Electronic Effects of Substituents on the Stabilities of Carbon–Carbon Double Bonds[1]

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Abstract: Equilibrium constants for reactions of the type *trans*-$\mathrm{XCH_2CH{=}CHY} \rightarrow$ *trans*-$\mathrm{XCH{=}CHCH_2Y}$ may be correlated simply in terms of double bond stabilization parameters for the substituents, but a considerably better correlation is obtained when allowance is made for interaction of $\mathrm{XCH_2}$ and Y or X and $\mathrm{CH_2Y}$ across the trans vinylene groups. Such interactions were calculated from Hammett para-substituent constants and a proportionality constant τ_v. The double bond stabilization parameter D_X is equal, within the precision of the linear free energy relationships used, to the free energy of reaction of vinyl-X with propylene to give allyl-X and ethylene. Its magnitude, which increases with increasing tendency of the substituent to stabilize a carbon–carbon double bond to which it is attached, increases in the order $\mathrm{SO_2Me} < \mathrm{Br} < \mathrm{SOMe} < \mathrm{Cl} < \mathrm{CH_2CO_2Me} < \mathrm{CN} < \mathrm{CH_2OMe} < \mathrm{NO_2} < \mathrm{CO_2Me} \sim \mathrm{SMe} \sim n\text{-}\mathrm{C}_n\mathrm{H}_{2n+1} < \mathrm{F} < \mathrm{Ph} < \mathrm{OMe}$.

In a study of the relative abilities of methoxy and methylthio substituents to stabilize double bonds,[2] it was noted that some literature observations appear to be inconsistent with any rationalization simply in terms of the "double bond stabilizing ability" of the substituents. This may be illustrated by the relative positions of the equilibria shown in eq 1,[3,4] 2,[5] 3,[3-6] and 4.[7] From a comparison of the first two equilibria

$$\underset{70\%}{\mathrm{EtCH{=}CHCO_2Me}} \rightleftharpoons \underset{30\%}{\mathrm{MeCH{=}CHCH_2CO_2Me}} \qquad (1)$$

$$\underset{68\%}{\mathrm{EtCH{=}CHCO_2^-}} \rightleftharpoons \underset{32\%}{\mathrm{MeCH{=}CHCH_2CO_2^-}} \qquad (2)$$

$$\underset{3\%}{\mathrm{MeOCH_2CH{=}CHCO_2Me}} \rightleftharpoons \underset{97\%}{\mathrm{MeOCH{=}CHCH_2CO_2Me}} \qquad (3)$$

$$\underset{30\%}{\mathrm{MeOCH_2CH{=}CHCO_2^-}} \rightleftharpoons \underset{70\%}{\mathrm{MeOCH{=}CHCH_2CO_2^-}} \qquad (4)$$

it would be concluded that the double bond stabilizing ability of the $\mathrm{CO_2^-}$ substituent (minus that of $\mathrm{CH_2CO_2^-}$) does not differ significantly from that of $\mathrm{CO_2Me}$ (minus that of $\mathrm{CH_2CO_2Me}$). From a comparison of the latter two equilibria, however, it would be concluded that the double bond stabilizing ability of $\mathrm{CO_2^-}$ (minus that of $\mathrm{CH_2CO_2^-}$) is considerably greater. The sparsity of equilibrium data on relevant reactions, uncertainties as to the cis–trans contents of some of the species involved, and other factors made it seem unprofitable at that time[2] to discuss our hypothesis that allowance for polar interactions of substituents across the carbon–carbon double bond would permit a greatly improved rationalization of electronic effects on equilibria in such reactions as 1–4. However, we now feel that subsequent observations have added sufficiently to the body of data to make a test of our hypothesis feasible.

Derivation of Equations. In correlating equilibrium constants for migrations of carbon–carbon double bonds an approach like that proposed by Zahn[8] and amplified by Allen[9] and others[10] for correlating thermochemical properties is useful. In this approach a given property of a compound is expressed as the sum of contributions from the various bonds in the molecule, plus contributions from interactions between bonds leading to a common atom, plus contributions (in some cases) for interactions between more widely separated groups. A reference point has been fixed by defining interactions between bonds to a common atom as zero if any of the bonds are to hydrogen. Such a scheme has been applied frequently to enthalpies of formation in the gas phase; since entropies (of electrically neutral species) are usually correlated more precisely by additivity schemes than enthalpies are,[11] free energies should also be correlatable. Thus the change in chemical free energy[12] in eq 5 will be expressed

$$\mathrm{CH_2{=}CHCH_2X + CH_2{=}CH_2 \longrightarrow CH_2{=}CHCH_3 + CH_2{=}CHX} \qquad (5)$$

as shown in eq 6, in which C refers to saturated and

$$\Delta G^{\text{chem}} = B(\mathrm{C_d{-}X}) + B(\mathrm{C{-}H}) - B(\mathrm{C_d{-}H}) - B(\mathrm{C{-}X}) - \Gamma_{\mathrm{C_dCX}} \qquad (6)$$

$\mathrm{C_d}$ to double bonded carbon atoms. The four B terms are bond contributions and $\Gamma_{\mathrm{C_dCX}}$ is the interaction between the bonds from X and $\mathrm{C_d}$ to the same saturated carbon atom in allyl-X. There is no $\Gamma_{\mathrm{C_dC_dX}}$ term in the equation for the free energy content of vinyl-X because a $\mathrm{C_d}$, by definition, is always attached to another $\mathrm{C_d}$; hence this interaction is absorbed into the $B(\mathrm{C_d{-}X})$ term. The parameter D_X, which refers to the effect on double bond stability of X as a vinyl substituent relative to its effect as an allyl substituent, will be defined as $-\Delta G^{\text{chem}}$, in which the negative sign is used in order to make the double bond stabilizing

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[2] J. Hine, L. G. Mahone, and C. L. Liotta, *J. Org. Chem.*, 32, 2600 (1967).

[3] S. J. Rhoads, J. K. Chattopadhyay, and E. E. Waali, *ibid.*, **35**, 3352 (1970).

[4] This is more recent and reliable than the data referred to previously.

[5] R. P. Linstead and E. G. Noble, *J. Chem. Soc.*, 614 (1934).

[6] The value at 92° is shown (instead of that at 300°) since it is to be compared with a value[7] at 100°.

[7] L. N. Owen and M. U. S. Sultanbawa, *J. Chem. Soc.*, 3098 (1949).

[8] C. T. Zahn, *J. Chem. Phys.*, **2**, 671 (1934).

[9] T. L. Allen, *ibid.*, 31, 1039 (1959).

[10] J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970, Chapter 7.

[11] *Cf.* S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **29**, 546 (1958).

[12] By ΔG^{chem} we mean the free energy change corrected for symmetry effects.[13]

[13] S. W. Benson, *J. Amer. Chem. Soc.*, **80**, 5151 (1958).

ability of X as a vinyl substituent increase as D increases and to make D positive for most substituents. Analogously, D_Y, which is the free energy of formation of allyl-Y and ethylene from vinyl-Y and propylene, may be expressed as shown in eq 7. It is clear from the

$$D_Y = B(C_d\text{-}H) + B(C\text{-}Y) - B(C_d\text{-}Y) - B(C\text{-}H) + \Gamma_{C_dCY} \quad (7)$$

definition that the reference substituent is hydrogen; that is, D_H is zero.

The equilibria we wish to correlate are of the type shown in eq 8. The trans compounds were chosen so

$$trans\text{-}XCH_2CH{=}CHY \rightleftharpoons trans\text{-}XCH{=}CHCH_2Y \quad (8)$$

as to minimize steric effects and thus permit us to focus on electronic effects. We shall express the free energy of this reaction as shown in eq 9, in which the B's

$$\Delta G_{XY}{}^{chem} = B(C_d\text{-}X) + B(C\text{-}Y) + \Gamma_{C_dCY} + I_{X.CH_2Y} - B(C_d\text{-}Y) - B(C\text{-}X) - \Gamma_{C_dCX} - I_{Y.CH_2X} \quad (9)$$

are bond contributions, the Γ's are interactions of pairs of bonds leading to a comon atom, and the I's are interactions of pairs of groups across the trans vinylene group. In terms of the double bond stabilization parameters, $\Delta G_{XY}{}^{chem}$ may be expressed as shown in eq 10. Following an approach that may be used to

$$\Delta G_{XY}{}^{chem} = D_Y - D_X + I_{X.CH_2Y} - I_{Y.CH_2X} \quad (10)$$

derive the Hammett and Taft equations,[14] we shall assume that the free energy of interaction of X and CH_2Y across a trans vinylene group is proportional to the product of substituent constants for the two groups. The proportionality constant, under a given set of conditions, will be denoted τ_v, as shown in eq 11.

$$I_{X.CH_2Y} = \tau_v\sigma_X\sigma_{CH_2Y} \quad (11)$$

Substituting such expressions for each of the I terms in eq 10 gives eq 12.

$$\Delta G_{XY}{}^{chem} = D_Y - D_X + \tau_v(\sigma_X\sigma_{CH_2Y} - \sigma_Y\sigma_{CH_2X}) \quad (12)$$

Equilibrium Constants for Double Bond Migration. The best test of eq 12 would be to apply it to a large number of equilibrium constants determined in the same solvent and at the same temperature. Since no such body of data exists, we have used data at a variety of temperatures (which should lead to deviations from the equation only to the extent that the entropy change differs from zero), but with a preference for 25° or as near to 25° as possible, and in the gas phase and in a variety of solvents. Since the reactions we are studying are not accompanied by major changes in the nature of the functional groups, there is a reasonable hope that solvent effects will not be very large (for electrically neutral X and Y groups, at least).

Equilibrium constants are listed in Table I for all the reactions of the type of eq 8 for which we found data in the literature, except for the isomerization of seven compounds of the type $ArCH_2CH{=}CHPh$ where Ar is a polynuclear aryl radical[15] (in which steric effects appear to be important) and the isomerization of five compounds of the type $RSO_2CH_2CH{=}CHSO_2R'$ (where analyses were based on melting point curves and the absolute value of ΔG was never larger than 0.3 kcal/mol).[16] Data on the n-butenes,[17] n-pentenes,[18] hexenes,[19] n-heptenes,[20] and allyl halides[21] obtained in the gas phase at higher temperatures (usually about 150–350°) were extrapolated to 25°. In cases where the authors did not show their analytical method was good for both geometric isomers of a compound, products (including some simply said to be trans) were assumed to contain the same ratios of cis and trans isomers as certain model compounds at equilibrium.[2,3,17–23] Data on the butenylbenzenes at 55° were taken rather than those at 200° or higher.[24] The value of ΔG^{chem} for the 1-methoxy-3-phenylpropenes obtained from the measurements of Kloosterziel and van Drunen[25] differs by less than 0.1 kcal/mol from the value that may be calculated from the unpublished results of Doering and Vollrath quoted (without information on geometric isomer contents) by Broaddus.[26] The value listed for methyl 4-methoxybutenoates was obtained by combining the free energy of transformation of the 2-butenoates to the *cis*-butenoate at 35°[2] with the free energy of cis–trans isomerism of the 3-butenoate at 25°.[3] The data obtained at 92°[3] give a ΔG^{chem} about 0.2 kcal/mol less negative. The results obtained with the nitropropenes in n-heptane were used rather than the considerably different value in ether.[27]

The data used[2,3,5,7,17–31] include cases in which the equilibria were not approached from both sides, cases in which the equilibria are so one sided as to make the calculated values of ΔG^{chem} of reduced reliability, and various other uncertainties. The last figure given in most of the entries in Table I can rarely be considered to be significant. Nevertheless, we shall use the data shown because the highly reliable data do not constitute a large enough set to permit a good test of our equations.

Correlation of Data. Interactions of groups, especially when all are electrically neutral, across trans vinylene groups have not been studied in enough detail for there to be an obviously preferable way of calculating the interaction energies denoted by I's in eq 9–11. Ionization constants[32] and rates of reaction[33] of trans 3-substituted acrylic acids have been correlated

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[14] J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, Section 4-1.

[15] D. R. Ross and E. S. Waight, *J. Chem. Soc.*, 6710 (1965).

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[33] J. Hine and W. C. Bailey, Jr., *ibid.*, **81**, 2075 (1959).

Table I. Equilibria in Transformations of *trans*-$XCH_2CH{=}CHY$ to *trans*-$XCH{=}CHCH_2Y$

X	Y	% reactant trans	% product trans	Solvent	Temp, °C	K	ΔG^{chem}, kcal/mol	Ref
H	Me	80^{a}		Gas	25	0.041^{a}	$2.95^{a,b}$	17
H	Et	81^{a}		Gas	25	0.024^{a}	$2.87^{a,c}$	18
H	*n*-Pr	80^{a}		Gas	25	0.015^{a}	$3.14^{a,c}$	19
H	*n*-Bu	81^{a}		Gas	25	0.018^{a}	$3.04^{a,c}$	20
H	*i*-Pr	84^{a}		Gas	25	0.065^{a}	$2.27^{a,c}$	19
Me	*n*-Pr	86^{a}	81^{a}	Gas	25	1.1^{a}	-0.04^{a}	20
H	F	22^{a}		Gas	25	0.0091	$3.43^{a,c}$	21
H	Cl	21^{a}		Gas	25	0.072	$2.21^{a,c}$	21
H	Br	21^{a}		Gas	25	0.86	$0.74^{a,c}$	21
Me	Ph	92^{d}	78^{e}	Me_2SO	55	0.060	1.83	24
Et	OMe	45^{f}	86^{g}	*n*-Pentane	20	0.13	1.21	28
Me	CH_2OMe	86^{g}	80^{e}	*n*-Pentane	20	1.5	−0.25	28
H	$(CH_2)_2OMe$	80^{e}		*n*-Pentane	20	0.14	1.79^{c}	28
Ph	OMe	36	94^{d}	Me_2SO	23	1.3	−0.15	25
Me	CO_2Me	93	75^{e}	Octane	117	0.36	0.80	3
n-Bu	CO_2Me	88^{d}	81^{g}	Octane	125	0.42	0.69	28
n-Pr	CH_2CO_2Me	81^{g}	81^{g}	Octane	125	2.5	−0.72	28
Et	$(CH_2)_2CO_2Me$	81^{g}	81^{g}	Octane	125	1.2	−0.12	28
Me	$(CH_2)_3CO_2Me$	81^{g}	75^{e}	Octane	125	1.1	−0.08	28
H	$(CH_2)_4CO_2Me$	75^{e}		Octane	125	0.063	3.05^{c}	28
MeO	CO_2Me	86^{h}	47^{i}	*t*-BuOH	35	50^{j}	−2.39	2,3
H	CO_2Na	87^{d}		H_2O	150	0.024	4.08^{c}	29
Me	CO_2Na	87^{d}	74^{e}	H_2O	150	0.40	0.77	29
Et	CO_2Na	87^{d}	80^{g}	H_2O	150	0.32	0.95	29
MeO	CO_2Na	81^{k}	50^{k}	H_2O	100	1.4	−0.27	7
MeS	OMe	66	67	Me_2SO	50	0.031	2.23	2
MeS	CO_2Me	93^{d}	59	*t*-BuOH	35	0.86	0.09	2
n-Pr	SMe	57	86^{g}	Me_2SO	27	0.75	0.18	23
n-C_9H_{19}	SMe	61	86^{g}	Me_2SO	27	0.71	0.20	23
H	SOMe	88^{l}		*t*-BuOH	27	0.24	1.50^{c}	23
n-Pr	SOMe	88^{l}	86^{g}	*t*-BuOH	27	23	−1.89	23
n-C_9H_{19}	SOMe	88^{l}	86^{g}	*t*-BuOH	27	23	−1.89	23
H	SO_2Me	94		Et_3N	90	0.83	0.92^{c}	23
Me	SO_2Bu-*n*	98^{m}	80^{e}	*t*-BuOH	35	4.3	−0.89	30
H	CN	41		*t*-BuOH	30	0.012	3.31^{c}	31
Me	CN	50	66	*t*-BuOH	30	0.54	0.37	31
H	NO_2	97		*n*-Heptane	25^{n}	0.0018^{n}	4.40^{c}	27

[a] Extrapolated from ΔH and ΔS values determined at higher temperatures. [b] Corrected for a symmetry factor $(K_\sigma)^{12}$ of 6. [c] Corrected for a symmetry factor $(K_\sigma)^{12}$ of 3. [d] ΔG for cis to trans isomerization assumed to be the average of the values for methyl crotonate (∼ −1.s kcal/mol),[22] methyl 2-pentenoate (∼−2.1 kcal/mol),[3] and methyl 4-methoxy-2-butenoate (∼−1.1 kcal/mol).[3] [e] Assumed the same as fo6 2-hexene at the same temperature.[19] [f] Assuming the product of the dehydrohalogenation of *n*-BuCHClOMe was the equilibrium cis–tranr mixture. [g] Assumed the same as for 3-heptene at the same temperature.[20] [h] ΔG for cis–trans isomerization assumed to be the same as reported at 92°.[3] [i] ΔG for cis–trans isomerization assumed to be the same as reported at 25.°[3] [j] See text for method of calculation. [k] Assumed the same as for the methyl ester at 92°.[3] [l] ΔG for cis to trans isomerization assumed to be the average of the values for RCH=CHSMe (−0.2 kcal/mol)[23] and for $MeCH{=}CHSO_2Me$ (−2.3 kcal/mol).[23] [m] ΔG for cis to trans isomerization assumed to be the same (−2.3 kcal/mol) as for methyl propenyl sulfone.[23] [n] Average of values at 20 and 30°.

satisfactorily by use of Hammett para-substituent constants. Apparently the mixture of polar and resonance effects that controls interactions across a trans vinylene group is rather similar to that which controls interactions across a *p*-phenylene group. By the same argument used previously for interactions across phenylene groups,[34] we may express τ_v as shown in eq 13,

$$\tau_v = \frac{2.3RT\rho^2}{\log K_1 - \log (4K_2)} \qquad (13)$$

in which ρ is the reaction constant for trans 3-substituted acrylic acids and K_1 and K_2 are the first and second ionization constants of fumaric acid. The factor $2.3RT$ arises because we are calculating ΔG rather than log K values. The data of Charton and Meislich give a value of 8.9 kcal/mol for τ_v in aqueous solution at 25°. Somewhat larger values might be expected for this measure of the efficiency of transmission of polar effects in media of lower dielectric constant. One measure of the effect of medium on τ's for interactions across phenylene groups shows little effect on going from water to decalin but a 10–20% increase on going to the gas phase.[35] It may also be significant that τ_v relates to interactions of electrically neutral substituents. This is also true for the disproportionations of alkylbenzenes and halobenzenes, for which Hammett substituent constants did not give a very good correlation, but for which larger values of τ_p and τ_m were required than those obtained from data on the ionization of benzoic acids, phenols, and anilines.[36]

Since substituent constants will be obtained from other sources, eq 12 contains only one disposable parameter (D_X) whose value depends on the nature of X. For this reason a correlation using eq 12 will be trivial only in the cases of substituents for which we have only one equilibrium constant. A comparison of the first four entries in Table I, as well as various

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(34) J. Hine, *ibid.*, **81**, 1126 (1959).

(35) J. Hine, H. W. Haworth, and O. B. Ramsay, *ibid.*, **85**, 1473 (1963).

(36) J. Hine and H. E. Harris, *ibid.*, **85**, 1476 (1963).

other pairs of entries, shows that various primary alkyl groups all have essentially the same effect on the equilibria studied and that no clear trend accompanies increases in chain length in this series. For this reason we have treated all primary alkyl substituents as identical. Because of the uncertainty in and solvent dependence of substituent constants for electrically charged substituents, we have left the data on sodium salts out of our correlations. For reasons to be described later, the data on sulfones were also omitted. This leaves us with 20 equilibrium constants dealing with seven substituents (not counting the reference substituent, hydrogen), each of which appears as both X and CH_2X in the equations for at least two equilibrium constants. Exner's extensive collection of Hammett substituent constants[37] contained all the needed σ_X values, but four σ_{CH_2X} values were missing. From a plot of the para-substituent constants for CH_2X *vs.* the inductive substituent constants for X for the eight substituents for which both values are listed[37] a fairly satisfactory straight line was obtained. From this line and the listed inductive substituent constants, values of σ for the other CH_2X groups were calculated.

To examine the consequences of neglecting interactions across the trans vinylene group we first used a least-squares treatment to calculate values of D_X with the τ_v term in eq 12 set equal to zero. From the values obtained, which are listed in the next to the last column of Table II, the 20 values of ΔG^{chem} relating to substituents appearing in two or more equilibria may be calculated with an average deviation of 0.21 and a standard deviation of 0.37 kcal/mol. When τ_v was instead treated as a disposable parameter a value of 13.4 with a standard deviation of 2.4 was obtained. From the values of D_X also obtained, which are listed in the last column of Table II, the 20 ΔG^{chem} values may be calculated with an average deviation of 0.12 and a standard deviationof 0.20 kcal/mol. A correlation using the τ_v value 8.9 calculated for aqueous solutions gives a standard deviation of 0.22 kcal/mol and about the same D_X values as those obtained with a τ_v of 13.4. The significant improvement obtained in the correlation when interactions across the vinylene group are allowed for and the fact that the optimum value of τ_v is around that expected provide evidence for the reality of such interactions. They could perhaps be calculated better by some other treatment, but since the double bond stabilization terms in eq 12 tend to be the dominant terms and since the ΔG^{chem} values in Table I refer to a variety of experimental conditions, it was not felt to be worthwhile to attempt a detailed analysis of the origin and magnitudes of the interactions across the vinylene groups.

Table II. Double Bond Stabilization Parameters for Various Substituents[a]

X	σ_{CH_2X}[b]	D_X, kcal/mol $\tau_v = 0$	D_X, kcal/mol $\tau_v = 13.4$
OMe	0.03[c]	5.07 ± 0.29	5.17 ± 0.15
Ph	−0.09	5.05 ± 0.35	4.90 ± 0.19
F	0.15[c]	3.43[d]	3.34[d]
$(CH_2)_4CO_2Me$	−0.14[e]	3.1[d,f]	3.3[d,f]
n-C_nH_{2n+1}	−0.14[e]	3.04 ± 0.17	3.18 ± 0.09
SMe	−0.02[c]	3.15 ± 0.28	3.17 ± 0.15
CO_2Me	0.04[c,g]	3.38 ± 0.28	3.15 ± 0.15
$(CH_2)_3CO_2Me$	−0.14[e]	2.96[d]	3.10[d]
$(CH_2)_2CO_2Me$	−0.14[e]	2.92[d]	3.06[d]
NO_2	0.23[c]	4.4[d,f]	2.9[d,f]
CH_2OMe	−0.14[e]	2.79[d]	2.62[d]
i-Pr	−0.14[e]	2.27[d]	2.53[d]
CN	0.18	3.36 ± 0.29	2.30 ± 0.24
CH_2CO_2Me	−0.14[e]	2.32[d]	2.12[d]
Cl	0.12	2.21[d]	1.80[d]
SO_2Bu-*n*	0.17[h]	2.15[d,i]	1.24[d,i]
SOMe	0.16[c]	1.27 ± 0.25	0.71 ± 0.17
Br	0.14	0.74[d]	0.31[d]
H	−0.14	0.000	0.000
SO_2Me	0.17[h]	0.92[d,i]	−0.44[d,i]

[a] Uncertainties listed are standard deviations. [b] From ref 37 unless otherwise noted. [c] Calculated from σ_I as described in the text. [d] Based on the equilibrium constant for only one reaction. [e] Taken as equal to σ_{Me}. [f] Based on an equilibrium in which 1% or less of the minor component was present and therefore relatively uncertain. [g] Based on σ_I for CO_2R. [h] Taken as σ for SO_2R. [i] It is implausible that *D* for SO_2Bu-*n* should be so different from that for SO_2Me; see text.

Also listed in Table II are *D* values for most of the substituents that figured in only one of the equilibria covered in Table I. No σ values were available for $(CH_2)_nX$ where X is methoxy and carbomethoxy and *n* is 2 or more, but it was assumed that the values were the same as for the methyl group since the σ values used for CH_2OMe and CH_2CO_2Me are both within 0.04 of the value for hydrogen. No *D* value is listed for $(CH_2)_2OMe$ because the value obtained (2.04 kcal/mol) is implausible in differing so greatly from the values for primary alkyl groups and because it is based on a measurement of only 1% of the minor component present at equilibrium and hence may be considerably in error.

Discussion

Just as the values of *D* in the last column of Table II differ from those in the adjacent column, they may differ from other measures of the effects of substituents on the stability of double bonds because of differences in definitions of reference substituents and reference reactions, differences in data used to evaluate parameters, and for many other reasons. In addition to the quantitative data covered in Table I there are many semiquantitative and qualitative observations that are consistent with the *D* values in the last column of Table II. For example, it may be calculated from these parameters that the isomerizations of allyl methyl ether and allyl methyl sulfide to the corresponding *trans*-propenyl compounds at 25° should proceed to the extents of 99.96 and 99.5%, respectively, at equilibrium. Experimentally both these allyl compounds have been found to isomerize to the corresponding propenyl compounds to an extent greater than 99% at room temperature.[38,39] Although the propenyl products observed were mostly cis, the trans isomers are of comparable stability and therefore isomerization to trans products would proceed to about the same extent.

In order to analyze the data on carboxylic acid salts we need substituent constants for the CO_2^- and $CH_2CO_2^-$ groups. Values ranging from −0.05 to 0.16

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(37) O. Exner, *Collect. Czech. Chem. Commun.*, 31, 65 (1966).

(38) C. C. Price and W. H. Snyder, *J. Amer. Chem. Soc.*, 83, 1773 (1961).

(39) C. C. Price and W. H. Snyder, *J. Org. Chem.*, 27, 4639 (1962).

may be calculated for σ_p for the CO_2^- group,[40] but no values appear to have been reported for the $CH_2CO_2^-$ group. We have taken the recommended value (0.0)[40] for CO_2^- and have treated σ for $CH_2CO_2^-$ as a disposable parameter. The value of $D_{CO_2^-}$ was treated as a second disposable parameter. A least-squares treatment of the four equilibrium constants in Table I involving carboxylate salts in terms of eq 12 gave optimum values of −0.23 and 3.85 kcal/mol for $\sigma_{CH_2CO_2^-}$ and $D_{CO_2^-}$, respectively. The four values of ΔG^{chem} may be calculated from these parameters with an average deviation of 0.24 kcal/mol. This is larger than the average deviation obtained in correlating the other data, and the value of σ is somewhat more negative than we had expected for the $CH_2CO_2^-$ group. However, the equilibrium constant for the isomerization of the 4-methoxycrotonate ion is one that is rendered particularly unreliable by the possibility that the product was largely cis instead of being the cis–trans equilibrium mixture. (Basic isomerization of the corresponding methyl ester gives almost entirely the cis product with relatively little of the trans product being formed even after 60 half-lives.)[2] If the product formed in isomerization of the salt is all *cis*-4-methoxy-3-butenoate and if the trans isomer has the same stability, then ΔG^{chem} should be −0.78 instead of −0.26 kcal/mol. A least-squares treatment with this value of ΔG^{chem} gives a σ of −0.09 for $CH_2CO_2^-$ and a value of 3.94 kcal/mol for $D_{CO_2^-}$.

From these parameters, the four values of ΔG^{chem} for carboxylate salts may be calculated with an average deviation of 0.12 kcal/mol. Regardless of which of the two preceding sets of parameters for the carboxylate anion substituent is correct, the relative positions of the four equilibria shown in eq 1–4 may be explained at least qualitatively by adding interactions across the vinylene group to the factors ordinarily considered in discussing such equilibria. Thus, as measured by D values, the carboxylate anion substituent is a better double bond stabilizer than the carbomethoxy substituent. This factor by itself would make equilibrium 2 lie further to the left than 1 and 4 further to the left than 3. The largest interaction across a vinylene group is the stabilizing interaction between the electron-donating methyl group and the electron-withdrawing carbomethoxy group in methyl crotonate. This interaction makes equilibrium 1 lie further to the left than it otherwise would and thus creates the illusion that the carbomethoxy substituent is as good a double bond stabilizer as a carboxylate anion. The second largest interaction is a destabilizing interaction between the electron-donating methoxy and $CH_2CO_2^-$ substituents in the 4-methoxy-3-butenoate ion. This interaction makes equilibirum 4 lie further to the left than it would otherwise and thus makes the carboxylate anion substituent appear to be an even better double bond stabilizer than it actually is.

A case that also illustrates the reality of the τ_v term in eq 12 and that is not beclouded by as much uncertainty arising from cis–trans isomerism and unknown substituent constants may be found in comparing the methoxy and carbomethoxy substituents. As shown in Table I, ΔG^{chem} for eq 14 is 1.21 kcal/mol. If there

$$trans\text{-}EtCH_2CH{=}CHOMe \longrightarrow trans\text{-}EtCH{=}CHCH_2OMe \quad (14)$$

were no τ_v term in eq 12 this would mean that D_{OMe} is 1.21 kcal/mol larger than D for an alkyl group. Both entries in Table I for reactions of the type of eq 15

$$trans\text{-}RCH_2CH{=}CHCO_2Me \longrightarrow trans\text{-}RCH{=}CHCH_2CO_2Me \quad (15)$$

agree that ΔG^{chem} is within 0.06 of 0.75 kcal/mol. In the absence of a τ_v term this corresponds to D_{CO_2Me} being 0.75 kcal/mol larger than D_R. Combination of the values 1.21 and 0.75 kcal/mol would then lead to a prediction of −0.46 kcal/mol for the isomerization shown in eq 16. This differs by almost 2 kcal/mol

$$trans\text{-}MeOCH_2CH{=}CHCO_2Me \longrightarrow trans\text{-}MeOCH{=}CHCH_2CO_2Me \quad (16)$$

from the experimental value (−2.39 kcal/mol) listed in Table I. This difference is explained by interactions across the trans vinylene group. Since the σ values for CH_2OMe and CH_2CO_2Me are rather small, these interactions will be small in the products of eq 14 and 15 and in both the reactants and products of eq 16. The reactant in eq 14, however, is destabilized by the interaction of the electron-donating methoxy group and the electron-donating *n*-propyl group. When this destabilization is allowed for, $D_{OMe} - D_R$ becomes considerably larger than 1.21 kcal/mol. The reactant in eq 15, on the other hand, is stabilized by interaction of the electron-donating alkyl group and the electron-withdrawing carbomethoxy group. When this is allowed for, $D_{CO_2Me} - D_R$ becomes much smaller than 0.75 kcal/mol. The overall result is that $D_{CO_2Me} - D_{OMe}$ is now expected to be much more negative than −0.46 kcal/mol.

The effects of interactions across vinylene groups show up to the greatest extent in the cases of the most highly polar groups. For example, Table II shows that the nitro, cyano, and alkylsulfonyl groups had to be assigned double bond stabilization parameters more than 1 kcal/mol larger when interactions across the vinylene group were neglected as when such interactions were considered. Particularly large interactions might be expected when one of the groups is a reasonably strong resonance electron-donating substituent and the other a resonance electron-withdrawing substituent.

In at least one case the D values in the last column of Table II show a clear internal inconsistency. We can think of no plausible reason why the value of D for the *n*-butylsulfonyl group should be 1.6 kcal/mol larger than that for the methylsulfonyl group as shown in Table II. In a study of the ethylsulfonyl, *n*-propylsulfonyl, *n*-butylsulfonyl, *tert*-butylsulfonyl, and benzylsulfonyl groups there appeared to be a small but not clearly significant tendency for the double bond stabilizing ability of RSO_2 groups to decrease as R became larger.[16] From the value of D listed for the methylsulfonyl group the isomerization of *trans*-1-methylsulfonyl-1-hexene to *trans*-1-methylsulfonyl-2-hexene may be calculated to proceed to an extent of 98.7% at equilibrium at 25°. This *may* be in fair agreement with the facts since the reaction has been reported to proceed past 99% reaction at room temperature (cis–trans contents of reactants and products not determined).[23] According to D for the *n*-butylsulfonyl group, however, the reaction should

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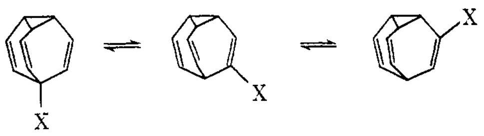
[40] D. H. McDaniel and H. C. Brown, *ibid.*, 23, 420 (1958).

go only 82% to completion at 25° if D for methylsulfonyl is the same as for n-butylsulfonyl. Our belief that the two D values should be similar makes us suspect experimental error. Both studies of sulfones appear to be reliable, but it may be significant that the 1-n-butylsulfonylbutenes were analyzed on the basis of their relative reactivities toward bromine,[30] which is not as specific a method as might be desired.

The D values listed for the halogens are reflections of the fact that in the equilibrium between the allyl and *trans*-propenyl halides the propenyl isomer is markedly favored in the case of the fluoride, less favored in the case of the chloride, and only slightly favored in the case of the bromide.[21] These observations may seem anomalous when compared with data on the halobullvalenes.[41] In the case of chloro- and bromobullvalene, the vinyl-substituted compounds (**2** and **3**) are so stable that no other isomers were detected. However, in spite of the fact that there is only one bridgehead position compared to six vinyl positions, fluorobullvalene exists largely as the bridgehead isomer **1**. After allowing for statistical effects, bridgehead fluorobullvalene is about 1.5 kcal/mol more stable than one of the vinyl isomers (probably **2**) and 1.9 kcal/mol more stable than the other. Let us analyze this substituent effect in terms of bond contributions and interactions of bonds leading to a common atom, neglecting interactions across vinylene groups. In these terms the free energy of a bridgehead to vinyl isomerization of fluorobullvalene may be expressed as shown in eq 17. The analogous expression for the isomerization of allyl fluoride to *trans*-propenyl fluoride is eq 18, which may be combined with eq 17 to give eq 19. Values for the two parameters in eq 19 do not appear to have been determined, but there is no obvious reason why they should not be of a suitable order of magnitude to satisfy eq 19. (Γ_{CCF} is −4.14 kcal/mol.)[10] Hence it is not obvious that there is any conflict between the results obtained with fluorobullvalene and those obtained with allyl fluoride. It is interesting to note that, although diethyl oxaloacetate is 79% enolized, diethyl fluorooxaloacetate contains too little enol to detect.[42] On the other hand, ethyl acetoacetate is 8% enolized, whereas ethyl α-fluoroacetoacetate is 15% enolized (as is ethyl α-chloroacetoacetate).[43]



1 **2** **3**

$$B(\mathrm{C_d{-}F}) + B(\mathrm{C{-}H}) - B(\mathrm{C_d{-}H}) - B(\mathrm{C{-}F}) + \Gamma_{\mathrm{CC_dF}} - 3\Gamma_{\mathrm{C_dCF}} \sim 1.7 \text{ kcal/mol} \quad (17)$$

$$B(\mathrm{C_d{-}F}) + B(\mathrm{C{-}H}) - B(\mathrm{C_d{-}H}) - B(\mathrm{C{-}F}) - \Gamma_{\mathrm{C_dCF}} = 3.5 \text{ kcal/mol} \quad (18)$$

$$2\Gamma_{\mathrm{C_dCF}} - \Gamma_{\mathrm{CC_dF}} \sim -5.2 \text{ kcal/mol} \quad (19)$$

The tendency for electron-withdrawing substituents to destabilize double bonds, which has been noted before,[28,44] may be seen in the relative values of D listed in Table II for substituents that attach themselves *via* saturated carbon atoms: $n\text{-}C_nH_{2n+1} > CH_2OMe > CH_2CO_2Me$. Other factors are also important, however. The methoxy and fluoro substituents, in spite of being attached *via* highly electronegative atoms, are among the best double bond stabilizers. This is presumably a result of the electron delocalization arising from the overlap of the filled 2p orbitals of the substituent with the 2pπ systems of the carbon–carbon double bonds. Such overlap should be less efficient when the filled orbital of the substituent is 3p, as in the case of methylthio and chloro substituents, and indeed the D values for these substituents are smaller than for methoxy and fluoro in spite of the lesser electronegativity of the atoms *via* which the methylthio and chloro substituents are attached. Overlap of the 2pπ system of the substituent with that of the double bond must add to the double bond stabilizing abilities of the phenyl, carbomethoxy, nitro, and cyano substituents. The fact that the methylsulfonyl and methylsulfinyl groups are much poorer double bond stabilizers than the nitro and cyano groups, which are comparably strong electron withdrawers, suggests that interaction of these substituents with carbon–carbon double bonds leads to considerably less electron delocalization.

In spite of the plausibility of the preceding rationalization of the relative magnitudes of observed D values, it is not clear how such a rationalization in terms of the polar and electron-delocalizing properties of substituents could be developed into a quantitative correlation that would also cover such reversals of substituent effects as that which appears to take place with the halogen substituents in the bullvalene and allyl–propenyl rearrangements. This is but one of many possible illustrations of the fact that until we develop a satisfactory set of qualitative explanations and quantitative correlations for the energies of interactions of pairs of bonds to a common atom our rationalizations of structural effects on rates and equilibria will be quite incomplete.

To assess the utility of our D values, let us see how well the equilibrium constants from which they were determined may be calculated by the use of other schemes. Of the various additivity schemes for calculating thermochemical properties, the group contribution scheme of Benson and coworkers[11,45] may offer the best combination of detailed parameterization and applicability to a wide range of compounds. In terms of these group contributions D_X may be expressed as shown in eq 20, in which [X–(C)] and [X–(C$_d$)] should be taken to include any additional contributions made necessary by the nature of X. Only for hydrocarbon substituents are all the required group contributions to the enthalpy and entropy available. For methyl, ethyl and higher primary alkyl, isopropyl, and phenyl substituents, D values of 3.28, 2.98, 2.97, and 4.77 kcal/mol, respectively, may be calculated, all in reason-

$$D_X = [\mathrm{C_d{-}(H)_2}] + [\mathrm{C{-}(C_d)(X)(H)_2}] + [\mathrm{X{-}(C)}] - [\mathrm{C{-}(H)_3(C_d)}] - [\mathrm{C_d{-}(H)(X)}] - [\mathrm{X{-}(C_d)}] \quad (20)$$

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[41] J. F. M. Oth, R. Merényi, H. Röttele, and G. Schröder, *Tetrahedron Lett.*, 3941 (1968).

[42] W. D. Kumler, E. Kun, and J. N. Shoolery, *J. Org. Chem.*, 27, 1165 (1962).

[43] J. L. Burdett and M. T. Rogers, *J. Amer. Chem. Soc.*, **86**, 2105 (1964).

[44] R. W. Taft, Jr., and M. M. Kreevoy, *ibid.*, **79**, 4011 (1957).

[45] S. W. Benson, *et al.*, *Chem. Rev.*, **69**, 279 (1969).

able agreement with the values in Table II. Most of the required group contributions to the entropy are missing for methoxy and methylthio substituents, but enthalpy components of *D* of 8.44 and 2.87 kcal/mol, respectively, may be calculated. The latter value is near ours, but unless there is a remarkably large entropy contribution (11 eu) the value for methoxy is significantly larger than ours. For none of the other substituents are there enough parameters even to calculate the enthalpy component of *D*.

Electrophilic Substitution at Saturated Carbon. LI. Varieties of Pathways for Substituted-Ammonium Carbanide Ion Pairs to Reorganize[1]

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Abstract: The stereochemical capabilities in *tert*-butyl alcohol of tertiary substituted-ammonium 3-*tert*-butyl-1-methylindenyl ion pairs have been examined. Changes in charge distribution in the protonated tertiary amine change the fate of the ion pair. Treatment of (−)-(*R*)-3-*tert*-butyl-1-methylindene ((−)-**1**-*h*) in *tert*-butyl alcohol-*O*-*d* (ROD) or (−)-(*R*)-3-*tert*-butyl-1-deuterio-1-methylindene ((−)-**1**-*d*) in *tert*-butyl alcohol-*O*-*h* (ROH) with triethylenediamine (TDA) or pentamethylguanidine (PMG) gave several reactions. Hydriodides of the tertiary bases were present in representative runs. Careful kinetics were studied for PMG-catalyzed isomerization of **1** to **2** and of racemization of equilibrated (−)-**1**-*h* and (+)-**2**-*h* in ROH. The results suggested the following conclusions. (1) For **1**-*h* in ROD, the rate of isomerization exceeds that of racemization of the system by factors of 24–53 with the charge-delocalizing base (PMG), but by a factor of 4×10^4 with the charge-localizing base (TDA). (2) For **1**-*h* and **2**-*h* in ROD, PMG produced a dominant isoinversion component, whereas TDA produced a less dominant isoinversion component. (3) The isoinversion components were demonstrated to be due neither to a carbanion–carbon acid proton transfer nor to concerted thermal isomerizations with PMG as base. (4) The *suprafacial*, base-catalyzed isomerization reaction of (−)-**1**-*h* to (+)-**2**-*h* occurs by a conducted tour mechanism by the amine of the proton along the π face of the anion from the 1 to the 3 position, where collapse to the covalent state occurs. (5) The slower isoinversion reaction (*antarafacial*, intramolecular proton transfer) passes through a relatively nonstructured, achiral contact ion pair of higher energy than the structured ion pair of the conducted tour mechanism. (6) The dominant isotope effects of the system are in collapse of contact ion pairs to **2**, and in isotopic drowning of the amine's conjugate acid in the medium.

Earlier work demonstrated that charge-delocalizing tertiary amines such as pentamethylguanidine (PMG) or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) affected the reactions of carbon acids differently from charge-localizing tertiary amines such as triethylenediamine (TDA).[2] In *tert*-butyl alcohol, 2- and 3-substituted 9-methylfluorene systems underwent PMG- and DBN-catalyzed isoinverson reactions in the absence of "conducted tour" functional groups. The data pointed to a nonstructured, contact ion-pair mechanism for isoinversion, with charge delocalization in both cation and anion. With TDA or tripropylamine as bases, isoinversion was observed only when the negative charge of the carbanion could be distributed by resonance on electronegative atoms, and a conducted-tour mechanism for isoinversion through contact ion pairs was available. In the absence of such groups, these charge-localizing tertiary amines largely gave racemization with isotopic exchange, presumably through solvent-separated ion pairs. A small bias toward isotopic exchange with retention was detectable, however. In the latter systems, invisible, but dominant, reactions of ionization and collapse to starting material seemed probable based on isotope effects, and on the fact that introduction of traces of secondary amine into the tertiary amine led to isotopic exchange with high retention of configuration.[2]

In the present study, the behavior of (−)-(*R*)-3-*tert*-butyl-1-methylindene ((−)-**1**-*h*)[3] in *tert*-butyl alcohol-*O*-*d* or (−)-(*R*)-3-*tert*-butyl-1-deuterio-1-methylindene[3a,b] ((−)-**1**-*d*) in *tert*-butyl alcohol-*O*-*h* with tertiary amines was examined. These hydrocarbons provide many advantages for mechanistic study. (1) Isotopic exchange, rearrangement, and racemization reactions catalyzed by amine bases occur in a variety of solvents without side reactions at convenient temperatures.[3] (2) The absolute configurations and maximum rotations of **1** and **2** are known.[3b,4] (3) The equilibrium constants between starting olefin **1** and the product **2** of allylic rearrangement are known at 25° (7.5), 48° (6.6), and 102° (6.0).[3b] (4) Isomers **1** and **2** can be separated by glc without thermal reac-

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(1) This investigation was supported by the U. S. Public Health Service Research Grant No. GM 12640-06 from the Department of Health, Education, and Welfare.

(2) K. C. Chu and D. J. Cram, *J. Amer. Chem. Soc.*, **94**, 3521 (1972).

(3) (a) J. Almy, R. T. Uyeda, and D. J. Cram, *ibid.*, **89**, 6769 (1967); (b) J. Almy and D. J. Cram, *ibid.*, **91**, 4459 (1969); (c) A. Weidler, *Acta Chem. Scand.*, 17, 1798 (1963); (d) A. Weidler and G. Bergson, *ibid.*, **18**, 1484 (1964).

(4) In ref 3b, the sign of rotation is coupled with the correctly drawn configuration for (+)-**2**, but (+)-**2** and its two precursors are incorrectly labeled *S*; they should have been labeled *R*. We thank Professor W. Klyne for calling our attention to this error.