 126-98-7; **13**, 764-42-1; **14**, 7700-07-4; **15**, 7700-08-5; **16**, 96-33-3; **17**, 79-06-1; **18**, 1187-59-3; **19**, 2210-25-5; **21**, 2210-24-4; **22**, 7700-09-6; **23**, 110-26-9; **24**, 2680-03-7; **25**, 2675-94-7; **26**, 10043-37-5; **27**, 6342-17-2; **28**, 959-52-4.

Acknowledgment.—Appreciation is expressed to Mr. Paul Shashaty for his technical assistance.

(10) (a) J. B. Conant and R. E. Hussey, *J. Am. Chem. Soc.*, **47**, 476 (1925); (b) P. G. Kletzke, *J. Org. Chem.*, **29**, 1363 (1964).