and in that of aldehydes by the aprotic donors. Anyway, the relative strength of the coordinating power of hydrogen donors and hydrogen acceptors is one of the important factors to control the reaction mechanisms of transfer hydrogenations.

In the reduction at 80 °C in bromobenzene, tetralin, 1,2-dihydronaphthalene, and 1,4-dihydronaphthalene reduced n-hexaldehyde at the initial rate of 3.2, 8.5, and 2.5×10^{-3} mol $\mathrm{l.}^{-1}$ min^{-1}, respectively. 1,4-Dihydronaphthalene showed the lowest reduction rate, and the rate of the isomerization to 1,2-dihydronaphthalene was far higher than that of the reduction of the aldehyde. We formerly considered that the driving force of the hydrogen transfer from tetralin was the increase of the aromatization energy caused by the formation of naphthalene. However, the dehydrogenation rate of dihydronaphthalenes was not so much higher than that of tetralin. Moreover, it was found that the main product in the earlier stage of the reduction of aldehydes by tetralin was not naphthalene but 1,2-dihydronaphthalene. These results show that the driving force of the hydrogen-donating ability of tetralin was not derived from the stabilization by the aromatization. We now consider that the hydrogen donating abilities of the aprotic donors examined were affected by the stabilities of the cationic intermediates.

Experimental Section

All the transfer hydrogenations and kinetic measurements were carried out by the method reported previously.[3,5,6,8,10]

Materials. Chlorotris(triphenylphosphine)rhodium(I),[12] dichlorotris(triphenylphosphine)ruthenium(II),[13] hydridotetrakis(triphenylphosphine)rhodium(I),[14] and dihydridotetrakis(triphenylphosphine)ruthenium(II)[14] were prepared by methods reported in the literature. Aldehydes were purified by distillation followed by dehydration with molecular sieves. Tetralin, indan, 1,2-dihydronaphthalene, and dioxane were purified by distillation and dried by usual methods. All solvents were purified by distillation. 1,4-Dihydronaphthalene and 3,4-dichloroethylbenzene were synthesized by methods of Cook[15] and Marvel,[16] respectively.

Registry No.—Cycloheptene, 628-92-2; hexyl alcohol, 111-27-3; dihydridotetrakis(triphenylphosphine)ruthenium(II), 19529-00-1.

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A Survey of Structural Effects on Formation Constants in C–H Hydrogen Bonding[1]

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Formation constants, K, for the association of a variety of C–H donors with HMPA have been measured by application of Higuchi's iterative method to ^{1}H NMR data for CCl_4 solutions at 35 °C. Infrared shifts have been measured using $Me_2SO\text{-}d_6$ in CCl_4 or $CDCl_3$. The donors include sp^3, sp^2, and sp systems. As previously reported, K's correlate so poorly with ir shifts that the latter have no predictive value as to the strength of H-bond complex formation for C–H donors. The largest K's are found in sp^3 systems because of the possibility of three electronegative α substituents. K's for terminal acetylenes are more sensitive to their single β substituent, covering a range of at least 100-fold. K's are reported for the first time for vinyl and aromatic C–H bonds; those for the latter are small. Substituents affect K values for sp^3 systems in the order $CN \simeq NO_2 > SCN, p\text{-}O_2N\text{-}C_6H_4 > F, Cl, Br > CONMe_2 > CO_2R \geq C_6H_5$, which differs markedly from that observed for Bronsted proton transfer in solution. Similar orders are followed in the sp^2 and sp series. Substituent effects are only crudely correlated by Taft σ_I constants. It is suggested that substituent effects in C–H hydrogen bonding reflect a greater contribution from the through-bond inductive effect than in other systems.

The participation of C–H bonds in hydrogen bonding has long been recognized, as for chloroform and terminal acetylenes.[2] Their hydrogen bonds with strong acceptors, such as pyridine and Me_2SO, as well as with weaker ones such as acetone, are readily detected by ir and ^{1}H NMR spectral shifts. A detailed survey of ir shifts by Allerhand and Schleyer,[3] utilizing fully deuterated Me_2SO and pyridine, has shown clearly that certain vinyl and aromatic C–H bonds also undergo hydrogen bonding, and that shifts for saturated systems are enhanced much more by an α-cyano group than by α-

chlorine or α-bromine. Some studies by ^1H NMR have been carried out, but these were restricted to haloforms and related polyhalides[4] and phenylacetylene.[5] Formation constants have been reported for very few donors.

The available data raise questions about the extent of hydrogen bonding by C–H bonds which can only be answered with formation constants. How is hydrogen bonding ability affected by hybridization at carbon? Is there any correlation between ir shifts and formation constants? Does an increase in the ir shift due to an α-cyano group in fact signal an increase in the formation constant, and if so, do any other substituents, especially nitro, rival cyano in their effect on C–H hydrogen bonding ability? What is the order of substituent effects, and what factors determine this order?

We have previously reported[6] formation constants for several donors with the strong acceptor hexamethylphosphoramide (HMPA) in CCl_4 at 35 °C. We found the constants, or K's, to fall in the order $Br_2CHCN \sim F_2CHCN > HCCl_3 > Cl_2C{=}CHCl \sim C_6H_5C{\equiv}CH$ and to fail completely to correlate with ir shifts, $-\Delta\bar{\nu}$.

We shall here present more precise formation constants for a greater variety of donors, and discuss the effects of substituents and hybridization on these.

Results

Infrared Shifts. Infrared shifts, $-\Delta\bar{\nu}$, have been measured for a few compounds using 1.0 M $Me_2SO\text{-}d_6$ in CCl_4 or $CDCl_3$ in well matched 0.5 or 1.0 mm sodium chloride cells. The values, in cm^{-1}, are reported in Tables I and II along with those previously measured.[6] $Me_2SO\text{-}d_6$ has been used for the sake of continuity with the work of Allerhand and Schleyer,[3] because the preparation of HMPA-d_{18} would probably be costly out of proportion to its usefulness, and because the few K's which we have measured by ^1H NMR using Me_2SO are reasonably proportional to K's for HMPA. Deuterium labeled acceptors are necessary in ir work to prevent the C–H stretching region from being rendered opaque by the more concentrated acceptor.

Measurement of Formation Constants. Two modifications have been introduced into our procedure for measuring hydrogen bond formation constants. The first, allowing a great improvement in the precision of δ, is the use of internal lock combined with sidebanding and frequency counting equipment. These features were absent from the spectrometer previously available to us.

The second modification is the Higuchi iterative method[7] of calculating K, involving eq 1, which is derived without any simplifying approximations for 1:1 complexing only. The advantages of the Higuchi method are that it is convergent, it is readily adaptable to digital computer programming, and it permits the easy identification of divergent data points.

$$\frac{C_b}{\delta_{obsd} - \delta_a} = \frac{C_a + C_b - C_c}{\delta_c - \delta_a} + \frac{1}{K(\delta_c - \delta_a)} \qquad (1)$$

In eq 1, C_a and C_b are total concentrations of acid (donor) and base (acceptor), respectively, and C_c that of 1:1 complex, δ_{obsd} is the chemical shift of donor in the presence of acceptor at concentration C_b, δ_a the shift of donor in the absence of acceptor, δ_c the (usually hypothetical) shift of the complexed proton, and K the formation constant.

Equation 1 is applied by plotting the left side vs. $(C_a + C_b)$; the slope is used as an approximation to $1/(\delta_c - \delta_a)$ for calculation of trial values of C_c via eq 2, and a second plot, using $(C_a + C_b - C_c)$, is constructed, giving an improved value of $1/(\delta_c - \delta_a)$.

$$C_c = C_a \frac{\delta_{obsd} - \delta_a}{\delta_c - \delta_a} \qquad (2)$$

This cycle of calculations and plots is repeated until the slope remains constant within desired limits. The final plot is examined, deviant points rejected, the iterative procedure repeated, and finally $(\delta_c - \delta_a)$ and K calculated (from eq 1, K = slope/intercept).

In the present study, the Higuchi method has given plots of excellent linearity in most cases for which $K \geq 1.0\ M^{-1}$, and acceptable plots for $0.2 \leq K \leq 1.0$. In some cases, e.g., phenyldinitromethane, the Higuchi method succeeded where the previous method[1,6] had failed,[1] viz., calculating K for a wide range of trial values of $(\delta_c - \delta_a)$ and choosing that value for which the K's had the smallest percent standard deviation. In other cases it gave results in good agreement with those of the other method. The Higuchi method failed only for very weak donors giving small shifts, e.g., *tert*-butylacetylene and 1,3,5-trichlorobenzene, and, as indicated above, where K was much less than $0.2\ M^{-1}$.

Attempts to determine K's much smaller than $0.2\ M^{-1}$ by using higher HMPA concentrations than 1.5 M usually led to curvature of Higuchi plots. This is a reasonable consequence of the effect on chemical shift of changing bulk diamagnetic anisotropy. In the case of *tert*-butylacetylene, this effect was so marked that the Higuchi plot actually had a negative slope. Although good plots were obtained for phenylacetylene in both CCl_4 and cyclohexane, $\delta_c - \delta_a$ was twice as great in CCl_4 (4.0 vs. 2.0 ppm in cyclohexane). For donors with larger K's, $\delta_c - \delta_a$ values were more nearly the same in the two solvents. The results for phenylacetylene in CCl_4 are therefore also rendered unreliable because of the bulk anisotropy effect.

The principal limitation of the Higuchi method is its restriction to 1:1 complexing. It is desirable to overcome this limitation, since certain compounds with two or more protons are of considerable interest, e.g., malononitrile and fumaronitrile, typical of disubstituted methanes and ethylenes. We believe that we have approached success in these two cases, by the simple expedient of repeating the measurements at the lowest concentrations consistent with observation of the proton resonance, thus minimizing the concentration of 2:1 complex. Indeed, the plots were linear, although they had been concave down at higher concentrations, $C_a \sim 0.1$ M and $0.1 < C_b < 1.0$ M. The K's were much greater than before (cf. Tables I and II; previous values were, malononitrile, ca. 10 M^{-1}, and fumaronitrile, 3.0 M^{-1}) and $\delta_c - \delta_a$ values were much smaller.

Conceivably a further reduction in concentration would further increase the K's. Evidence that this might *not* be so was obtained for malononitrile by measuring K_2 and using it to estimate the concentration of 2:1 complex in dilute solutions. A K value of 60 M^{-1} (Table I) implies that at 1.0 M HMPA, 0.1 M malononitrile is ca. 98% complexed. Using δ_c measured for the 1:1 complex as "δ_a" for the 2:1 complex, data for four points from 1.29 to 3.06 M HMPA gave a linear plot and $K_2 = 0.20 \pm 0.01\ M^{-1}$;[8] denoting the chemical shift of the 2:1 complex as δ_c', $\delta_c' - \delta_c$ was 1.8 ppm. From these values of K_1 and K_2 we estimate that at 1.0 M HMPA and ca. 0.1 M malononitrile, about 20% of the donor is present as 2:1 complex, but less than 2% at 0.1 M HMPA and 0.02 M malononitrile.

Measured Formation Constants. Tables I and II present data for C(sp^3)–H donors and for C(sp^2)–H and C(sp)–H donors, respectively, all with HMPA in CCl_4 at 35 °C. Table III presents data for a few donors with acceptors other than HMPA. Figures 1 and 2 show Higuchi plots for several representative donors with HMPA in CCl_4, having either high or low K values. As noted above, linearity is excellent, although some scatter is evident when K is low. Standard deviations determined in several cases are included in Tables I–III. A more crucial measure of precision is of course the reproducibility of the K values. Three separate runs with Br_2CHCN and two runs with chloroform, shown in Table I, gave such

Table I. Formation Constants of C(sp^3)–H Donors with HMPA in CCl_4 at 35 °C

Registry no.	Donor, AH	[AH], M	Range of [HMPA], M	No. of points	$\delta_c - \delta_a$ obsd, ppm	K, M^{-1}	$-\Delta\bar{\nu}$, cm^{-1}
67-66-3	$HCCl_3$	0.03	0.03–0.3	7	1.79	2.35	29[a]
		0.10	0.5–1.5	3	1.83	2.12	
75-25-2	$HCBr_3$	0.10	0.1–0.8	7	1.71	2.0	50[a]
75-95-6	Br_3CCHBr_2	0.10	0.2–0.9	7	1.81	1.12 ± 0.03	58[a]
74-95-3	CH_2Br_2	0.10	0.2–1.5	7	0.77	0.68	3, 11[a]
618-31-5	$C_6H_5CHBr_2$	0.11	0.2–1.0	6	1.60	0.68 ± 0.03	
619-75-0	p-$O_2NC_6H_4CHBr_2$	0.10	0.2–1.2	7	1.33	5.54 ± 0.15	
359-12-6	F_2CHCN	0.13	0.2–1.0	7	1.25	10.7	0
3018-12-0	Cl_2CHCN	0.12	0.1–0.8	7	2.08	20.6 ± 1.1	66
3252-43-5	Br_2CHCN	0.09	0.1–1.0	7	2.21	17.3	80[a]
		0.10	0.1–1.0	5	2.23	16.0	
		0.23	0.2–1.2	7	2.22	16.2	
107-14-2	$ClCH_2CN$	0.03	0.05–0.3	7	0.76	4.6	15[a]
4553-07-5	$C_6H_5CH(CN)CO_2Et$	0.05	0.2–1.6	7	1.70	1.30	
109-77-3	$CH_2(CN)_2$	0.02	0.03–0.14	7	0.98	60.0 ± 0.6	45, 75[b]
1885-22-9	$BrCH(CN)_2$	0.05	0.08–0.3	7	2.86	205	123
598-91-4	Br_2CHNO_2	0.25	0.1–1.0	6	1.98	10.3	80
611-38-1	$C_6H_5CH(NO_2)_2$	0.03	0.03–0.27	6	1.88	28.8	0
5468-76-8	$Cl_2CHCONMe_2$	0.09	0.1–1.0	4	1.48	1.44 ± 0.01	
116-54-1	Cl_2CHCO_2Me	0.08	0.1–1.0	4	1.75	0.68 ± 0.02	26[a]
6317-18-6	$CH_2(SCN)_2$	0.05	0.4–0.7	4	0.875[c]	8.2 ± 0.6[c]	15
6262-51-7	c-C_3HCl_5	0.10	0.2–1.0	7	3.00	0.59 ± 0.03	88[a,d]

[a] Reference 3. [b] C–H stretch band a doublet in pure $CDCl_3$, but broad singlet in presence of Me_2SO-d_6. [c] In CS_2; donor insoluble in CCl_4; in CS_2, Br_2CHCN had $K = 20.7 \pm 1.6$ M^{-1}. [d] Pyridine-d_5 as acceptor.

Table II. Formation Constants of C(sp^2)–H and C(sp)–H Donors with HMPA in CCl_4 at 35 °C

Registry no.	Donor, AH	[AH], M	Range of HMPA, M	No. of points	$\delta_c - \delta_a$, obsd, ppm	K, M^{-1}	$-\Delta\bar{\nu}$, cm^{-1}
598-16-3	$Br_2C{=}CHBr$	0.1	0.2–1.5	5	2.20	0.23	40[a]
79-01-6	$Cl_2C{=}CHCl$	0.1	0.2–1.4	7	2.70	0.27	41[a]
764-42-1	E-$NC\text{-}CH{=}CHCN$ (fumaronitrile)	0.015	0.04–0.25	7	0.90	14.5	45
123-06-8	$C_2H_5OCH{=}C(CN)_2$	0.05	0.2–1.0	7	1.38	18.1	55
4786-24-7	$(CH_3)_2C{=}CHCN$	0.2	0.5–2.0	4	0.90	0.26	
1885-38-7	E-$C_6H_5CH{=}C\mathbf{H}CN$ (α)	0.1	0.5–2.0	5	1.10	1.24	
				7	1.13	1.12	
5153-67-3	E-$C_6H_5CH{=}C\mathbf{H}NO_2$ (α)	0.1	0.5–2.0	7	0.97	1.06	
	E-$C_6H_5C\mathbf{H}{=}CHCN$ (β)	0.1	0.5–2.0	5	0.32	0.66	
				7	0.18	1.25	
	E-$C_6H_5C\mathbf{H}{=}CHNO_2$ (β)	0.1	0.5–2.0	4	0.36	1.24	
108-70-3	1,3,5-$C_6H_3Cl_3$	0.25	0.2–3.0			b	27
95-94-3	1,2,4,5-$C_6H_2Cl_4$	0.25	0.5–1.5	4	2.20	0.073	40[a]
	1,2,4,5-$C_6H_2Cl_4$	0.1	0.7–1.8	5	1.02[c]	0.59[c]	40
608-93-5	C_6HCl_5	0.05	0.7–2.0	4	3.07	0.092	
				5	3.40	0.085	
	C_6HCl_5	0.05	0.5–2.0	7	1.57[c]	0.69[c]	
				5	1.60[c]	0.66[c]	
117-18-0	3-NO_2-1,2,4,5-C_6HCl_4	0.05	0.1–1.0	6	1.81	0.49	45[a,d]
327-54-8	1,2,4,5-$C_6H_2F_4$	0.05	0.3–1.0	5	1.27	0.45 ± 0.01	50
	1,2,4,5-$C_6H_2F_4$	0.025	0.1–0.3	3	1.11[c]	2.58[c]	50
917-92-0	t-$BuC{\equiv}CH$	0.1	0.2–2.0			e	82[a,f]
536-74-3	$C_6H_5C{\equiv}CH$	0.23	0.25–1.7	7	4.0	0.15 ± 0.02	105
106-96-7	$BrCH_2C{\equiv}CH$	0.08	0.6–1.4	5	2.09	0.53 ± 0.01	102[a]
623-47-2	$C_2H_5O_2CC{\equiv}CH$	0.1	0.3–0.85	4	2.69	1.66 ± 0.02	
1070-71-9	$NCC{\equiv}CH$	0.08	0.3–1.0	7	3.08	12.1 ± 0.6	155

[a] Reference 3. [b] Too small to measure; plot scattered. [c] In cyclohexane solvent. [d] With 2 M pyridine-d_5 in CCl_4. [e] Too small to measure; Higuchi plot had negative slope. [f] Reported for 1-hexyne.

good agreement that runs with other compounds were not repeated unless the Higuchi plot showed excessive scatter or curvature.

Inspection of the K values of Tables I–III reveals several regularities. Chloroform and bromoform have nearly equal constants, as reported previously for THF in cyclohexane;[4] the three dihalonitriles studied also have similar K's within a factor of 2. All the nitriles have sizable K's, as do both nitro compounds of Table I. The constant for bromomalononitrile is the largest one known to us for C–H bonds, and is consistent with K's for other α-bromo and α-cyano compounds. Trichloro- and tribromoethylene have similar K's.

Substituent effects in the sp^3 series are consistent, since the effects of substitution of certain groups for others, evaluated

Table III. Formation Constants with Various Acceptors and Solvents at 35 °C

Donor	Acceptor	Solvent	No. of points	$\delta_c - \delta_a$, ppm	K, M^{-1}
$HCCl_3$	HMPA	CCl_4	7	1.79	2.35
	HMPA	c-C_6H_{12}	7	1.90	12.0
$HCCl_3$	Me_2SO	CCl_4	7	1.01	0.94
Br_2CHCN	HMPA	CCl_4	5–7	2.22[a]	16.5[a]
Br_2CHCN	Me_2SO	CCl_4	5	1.26	5.58
Br_2CHCN	DMF	CCl_4	7	1.23	3.59
Br_2CHCN	HMPA	c-C_6H_{12}	6	2.39	70.6
Br_2CHCN	HMPA	CS_2	7	2.22	20.7
Br_2CHCN	HMPA	Benzene	6	4.50	6.20
$CH_2(CN)_2$	HMPA	CCl_4	7	0.98	60
$CH_2(CN)_2$	Acetone	CCl_4	6	0.48	3.39 ± 0.04
$CH_2(CN)_2$	DMF	CCl_4	3	0.56	11.4 ± 0.23
$C_6H_5CH(CN)_2$[b]	Acetone	CCl_4	4	0.92	1.70 ± 0.03
$C_6H_5CH(CN)_2$[b]	DMF	CCl_4	6	1.25	5.28
$C_6H_5CH(NO_2)_2$	Acetone	CCl_4	7	0.89	1.69 ± 0.02

[a] Mean of three runs; cf. Table I. [b] Registry no., 3041-40-5.

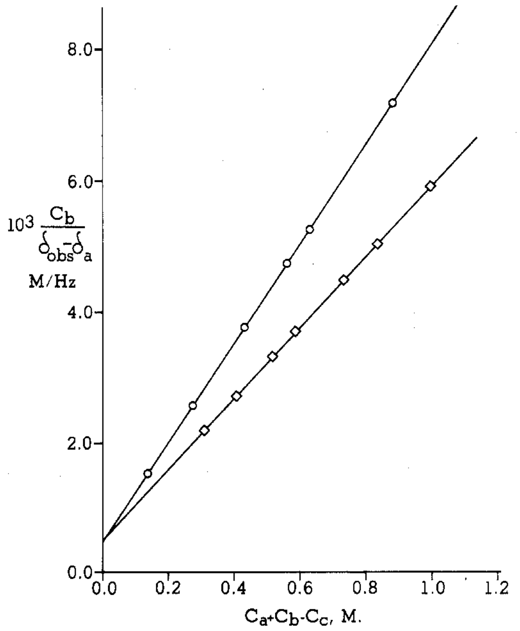

Figure 1. Higuchi plots for "strong" donors with HMPA in CCl_4, 35.0 °C: ○, Br_2CH-CN, c 0.09 M; ◇, H–C≡C–CN, c 0.08 M. The coincidence of the intercepts is not significant.

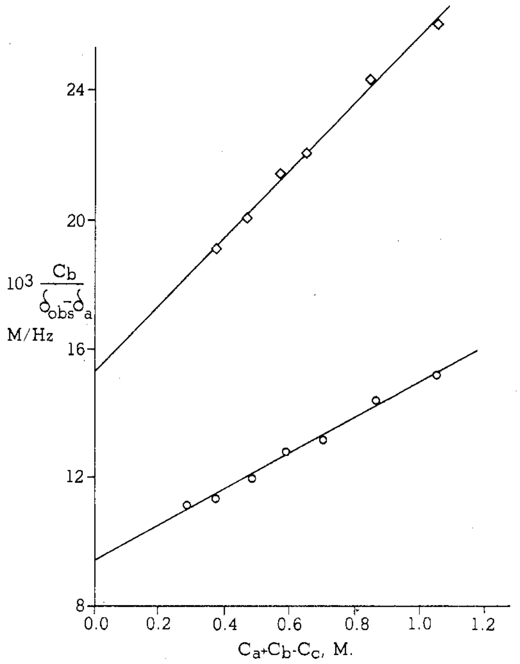

Figure 2. Higuchi plots for "weak" donors with HMPA in CCl_4, 35.0 °C: ○, pentachlorocyclopropane, c 0.10 M; ◇, $PhCHBr_2$, 0.11 M.

in more than one way and tabulated in Table IV, are in fair to good agreement. In these comparisons, $ClCH_2CN$ is used as a model for $BrCH_2CN$, as justified by the similarities of other Cl-Br analogues; K is divided by two for disubstituted methanes to correct for the presence of two C–H bonds.

Certain regularities in $\delta_c - \delta_a$ values also appear: thus, for dibromomethane, the observed value of 0.77 ppm is essentially one-half of that for benzal bromide ($C_6H_5CHBr_2$), 1.60 ppm, as expected if only one of the two protons of the former is complexed and if the effect of phenyl on δ_c is the same as on δ_a. (The dibromomethane experiment was not repeated at lower concentrations, as K was much smaller than for malononitrile.) A similar relationship holds for malononitrile and phenylmalononitrile with both acetone and DMF as acceptors. (We were unable to measure K for phenylmalononitrile and HMPA, as the proton resonance always broadened and disappeared in the presence of HMPA. A small amount of proton transfer, forming ion pairs, may have taken place at a net rate comparable to the relaxation time.)

Our results can be compared with previously reported results of other workers evidently only in the single case of chloroform–HMPA. Drago and co-workers[9] report $K = 15.0$ M^{-1} at 29.0 °C in cyclohexane. Extrapolation to 35.5 °C using $\Delta H° = -5$ kcal/mol gives $K = 13.0$ M^{-1}. We subsequently obtained $K = 12.0$ M^{-1}, in good agreement, and $\delta_c - \delta_a = 1.90$ ppm, in excellent agreement with 1.92 ppm reported by Drago et al. The anomalously large value of K in cyclohexane as compared to CCl_4 has now been observed for several donors of widely differing K's, and is under investigation.

Discussion

The data presented in Tables I–III contain enough regularities to inspire confidence in their validity, but they contain several significant surprises. The ensuing discussion will focus exclusively on equilibrium constants, in which we are principally interested. Absolute values of $\delta_c - \delta_a$ are of unknown significance at this point, except for a crude trend to higher values where K values are large.

Formation Constants and Infrared Shifts. First, our results confirm our previous observation that K and $-\Delta\bar{\nu}$ are not correlated for C–H bonds generally, and only vaguely within a group, e.g., the C(sp^3)–H series. Two donors with

Table IV. Effect of Substituent Changes on K for $C(sp^3)$–H Systems

New group	Group replaced	Compds compared	K values[a]	Ratio of K's
CN	Br or Cl	$CH_2(CN)_2/ClCH_2CN$	30./2.3	13.0
CN	Br or Cl	$Br_2CHCN/HCBr_3$	16.5/2.0	8.3
CN	Br or Cl	$BrCH(CN)_2/Br_2CHCN$	205/16.5	12.4
Br	H	$Br_2CHCN/ClCH_2CN$	16.5/2.3	7.2
Br	H	$BrCH(CN)_2/CH_2(CN)_2$	205/30.	6.8
Br	H	$HCBr_3/CH_2Br_2$	2.0/0.34	5.9
CN	H	$BrCH(CN)_2/ClCH_2CN$	205/2.3	89
CN	H	Br_2CHCN/CH_2Br_2	16.5/0.34	49
NO_2	H	Br_2CHNO_2/CH_2Br_2	10.3/0.34	30

[a] Cf. Table I.

large K's, F_2CHCN and $PhCH(NO_2)_2$, have $-\Delta\bar{\nu} = 0$; phenylacetylene and pentachlorocyclopropane have small K's but large values of $-\Delta\bar{\nu}$. Bromomalononitrile, with the largest K, 205 M^{-1}, has a smaller $-\Delta\bar{\nu}$ than cyanoacetylene, $K = 12\ M^{-1}$, although the latter value is large for an acetylene. Figure 3 is a plot of log K vs. $-\Delta\bar{\nu}$ for the $C(sp^3)$–H donors studied; it is little better than a scatter diagram in which scarcely any trend is discernible. Factors which perturb the C–H bond and cause the observed shift must be related in a complex way to those which determine $-\Delta F°$, i.e., log K. It is clear that infrared shifts may not be used to make predictions about the magnitude of the formation constant.

Correlations of thermodynamic parameters with ir shifts were evidently first suggested by Badger and Bauer,[10] who did not expect generality. Subsequent work has confirmed such skepticism while revealing many examples of good correlations for limited ranges of donors or acceptors or both.[11] Several factors must contribute to the lack of correlation for C–H donors. One is that changes in the structure of the donor occur closer to the C–H bond than to the O–H bond in systems such as substituted phenols. Another is a fundamental difference between the ir and NMR methods: the ir shift is characteristic of a species of very definite structure (A–H and H–B distances and A–H–B angle), while the NMR measurement takes into account all possible interactions between A–H and B.

Substituents and Formation Constants. The effect of substituents on formation constants is qualitatively similar for the three main classes of C–H bonds, i.e., independent of hybridization. Thus, for the $C(sp^3)$–H series, the order is CN $\simeq$ NO_2 > SCN, p-O_2N-C_6H_4 > F, Cl, Br > $CONMe_2$ > CO_2R ≥ C_6H_5. This order is followed also in sp^2 and sp systems which have thus far been studied. The failure of K for Cl_2CHCO_2Me to rival that for Cl_2CHCN, or even greatly to exceed that for CH_2Br_2, was particularly unexpected.

These substituent effects are worth examining, since they may shed some light on the nature of the C–H H bond. We shall adopt a working model of the H bond which is consistent with the bulk of theoretical work carried out in recent years and discussed by, among others, Coulson,[12] Murrell,[13] and Kollman and Allen.[14] In valence bond terms, at least three structures, **1–3**, contribute to the H bond. Electrostatic attraction is represented by **2**, while **3** illustrates charge transfer. Repulsive and dispersion contributions are also important but are not represented by distinct structures here. The view is generally held that **2** is the dominant attractive contribution to weak, long H bonds. Structure **3** becomes important for stronger, shorter H bonds. Valence bond theory thus suggests localization of electrons on A, and results of MO calculations strongly support this view. According to Kollman and Allen, both B and A gain electrons, while H loses electrons; the gain by A is greater than that of B; atoms attached to B lose electrons, while those attached to A gain electrons. Apparently the only C–H system mentioned by Kollman and Allen is HCN: its dimer is said to have a long H bond (3.2 Å), for which the electrostatic model should work well.

$$\underset{\mathbf{1}}{A{-}H\cdots{:}B} \longleftrightarrow \underset{\mathbf{2}}{A{:}^- \ \overset{+}{H} \ {:}B} \longleftrightarrow \underset{\mathbf{3}}{A{:}^- \ H{-}B^+}$$

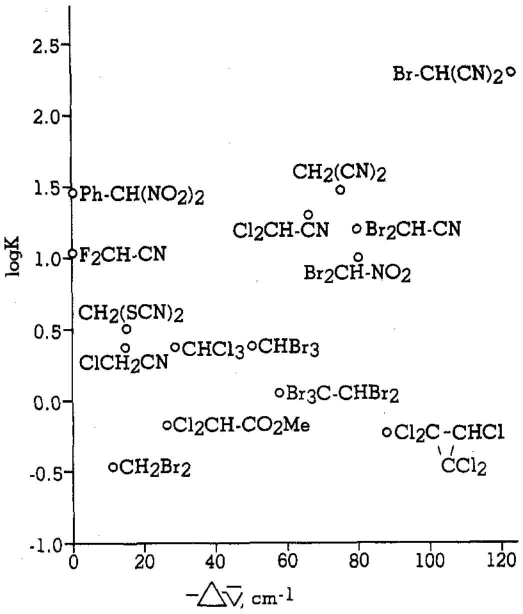

Figure 3. Relation between donor–HMPA formation constants (K's) and infrared C–H stretching wavenumber shifts.

Substituent effects on C–H H bonding can evidently arise in several ways: (1) interaction with the charge generated on A, which may be subdivided into field, σ-inductive, and delocalization (resonance) components; (2) electrostatic attraction between the electronegative B and the electropositive end of the substituent; (3) steric interference between B and bulky substituents on A.

It is doubtful that resonance effects in A–H are very significant.[32] If they were, the substituent order would more nearly resemble that in Bronsted acidity, in which lone pairs are fully formed and the effect of substituents may largely be explained by delocalization. In carbon acidity, NO_2 is much more effective than CN, and CO_2R only slightly less effective than CN. Thus, in aqueous solution, nitromethane and dinitromethane have pK_a's of ca. 10 and 4, respectively, while that of acetonitrile is estimated to be 25, of malononitrile 12, and diethyl malonate ca. 13.3.[15] Not too surprisingly, this suggests that in C–H H bonding the degree of charge redistribution toward carbon is modest.

The two principal nonconjugative effects, the σ-inductive and field effects,[16] are probably important in C–H H bonding. The separation of these effects has never been achieved;[16b] although there is conclusive evidence for the field effect[16c] and fairly good evidence for the σ-inductive effect, disagreements have arisen as to their relative importance.[17] Both effects are probably encompassed by the most successful measure of nonconjugative polar effects, the Taft σ_I constants.[18] These fall in the order Me_3N^+ > NO_2 > CH_3SO_2, CN > F, Cl, Br > I, OC_6H_5, CF_3 > CO_2Et, COMe > OCH_3, C_6H_5, which agrees with the H-bonding order with respect to CN vs. both NO_2 and carbonyl substituents. However, this correlation is qualitative, not quantitative, as shown by the scatter in Figure 4, a plot of log K vs. the sum of the σ_I constants for $C(sp^3)$–H donors. A line through the points for the dibromo- and dichloroacetonitriles, dibromomethane, and α,α-dibromotoluene gives a ρ value of ca. +2.7. It is noteworthy that other systems fail to correlate with σ_I, e.g., the substituent chemical shifts in ^{19}F

NMR spectra of maleic anhydride adducts of 10-substituted 9-fluoroanthracenes.[19]

The failure of the Taft correlation to be quantitative may be attributed to several causes. The first is that steric effects are important. This would account for several of the points in Figure 4 falling below the arbitrary line mentioned above. Second, there may be a different blend of σ-inductive and field effects than in the reactions used to define σ_I, and substituents may differ in their effectiveness by the two mechanisms. One theoretical conclusion given above, viz., that substituents on A gain electrons, is compatible with the σ-inductive effect in that gain of electrons by an electronegative group is energetically favorable. A third possible reason for failure of the correlation might be the increasing importance of charge transfer for the strongest C–H donors. A final and more troublesome reason is the fact that the NMR method measures all modes of interaction of A–H and B, not just those giving a linear, three-center hydrogen bond. The possible interactions may clearly vary uncontrollably with the substituent.

Substituent Effects in Unsaturated Donors. Substituent effects in the sp^2 and sp series are quite large, although we cannot yet evaluate these in as much detail as for the sp^3 series. Replacement of three halogens in the trihaloethylenes by two nitrile groups increases *K* by 54- to 63-fold. The size of *K* for fumaronitrile suggested study of analogues with only one cyano group, as well as a compound with a vinylic nitro group. From the *K*'s for β,β-dimethylacrylonitrile ($Me_2C{=}CHCN$) and the α proton of (*E*)-cinnamonitrile ($PhCH{=}CHCN$), one can see that the second cyano group of fumaronitrile is an important contributor to the size of its *K* (7.2 M^{-1} per proton). This is also evident from the large *K* of 18.1 M^{-1} for ethoxymethylenemalononitrile [$EtOCH{=}C(CN)_2$], which has only β-cyano groups. The effect of the nitro group in (*E*)-β-nitrostyrene ($PhCH{=}CHNO_2$) on the α proton is essentially identical with that of cyano in (*E*)-cinnamonitrile, consistent with results in the C(sp^3)–H series. The β-phenyl group evidently has a significant *K*-enhancing effect in both compounds, relative to β,β-dimethyl substitution in β,β-dimethylacrylonitrile. The results for the β protons of both cinnamonitrile and β-nitrostyrene are intriguing, both in the sizable *K*'s and the very small values of $\delta_c - \delta_a$. A study of the stereochemistry of the β-substituent effect, utilizing the *Z* isomers, as well as angelo- and tiglonitriles (*E*- and *Z*-$MeCH{=}CMeCN$, respectively) would be of interest, but the small shifts would complicate the interpretation.

The aromatic compounds studied provide good examples of the poor predictive powers of ir shifts, in view particularly of our failure to measure *K* for 1,3,5-trichlorobenzene. Even the *K*'s for 1,2,4,5-tetrachlorobenzene and pentachlorobenzene in CCl_4 are questionable since the $(\delta_c - \delta_a)$'s are more than twice as large as the values obtained in cyclohexane. Use of cyclohexane as solvent (vide supra) rendered these *K*'s readily measurable, and revealed the substituent effect orders 4-NO_2 > 4-Cl, and 1,2,4,5-F_4 > 1,2,4,5-Cl_4. One would thus expect 1,3,5-trinitrobenzene to show a sizable *K*, but curiously the chemical shift of its protons moves to *higher* field, rather than lower, in HMPA relative to CCl_4. We are currently investigating methylated analogues, e.g., TNT, to gain insight into this anomaly.

The effects of substituents on *K*'s for acetylenes are particularly impressive when one considers that only β substituents are possible, and only one of these. Replacement of phenyl by cyano increases *K* by nearly 100-fold, by carboethoxy, 11-fold, and even by γ-bromine, by threefold. From the fact that *K* for *tert*-butylacetylene was too small to measure, a phenyl group is *K* enhancing relative to alkyl. These observations are in quantitative contrast to those for C(sp^3)–H donors, and suggest that electrical effects are more effectively transmitted through a triple bond than a single bond. This is consistent with the greater polarizability of π than σ electrons, and suggests operation of the π-inductive effect, recently demonstrated by Fukunaga and Taft.[20] Although the π orbitals are of course orthogonal to the C–H bonding orbital, polarization of π electrons toward the substituent would reduce the net charge developed at the carbon atom by H bonding.

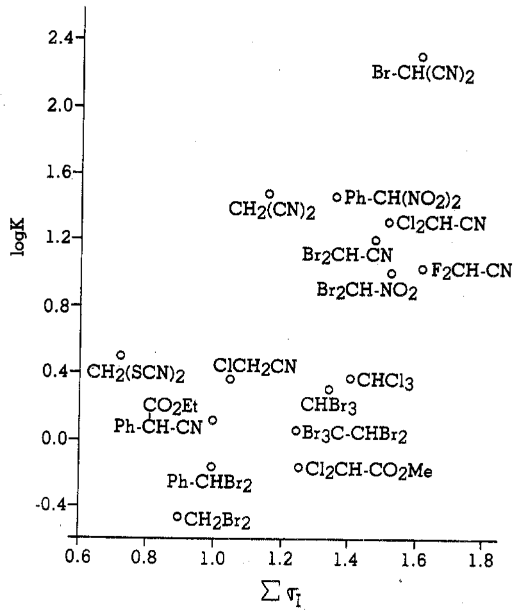

Figure 4. Relation between *K*'s and sum of Taft σ_I values (cf. ref 18).

Measurement of Small *K*'s. We close with mention of the problem that certain *K*'s proved too small to measure by means of our materials and techniques. One solution would be to find another acceptor even stronger than HMPA. Although tetraalkylammonium chlorides and bromides have much larger ir shifts than Me_2SO,[21] the measured *K*'s for chloroform with quaternary ammonium halides are reported to be nearly the same as for chloroform with HMPA.[22]

Another approach to measurement of small *K*'s is the method of Homer et al.,[23] who used Benesi and Hildebrand's data treatment method[24] to obtain *K*'s at acceptor mole fractions approaching unity. Such conditions eliminate uncertainties due to variation of bulk susceptibility with changing acceptor concentration. The method would be inapplicable to strong donors, which approach complete complexing at high acceptor concentration. Finally, the ir method may meet with greater success than NMR because of its greater sensitivity to low concentrations of complexed species, as well as its specificity to H bonding and freedom from the bulk anisotropy problem.

Experimental Section

Materials. Carbon tetrachloride and cyclohexane, reagent grade, were stored over Linde Type 4 molecular sieves. Hexamethylphosphoramide (HMPA), Aldrich Chemical Co., was generally used as received; for a few experiments it was vacuum distilled from benzenepentacarboxylic acid to remove any dimethylamine present; its water content was shown by Karl Fischer titration to be less than 6 mol %.[25] Most C–H donors were purchased as reagent grade materials and were used as received. Benzal bromide, $PhCHBr_2$, Aldrich, fumed in air; it was washed with aqueous sodium bicarbonate, then water, dried, and vacuum distilled before use. On standing a few days, it fumed again. Methylene bisthiocyanate, $CH_2(SCN)_2$, was kindly donated by the Stauffer Chemical Co.

Several nitriles were prepared by dehydration of the corresponding amides with P_2O_5; those amides not available commercially were prepared from the acid chlorides or methyl or ethyl esters. Difluoro-, dichloro-, and chloroacetonitriles and phenylmalononitrile were prepared in this way; their boiling or melting points agreed with reported values, and spectral data supported the assigned structures. Bromomalononitrile was prepared by the method of Freeman,[26] mp 64.8–65.2 °C (lit.[26] 64.5–65.1 °C). Dibromonitromethane was prepared by two-stage bromination of nitromethane,[27] bp 60 °C (13 Torr) [lit.[28] 52 °C (16 Torr)]. Phenyldinitromethane was prepared by oxidative nitration[29] of phenylnitromethane (α-nitrotoluene, K & K Chemicals); it had mp 75–77 °C (lit.[30] 78–80 °C). Pentachlorocyclopropane was prepared from trichloroethylene and dichlorocarbene (from sodium trichloroacetate) as described by Tobey and West,[31] bp 55 °C (10 Torr) [lit.[31] 56 °C (7 Torr)].

Infrared Spectra. Infrared spectra were recorded on a Perkin-Elmer Model 257 spectrophotometer, wavenumber accuracy ca. ±5 cm^{-1}, calibrated vs. polystyrene film. Values of $\tilde{\nu}$ were measured for ca. 0.1 M solutions in CCl_4 or $CDCl_3$ and again in the same solvent containing 1.0 M dimethyl sulfoxide-d_6. Cells, with NaCl windows, had path length either 1.0 mm, as used by Allerhand and Schleyer,[3] or 0.5 mm, and were well matched.

NMR Measurements. Solutions were prepared in 2-ml volumetric flasks by weighing the donor and acceptor, adding several drops of Me_4Si, and adding solvent to the mark. Some compounds, e.g., bromomalononitrile, were decomposed by neat HMPA; decomposition was prevented by adding ca. 1 ml of CCl_4 to the weighed donor before weighing the HMPA. Solutions were transferred to NMR tubes which were immediately stoppered and measurements were made within a few hours.

All chemical shifts were measured using a Varian T-60 spectrometer, probe temperature 35.5 °C, equipped with internal lock, Hewlett-Packard test oscillator Model 650A, and Beckman counter and timer Model 6155A. Me_4Si was employed for the lock signal. For each sample, the donor peak was centered on 100-Hz sweep width, the oscillator tuned to give a Me_4Si sideband null pattern first at the low field end of the scale, then at the high field end, and the period (1/frequency) of each pattern recorded. The chemical shift was calculated by solving a proportion among the frequencies of the null patterns and the distances between patterns and sample signal on the paper.

Formation Constants. These were calculated by the method of Higuchi et al.,[7] as outlined in the text. Least-squares refinement of plots for each iteration was aided by a Hewlett-Packard programmable calculator; iteration was carried out until $\delta_c - \delta_a$ was constant within ±0.1 Hz, not more than five cycles usually being required. Some data have also been treated using a FORTRAN IV program written by J.M.T. The resulting points were plotted; those points which were more than two standard deviations from the least-squares line were rejected; and the calculation was repeated. In most cases only one or two points of seven were rejected; with phenyldinitromethane one point diverged slightly from the line, the others appearing to lie precisely on the line. Points tended to scatter more the smaller K was; with 1,3,5-trichlorobenzene scatter was so severe as to permit values of K over a range of severalfold; with *tert*-butylacetylene the slope of the plot was negative (cf. text).

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