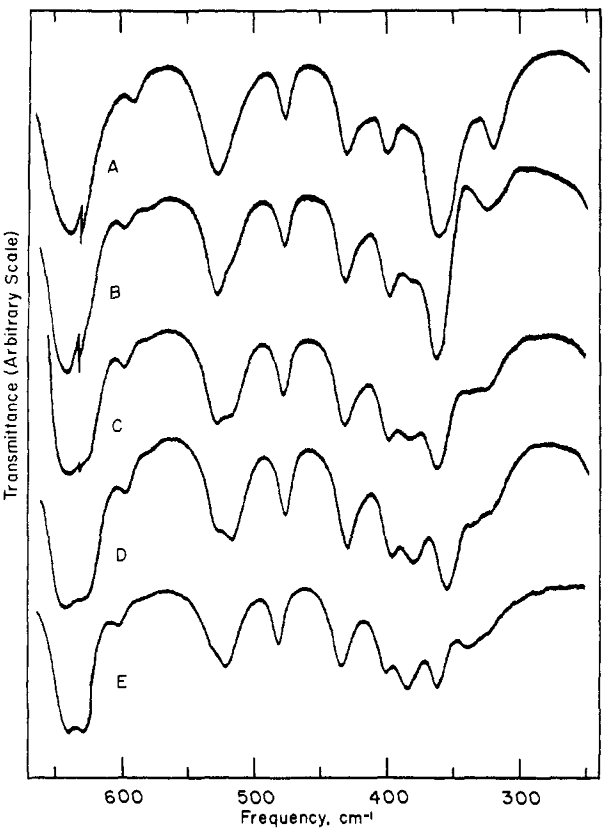

Figure 1. Far-infrared spectra of $V(dpm)_2Cl_2$ in (A) Nujol mull, (B) carbon tetrachloride, (C) benzene, (D) chloroform, and (E) dichloromethane. Solution spectra are arranged in order of increasing solvent dielectric constant. The discontinuities at ~630 cm^{-1} are due to a grating change.

band to be assigned to the cis isomer and the 362-cm^{-1} band to the trans isomer. Thus, $V(dpm)_2Cl_2$ has the trans configuration in the solid state, and it is the cis isomer which increases in concentration with increasing solvent dielectric constant. If one assumes that *cis*-$V(dpm)_2Cl_2$ and *cis*-$Ti(dpm)_2Cl_2$[6] have the same orientation molar polarization (1336 cm^2), the equilibrium constant for isomerization of $V(dpm)_2Cl_2$, K = [cis]/[trans], can be estimated to be 0.33 in carbon tetrachloride and 0.59 in benzene.

Similar results were obtained for $V(dpm)_2Br_2$, K = 0.18 in benzene, and, again, the trans isomer is present in the solid state. These results are of considerable interest in view of the fact that only the cis isomer has been found for dichloro- and dibromobis(β-diketonato)titanium(IV) complexes.[7] Steric effects may be an important determinant of the trans configuration in the case of the vanadium complexes since the crystal radius of V^{4+} (0.60 Å) is appreciably smaller than that of Ti^{4+} (0.68 Å).[8] It is pertinent to note that both cis and trans isomers have been found for $Ge(dpm)_2Cl_2$ and $Ge(dpm)_2Br_2$[9] ($r_{Ge^{4+}}$ = 0.53 Å), whereas only the cis isomer is known in the case of dihalobis(β-diketonato)tin(IV) complexes[7c,10] ($r_{Sn^{4+}}$ = 0.71 Å). The existence of both cis and trans isomers for $Ti(acac)_2I_2$[11] but only the cis isomer for $Ti(acac)_2X_2$ (X = F, Cl, or Br) also suggests the importance of a steric effect.

The cis configuration is indicated for the pseudohalide complexes $V(dpm)_2(NCX)_2$ by the presence of two CN stretching bands in the infrared spectra [2166 and 2206 cm^{-1} for $V(dpm)_2(NCO)_2$, 2010 and 2060 cm^{-1} for $V(dpm)_2(NCS)_2$-CH_2Cl_2 solution] and by the dipole moment of $V(dpm)_2(NCO)_2$ (8.38 ± 0.22 D, C_6H_6 solution). The frequencies of the NCX vibrations and the integrated intensities of the CN stretching bands are consistent with an N-bonded attachment of the pseudohalide ligands.

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[6] Low-temperature nmr spectra indicate that $Ti(dpm)_2Cl_2$ is 100% cis in dichloromethane. It is probably cis in the solid state as well, since its far-infrared spectrum is unchanged on going from the solid to dichloromethane solution.

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Acidity of Hydrocarbons. XLIX. Equilibrium Ion Pair Acidities of Fluorinated Benzenes for Cesium Salts in Cyclohexylamine. Extrapolation to pK of Benzene[1]

Sir:

The hydrogen isotope exchange rates of the ortho, meta, and para hydrogens in fluorobenzene with lithium cyclohexylamide in cyclohexylamine relative to benzene have been shown to be almost identical with the partial rate factors for exchange of ortho, meta, and para fluorine substituents in hydrogen isotope exchange of polyfluorobenzenes with methanolic sodium methoxide (Table I).[2,3] Arguments have been presented that these substituent rate effects also represent substituent

Table I. Partial Rate and Equilibrium Factors

Fluorine position	R_f,[a] NaOMe, MeOH	log k_{rel},[b] LiCHA	ΔpK[c]
Ortho	5.25	5.43	5.7
Meta	2.07	1.95	2.3
Para	1.13	1.03	1.1

[a] Partial rate factors at 40° (ref 3). [b] Relative rates for tritium exchange of fluorobenzene with lithium cyclohexylamide in cyclohexylamine at 25° (ref 2). [c] Calculated from the following equations: pK(benzene) − pK(C_6F_5H) = 2*o*-F + 2*m*-F + *p*-F; pK(benzene) − pK(1,2,3,4-$C_6F_4H_2$) = *o*-F + 2*m*-F + *p*-F; pK(benzene) − pK(*o*-$C_6H_4F_2$) = *o*-F + *m*-F.

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[1] This research was supported in part by National Institutes of Health, U. S. Public Health Service Grant No. GM-12855.

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Table II. Equilibrium Measurements for Fluorinated Benzenes

Compd[a]	Indicator hydrocarbon[b]	$[ArH]_0$,[c] 10^3 *M*	$[Ar^-Cs^+]_e$,[d] 10^4 *M*	$[RH]_0$,[e] 10^2 *M*	$[R^-Cs^+]_e$,[f] 10^3 *M*	p*K*[g]
C_6F_5H	*t*-BuF	14.27	7.68	19.28	12.33	25.65[h]
C_6F_5H	*t*-BuF	20.94	5.97	19.55	12.53	25.96[h]
1,2,3,4-$C_6F_4H_2$	DBM	9.34	0.87	1.61	0.121	31.20
1,2,3,4-$C_6F_4H_2$	TPM	10.37	2.75	5.54	0.399	31.67
1,2,3,4-$C_6F_4H_2$	TPM	2.87	1.43	3.81	0.311	31.70
o-$C_6H_4F_2$	TTM	10.04	0.323	5.16	0.385	34.70
o-$C_6H_4F_2$	TTM	23.61	0.409	6.39	0.623	35.10
o-$C_6H_4F_2$	TTM	32.49	0.406	3.77	0.320	35.15

[a] The fluorobenzenes (Pierce Chemical Co.) were purified by gc before use. [b] *t*-BuF ≡ 9-*t*-butylfluorene, p*K* = 24.23; DBM ≡ di-*p*-biphenylylmethane, p*K* = 30.83; TPM ≡ triphenylmethane, p*K* = 31.45; TTM ≡ tri-*p*-tolylmethane, p*K* = 33.04 (ref 5 and 6). [c] Concentration of fluorinated hydrocarbon added. [d] Equilibrium concentration of arylcesium determined as $[R^-Cs^+]_0 - [R^-Cs^+]_e$. [e] Concencentration of indicator hydrocarbon before addition of ArH. [f] Directly measured concentration of indicator carbanion. [g] p*K* of ArH per hydrogen at 34°. [h] These measurements were complicated by a decomposition of the reaction mixtures, undoubtedly because of elimination of CsF from the intermediate carbanion to form the corresponding tetrafluorobenzyne. $[R^-Cs^+]_e$ was obtained by following the spectrum as a function of time and extrapolating back to the time of mixing.

effects on equilibrium acidity. We wish to report measurements of equilibrium ion pair acidities for some polyfluorobenzenes for comparison with the kinetic results. The equilibrium measurements relate to eq 1, in which RH is the hydrocarbon used as indicator, ArH is the fluorinated benzene, and the solvent is cyclohexylamine.

$$ArH + R^-Cs^+ \overset{K}{\rightleftharpoons} Ar^-Cs^+ + RH \qquad (1)$$

$$K = \frac{[Ar^-Cs^+]_e[RH]_e}{[ArH]_e[R^-Cs^+]_e}$$

The indicator carbanion can be measured spectrophotometrically, but the aryl anions do not absorb in the visible region. The concentration of Ar^-Cs^+ was determined from the change in spectrum on adding a known amount of fluorinated hydrocarbon to a known mixture of the indicator hydrocarbon and its cesium salt. This method makes high demands on purity and technique, but we have used it previously with success on acetylenic hydrocarbons.[4] The present results are summarized in Table II and show excellent reproducibility; in particular, 1,2,3,4-tetrafluorobenzene (TFB) could be examined with two indicator hydrocarbons, di-*p*-biphenylylmethane (DBM) and triphenylmethane (TPM), with concordant results. The average p*K* values for the three fluorinated benzenes are summarized in Table III relative to 9-phenylfluorene (p*K* = 18.49).

Table III. p*K* Values of Fluorinated Benzenes

Compound	p*K* (per hydrogen), 34°
Pentafluorobenzene	25.81 ± 0.16
1,2,3,4-Tetrafluorobenzene	31.52 ± 0.21
o-Difluorobenzene	34.98 ± 0.19
Benzene	43.0 ± 0.2

There are several ways in which these results can be extrapolated to a p*K* for benzene. A plot of the predicted rates of exchange in NaOMe-MeOH using the partial rate factors in Table I *vs.* the p*K* values in Table III is linear (slope = −0.92) and extrapolates to p*K*(benzene) = 42.93. Alternatively, experimental exchange rates can be used for C_6HF_5 and 1,2,3,4-$C_6H_2F_4$ with a calculated rate for *o*-$C_6H_4F_2$. This plot is also linear (slope = −0.83) and, with the corresponding rate constant for benzene at 40°, log k_2 = −15.7,[7] gives p*K*(benzene) = 43.27. In a third procedure, the relative rates of LiCHA exchange in Table I are treated as partial rate factors to derive expected exchange rates for the polyfluorobenzenes. These rates give a linear Brønsted plot with the p*K* values in Table III (slope = −0.92) and yield p*K*(benzene) = 42.90. The average value from the three methods is p*K*(benzene) = 43.0 ± 0.2 (per hydrogen). With this value, partial equilibrium factors for *o*-, *m*-, and *p*-F can be derived, and are summarized in Table I. The agreement with the kinetic substituent effects reflects the near-unity Brønsted slopes found above.

The p*K* values summarized in Table III are expected to be reasonably accurate measures of equilibrium 1. The p*K* values obtained in our past work for hydrocarbons with highly conjugated carbanions are plausibly considered to be approximately on the dilute aqueous solution standard state, because solvation energy differences among such ions are expected to be relatively small. This assumption does not extend to the localized anions of the phenide type considered in this paper, and there remains the question of whether the p*K* values in Table III bear any relationship to aqueous solution values. The similarity of results in two such different media as methanol and cyclohexylamine is encouraging and suggests that the effects of hydrogen-bond solvation in hydroxylic solvents may be rather similar to the effects of ion pairing in nonpolar solvents; nevertheless, most experimental work with aryl-type carbanions is carried out as ion pairs in aprotic media, and for such systems the p*K* data in Table III should have quantitative significance. Within this framework the derived p*K* for benzene should represent the most accurate determination to date.

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