Relative Reactivities and Linear Free-Energy Relationships in Competitive Addition of Substituted Phenyl Radicals to Vinyl Monomers

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Relative rate constants have been determined for the addition of phenyl and substituted phenyl radicals to styrene, methyl methacrylate, methyl acrylate, and methacrylonitrile, all relative to acrylonitrile. These data have been correlated with σ^0 constants for substituents in the radical by an expression in which the slope ($\rho_M - \rho_{AN}$) corresponds to the difference in polar response. These and other findings are discussed in terms of theories regarding reactivity in radical addition reactions and, particularly, with respect to a general treatment of such data based on studies of polymer radicals.

Rate data for and current theories concerning intrinsic reactivities and polar effects in addition reactions of radicals to olefins are based almost exclusively on studies of polymerization.[1-3] Although easily obtained, such data normally include a variable and unknown steric parameter. In order to circumvent this problem there have been several fragmentary attempts to determine reactivities for types of radicals in which polar effects could be varied while the steric factor remained constant, *e.g.*, substituted benzoyloxy[4] and cumyloxy radicals.[5]

Our approach to this problem involved the use of substituted phenyl radicals in competitive Meerwein reactions.[6] Subsequent to this preliminary communication Schrauzer reported the preparation of a π complex of acrylonitrile and cuprous chloride and the suggestion that Meerwein adducts are formed by the reaction of such complexes with diazonium cations.[7] This type of mechanism has appeared intuitively attractive to many and, if operative, would complicate the interpretation of data from competitive Meerwein reactions. Therefore, a detailed examination of the products of several Meerwein reactions at various initial cupric chloride concentrations was made and has revealed that complexes of monomer with both cuprous and cupric chloride[8] are mechanistically unimportant.[9] Furthermore, there is a considerable body of evidence that implies that the free phenyl or substituted phenyl radical is the intermediate in Meerwein reactions and that it is this entity that adds to monomer.[9] The aryl radicals are generated by a redox reaction between diazonium cation and dichlorocuprate(I) anion which in turn is produced from acetone, one of the solvents, and cupric chloride as indicated in reactions A and B. If both monomer (M) and acrylonitrile (AN) are present, these compete for the aryl radical and yield the corresponding adducts in proportion to the rate constants for addition, k_M and k_{AN}, as shown in reactions C and D. Thus, at equal and large excess concentration of the two monomers, the relative rate constants, k_M/k_{AN}, for addition of phenyl and substituted phenyl radicals may be determined simply by measuring the molar ratio of the two adducts. Polymerization has not been observed previously at the concentration of cupric chloride used in this study and was not detected here. Competitive kinetics based on product analyses are valid only if addition of the aryl radical to both monomers is not reversible. This possibility was tested by subjecting methyl maleate to a Meerwein reaction with *p*-chlorobenzenediazonium chloride. Before reaction this sample of methyl maleate contained approximately 0.37% of methyl fumarate (glpc). After reaction, the content of methyl fumarate had decreased to about 0.31% (glpc). Since both methyl maleate and methyl fumarate are known to yield Meerwein adduct with this diazonium salt[8b] and the latter ester is the more stable isomer,[10] it is apparent that addition of the *p*-chlorophenyl radical to methyl maleate is essentially irreversible.

$$\mathrm{Cl^- + 2CuCl_2 + CH_3COCH_3 \longrightarrow 2CuCl_2^- + H^+ + ClCH_2COCH_3} \quad \text{(A)}$$

$$\mathrm{G{-}C_6H_4N_2^+ + CuCl_2^- \longrightarrow G{-}C_6H_4\cdot + N_2 + CuCl_2} \quad \text{(B)}$$

$$\mathrm{G{-}C_6H_4\cdot + CH_2{=}CHR \longrightarrow G{-}C_6H_4CH_2\dot{C}HR \xrightarrow{CuCl_n^{2-n}} G{-}C_6H_4CH_2CH(Cl)R} \quad \text{(C)}$$

$$\mathrm{G{-}C_6H_4\cdot + CH_2{=}CHCN \longrightarrow G{-}C_6H_4CH_2\dot{C}HCN \xrightarrow{CuCl_n^{2-n}} G{-}C_6H_4CH_2CH(Cl)CN} \quad \text{(D)}$$

The results of competitive Meerwein reactions between methacrylonitrile, methyl acrylate, methyl methacrylate, styrene, and acrylonitrile with a number of substituted phenyl radicals are listed in Table I. The amounts of the various adducts were determined by glpc using authentic samples to locate the compounds and to measure factors. In the earlier work a chemical method of analysis was employed. This involved a determination of total chlorine in both adducts and nitrile nitrogen as ammonia. Although these data were not used in quantitatively assaying substituent effects, they are recorded in Table I in parentheses because relative reactivities determined in this manner provide

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[1] C. Walling, "Free Radical in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, Chapter 4.

[2] J. C. Bevington, "Radical Polymerization," Academic Press, New York, N. Y., 1961, Chapter 4.

[3] A. D. Jenkins, "Advances in Radical Chemistry," G. H. Williams, Ed., Academic Press, New York, N. Y., 1967, Chapter 4.

[4] Reference 2, p 45.

[5] Reference 2, p 51.

[6] S. C. Dickerman, I. S. Megna, and M. M. Skoultchi, *J. Amer. Chem. Soc.*, **81,** 2270 (1959).

[7] G. N. Schrauzer, *Chem. Ber.*, **94,** 1891 (1961).

[8] (a) A mechanism involving complexes of cupric chloride and monomer has been suggested by O. Vogl and C. S. Rondestvedt, Jr., *J. Amer. Chem. Soc.*, **77,** 3067 (1955); (b) **78,** 3799 (1956).

[9] S. C. Dickerman, D. DeSouza, and N. Jacobson, *J. Org. Chem.*, **34,** 710 (1969). For discussion and additional references, consult this paper.

[10] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 344.

TABLE I

MONOMER–ACRYLONITRILE AND MONOMER–METHACRYLONITRILE REACTIVITY RATIOS FOR ADDITION OF PHENYL AND SUBSTITUTED PHENYL RADICALS[a,b]

G in G—C_6H_4	k_{MAN}/k_{AN}	k_{MA}/k_{AN}	k_{MMA}/k_{AN}	k_S/k_{AN}
p-NO_2			1.78 ± 0.02 (1.9)	2.91 ± 0.02
m-NO_2	1.77 ± 0.03	1.28 ± 0.01	1.98 ± 0.01 (2.0)	5.01 ± 0.12
m-Br			(1.6)	
m-Cl	1.40 ± 0.03	1.08 ± 0.02 (1.1)	(1.7)	2.21 ± 0.02 (1.8)
m-F			1.44 ± 0.01 (1.5)	
p-Br			(1.6)	
p-Cl		(0.97)	1.42 ± 0.01 (1.6)	1.79 ± 0.07 (1.5)
p-F		(0.84)	1.25 ± 0.01 (1.6)	(1.2)
m-OCH_3	1.06 ± 0.04	0.751 ± 0.012	1.09 ± 0.01 (0.99)	1.22 ± 0.06
H		0.719 ± 0.005 (0.79)	1.00 ± 0.01 (1.1)	1.04 ± 0.04 (0.86)
m-CH_3			0.985 ± 0.009	0.930 ± 0.024
p-CH_3		(0.81)	0.769 ± 0.004 (1.1)	0.789 ± 0.011 (0.78)
p-OCH_3			0.819 ± 0.017 (0.98)	0.666 ± 0.033
3,5-Cl_2		(1.3)	(2.2)	(2.8)
2,4-Cl_2		(1.1)	(2.0)	(3.1)
		k_{MA}/k_{MAN}	k_{MMA}/k_{MAN}	k_S/k_{MAN}
m-Cl		(0.74)	(1.2)	(1.3)
p-Cl		(0.68)	(1.2)	(1.2)
H		(0.69)	(0.93)	(0.74)

[a] Methacrylonitrile (MAN), acrylonitrile (AN), methyl acrylate (MA), methyl methacrylate (MMA), and styrene (S). [b] The reactivity ratios at 25–30° were determined by product analysis of competitive Meerwein reactions. The unparenthesized data were obtained by glpc and represent a total of six determinations on two reaction mixtures, except for one set of five and one of ten, with the indicated standard error in the average. The ratios enclosed in parentheses were obtained by a chemical method of analysis.

additional evidence for the operation of such an effect. An examination of the data reported in Table I reveals the existence of a rather small but, nevertheless, real substituent effect that is beyond experimental error.[11] In every instance the addition of an electron-withdrawing group to the phenyl radical leads to an increase in the reactivity of monomer relative to acrylonitrile. The converse effect is observed with electron-releasing groups.

The data may be quantitatively assayed for substituent effects by assuming a linear free-energy relationship for the individual monomers, eq 1 and 2. Subtraction of the second expression from the first and rearrangement of terms gives eq 3. Two pairs of monomers, styrene–acrylonitrile and methyl methacrylate–acrylonitrile, were investigated extensively and

$$\log (k_M)_G - \log (k_M)_H = \rho_M \sigma_G{}^0 \quad (1)$$

$$\log (k_{AN})_G - \log (k_{AN})_H = \rho_{AN} \sigma_G{}^0 \quad (2)$$

$$\log (k_M/k_{AN})_G = \sigma_G{}^0(\rho_M - \rho_{AN}) + \log (k_M/k_{AN})_H \quad (3)$$

plots of $\log (k_S/k_{AN})_G$ and $\log (k_{MMA}/k_{AN})_G$ against the various types of σ constants for *meta* and *para* substituents in the radical established correlation with σ^0 constants[12] as anticipated in eq 1–3.[13] These linear free-energy relationships are plotted in Figures 1 and 2.

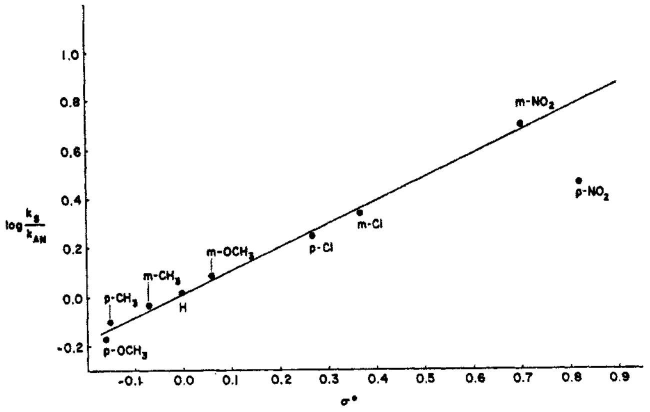

Figure 1.—Effect of substituents in the phenyl radical on the reactivity of styrene (S), relative to acrylonitrile (AN), in homolytic addition excluding the reactivity ratio for the *p*-nitrophenyl radical.

In both instances, but particularly noticeable for styrene–acrylonitrile, the relative reactivity for the *p*-nitrophenyl radical is below the line determined by

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[11] It is not surprising that the effect is small since phenyl and substituted phenyl radicals appear to be the most reactive and least selective radicals studied to date.

[12] R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1865 (1960).

[13] Correlation with σ^0 constants rather than another type of substituent constant is not unexpected in view of the fact that addition to monomer yields an insulated series of radicals.

TABLE II

PARAMETERS FOR VARIOUS LINEAR FREE-ENERGY RELATIONSHIPS

Monomers[a]	Points	Slope,[b] $\rho_M - \rho_{AN}$	Corr coeff, r	Intercept	
				Calcd[c]	Found[d]
S-AN	7[e]	0.95	0.996	0.0141	0.0182
S-AN	4[f]	0.94	0.998	0.0255	0.0182
MMA-AN	8[e]	0.46	0.983	0.0009	0.0000
MMA-AN	4[f]	0.40	0.999	0.0166	0.0000
MA-AN	3[f]	0.38	0.969	−0.1449	−0.1433
MAN-AN	3[f]	0.35	0.997	0.0089	.... [g]

[a] Styrene (S), acrylonitrile (AN), methyl methacrylate (MMA), methyl acrylate (MA), and methacrylonitrile (MAN). [b] Of regression line. [c] Calculated for regression line at $\sigma^0 = 0$. [d] Found for $\log (k_M/k_{AN})_H$. [e] Both *meta* and *para* substituents excluding *p*-nitro; see Table I. [f] *meta* substituents only; see Table I. [g] Adducts not separable.

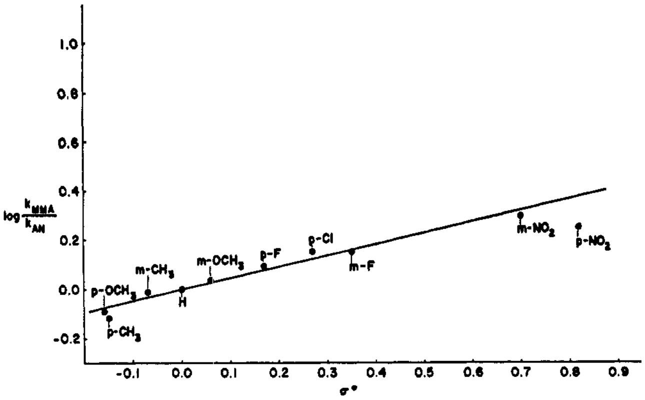

Figure 2.—Effect of substituents in the phenyl radical on the reactivity of methyl methacrylate (MMA), relative to acrylonitrile (AN), in homolytic addition excluding the reactivity ratio for the *p*-nitrophenyl radical.

the other substituents. Although nitro groups are notoriously misbehaved in radical reactions, there does not appear to be any generally accepted explanation.[14] Changes in mechanism including formation and addition of *p*-nitrophenylcopper and *p*-nitrophenyl anion were considered but rejected since neither is consistent with formation of Meerwein adduct. However, it is possible that we are observing a breakdown in kinetic control. Certainly, the *p*-nitrobenzenediazonium cation is reduced faster than any other diazonion ion that was studied and, consequently, these reaction mixtures must contain the highest concentration of radicals.[15]

Several reactivity ratios for methacrylonitrile–acrylonitrile and methyl acrylate–acrylonitrile were also determined and these data are correlated with σ^0 constants in Figures 3 and 4. The slopes or $\rho_M - \rho_{AN}$ values obtained from the regression lines and the corresponding correlation coefficients are summarized in Table II. Equation 3 contains the term $\log (k_M/k_{AN})_H$, which represents the reactivity ratio for the phenyl radical. Thus, this term may be evaluated by direct measurement and also from the intercept of the regression line at $\sigma^0 = 0$. A comparison of such data is given in Table II. Values of $\rho_M - \rho_{AN}$ for *meta*-substituted phenyl radicals stand in the following order: styrene > methyl methacrylate > methyl acrylate methacrylonitrile > acrylonitrile. This reactivity sequence has physical significance in that it represents the ultimate order of reactivity for the addition of electrophilic radicals. In this connection it is pertinent to observe that this sequence is exactly that expected for the addition of a cation.[16] Conversely, the opposite sequence, acrylonitrile > methacrylonitrile > methyl acrylate > methyl methacrylate > styrene represents the ultimate order of reactivity in addition of nucleophilic radicals and carbanions.[17] Another pertinent observation is the large number of different reactivity sequences that are revealed both within and outside the range of σ^0 constants, which were investigated. These are illustrated in Figure 5.

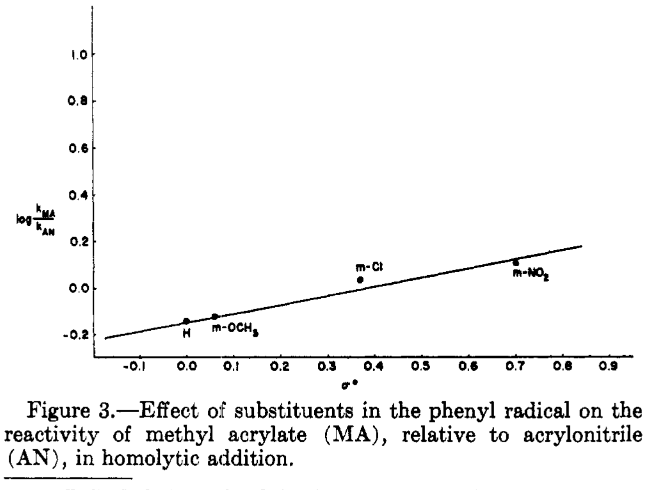

Figure 3.—Effect of substituents in the phenyl radical on the reactivity of methyl acrylate (MA), relative to acrylonitrile (AN), in homolytic addition.

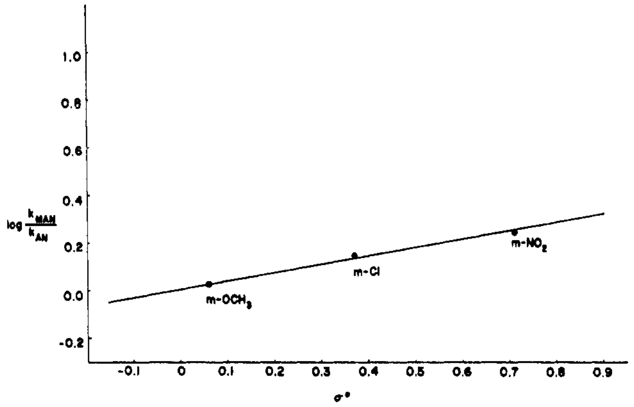

Figure 4.—Effect of substituents in the phenyl radical on the reactivity of methacrylonitrile (MAN), relative to acrylonitrile (AN), in homolytic addition.

The tendency for alternation in copolymerization has

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(14) R. W. Taft, Jr., and I. C. Lewis, *J. Amer. Chem. Soc.*, **81**, 5343 (1959).

(15) Presumably the phenyl radical is somewhat less selective than the *p*-nitrophenyl radical; however, the former is generated much more slowly.

(16) The reactivities of these monomers in cationic addition or cationic polymerization have not been established. For a recent review of cationic polymerization, see D. C. Pepper, "Friedel-Crafts and Related Reactions," Vol. II, G. A. Olah, Ed., Interscience Publishers, New York, N. Y., 1964. Chapter 30.

(17) At one time it was thought that studies of anionic copolymerization would provide at least qualitative orders of reactivity. However, this hope does not appear to have been realized.

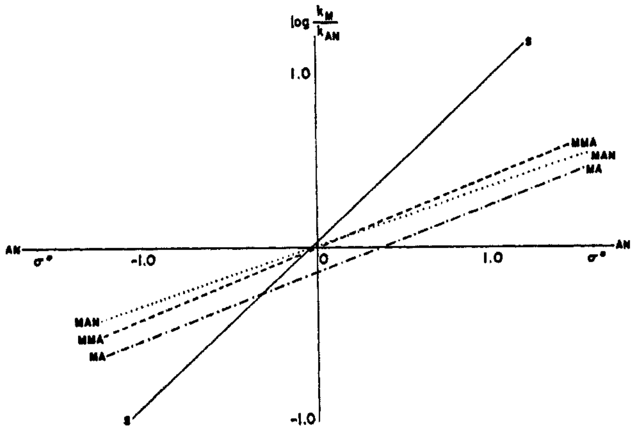

Figure 5.—Polar response of styrene (S), methyl methacrylate (MMA), methyl acrylate (MA), and methacrylonitrile (MAN), relative to that of acrylonitrile (AN), in addition of substituted phenyl radicals.

been interpreted in terms of the donor–acceptor character of the radical–monomer pairs.[18] The operation of such an effect in these systems leads to the conclusion that the *m*-methoxyphenyl and *m*-methylphenyl radicals, which correspond to the more stable cations, should exhibit enhanced preference for addition to acrylonitrile.[19] Since this is not observed it must be concluded that dipole–dipole interactions are responsible for the polar responses observed here. Thus, the large value of $\rho_S - \rho_{AN}$ is a relection of both a low or zero and a large postive charge at the terminal carbon atoms of the double bonds in styrene and acrylonitrile, respectively.[20] Actually, the dipole moments of styrene,[21a] methacrylonitrile,[21b] methyl methacrylate,[22a] methyl acrylate,[22b] and acrylonitrile[23] have been measured and conform to the following sequence: styrene < methyl methacrylate = methyl acrylate < methacrylonitrile < acrylonitrile. Although a rigorous comparison should involve only that component of the molecular dipole moment associated with the carbon–carbon double bond, the agreement with the order of $\rho_M - \rho_{AN}$ values is encouraging. Furthermore, a consideration of dipole moments provides an explanation for a peculiar feature of our findings. That is, the fact that the magnitude of $\rho_{MAN} - \rho_{AN}$ (0.35) must be due to solely methyl substitution; yet for the esters $\rho_{MMA} - \rho_{MA}$ is essentially zero. As indicated earlier identical dipole moments have been reported for methyl methacrylate and methyl acrylate. Both anomalies may be resolved by accepting the suggestion that the *s-cis* conformation, with respect to two double bonds, makes a significant contribution to the molecular dipole moment of methyl acrylate but not to methyl methyacrylate.[22] If the introduction of an α-methyl group into methyl acrylate leads to an increase in the population of the *s-trans* conformation, the over-all effect would be largely self-compensating with respect to dipole moment and, thus, to polar response in radical addition.

Copolymerization data for the several monomers investigated in this study have been treated in various ways.[1–3] The most direct comparison is with the treatment originally reported by Bamford, Jenkins, and Jonhston,[24a] and developed by Bamford and Jenkins.[24b] This approach leads to eq 4 in which the α and β terms represent polar response and intrinsic reactivities, respectively. Equations 4 and 3 are of exactly the same form; therefore, values of $\alpha_M - \alpha_{AN}$ and $\rho_M - \rho_{AN}$

$$\log (k_M/k_{AN})_G = \sigma_G(\alpha_M - \alpha_{AN}) + \beta_M - \beta_{AN} \qquad (4)$$

should be directly related. These quantities are listed in Table III and comparison reveals only one serious discrepancy, *i.e.*, the polar response of methyl acrylate. However, if the α value for methyl acrylate is calculated from a relationship suggested by these workers,[25] rather than from reactivity data, there is a one to one correspondence between the sequence of $\rho_M - \rho_{AN}$ values and that predicted from the differences in α values. A similar comparison of β terms with reactivity data for the phenyl radical is not possible since all of the monomers except methyl acrylate possess about the same reactivity toward this radical. Nevertheless, the linear free-energy relationships reported here strongly support the essential features of the "patterns of reactivity" approach to the reactivity of polymer radicals.

TABLE III

POLAR RESPONSE OF MONOMERS RELATIVE TO ACRYLONITRILE FOR ADDITION OF SUBSTITUTED PHENYL AND POLYMER RADICALS.

Monomer (M)	$\rho_M - \rho_{AN}$[a]	$\alpha_M - \alpha_{AN}$[b]
Acrylonitrile (AN)	0	0
Methacrylonitrile	0.35	0.50
Methyl acrylate	0.38	0
Methyl methacrylate	0.40	1.5
Styrene	0.95	3.0

[a] Substituted phenyl radicals: this research. [b] Polymer radicals: calculated from the data given in ref 3, p 185.

Experimental Section

Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Inc., Woodside, N. Y. 11377. Product analyses were accomplished on F & M Model 500, 810 and 5750 gas chromatographs. In one instance a Microtek Model 2500R instrument was used.

Reagents.—Acrylonitrile, methyl acrylate, methyl methaacrylate, and styrene were purchased from Matheson Coleman and Bell. Methacrylonitrile was obtained from A. D. MacKay Co. and from E. I. du Pont de Nemours and Co. Several of the monomers contained inhibitor that was removed by extraction with dilute sodium hydroxide saturated with sodium chloride. The monomers, which have been freed of inhibitor, were washed with water, dried (Na_2SO_4), distilled, and stored for short periods of time under nitrogen. The other monomers were redistilled before use. Methyl maleate (9240) and methyl fumarate (7545) were purchased from Eastman Organic Chemicals and were used as supplied. Other chemicals were generally of reagent grade.

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(18) C. Walling, E. R. Briggs, K. B. Wolfstirn, and F. R. Mayo, *J. Amer. Chem. Soc.*, **70,** 1537 (1948); ref 1, p 134.

(19) This follows from observations that *m*-methoxy and *m*-methyl groups abnormally accelerate the solvolysis of the corresponding benzenediazonium cations. An interesting suggestion for the mode of interaction has been offered by R. W. Taft, Jr., *ibid.* **83,** 3350 (1961).

(20) This type of explanation was first proposed by C. C. Price, *J. Polym. Sci.*, **1,** 83 (1946): also see ref 1, pp 132–134.

(21) (a) N. B. Hannay and C. P. Smyth, *J. Amer. Chem. Soc.*, **68,** 244 (1946); (b) **68,** 1357 (1946).

(22) (a) R. W. LeFevre and K. M. S. Sundaram, *J. Chem. Soc.*, 1880 (1963); (b) 3188 (1963).

(23) W. S. Wilcox, J. H. Goldstein, and J. W. Simmons, *J. Chem. Phys.*, **22,** 516 (1954).

(24) (a) C. H. Bamford, A. D. Jenkins, and R. Johnston, *Trans. Faraday Soc.*, **55,** 418 (1959). (b) C. H. Bamford, and A. D. Jenkins, *J. Polym. Sci.*, **53,** 149 (1961); *Trans. Faraday Soc.*, **59,** 530 (1963).

(25) Equation 16 in ref 3: $\alpha = -5.3\sigma$ where σ is the usual substituent constant for the ester group.

TABLE IV
NEW MEERWEIN ADDUCTS PREPARED DURING THIS INVESTIGATION

					Anal., %							
					C		H		Cl		N	
Compd	Substituent	Yield, %	Mp or bp(mm), °C	Molecular formula	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
	Group (G) in G—$C_6H_4CH_2CH(Cl)CN$											
1	*m*-Cl	45	122 (0.3)	$C_9H_7Cl_2N$	54.00	54.22	3.50	3.65	35.45	35.63	7.00	7.18
2	*m*-F	26	96 (1.8)	C_9H_7ClFN	58.70	58.48	3.80	3.76			7.61	7.94
3	*p*-F	28	109 (3.8)	C_9H_7ClFN	58.70	58.42	3.80	3.93	19.29	19.25	7.61	7.68
4	*m*-Br	15	112 (0.3)	$C_9H_7BrClN^a$	44.20	44.40	2.86	3.08	14.50	14.35	5.72	5.98
5	*m*-OCH_3	43	105 (0.3)	$C_{10}H_{10}ClNO$	61.23	61.25	5.10	5.11			7.15	7.04
6	*m*-CH_3	27	75 (0.3)	$C_{10}H_{10}ClN$	66.67	66.71	5.55	5.77	19.72	19.75	7.77	7.56
	Group (G) in G—$C_6H_4CH_2C(Cl)(CH_3)CN$											
7	*m*-Cl	19	92 (0.1)	$C_{10}H_9Cl_2N$	56.00	55.81	4.24	4.48	33.00	32.80	6.44	6.88
8	*m*-OCH_3	57	101 (0.5)	$C_{11}H_{12}ClNO$	63.20	63.14	5.74	5.82	17.00	17.07	6.70	6.81
	Group (G) in G—$C_6H_4CH_2CH(Cl)CO_2CH_3$											
9	H	24	80 (0.4)	$C_{10}H_{11}ClO_2$	60.50	61.36	5.56	5.95	17.80	17.30		
10	*m*-NO_2	56	83–84	$C_{10}H_{10}ClNO_4$	49.50	48.91	4.10	4.46	14.60	14.45	5.75	5.85
11	*m*-Cl	39	105 (0.8)	$C_{10}H_{10}Cl_2O_2$	51.60	51.63	4.30	4.59	30.40	30.64		
12	*m*-OCH_3	21	100 (0.4)	$C_{11}H_{13}ClO_3$	58.10	57.93	5.70	5.34	15.56	15.49		
	Group (G) in G—$C_6H_4CH_2C(Cl)(CH_3)CO_2CH_3$											
13	*m*-F	35	94 (1.6)	$C_{11}H_{12}ClFO_2$	57.14	56.83	5.22	5.12	15.37	15.11		
14	*p*-F	36	97 (1.7)	$C_{11}H_{12}ClFO_2$	57.14	56.98	5.22	5.19	15.37	15.04		
15	*m*-OCH_3	44	110 (0.8)	$C_{12}H_{15}ClO_3$	59.26	59.01	6.20	6.84	14.67	15.02		
16	*m*-CH_3	31	89 (0.7)	$C_{12}H_{15}ClO_2$	63.44	63.13	6.64	6.84	15.64	15.22		
	Ar in $ArCH_2CH(Cl)C_6H_5$											
17	*m*-$NO_2C_6H_4$	23	71–72^b	$C_{14}H_{12}ClNO_2$	64.50	64.15	4.62	4.52	13.68	13.41	5.35	5.28
18	2,4-$Cl_2C_6H_3$		62–63	$C_{14}H_{11}Cl_3$	58.87	58.90	3.88	3.86			37.25	37.10

[a] Calcd for C_9H_7BrClN: Br, 32.60. Found: 32.77. [b] Reported mp 64° by K. G. Tashchuk and A. V. Dombrovskii, *Zh. Organ. Khim.*, 1 (11), 1995 (1965); *Chem. Abstr.*, 64, 9617 (1966).

In several instances only practical grades were available and these were purified by recrystallization or distillation until the melting or boiling point agreed with literature values.

Meerwein Adducts.—The analytical method (glpc) required authentic samples of both known and new Meerwein adducts. These were prepared by the standard method recommended by Rondestvedt in a comprehensive review of the Meerwein reaction.[26] The physical constants of the known adducts were in good agreement with those reported by the numerous workers listed in this compilation.[25] The adduct from styrene and diatomized *p*-nitroaniline, *p'*-nitro-α-chlorobibenzyl, is not listed but has been reported.[27] That from methyl acrylate and *p*-chloroaniline is described in the accompanying paper.[9] The new adducts (**1**–**18**), which were prepared during this study, are listed in Table IV with physical constants and analytical data. Yields are also recorded in this table; however, no attempt was made to find optimum reaction conditions.

Competitive Meerwein Reactions.—A 1-l. erlenmeyer flask, fitted with a thermometer and a gas buret, was flushed with nitrogen. Acetone (160 ml), acrylonitrile (5.30 g, 0.100 mol), monomer (0.100 mol), and a solution of 0.85 g of cupric chloride dihydrate in 20 ml of water were added to the flask and maintained at laboratory temperatures under nitrogen for 30 min. To this solution was added 0.005 mol of diazonium chloride that had been prepared in the usual manner from 0.005 mol of the appropriate amine, 8 ml of 6 *F* hydrochloric acid, and 0.005 mol of sodium nitrite in 12 ml of distilled water. After addition of the solution of the diazonium salt, the homogeneous reaction mixtures were allowed to stand at ambient temperatures until the evolution of nitrogen ceased and a negative test was obtained with 2-naphthol. At this point the mixture was placed in a separatory funnel and 500 ml of water were added. The two-phase system that formed was extracted with three 50-ml portions of chloroform. The combined extracts were washed with water and in some instances with 1 *F* sodium hydroxide solution and then water. The water and dilute sodium hydroxide solutions used in washing were extracted with three 25-ml portions of chloroform and the combined extracts were dried (Na_2SO_4) and concentrated under reduced pressure and at a bath temperature not exceeding 45°, to a volume of about 5 ml for analysis by glpc.

Test of Reversibility of Addition in Meerwein Addition.—A solution of 28.8 g (0.200 mol) of methyl maleate and 8.50 g (0.050 mol) of cupric chloride dihydrate in 160 ml of acetone and 10 ml of water was treated with 30 ml of an aqueous solution of *p*-chlorobenzenediazonium chloride. The latter was prepared in the usual manner from 6.40 g (0.050 mol) of *p*-chloroaniline, 25 ml of 6 *N* hydrochloric acid, and a solution of 3.6 g of sodium nitrite in 5 ml of water. After about 2 hr, the reaction mixture was worked up as described above except that the chloroform extracts were not concentrated. Before reaction the sample of methyl maleate was found to contain 0.37%, by area, of a component having exactly the same retention time as an authentic sample of methyl fumarate. After reaction the amount of methyl fumarate in the recovered reactants has decreased to 0.31%, by area. These analyses were accomplished by glpc using a pair of $\frac{1}{8}$ in. by 6 ft columns packed with 10% XF 1150 on 80–100 mesh Chromosorb W. A column temperature of 100° was employed in conjunction with a flame-ionization detector.

Analytical Methods.—The procedure for analysis by glpc involved the use of authentic samples of the adducts to determine that column and those operating conditions that would affect a separation. Accurately weighed samples of the adducts, in about the proportions indicated by a preliminary examination of the experimental mixture, were dissolved in an appropriate solvent and injected to measure relative factors. Alternate injections of this solution and the experimental mixture of Meerwein adducts were then made and the molar ratio of adducts was calculated in the usual manner. This procedure was followed without exception for the systems methyl acrylate–acrylonitrile, methyl methacrylate–acrylonitrile, and methacrylonitrile–acrylonitrile. However, the styrene–acrylonitrile system presented problems. First, the Meerwein adducts from styrene are so susceptible to dehydrohalogenation that purification of liquid adducts is difficult. Therefore, the solid, *p'*-chloro-α-chlorobibenzyl,[28] was used as the standard for all Meerwein adducts derived from styrene except those from *p*- and *m*-nitrobenzenediazonium chlorides. Second, in contrast to the behavior of the adducts from the other monomers, those obtained from styrene invariably exhibited two peaks in the glp chromatograms. The larger of these areas had the longer retention time and was assigned to the corresponding *trans*-stilbene and the smaller to the *cis* isomer. These assignments were checked by comparing the retention times of authentic *cis*- and *trans*-stilbene with the retentions times of the peaks observed during analysis for α-chlorobibenzyl. An authentic sample of *trans*-*p*-chlorostilbene was used similarly. It is unlikely that these procedures introduced a significant error since the substituents had little effect on retention times and on the relative amounts of the *cis*- and *trans*-stilbenes produced by thermal dehydrohalogenation during analysis. The columns and operating conditions used in any particular analysis may be obtained by writing the senior author.

The monomer reactivity ratios reported in parentheses in Table I were calculated by eq 5. This differential method of

$$k_M/k_{AN} = \frac{(\text{equiv Cl/g}) - (\text{equiv NH}_3\text{/g})}{\text{equiv NH}_3\text{/g}} \quad (5)$$

analysis is based on a determination of aliphatic chlorine by reaction with sodium methoxide followed by titration of the liberated chloride ion and nitrile nitrogen as ammonia by hydrolysis,[29] distillation, and titration. Both adducts provide chloride ion but only that from acrylonitrile or methacrylonitrile furnished the ammonia. The samples from competitive Meerwein reactions were prepared for analysis as described above. Although this method gave good results with mixtures of authentic samples of Meerwein adducts, it was less satisfactory when applied to the competitive reactions as indicated by a comparison of the data in Table I.

Registry No.—*p*-Nitrophenyl radical, 2395-99-5; *m*-nitrophenyl radical, 3522-58-5; *p*-bromophenyl radical, 2973-44-6; *m*-chlorophenyl radical, 3474-40-6; *p*-fluorophenyl radical, 2973-47-9; *p*-bromophenyl radical, 2973-43-5; *p*-chlorophenyl radical, 2396-00-1 *p*-fluorophenyl radical, 2973-46-8; *m*-methoxyphenyl radical, 18815-11-7; phenyl radical, 2396-01-2; *m*-methylphenyl radical, 3474-41-7; *p*-methylphenyl radical, 2396-02-3; *p*-methoxyphenyl radical, 2396-03-4; 3,5-dichlorophenyl radical, 18815-15-1; 2,4-dichlorophenyl radical, 18827-98-0; acrylonitrile, 107-13-1; methyl acrylate, 96-33-3; methyl methacrylate, 80-62-6; styrene, 100-42-5; methacrylonitrile, 126-98-7; **1**, 18826-39-6; **2**, 18826-40-9; **3**, 18826-41-0; **4**, 18826-42-1; **5**, 18826-43-2; **6**, 17849-34-2; **7**, 18826-45-4; **8**, 18826-46-5; **9**, 18841-64-0; **10**, 18826-47-6; **11**, 14437-13-9; **12**, 18826-48-7; **13**, 18826-49-8; **14**, 18826-50-1; **15**, 18826-51-2; **16**, 18826-52-3; **17**, 4714-20-9; **18**, 18826-54-5.

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