Application of the Hammett Equation to Nonaromatic Unsaturated Systems. IX. Electrophilic Addition to Olefins. X. Nucleophilic Addition to Olefins

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Data for fifteen sets of rates of electrophilic addition to substituted ethylenes were correlated with the extended Hammett equation. Significant correlations were obtained for the majority of the sets studied. The results show that, while in the majority of the sets the localized effect is predominant, in a minority of the sets the delocalized effect is predominant. The results are accounted for in terms of the reaction mechanism. Sets for which the localized effect is predominant are believed to react *via* a bridged intermediate, whereas sets for which the delocalized effect predominates are thought to react *via* a carbonium ion intermediate. Data on the orientation observed in the addition of BH_3 to substituted ethylenes were also studied. The orientation is governed largely by the delocalized effect. Data for eight sets of rates of nucleophilic addition to substituted ethylenes were correlated with the extended Hammett equation using σ_R constants, with the extended equation using σ_R^- constants, and with the equation $Q_X = \beta\,\sigma_{R,X} + h$. Best results were obtained with the equation above. Of the eight sets examined, six gave significant correlation. The large values of β observed are in accord with rate-determining formation of a carbanion intermediate. The transition state is closer to the carbanion than it is to the reactants. Although values of β obtained from correlation with the equation are temperature dependent, they are not a linear function of $1/T$.

In a previous paper of this series,[1] the effect of substituents on diene and dienophile reactivity in the Diels–Alder reaction was studied. It seemed of interest to extend our investigation to the effect of substituents upon electrophilic addition to the double bond. The first attempt to correlate rates of electrophilic addition to the double bond with a linear free-energy relationship was reported by de la Mare[2] who used the σ_p^+ constants and the simple Hammett equation to correlate rates of addition of chlorine to 3,3-disubstituted acrylic acids. The Taft modification of the Hammett equation has been used by Dubois and coworkers to correlate the rates of bromination of substituted ethylenes.[3-6] The use of eq 1, in which the E_S

$$Q_X = \rho^*\Sigma\sigma^*_X + \delta\Sigma^*E_{S,X} + h \qquad (1)$$

values are the Taft steric parameter, has been reported by Dubois and Bienvenue-Goetz.[6] A correlation of values of $\Delta\Delta G^{\ddagger}_{\psi}$ with $\sigma_R{}^\circ$ constants was reported by Dubois and coworkers[7] for bromination of substituted ethylenes. The $\Delta\Delta G^{\ddagger}_{\psi}$ were obtained from eq 2, where

$$\Delta\Delta G^{\ddagger} = \Delta\Delta G^{\ddagger}_{po} + \Delta\Delta G^{\ddagger}_{\psi} \qquad (2)$$

$\Delta\Delta G^{\ddagger}_{po}$ is the polar contribution and $\Delta\Delta G^{\ddagger}_{\psi}$ is the resonance contribution to the free energy. The $\Delta\Delta G^{\ddagger}_{po}$ is calculated from the correlation of log k for the olefins bearing substituents which do not conjugate with the double bond.

No systematic examination of electrophilic additions by means of the extended Hammett equation[8] (eq 3) is

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h \text{ (Hammett equation)} \qquad (3)$$

extant in the literature. Rate data taken from the literature for the addition of chlorine, bromine, hydronium ion, trifluoroacetic acid, and mercuric ion were correlated with eq 3. Data used are presented Table I. The sources of most of the substituent constants used are reported in previous papers of this series;[1,9] substituent constants from other sources are set forth in Table II. In several of the sets studied, the compounds are multiply substituted. Correlations in these sets were made with eq 4 which neglects interaction terms.[10]

$$Q_X = \alpha\Sigma\sigma_{I,X} + \beta\Sigma\sigma_{R,X} + h \qquad (4)$$

The effect of substituents on orientation in the addition of BH_3 to the double bond was also studied. In the reaction of BH_3 with a substituted ethylene, the boron may bond to either carbon 1 or carbon 2. The overall rate constants for the reaction is given by

$$k_T = k_1 + k_2 \qquad (5)$$

where

$$k_1 = p_1k_T;\ k_2 = p_2k_T \qquad (6)$$

The quantities p_1 and p_2 denote the per cent of the product with boron bonded to carbon and carbon 2, respectively. Now, applying the extended Hammett equation (eq 4) to the partial rate constants k_1 and k_2 for the reaction of a substituted ethylene gives eq 7 and 8.

$$\log k_{1,X} = \log p_{1,X}k_T = \alpha_1\sigma_{I,X} + \beta_1\sigma_{R,X} + h_1 \qquad (7)$$

$$\log k_{2,X} = \log p_{2,X}k_T = \alpha_2\sigma_{I,X} + \beta_2\sigma_{R,X} + h_2 \qquad (8)$$

Subtraction of eq 8 from eq 7 gives

$$\log\left(\frac{k_{1,X}}{k_{2,X}}\right) = \log\left(\frac{p_{1,X}}{p_{2,X}}\right) = (\alpha_1 - \alpha_2)\sigma_{I,X} + (\beta_1 - \beta_2)\sigma_{R,X} + k_1 - k_2 \qquad (9)$$

or

$$\log\left(\frac{p_{1,X}}{p_{2,X}}\right) = \alpha'\sigma_{I,X} + \beta'\sigma_{R,X} + h' \qquad (10)$$

equivalent to eq 4. The data on orientation in the addition of BH_3 to substituted ethylenes are presented in Table I.

We have also examined nucleophilic addition reactions of substituted olefins. The first attempt to apply a linear free-energy relationship to the reactivity of sub-

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(1) M. Charton, *J. Org. Chem.*, **31**, 3745 (1966).

(2) P. B. D. de la Mare, *J. Chem. Soc.*, 3823 (1960).

(3) J. E. Dubois and G. Mouvier, *Tetrahedron Lett.*, 1325 (1963).

(4) J. E. Dubois and E. Bienvenue-Goetz, *J. Chim. Phys.*, 780 (1966).

(5) J. E. Dubois and G. Mouvier, *Bull. Soc. Chim. Fr.*, 1441 (1968).

(6) J. E. Dubois and E. Bienvenue-Goetz, *Bull. Soc. Chim. Fr.*, 2094 (1968).

(7) J. E. Dubois, P. Alcais, G. Barbier, and E. Bienvenue-Goetz, *Bull. Soc. Chim. Fr.*, 2113 (1966).

(8) R. W. Taft and I. C. Lewis, *J. Amer. Chem. Soc.*, **80**, 2436 (1958).

(9) M. Charton, *J. Org. Chem.*, **30**, 522, 557, 974 (1965).

(10) S. I. Miller, *J. Amer. Chem. Soc.*, **81**, 161 (1959).

TABLE I

DATA USED IN THE CORRELATIONS

1. Substituted Ethylenes + Chlorine in Acetic Acid at 24° [a] (k_{rel})

$CHCl_2$, 0.60; Br, 0.28; SO_3H, 0.11; CO_2Et, 0.056; CO_2H, 0.018; CCl_3, 0.006; SO_2Me, 0.001; CN, 0.0001

2. Substituted Ethylenes + Chlorine in Aqueous Acetic Acid[b] (k_{rel})

Me, 2.0; H, 1.0; CH_2F, 3.4×10^{-2}; CH_2Cl, 1.9×10^{-2}; CH_2Br, 1.3×10^{-2}; CH_2CN, 2.7×10^{-3}; $CHCl_2$, 2.6×10^{-5}; Br, 1.3×10^{-5}; CCl_3, 2.9×10^{-7}

3. Trans-2′-Substituted Styrenes + Chlorine in Acetic Acid at 24° [a] (k_{rel})

Bz, 61.0; Br, 30.0; 3-$O_2NC_6H_4$, 15.0; CO_2Me, 10.0; CO_2H, 4.9; CHO, 1.8; CN, 0.022; NO_2, 0.020.

4. Substituted Ethylenes + Bromine in Aqueous Perchloric Acid at 25° [c] (k)

CO_2Et, 1.06×10^{-1}; CH_2CN, 440.0; H, 3.9×10^5; CH_2OH, 6.7×10^5; Me, 4.5×10^6; $CH_2NMe_3{}^+Br^-$, 2.8×10^{-1}

5. Substituted Ethylenes with Br_3^- in Aqueous Perchloric Acid at 25° [c] (k)

CO_2Et, 6.7×10^{-2}; $CH_2NMe_3{}^+Br^-$, 9.1×10^{-2}; CH_2CN, 100.0; H, 2.0×10^4; CH_2OH, 6.9×10^4; Me, 3.2×10^5

6. Trans-1,2-Disubstituted Ethylenes + Bromine in Aqueous Perchloric Acid at 25° [c] (k)

CO_2Et, CO_2Et, 3.4×10^{-5}; CO_2Et, Me, 2.76; Cl, CH_2OH, 3.08; Ph, $CH_2NMe_3{}^+Br^-$, 37.0; CO_2Et, Ph, 220.0

7. Trans-1,2-Disubstituted Ethylenes + Br_3^- in Aqueous Perchloric Acid at 25° [c] (k)

CO_2Et, CO_2Et, 3.7×10^{-4}; CO_2Et, Me, 1.04; Cl, CH_2OH, 0.31; Ph, $CH_2NMe_3{}^+Br^-$, 4.8; CO_2Et, Ph, 2.3

8. Substituted Ethylenes + Bromine in Acetic Acid at 24° [a] (k)

Ph, 11,000; Bu, 2000; H, 84.0; CH_2OAc, 10.0; CH_2OBz, 14.0; CH_2Cl, 1.6; CH_2Br, 1.0; CH_2CN, 0.23; Br, 0.0011; CO_2Et, 0.004

9. Trans-2′-Substituted Styrenes + Bromine in Acetic Acid at 24° [a] (k)

CH_2Cl, 77.0; Ph, 18.0; Br, 0.11; CO_2H, 0.019; H, 11,000

10. Substituted Ethylenes + Bromine in MeOH 0.2 M in NaBr at 25° [d] (log k)

H, 1.481; Et, 3.462; Pr, 3.320; Bu, 3.299; *sec*-Bu, 2.966; CH_2-*t*-Bu, 2.539; OEt, 8.54; OAc, 3.36

11. Substituted Ethylenes + Bromine in Acetic Acid + HBr at 24° [a] (k_{rel})

CH_2OBz, 9.0; CH_2Cl, 3.8; CH_2Br, 2.2; Br, 0.012; CO_2H, 0.44

12. Trans-2′-Substituted Styrenes + Br_2 in Acetic Acid + HBr at 24° [a] (k_{rel})

CH_2Cl, 16.0; Ph, 8.0; Br, 0.07; CN, 4.0; NO_2, 1.0

13. 2-Substituted Propenes + H_3O^+ in 29.6% Aqueous Perchloric Acid at 38° [e] (k_{rel})

H, 1.0; CH_2Cl, 1.0; CH_2OMe, 30.0; Ph, 5000; Me, 8000; Et, 10,000; *t*-Bu, 8000

14. 2-Substituted Propenes + Trifluoroacetic Acid in Trifluoroacetic Acid at 25° [f] (k)

H, 4.81; F, 340.0; Cl, 1.70; Br, 0.395

15. Substituted Ethylenes + Mercuric Perchlorate in Water at 25° [g] (k)

H, 5100; Me, 100,000; Et, 80,000; CH_2OH, 1120; CH_2CH_2OH, 8400; $MeCHOHCH_2$, 6100; CH_2Cl, 11.0; CH_2CN, 4.3

16. Orientation in the Reaction $XCH{=}CH_2 + B_2H_6$ in THF at 0° [h] ($\log p_1/p_2$)

Et, 1.195; Ph, 0.6021; $PhCH_2$, 0.9542; $ClCH_2$, 0.1761; Me_3Si, 0.3076; CF_3, −0.4543; $ClCH_2CH_2$, 0.6585; EtO_2CCH_2, 0.6886

21. Rates of Addition of Diglycine Anion to Substituted Ethylenes in H_2O, $\mu = 1.2$; pH = 8.75 at 30° (10^4k_2, $M^{-1}\,sec^{-1}$)[i]

CO_2NH_2, 2.00; CO_2Me, 46.0; CN, 13.7; SO_2Me, 90.0

22. Rates of Addition of Glycine Anion to Substituted Ethylenes in H_2O, $\mu = 1.2$; pH = 8.75; 30° ($10^4k_2\,M^{-1}\,sec^{-1}$)[i]

$CONH_2$, 6.30; $PO(OCH_2CH_2Cl)_2$, 20.9; CO_2Me, 182.0; CN, 50.0; SO_2Me, 306.0; Ac, 4000.0

23. Rates of Addition of ε-Aminocaproic Acid Anion to Substituted Ethylenes in H_2O, $\mu = 1.2$; pH = 8.75, 30° ($10^{-4}k_2\,M^{-1}\,sec^{-1}$)[i]

$CONH_2$, 16.9; CO_2Me, 528.0; CN, 203.0; SO_2Me, 1120.0

24. Rates of Addition of DL-α-Alanine Anion to Substituted Ethylenes in H_2O, $\mu = 1.2$; pH = 8.75; 30° ($10^4k_2\,M^{-1}\,sec^{-1}$)[i]

$CONH_2$, 3.50; $PO(OCH_2CH_2Cl)_2$, 10.7; CO_2Me, 111; CN, 35.3; Ac, 2280

25. Rates of Addition of Methoxide to Substituted Ethylenes in MeOH at 24° (k_2 l. $mol^{-1}\,min^{-1}$)[j]

Ac, 26.4; $EtSO_2$, 2.46; CN, 0.732; CO_2Me, 0.21; EtCO, 14.1

26. Rates of Addition of Morpholine to Substituted Ethylenes in MeOH at 0° ($10^4k_2\,M^{-1}\,sec^{-1}$)[k]

$PO(OEt)_2$, 0.233; $CONH_2$, 0.561; CN, 14.4; CO_2Me, 32.8; Ts, 187.0; Ac, 3770.0; CHO, 6490.0; Bz, 20,800

27. Rates of Addition of Morpholine to Substituted Ethylenes in Methanol at 30° ($10^4k_2\,M^{-1}\,sec^{-1}$)[k]

$PO(OEt)_2$, 1.43; $CONH_2$, 3.57; CN, 56.8; CO_2Me, 104.0; Ts, 755; CO_2Ph, 1410.0; Ac, 12,000; CHO, 12,800; Bz, 40.500

28. Rates of Addition of Morpholine to Substituted Ethylenes in MeOH at 45° ($10^4\,k_2\,M^{-1}\,sec^{-1}$)[k]

$PO(OEt)_2$, 33.1; $CONH_2$, 65.1; CN, 106.0; CO_2Me, 162.0; Ts, 1200; CO_2Ph, 2270; Ac, 23.300; CHO, 17,000; Bz, 49,200

[a] P. B. D. de la Mare and R. Bolten, "Electrophilic Additions to Unsaturated Systems," Elsevier, Amsterdam, 1966, p 84. [b] J. R. Shelton and L. H. Lee, *J. Org. Chem.*, **25**, 428 (1960). [c] R. P. Bell and M. Pring, *J. Chem. Soc. B*, 1119 (1966). [d] J. E. Dubois and G. Mouvier, *Tetrahedron Lett.*, 1325 (1963); J. E. Dubois, P. Alcais, G. Barbier, and E. Bienvenue-Goetz, *Bull. Soc. Chim. Fr.*, 2113 (1966). [e] R. W. Taft, Q. N. Report 1960, p 6 (cited in ref *a*). [f] P. E. Peterson and R. J. Bopp, *J. Amer. Chem. Soc.*, **89**, 1283 (1967). [g] J. Halpern and H. B. Tinker, *J. Amer. Chem. Soc.*, **89**, 6427 (1967). [h] H. C. Brown and K. A. Keblys, *J. Amer. Chem. Soc.*, **86**, 1795 (1964). [i] Reference 11. [j] R. N. Rign, G. C. Tesoro, and D. R. Moore, *J. Org. Chem.*, **32**, 1091 (1967). [k] Reference 12; k_{rel} indicates relative reaction rates.

stituted ethylenes undergoing nucleophilic addition is that of Friedman and Wall.[11] These authors proposed the equation

$$\log k_X = P_V + \log k_{CN} \qquad (11)$$

where k_X represents the rate constant for the reaction of the substituted ethylene bearing the X substituent with the anion of some amino acid, k_{CN} represents the rate constant for the reaction of acrylonitrile with the same nucleophile, and P_V is a measure of the electrical effect of X relative to that of the cyano group. These authors also reported nearly linear plots of log k_X against $\sigma - \sigma^\circ$ and against σ_R. A plot of log k_X against $\sigma^- - \sigma^\circ$ was said to give only qualitative correlation. Shenhav, Rappoport, and Patai[12] have re-

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(11) M. Friedman and J. S. Wall, *J. Org. Chem.*, **31**, 2888 (1966).

(12) H. Shenhav, Z. Rappoport, and S. Patai, *J. Chem. Soc. B*, 469 (1970).

TABLE II

SUBSTITUENT CONSTANTS

X	*I*	Source	*R*	Source
CH_2OMe			−0.08	*a*
CH_2OBz	0.15	*b*	−0.05	*c*
$CH_2NMe_3{}^+Br^-$	0.25	*b*	0.0	*c*
CH_2F	0.18	*b*	−0.04	*c*
$3\text{-}O_2NC_6H_4$	0.19	*d*	−0.01	*e*
CH_2CH_2OH	0	*f*	−0.10	*c*
$MeCHOHCH_2$			−0.13	*c*
CH_2OAc	0.14	*g*	−0.05	*c, g*
$CONH_2$			0.09	*h*
$PO(OCH_2CH_2Cl)_2$	0.52	*i*	0.08	*i*
$PO(OEt)_2$	0.52	*j*	0.08	*j*
$EtSO_3$			0.13	*k*
EtCO	0.29	*l*	0.19	*l*
CHO	0.31	*m*	0.14	*n*
CO_2Ph	0.42	*o*	0.14	*o*

[a] Calculated from $\sigma_R = \sigma_p - \sigma_I$ assuming $\sigma_{p,CH_2OMe} = \sigma_{p,CH_2OH}$. [b] Calculated from $\sigma_{I,XCH_2} = 0.3685\sigma_{I,X} - 0.01656$. [c] Calculated from $\sigma_R = \sigma_p - \sigma_I$. σ_p calculated from $\sigma_{p,XCH_2} = 0.5217\sigma_{I,X} - 0.1306$. [d] From p$K_a$ of $3\text{-}O_2NC_6H_4CH_2CO_2H$. [e] From $\sigma_R - \sigma_p - \sigma_I$. [f] From p$K_a$ of $HOCH_2CH_2CH_2CO_2H$. [g] M. Charton, *J. Org. Chem.*, **30**, 3346 (1965). [h] M. Charton, *J. Org. Chem.*, **28**, 3121 (1963). [i] Assumed equal to substituent constants for $PO(OEt)_2$. [j] Calculated from σ_m and σ_p values reported by L. D. Freedman and H. H. Jaffé, *J. Amer. Chem. Soc.*, **77**, 920 (1055). [k] Assumed equal to σ_R for $MeSO_2$. [l] M. Charton, *J. Org. Chem.*, **36**, 266 (1971). [m] Calculated from the equation $\sigma_{I,XCO} = 0.308\sigma_{m,X} + 0.31$. [n] Calculated from the σ_p value reported by K. Bowden and M. J. Shaw, *J. Chem. Soc. B*, 161 (1971). [o] Calculated from σ_m and σ_p values estimated as described in footnote *a*. Other values of σ_I are generally taken from M. Charton, *J. Org. Chem.*, **29**, 1222 (1964). Other values of σ_R are obtained as in footnote *e*, using σ_p values reported by D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

ported a correlation of the rate constants of the addition of morpholine to substituted ethylenes with the P_V values of Friedman and Wall. They also report a correlation of the rates with the σ_R values where $\rho = 48$. This correlation was limited to substituents with σ_R in the range of 0.10 to 0.15. Sufficient data is extant in the literature for eight sets of nucleophilic addition to substituted ethylenes. The sets studied are reported in Table I. The data were correlated with eq 1 and with the equation

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma^-{}_{R,X} + h \qquad (12)$$

where $\sigma^-{}_{R,X}$ is defined by

$$\sigma^-{}_{R,X} = \sigma^-{}_{p,X} - \sigma_{I,X} \qquad (13)$$

using the $\sigma^-{}_p$ values reported in the review of Ritchie and Sager.[13] The data have also been correlated with eq 14.

$$Q_X = \beta\sigma_{R,X} + h \qquad (14)$$

Results

The results of the correlations are presented in Table III. It should be noted that the magnitude of the multiple correlation coefficient is not the best measure of the goodness of fit of data to an equation with two or more independent variables. For such an equation, the best measure of goodness of fit is the confidence level of the F test for significance of regression. For correlation with an equation having only a single independent variable the confidence level of the "t" test for significance of the regression coefficient of that variable is the best measure of goodness of fit. We consider a confidence level (CL) of >99% to be excellent; 99.0% very good; 97.5–98%, good; 95% fair; 90%, poor; and <90%, not significant. The equation which gives the best correlation is that equation for which the highest confidence level is observed. It is therefore entirely possible to get a more significant correlation with an equation which possesses fewer independent variables than its competitor.

The value for SO_3H was excluded from set 1 as it is uncertain whether or not this group is ionized. The results obtained are excellent. Set 2 also gave an excellent correlation. Set 3 gave good results which were slightly improved by the exclusion of the value for X = Bz (set 3A). Sets 4 and 5 gave good correlation; sets 6 and 7 did not give significant results. Sets 8 and 10 gave excellent correlation; set 9 did not give significant results, perhaps owing to the small size of the set. The value for X = Ph was excluded from sets 8 and 9 as it obviously did not fit. Possibly this compound reacts by a different path. Set 11 gave good results. It is particularly significant that the values of α and β obtained for sets 12 are both significant and differ in sign. If the correlation is meaningful, this suggests a composite substituent effect made up of contributions from two or more steps. Set 13 gave very good correlation. Set 14 did not give significant results, again perhaps owing to the small size of the set. Set 15 gave an excellent correlation as did set 16.

The results for sets 26–28 are all slightly improved by the exclusion of the value for X = CHO. This is most likely due to the uncertainty in the value of σ_R for the formyl group. Of the eight nucleophilic addition sets studied, five gave significant correlation with eq 3. In all of these sets, however, α was not significant. No sets gave significant correlation with eq 12. Best results were obtained for correlations with eq 14; of the eight sets studied, six gave significant correlation with eq 14. The two sets which did not give significant correlation with σ_R had only four points each and encompassed a range of only 0.05 σ unit. Of the six sets which did give significant correlation with eq 14, one gave excellent, one gave very good, three gave good, and one gave poor correlation.

Discussion

Composition of the Electrical Effect.—Previously in this series of papers, the composition of the electrical effect was described by means of the parameter, ϵ, where

$$\epsilon = \beta/\alpha \qquad (15)$$

A more useful measure of the composition of the electrical effect may be defined as

$$P_R = \frac{\beta \times 100}{\alpha + \beta} \qquad (16)$$

where P_R is the per cent resonance effect. The quantities ϵ and P_R are related to each other by eq 17.

$$P_R = \frac{\epsilon \times 100}{\epsilon + 1} \qquad (17)$$

Values of P_R are given in Table IV.

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[13] C. D. Ritchie, and W. F. Sager, *Prog. Phys. Org. Chem.*, **2**, 323 (1963).

TABLE III

RESULTS OF CORRELATIONS

Set	α	β	h	R[a]	F[b]	r[c]	s_{estd}[d]	s_α[d]	s_β[d]	s_h[d]	n[e]
1	−9.72	−5.60	2.28	0.980	49.28[g]	0.244	0.369	1.35[h]	1.15[h]	0.601[i]	7
2	−13.5	−3.38	0.912	0.965	40.82[f]	0.378	0.696	1.55[f]	3.71[o]	0.397[l]	9
3	−7.14	−3.02	3.41	0.881	8.672[j]	0.012	0.756	1.79[i]	2.39[o]	0.781[h]	8
3A[r]	−6.22	−4.77	2.94	0.928	12.45[j]	0.121	0.603	1.50[i]	2.10[l]	0.667[i]	7
4	−22.4	2.29	6.10	0.974	28.15[j]	0.838	0.974	4.23[k]	10.5[q]	0.886[h]	6
5	−19.1	0.832	4.86	0.964	19.98[j]	0.838	1.01	5.43[k]	10.9[q]	0.920[i]	6
6	−10.7	−5.82	4.70	0.857	2.762[m]	0.376	1.94	6.85[o]	5.54[o]	3.33[o]	5
7	−8.35	−2.73	3.32	0.837	2.337[m]	0.376	1.43	5.05[o]	4.08[p]	2.45[o]	5
8	−13.0	−3.56	2.25	0.981	78.65[f]	0.133	0.440	1.04[f]	1.75[l]	0.238[f]	9
9	−9.76	−4.53	2.37	0.931	3.238[m]	0.178	1.09	3.93[o]	4.63[p]	1.15[o]	4
10	0.328	−13.2	1.64	0.973	44.79[f]	0.477	0.569	1.35[q]	1.61[f]	0.292[h]	8
11	−7.49	2.20	1.93	0.990	48.46[j]	0.330	0.228	0.895[i]	1.03[n]	0.239[i]	5
12	−3.72	6.80	2.01	0.990	48.64[j]	0.512	0.187	0.423[i]	0.816[i]	0.201[h]	5
13	−4.32	−32.9	−0.158	0.959	22.96[h]	0.447	0.651	3.46[q]	6.08[o]	0.587[h]	7
14	−8.48	−13.7	0.672	0.985	16.46[m]	0.879	0.375	1.88[n]	2.41[n]	0.375[o]	4
15	−18.3	−0.554	0.835	0.995	262.7[f]	0.694	0.187	1.12[f]	1.93[p]	0.174[h]	8
16	−1.26	−3.88	0.444	0.948	220.4[g]	0.428	0.192	0.492[l]	0.875[h]	0.0990[h]	8
21A	1.79	19.2	−1.45	0.797	0.873[m]	0.319	0.758	2.81[p]	2.14[p]	2.14[p]	4
21B	1.90	4.31	−1.17	0.678	0.424[m]	0.418	0.924	3.58[p]	9.33[p]	3.15[p]	4
21C		23.5	−1.09	0.699			0.635		17.0[o]		4
22A	1.70	19.4	−0.940	0.921	8.437[l]	0.376	0.495	1.61[o]	4.76[k]	1.05[o]	6
22B	0.995	8.14	−1.58	0.848	2.568[m]	0.193	0.773	2.49[p]	3.59[m]	1.98[p]	5
22C		17.5	0.0124	0.891			0.501		0.448[i]		6
23A	2.38	17.8	−0.514	0.794	0.855[m]	0.319	0.834	3.10[p]	23.5[p]	2.35[q]	4
23B	2.54	3.63	−0.140	0.698	0.476[m]	0.418	0.983	3.80[p]	9.93[p]	3.36[q]	4
23C		23.6	−0.0337	0.643			0.744		1.99[o]		4
24A	2.25	20.2	−1.45	0.911	4.862[m]	0.538	0.632	2.66[o]	6.76[l]	1.63[o]	5
24B	2.71	9.26	−2.81	0.865	1.491[m]	0.465	1.02	4.63[p]	5.41[o]	3.35[p]	4
24C		17.1	−0.211	0.877			0.601		5.42[l]		5
25A	2.13	18.5	−3.09	0.978	21.48[k]	0.674	0.260	1.13[n]	3.13[k]	0.848[l]	5
25B	0.895	7.53	−3.35	0.957	5.431[m]	0.426	0.450	1.83[p]	2.38[m]	1.57[o]	4
25C		14.5	−1.63	0.936			0.355		3.16[i]		5
26A$_1$	1.14	35.0	−2.81	0.841	6.044[l]	0.552	1.19	4.09[p]	11.5[k]	2.71[o]	8
26A$_2$	2.30	35.0	−3.47	0.874	6.489[l]	0.540	1.09	3.85[p]	10.6[k]	2.53[o]	7
26B	2.21	7.94	−2.60	0.882	3.505[m]	0.280	1.14	4.80[p]	3.02[n]	2.61[o]	5
26C$_1$		33.2	−2.14	0.838			1.09		8.82[i]		8
26C$_2$		31.6	−2.13	0.862			1.02		8.30[i]		7
27A$_1$	1.28	32.7	−2.02	0.861	8.576[k]	0.538	0.932	3.16[p]	8.84[i]	2.10[i]	9
27A$_2$	2.33	32.9	−2.62	0.892	9.699[j]	0.528	0.847	2.95[o]	8.04[h]	1.95[o]	8
27B	1.71	7.13	−1.49	0.877	3.337[m]	0.280	1.06	4.43[p]	2.78[n]	2.41[p]	5
27C$_1$		30.7	−1.27	0.857			0.874		6.99[h]		9
27C$_2$		29.6	−1.26	0.877			0.820		6.61[h]		8
28A$_1$	0.0555	25.9	−0.113	0.912	14.87[h]	0.538	0.568	1.93[q]	5.40[h]	1.28[q]	9
28A$_2$	0.817	25.1	−0.554	0.944	20.52[g]	0.528	0.464	1.62[p]	4.41[h]	1.07[p]	8
28B	−0.434	5.77	0.365	0.918	5.345[m]	0.280	0.707	2.97[q]	1.86[l]	1.61[q]	5
28C$_1$		24.8	−0.0806	0.912			0.526		4.21[h]		9
28C$_2$		23.9	−0.0758	0.941			0.435		3.50[f]		8

[a] Multiple correlation coefficient. [b] F test for significance of regression. [c] Partial correlation coefficient of σ_I on σ_R. [d] Standard deviation of the estimate, α, β, and h. [e] Number of points in the set. [f] 99.9% confidence level (CL). [g] 99.5% CL. [h] 99.0% CL. [i] 98.0% CL. [j] 97.5% CL. [k] 95% CL. [l] 90% CL. [m] <90% CL. [n] 80% CL. [o] 50% CL. [p] 20% CL. [q] <20% CL. [r] Sets labeled A, B, and C were correlated with eq 3, 12, and 14, respectively.

TABLE IV

VALUES OF P_R[a]

Set	P_R	Set	P_R	Set	P_R	Set	P_R
1	37	5	4	9	*c*	13	*e*
2	*b*	6	*d*	10	*e*	14	*d*
3	43	7	*d*	11	*b*	15	*b*
4	*c*	8	21	12	*d*	16	76

[a] For sets with $P_R > 50$, β is predominant, whereas, for sets with $P_R < 50$, α is predominant. [b] β is not significant for this set. [c] σ_I is a function of σ_R for this set. [d] Correlation is not significant for this set. [e] α is not significant for this set.

Mechanism of Electrophilic Addition.—In the majority of the sets studied (sets 1–5, 8, 11, 15) a large significant value of α was obtained, while β was small and in some cases not significant. Thus two major classes of electrophilic addition to olefins seem to exist in so far as substituent effects are concerned. We believe that this behavior may be accounted for in terms of the addition mechanism. The rate-determining step in the electrophilic addition to the double bond is the formation of an intermediate which may be either bridged or a free carbonium ion.[14] Thus i–iii obtain. Those sets for which β is predominant are the sets which are most likely to give rise to the free carbonium ion, **3**, as the substituents in these sets are all donors by resonance. This can readily be seen from the σ_R

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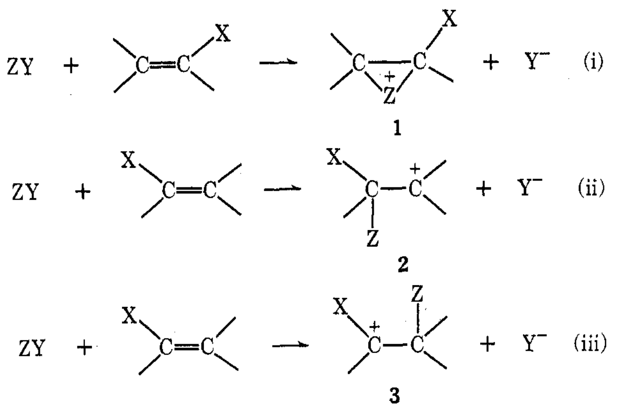
(14) While structures **1**, **2**, and **3** may well represent points in a spectrum of intermediate type, it is certainly conceivable that for a given set of substrates the intermediate is closest to one of these species, and they are therefore very useful for purposes of discussion.



values of these substituents. Those sets for which α is predominant may be accounted for in terms of the formation of intermediates **1** or **2**. Sets 1, 3A, and 8 gave significant although small values of β. It is difficult to account for this in terms of intermediate **2**. The results can, however, be accounted for in terms of intermediate **1** if the species resembles other three-membered rings in behavior. Sets 2, 4, 5, 8, and 11 include both donor and acceptor substituents. The successful correlation of these sets suggests that the same mechanism operates throughout the set. Then we may exclude free carbonium ion formation in these sets as the donor-substituted compounds would lead to **3** and the acceptor-substituted compounds would lead to **2** if free carbonium ions were to form. As substituent effects are not the same for **2** and **3**, this would result in a lack of correlation with eq 3. Then we conclude that in these sets the addition must proceed through the formation of the bridged intermediate **1**. Since all of the substituents in set 15 are donors by resonance with the exception of X = H, if a free carbonium ion were to form, it would be expected to be **3**. This intermediate should show a large and significant β value, however. We conclude therefore that in set 15 the reaction again proceeds by way of the bridged intermediate, **1**. The results obtained show that correlations with the extended Hammett equation are of use in describing the mechanism of the electrophilic addition to the double bond.

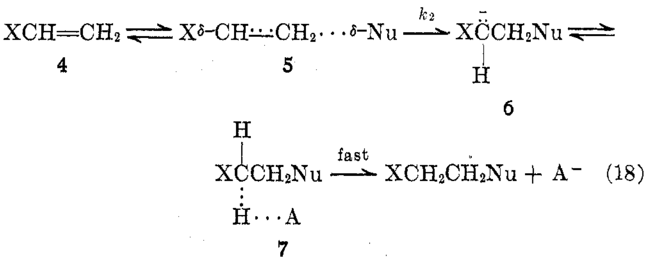
Magnitude of the Electrical Effect in Electrophilic Addition.—The β values observed for the sets in which α is predominant are smaller than the β values observed for substituent effects on dienophiles in the Diels–Alder reaction (the latter values must be corrected for multiple substitution by dividing by two). The β values observed for the sets in which β is predominant are large, in accordance with a mechanism proceeding *via* intermediate **3**. The α values obtained for sets in which α is predominant are also large.

Multiply Substituted Sets in Electrophilic Addition.—The failure to obtain significant correlation in sets 6 and 7 cannot be attributed to a change in mechanism. A comparison of the substituents in sets 6 and 7 with those present in sets 4 and 5 suggests that, if more than one mechanism occurs in sets 6 and 7, then it should also occur in sets 4 and 5. Since sets 4 and 5 are successfully correlated with eq 3, we may reject the multiple mechanism hypothesis. The lack of correlation may possibly be due to the neglect of interaction terms in the use of eq 4 or perhaps to steric factors.

Orientation in Electrophilic Addition.—The results of correlation with eq 10 show that orientation in electrophilic addition can be successfully represented by the extended Hammett equation. It would seem that orientation in the addition of BH_3 to substituted ethylenes is primarily dependent upon the delocalized electrical effect. There is one surprising point concerning the results. For that member of the set for which X = H, carbon 1 is equivalent to carbon 2 and therefore $p_1 = p_2$. Then $\log (p_1/p_2)_H = 0$ and therefore h' should be equal to zero. The value actually obtained is significantly different from zero. This may possibly be due to a constant steric effect.

Nucleophilic Addition.—Obviously, the electrical effect in nucleophilic addition to the double bond is almost purely a resonance effect. In magnitude the electrical effect is very large. The values of β obtained range from 14 to 32. This is comparable to the range of β observed for those electrophilic addition sets for which β was predominant, the range in that case being −13 to −33.[11]

The results are in accord with a mechanism involving the formation of a carbanion, **6**, by a rate-determining step (eq 18). The carbanion, **6**, in which



$$\underset{\mathbf{4}}{XCH{=}CH_2} \rightleftharpoons \underset{\mathbf{5}}{X^{\delta}\text{-}CH\overset{..}{-}CH_2\cdots{}^{\delta}\text{-}Nu} \xrightarrow{k_2} \underset{\mathbf{6}}{X\overset{-}{\underset{H}{C}}CH_2Nu} \rightleftharpoons$$

$$\underset{\mathbf{7}}{X\overset{H}{\underset{H\cdots A}{C}}CH_2Nu} \xrightarrow{\text{fast}} XCH_2CH_2Nu + A^- \qquad (18)$$

the substituent X is directly attached to the carbon bearing the negative charge, would be expected to show a large degree of resonance stabilization of the negative charge. Thus, a large positive value of β for this reaction is in agreement with the formation of **6** by a transition state, **5**, which is closer to **6** than to **4**. If the transition state were closer to **4** than to **6**, the resonance effect would not be predominant, and β would be much smaller.

The β values are a function of temperature as is shown by the results for sets $26C_2$, $27C_2$, and $28C_2$. Contrary to the literature[15] however, β is not linear in $1/T$. The β values ought to be dependent on both solvent and nucleophile. Thus, in the case of the nucleophile, let the reactivity as a function of nucleophile be given by the equation

$$Q_{Nu} = aN_{Nu} + h \qquad (19)$$

where N is a parameter characteristic of the nucleophile reactivity. When the nucleophile is held constant, and the substituent in the substituted ethylene is varied, the data may be represented by eq 20 where h_{Nu} represents the reactivity of the unsubstituted compound (ethylene itself). Then from eq 19

$$Q_{X,Nu} = \beta_{Nu}\sigma_{R,X} + h_{Nu} \qquad (20)$$

$$h_{Nu} = aN_{Nu} + h \qquad (21)$$

and

$$Q_{X,Nu} = \beta_{Nu}\sigma_{R,X} + aN_{Nu} + h \qquad (22)$$

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[15] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

According to Miller,[10] the quantity $Q_{X,Nu}$ can be written as eq 23 where $\chi\sigma_{R,X}N_{Nu}$ is the so-called interaction term.

$$Q_{X,Nu} = \beta\sigma_{R,X} + aN_{Nu} + \chi\sigma_{R,X}N_{Nu} + h \quad (23)$$

Setting eq 22 equal to eq 23 and dividing through by $\sigma_{R,X}$ gives eq 24 which predicts that the slopes of the

$$\beta_{Nu} = \chi N_{Nu} + \beta \quad (24)$$

line obtained from correlation with eq 17 will be a linear function of the nucleophilicity parameter, N. The same type of equation can be derived from the solvent variation. Thus,

$$\beta_{Sv} = \chi S_{Sv} + \beta \quad (25)$$

Unfortunately, the data available here do not permit a test of eq 24 and 25.

The results obtained would undoubtedly be much improved if a wider range of σ_R values could be studied. The largest range of σ_R studied in this work encompassed only 0.14 σ units. It is unlikely that a greater range of σ will be studied as no substituent with $\sigma_R > 0.21$ is known, and it is unlikely that a substituent with $\sigma_R < 0.07$ would react at a measurable rate.

It is interesting to note that, although σ_R^- values might have been expected to be the substituent constants most applicable to reactions involving carbanions, correlations with eq 12 are generally inferior to correlations with eq 3 in which σ_R constants were used. This is partly due to the fact that values of σ_R^- were not available for all substituents, and therefore in several cases all the members of the set could not be correlated by eq 12. Nevertheless, eq 12 is not successful in correlating this data. Thus no attempt was made to correlate data with the equation

$$Q_X = \beta\sigma^-_{R,X} + h \quad (26)$$

Why Increasing Concentrations of Ethylenediamine Cause the Rate of Exchange of Isobutyraldehyde-*2-d* to Rise, Then Fall, and Then Rise Again[1a,b]

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First-order rate constants for the deuterium exchange of about 0.06 M isobutyraldehyde-*2-d* in aqueous solution around pH 8.5 increase with increasing concentrations of added ethylenediamine and reach a maximum at diamine concentrations around 0.03 M. They then decrease, pass through a minimum around diamine concentrations of 0.1 M, and finally increase again. This behavior is explained in terms of the transformation of most of the limiting reagent to 2-isopropylimidazolidine (or its conjugate acid), which then catalyzes the exchange of remaining aldehyde. Exchange by this pathway is fastest when half the aldehyde has been transformed to imidazolidine. At higher concentrations of diamine most of the exchange arises from attack of the various bases present on the small amounts of iminium ions, such as $Me_2CDCH{=}NHCH_2CH_2NH_2^+$, which are present in equilibrium with the imidazolidine. Quantitative treatment of the data gives reasonable agreement with the experimental rate constants. A few measurements using N-methylethylenediamine also show a rate maximum and minimum, but N,N'-dimethylethylenediamine, which gives a considerably less basic and more hindered imidazolidine, shows no extrema.

In searching for bifunctional catalysts for the dedeuteration of isobutyraldehyde-*2-d*,[1b,2,3] it was observed that the rate of dedeuteration of ~0.06 M isobutyraldehyde-*2-d* in the presence of ethylenediamine around pH 8.38 at first increased, then decreased, and then increased again as the concentration of diamine was increased from zero to about 0.5 M. We developed a hypothesis, which included the formation of 2-isopropylimidazolidine and its action as a basic catalyst, to explain these results. To test this hypothesis (and for other reasons), the equilibrium constant for the formation of 2-isopropylimidazolidine from isobutyraldehyde and ethylenediamine was measured and the basicity constant of the imidazolidine was determined.[4] The way in which these results and additional kinetic measurements support our hypothesis will be described in the present paper.

Results

The kinetics of the dedeuteration of isobutyraldehyde-*2-d* in the presence of ethylenediamine at 35° were studied at various concentrations and various pH's. The reaction was followed in the manner described previously[5,6] by acidifying the reaction mixture to stop the reaction (and to hydrolyze any imines, imidazolidines, etc., to aldehyde), extracting the aldehyde, and making proton magnetic resonance measurements to determine the extent of deuteration of the aldehyde. Satisfactory first-order rate constants were obtained in the various runs and their values are collected in Table I. Rate constants for the runs at pH 8.37 ± 0.14 using 0.060 ± 0.007 M isobutyraldehyde-*2-d* are plotted as open circles against the concentration of ethylene-

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