$\nu_{max}^{CHCl_3}$ 2430, 2730, 2130, 1695, and 1325 cm^{-1}. The vapor phase chromatographic retention time (2 ft × 0.25 in. 20% silicone rubber column, 195°) was equal to that of an undeuterated sample. The deuterium content, calculated from the mass spectrum, was 0.3% d_0, 0.5% d_1, 2.4% d_2, 8.3% d_3, 19.4% d_4, 28.8% d_5, 25.3% d_6, 11.6% d_7, 3.0% d_8, and 0.5% d_9.[22]

To this diketone (6.07 g) in 100 ml of deuterium oxide and 100 ml of dioxane was added sufficient potassium carbonate to give a solution having pH 10. The mixture was heated to reflux for 18 hr. After the mixture had cooled, extraction with methylene chloride and removal of solvent from the dried extract yielded 6.0 g of product. After three successive exchanges, the colorless crystals (6.0 g) showed only two absorptions in the nmr spectrum for benzylic and aromatic protons in a ratio of 1.76:1 (in agreement with 82% d_2 incorporation in the benzene ring). The deuterium content, calculated from the mass spectrum, was 0.4% d_3, 0.9% d_4, 2.4% d_5, 6.9% d_6, 16.7% d_7, 29.1% d_8, 29.5% d_9, 13.9% d_{10}, and 0.3% d_{11}.[22] The infrared spectrum showed $\nu_{max}^{CHCl_3}$ 2380, 2210, 2130, and 1695 cm,$^{-1}$.

trans-**Bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene-3,3,5,6,8,8,11,13-d_8 (7).** The diketone **4** (744 mg, 3.28 mmol) was dissolved in 30.5 g of glacial acetic acid-1-*d* and warmed to 50°. Pyridinium hydrobromide perbromide[24,25] (1.05 g, 3.3 mmol) was added with stirring. The reaction mixture was maintained at 60° for 10 min. The cooled mixture was extracted with chloroform and the chloroform extracts were washed with two portions of deuterium oxide and four portions of saturated sodium bicarbonate, and finally with saturated sodium chloride. Evaporation of the solvent from the dried extract gave 601 mg of residue. Freshly distilled γ-collidine (2.2 ml) was added to the bromination product, and the resulting mixture was heated to 160° for 45 min. The cooled reaction mixture was diluted with chloroform and washed with cold 3% sulfuric acid until the washings were strongly acidic, then with water, saturated sodium bicarbonate, and water again. The dried chloroform extract was evaporated to dryness, and the residue was purified by sublimation at 120° (0.4 mm). The product (220 mg) was shown by its vapor phase chromatogram and infrared spectrum to be a mixture of the desired enedione 6 and the starting diketone **4**.

This mixture was treated with lithium aluminum hydride–aluminum chloride as described previously.[5] Following the work-up, 66 mg of olefin **1** was obtained, which had $\nu_{max}^{CS_2}$ 3010, 2915, 2870, 2850, 2820, 900, and 700 cm^{-1}. The deuterium content, calculated from the mass spectrum, was 0.4% d_4, 1.4% d_5, 6.2% d_6, 31.0% d_7, 60.2% d_8, and 0.8% d_9.[22]

trans-**Bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene-4,7-dione-3,3,8,-8,11,13-d_6 (5).** Treatment of the diketone **4** (5.0 g) with pyridinium hydrobromide perbromide in glacial acetic acid as described above afforded, after dehydrobromination with collidine, product having $\nu_{max}^{CHCl_3}$ 2220, 2150, 1695, 1675, and 970 cm^{-1}, which was purified by sublimation at 120° (0.4 mm). The deuterium content, calculated from the mass spectrum, was 0.2% d_1, 0.8% d_2, 4.0% d_3, 14.1% d_4, 30.9% d_5, 33.1% d_6, 9.7% d_7, 5.1% d_8, 1.7% d_9, and 0.4% d_{10}.[22] The use of undeuterated acetic acid in this bromination apparently resulted in essentially complete exchange of the deuterium atoms at C_5 and C_6 for hydrogen atoms.

Acknowledgment. We wish to thank Dr. John Fleming for his efforts in modifying the variable-temperature nmr probe used in this work for heteronuclear decoupling.

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[24] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1957, p 65.

[25] C. Djerassi and C. R. Scholz, *J. Amer. Chem. Soc.*, **70**, 417 (1948).

Acidity of Hydrocarbons. XXVII. Proton Exchange Rates of Fluorobenzene with Lithium Cyclohexylamide[1,2]

A. Streitwieser, Jr., and F. Mares[3]

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received August 18, 1967*

Abstract: Deuterium and tritium exchange in aryl positions of fluorobenzene and benzotrifluoride were studied with lithium cyclohexylamide in cyclohexylamine at 25°. Rates for D and *T* exchange relative to benzene are: fluorobenzene −2, 6.3×10^5, *3.4×10^5;* −3, 107, *86;* −4, 11.2, *9.1;* benzotrifluoride −3, 580, *390.* These rates are in only qualitative agreement with previous work and are interpreted with a field effect model for inductive effects. 2,5-Difluorotoluene-α-*d* is found to exchange 350 times faster than toluene-α-*d*.

A fluorine substituent has a powerful effect on the kinetic acidity of an aryl hydrogen. Pentafluorobenzene undergoes rapid hydrogen isotope exchange even with sodium methoxide in methanol at room temperature.[4] Hall, Piccolini, and Roberts[5] found the *o*-hydrogen of fluorobenzene to be about 10^6 more reactive than a benzene hydrogen toward potassium amide in liquid ammonia.[5] However, in this latter deuterium exchange work, experimental difficulties allowed the determination of only approximate rate constants for these reactions. Even for the slower *meta* and *para* positions, the kinetics of the reactions were not determined and rate constants were calculated from the amount of exchange at two times only. In order to obtain more precise values for these kinetic acidities, we undertook the present more detailed study of the fluorobenzene positions using the lithium cyclohexylamide–cyclohexylamine (LiCHA–CHA) system. Relative rates in this system have been shown previously to correspond closely to potassium amide–liquid ammonia results.[6] The *meta* position of benzotrifluoride and the α position of 2,5-difluorotoluene were included in the present study for additional comparisons.

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[1] Supported in part by Grant No. GM-12855 of the National Institutes of Health, U. S. Public Health Service.

[2] Paper XXVI: F. Mares and A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **89**, 3770 (1967).

[3] On leave from the Institute of Chemical Process Fundamentals, Prague, Suchdol 2, Czechoslovakia.

[4] A. Streitwieser, Jr., J. Hudson, and F. Mares, *ibid.*, **90**, 648 (1968).

[5] G. E. Hall, R. Piccolini, and J. D. Roberts, *ibid.*, **77**, 4540 (1955).

[6] A. Streitwieser, Jr., R. A. Caldwell, R. G. Lawler, and G. R. Ziegler, *ibid.*, **87**, 5399 (1965).

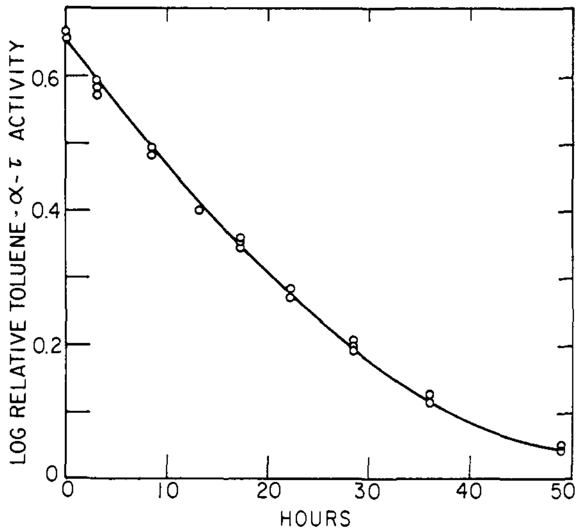

Figure 1. Log radioactivity plot for toluene-α-*t* with LiCHA in the presence of fluorobenzene demonstrating nonfirst-order kinetic behavior.

Experimental Section

Fluorobenzene-3-*d*(*t*) and -4-*d*(*t*), and 2,5-difluorotoluene-α-*d*(*t*) were prepared from the corresponding aryl bromide or benzyl chloride (prepared from 2,5-difluorobenzoic acid) (Pierce Chemical Co.) by quenching an ether solution of the Grignard reagent (~ 1 *M*) with deuterium oxide (50 ml/mole) enriched with tritium (50–100 mcuries/mole). The products were purified by fractional distillation. Purity was monitored by glpc, and the structures were verified by infrared and nmr. The products had >90% d_1 (mass spectroscopy) and had an activity of 10^5–10^6 dpm/mg.

Fluorobenzene-2-*d*(*t*). To a stirred solution of 0.036 mole of butyllithium in 50 ml of ether maintained at −90° was added 5.44 g (0.032 mole) of *o*-bromofluorobenzene. Immediately after the addition was complete, the mixture was quenched with 1.1 ml of methanol-*d* enriched with tritium (10 mcuries) in 10 ml of ether. After 1 hr, 3 ml more methanol-*d* was added. The product, separated from butyl bromide by preparative glpc in 43% yield, was 96% d_1 and had an activity of 16×10^5 dpm/mg.

Kinetics. The kinetic procedure was essentially that of Mares and Streitwieser[2] in which two compounds were present in each run with LiCHA and CHA. Deuterium analysis was by low-voltage mass spectroscopy and tritium analysis made use of the radio gas chromatography system previously described.[2] Multiple glpc analyses—often as many as five—were made for each point. With this radio gas chromatography system the relative amounts of the two substrates could also be monitored as a function of time (*vide infra*).

Kinetics

Figure 1 shows the results of tritium exchange for toluene-α-*d*(*t*) in a run that contained fluorobenzene-4-*d*(*t*). The kinetics is clearly not of pseudo first order since such kinetics would have given a straight line. The decrease of the reaction rate with time is paralleled by a decrease in base concentration as shown by titration. After 80 hr at 25° the base was completely neutralized. Figure 2 shows that the ratio of fluorobenzene to toluene decreases during the course of this run. In addition, an insoluble inorganic precipitate, probably lithium fluoride, gradually formed. Fluorobenzene is clearly unstable to the reaction conditions and probably decomposes *via* a benzyne mechanism. The comparable decomposition of aryl bromides is far more rapid[7] and gives N-arylcyclohexylamines.[8]

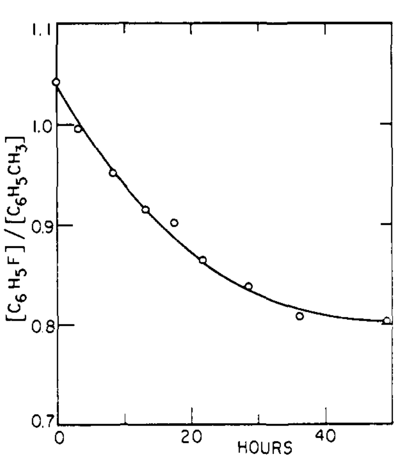

Figure 2. Reaction of toluene and fluorobenzene with LiCHA showing progressive loss of fluorobenzene.

In principle, to obtain rate constants in these circumstances, the system could be treated as a second-order reaction in which the concentration of base as a function of time is included explicitly together with the deuterium and tritium changes. However, it was far more convenient to obtain relative rates directly—in effect, the exchange of toluene is used as a time scale for comparing the exchange of undecomposed fluorobenzene. Since the reactivity of the internal standard, toluene, has been studied in detail,[9] such relative rates are completely useful.

For a simple first-order reaction such relative rates may be obtained from eq 1. The present system is

$$\log \frac{x_0 - x}{x_0 - x_\infty} = \frac{k_x}{k_y} \log \frac{y_0 - y}{y_0 - y_\infty} \qquad (1)$$

more complicated because of the necessity to take proper account of the back reaction inasmuch as the solvent hydrogen pool is not in general infinite compared to the substrate hydrogen pool.[7,10]

The rate of exchange of a simple compound, *i*, in a mixture is given by eq 2 or[11] eq 3 in which x_i is the measure of isotope in compound *i*, n_i is the number of equivalent positions being investigated, ρ, the relative probability that a given solvent proton is an isotope, is given by $\Sigma_i a_i(x_i^0 - x_i)/2b$, a_i is the concentration of *i*, and *b* is the concentration of CHA.

$$-\frac{dx_i}{dt} = k_i[x_i - n_i\rho] \qquad (2)$$

$$\ln \frac{x_i^0}{x_i} = k_i\left(t - n_i\int_0^t \frac{\rho}{x_i}\,dt\right) \qquad (3)$$

Note that the experimental measure of isotope content must be corrected for the m_i hydrogen positions that are in effective equilibrium with solvent; from the experimental quantity at each time there is substracted $m_i\rho$. For example, the *o*-hydrogens of fluorobenzene are far more reactive than the *p*- (*vide infra*). In studying loss of a *para* isotope, some of the isotope lost comes back to the *ortho* positions, and the total isotope con-

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(7) A. Streitwieser, Jr., and H. F. Koch, *J. Am. Chem. Soc.*, **86**, 404 (1964).

(8) G. R. Ziegler and R. I. Sadayasu, unpublished results.

(9) A. Streitwieser, Jr., R. A. Caldwell, M. R. Granger, and P. M. Laughton, *J. Phys. Chem.*, **68**, 2916 (1964).

(10) A. Streitwieser, Jr., D. E. Van Sickle, and W. C. Langworthy, *J. Am. Chem. Soc.*, **84**, 244 (1962).

(11) This equation is the same as eq 6 of ref 7. The inclusion of *a* in this latter equation is an error.

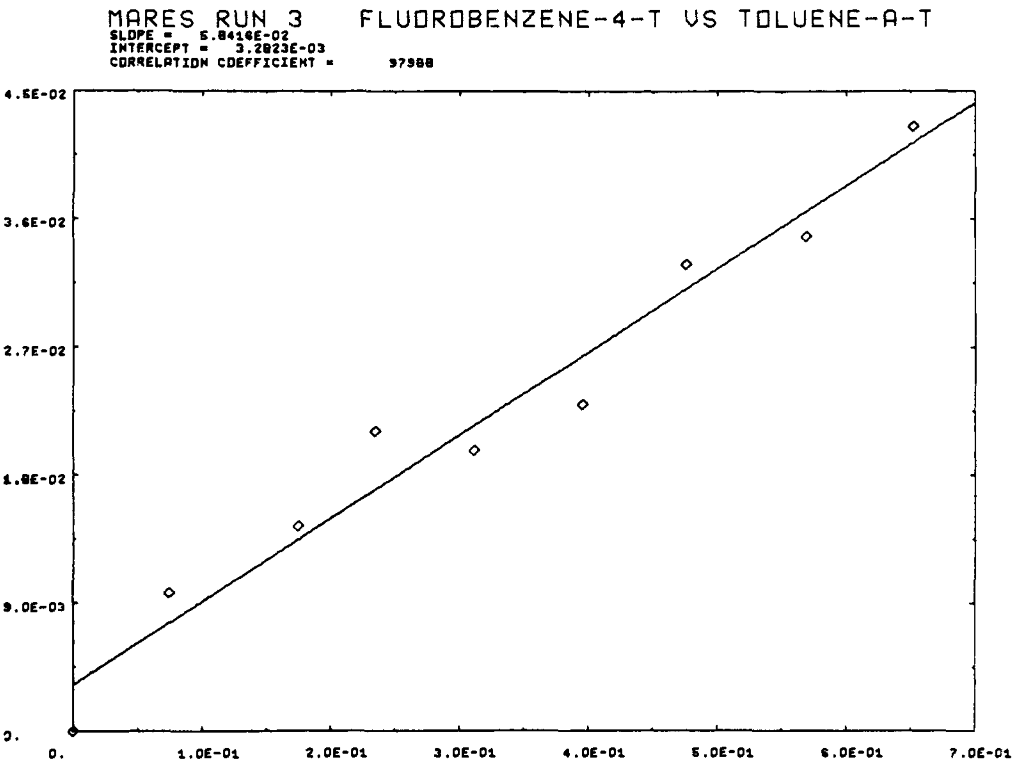

Figure 3. A direct reproduction of a computer output plot in run 3 showing the relative rate of loss of tritium from a mixture of toluene-α-$d(t)$ and fluorobenzene-4-$d(t)$ with LiCHA.

tent is somewhat higher than that of the *para* position alone. This correction is required not only for tritium kinetics but also for deuterium exchange in which the total deuterium in a molecule is assayed, such as by low-voltage mass spectrometry. In addition, in tritium counting by radio gas chromatography, the experimental counts/area quantity must be converted to counts/unit moles by use of relative thermal conductivities.[7]

For a mixture of two substrates with these corrections, the relative rate, k_i/k_j, is given as the slope of a plot of the two sides of eq 4; the values of the integrals were

$$\log x_i^0/x_i = \frac{k_i}{k_j}(\log x_j^0/x_j)\,\frac{t - n_i\int_0^t(\rho_l/x_i)\mathrm{d}t}{t - n_j\int_0^t(\rho_l/x_j)\mathrm{d}t} \qquad (4)$$

obtained graphically from plots of ρ_l/x *vs.* time. The least-squares slope was obtained by computer calculation which also plotted the results with a Calcomp plotter. An example of typical output is shown in Figure 3. The results obtained are summarized in Tables I and II. This method was not required for following exchange at the *ortho* position in fluorobenzene; exchange here is much more rapid than decomposition (by a factor of 2×10^4) and the standard kinetic procedure suffices.

Primary Isotope Effects. In almost all cases we were able to follow tritium and deuterium loss simultaneously. For reactions followed as a rate relative to a standard, the isotope effect can be calculated as

$$(k_D/k_T)_i = \frac{(k_i/k_0)_D}{(k_i/k_0)_T}(k_D/k_T)_0 \qquad (5)$$

Such values are also given in Table I. Alternatively, they could be obtained directly as relative rates using eq 4—both methods gave the same answers.

Note that the isotope effect for aryl hydrogen exchange in fluorobenzene varies from $k_D/k_T = 2.0$ for the *para* position to 3.0 for the *ortho* position. These values are all relatively high and effectively rule out any important contribution from internal return;[7,12] hence, the rate-determining step is that of aryl–H bond breaking. This result contrasts completely with that for exchange with pentafluorobenzene and sodium methoxide–methanol.[4] These isotope effects are also larger than those found for exchange with LiCHA at aryl positions of benzene, 1.6;[13] 1-naphthalene, 1.7;[13] 9-anthracene, 1.2;[14] and 1-pyrene, 1.2.[14] In these cases the low isotope effects were attributed to covalent bonding between the central carbon and the lithium at the transition state. The close proximity of lithium and exchanging hydrogen impedes the bending vibrations of the hydrogen and results in lowering of the isotope effect. We may now extend this argument one step further. Because lithium is a first row element it seems reasonable to expect a significant amount of π overlap between the aryl π system and the Li $2p_z$ orbital in monomeric lithium phenyl. Such overlap would have the effect of withdrawing electrons from the aryl π systems and of strengthening the Ar–Li bond. Such π interaction is expected to be more important for lithium 9-anthracyl or lithium 1-pyrenyl, and the observed lowered isotope effects for these compounds (*vide supra*) are in agreement with this hypothesis. Conversely, an electron-withdrawing substituent is ex-

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(12) D. J. Cram, C. A. Kingsbury, and B. Rickborn, *J. Am. Chem. Soc.*, **83**, 3688 (1961).

(13) A. Streitwieser, Jr., R. G. Lawler, and C. Perrin, *ibid.*, **87**, 5383 (1965).

(14) A. Streitwieser, Jr., and R. G. Lawler, *ibid.*, **87**, 5388 (1965).

Table I. Summary of Kinetic Runs at 25°

Run	Compound	[RH], M	[LiCHA],[a] M	$k_{D,rel}$[b]	$k_{T,rel}$[b]	k_D/k_T[c]
2	Fluorobenzene-4-*d*(*t*)	0.22		0.0455 ± 0.0032	0.0672 ± 0.014	1.9
	Benzotrifluoride-3-*d*(*t*)	0.171	~0.1	2.22 ± 0.088	2.58 ± 0.061	2.4
	Toluene-α-*d*(*t*)	0.194		(1)	(1)	2.8
3	Fluorobenzene-4-*d*(*t*)	0.21	~0.1	0.0421 ± 0.0007	0.059 ± 0.004	2.0
	Toluene-α-*d*(*t*)	0.19		(1)	(1)	2.8
4	Fluorobenzene-3-*d*(*t*)	0.21	~0.1	0.407 ± 0.011	0.574 ± 0.012	2.0
	Toluene-α-*d*(*t*)	0.21		(1)	(1)	2.8
7	Fluorobenzene-2-*d*(*t*)	0.184	0.00185[d]	6.90[e]	*e*	3.0[f]
	2,5-Difluorotoluene-α-*d*(*t*)	0.15		(1)		

[a] Probable initial formal concentration of base. [b] Equation 4. [c] Equation 5 for toluene: $k_D/k_T = 2.8$. [d] Titrated at the end of kinetic run. [e] Absolute second-order rate constants for fluorobenzene-2-*d*(*t*): $k_D = 13.8 \pm 0.3$ l./mole sec, $k_T = 4.56 \pm 0.18$ l./mole sec (*cf.* ref 9). [f] Calculated from the pseudo-first-order rate constants.

Table II. Summary of Relative Rates at 25°

	Rate rel to toluene		Rate rel to benzene	
Compound	D	T	D	T
Fluorobenzene-2	2400[a]	2250[a]	6.3×10^5 [a]	3.4×10^5 [a]
Fluorobenzene-3	0.41	0.57	107	86
Fluorobenzene-4	0.043	0.061	11.2	9.1
Benzotrifluoride-3	2.22	2.58	580	390
2,5-Difluorotoluene-α	350		9.1×10^4	
Toluene-α	(1)	(1)	260[b]	150[b]
Benzene	0.0038[b]	0.0067[b]	(1)	(1)

[a] Calculated from appropriate second-order rate constants. [b] Extrapolated to 25° from results at 50° using a ΔE^* of 3 kcal/mole. This value was found experimentally for the difference in activation energies between naphthalene-2 and toluene-α with LiCHA (*cf.* ref 9 and 13).

pected to diminish the importance of such π overlap, reduce the covalent bond strength of the Ar–Li bond, diminish the steric interaction of Li and H at the transition state for exchange, and lead to higher primary hydrogen isotope effects. The inductive effect of fluorine could have such an effect as well as giving the C–Li bond more ionic character. This argument is, of course, only suggestive, but it serves to rationalize the available primary isotope effect data for these exchange reactions.

Relative Rates. The results of Hall, Piccolini, and Roberts[5] were converted to approximate partial rate factors by Shatenshtein:[15] *ortho*, 10^6; *meta*, 10^3; and *para*, 10^2. From our results these relative rates will depend on whether deuterium or tritium exchange is followed because of differences in primary isotope effects for these compounds. For deuterium exchange, we find (Table II) *ortho*, 6.3×10^5; *meta*, 1.1×10^2; and *para*, 1.1×10, results that differ significantly from those cited above. However, because of the low precision of the KNH_2 studies, the differences are probably not significant—in none of the previous work was the decomposition of fluorobenzene taken into account. In our work, systematic errors are possible in the assay of LiCHA concentration required for conversion of the experimental pseudo-first-order rate constant to a second-order rate constant. The relative rates for *m*- and *p*-fluorine were determined by direct comparisons with standard compounds, and this source of error does not apply; hence, the relative rates cited for these substituents should be reasonably accurate. The relative rate for the *o*-fluorine did require the determination of a second-order rate constant, and a systematic error in the assay of base concentration is a possible source of inaccuracy; however, other results in these laboratories[16] show that the derived relative rate is probably accurate to about 10%.

Shatenshtein[15] has also shown that the kinetic acidities of various *o*-hydrogens in substituted benzenes correlate well with the σ_I value of the substituent; that is, inductive effects appear to be primarily important. The importance of simple electrostatic interactions with bond dipoles has long been recognized as an important mechanism of inductive effects.[17] More recently, this view has been emphasized by Dewar and Grisdale[18] and has been elegantly confirmed by Wilcox.[19] The actual calculation of the electrostatic interaction energy involved is complicated because the distances involved are of atomic dimensions and a uniform continuous dielectric medium cannot be assumed in a Coulomb's law application. The important simplification introduced by Kirkwood and Westheimer[20] in which the organic ion is placed within a cavity of low dielectric constant in a continuous dielectric medium is the basis of a computer program written by Wilcox.[21] We calculated the charge–dipole electrostatic energy for *o*-, *m*-, and *p*-fluorophenyl anions with this program but no attempt was made to achieve optimum parametrization.[22] A plot of log

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(15) A. I. Shatenshtein, *Advan. Phys. Org. Chem.*, **1**, 155 (1963).

(16) Experiments of Dr. F. Mares and D. Holtz to be published.

(17) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 129.

(18) M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.*, **84**, 3548 (1962).

(19) C. F. Wilcox, Jr., unpublished results.

(20) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506, 513 (1938); *cf.* also C. Tanford, *J. Am. Chem. Soc.*, **79**, 5348 (1957).

(21) We are indebted to Professor Wilcox for a copy of his program.

(22) A cavity of dielectric constant, ϵ 2, with a radius of 1.5 A was centered at the center of the benzene ring. A unit point dipole was placed at the center of the C–F bond and a point negative charge was placed at the center of the appropriate C–H bond. The region outside the cavity was treated as a continuous dielectric with ϵ 6. The results scaled to a dipole moment of 1.5 D. are: *para*, 1.04; *meta*, 2.04; *ortho*, 5.79 kcal/mole.

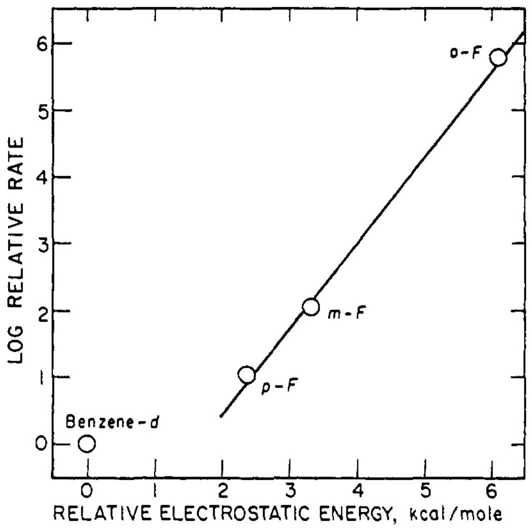

Figure 4. Results of a Kirkwood-Westheimer inductive field effect calculation applied to fluorophenyl anions and compared to kinetic acidities of fluorobenzenes.

k_{rel} for these positions *vs.* the calculated electrostatic energies, as in Figure 4, is adequately linear. Benzene itself does not fall on this line presumably because optimum parameters were not chosen; nevertheless these results do show that ordinary inductive field effects can account for the positional effects of a substituent in stabilizing a phenyl anion.

The kinetic acidity of the *meta* position of benzotrifluoride relative to benzene reported in Table II, 4.6 × 10^2, is also considerably lower than that obtained by Hall, Piccolini, and Roberts,[5,15] 10^4. Benzotrifluoride is also unstable toward LiCHA and probably also to KNH_2; possibly this decomposition, which was not considered in the earlier work, is responsible for the discrepancy. The rate enhancement caused by a *m*-trifluoromethyl group is about five times that of *m*-fluorine. The dipole moment of benzotrifluoride, 2.6 D., is considerably greater than that of fluorobenzene, 1.5 D.,[23] but a larger charge–dipole distance is involved with the CF_3 group. We plan to obtain accurate kinetic acidities for other substituted benzenes and defer more extensive calculations of electrostatic energies until more extensive such data have been obtained.

Finally, we may mention 2,5-difluorotoluene. From the reactivities of *m*- and *o*-fluorotoluene,[6] we can derive an estimated rate ratio, 2,5-difluorotoluene-α-*t*-toluene-α-*t*, of 260 at 50°. This estimate compares well with the value, 350 at 25°, found experimentally in the present work for deuterium exchange.[24]

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[23] Summarized in A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963. The "best value" cited for fluorobenzene is in error and has been revised to 1.463 D. (Dr. McClellan, personal communication).

[24] Note that if the relative rate is due entirely to an energy of activation difference the extrapolated relative rate for tritium exchange at 25° is 414.

Acidity of Hydrocarbons. XXVIII. Hydrogen Isotope Exchange of Polyfluorobenzenes with Sodium Methoxide in Methanol[1,2]

A. Streitwieser, Jr., J. A. Hudson, and F. Mares[3]

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received August 18, 1967*

Abstract: Rates are reported for hydrogen isotope exchange with sodium methoxide–methanol of pentafluorobenzene, the tetrafluorobenzenes, and 1,3-difluorobenzene. The results give the following log partial rate factors at 40°: *ortho*, 5.25; *meta*, 2.07; *para*, 1.13. The exchange reaction of pentafluorobenzene shows no primary isotope effect and appears to be of the internal return type. The relative rates are shown to be approximately equal to the relative equilibrium acidities.

The pronounced effects of fluorine substituents on kinetic acidities of aryl hydrogens[4] prompted a study of the kinetic acidity of pentafluorobenzene which was first synthesized only a decade ago[5] and which has recently become commercially available. Preliminary kinetic studies showed that the compound undergoes hydrogen isotope exchange quite rapidly even with dilute sodium methoxide in methanol; hence, a detailed study was undertaken that included the tetrafluorobenzenes and *m*-difluorobenzene.

Experimental Section

Polyfluorobenzenes. Commercial products (Pierce Chemical Company, Rockford, Ill.) were used without further purification. Purity was monitored by refractive index and by glpc using the following columns: Dow 710, a 1:4 mixture of Bentone 34 and SE 52, and QF 1, each 20% on Chromosorb W. All of the fluorobenzenes showed one peak except for 1,2,4,5-tetrafluorobenzene which contained traces of 1,2,3,5-tetrafluorobenzene and pentafluorobenzene and about 5% 1,2,3,4-tetrafluorobenzene.

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[1] Supported in part by Grant No. GM-12855 of the National Institutes of Health, U. S. Public Health Service, and by a grant from the Petroleum Research Fund of the American Chemical Society.

[2] Paper XXVII: A. Streitwieser, Jr., and F. Mares, *J. Am. Chem. Soc.*, **90**, 644 (1968).

[3] On leave from the Institute of Chemical Process Fundamentals, Prague, Suchdol 2, Czechoslovakia.

[4] *Cf.* summaries by A. I. Shatenshtein, *Advan. Phys. Org. Chem.*, **1**, 187 (1963), and A. Streitwieser, Jr., and J. H. Hammons, *Progr. Phys. Org. Chem.*, **3**, 41 (1965).

[5] R. Stephens and J. C. Tatlow, *Chem. Ind.* (London), 821 (1957).