

by treating the initial activities as intercepts to be fitted during each iteration, again by a Newton-Raphson procedure.

At each iteration, convergence is tested by inspecting whether all rate constants have changed by less than a fixed proportion (arbitrarily selected as 0.1%) during that iteration. Upon convergence, the second-order rate constants are converted to pseudo-first-order rate constants, at zero substrate concentration, for print-out.

One further pitfall should be mentioned. A rate constant of zero or infinity will also produce a zero value for f_j . This corresponds to *maximizing* the sum of the squares of the deviations, and divergence to such a value can occur if the initial guess at the rate constant is badly in error. However, in such a situation, it can be shown that f_j' must be negative. When this occurs, the rate constant must be increased or decreased (depending upon the sign of f_j) by an order of magnitude, to force the convergence to a finite rate constant.

With this solution it is possible to take explicit ac-

count of other positions in a substrate molecule which acquire radioactivity as the reaction proceeds. Positions which exchange very rapidly may be considered to be a part of the solvent pool. The activity at a position which exchanges at a rate comparable to that of the position initially radioactive may be calculated for the parent position, since the counting method assumed does not distinguish among the various positions of a molecule. Finally, the resulting residuals between calculated and experimental activities are used to derive approximate standard deviations in the rate constants.

This program was written in IBM Fortran language. As an example of its versatility, a kinetic run consisting of benzene-*t*, toluene-2-*t*, and 2-phenylbutane-2-*t*, with three rate constants to be fitted, eight distinguishable hydrocarbon positions, and one set of benzylic hydrogens (assumed rapidly exchanging), was analyzed in less than 2 min. on the IBM 7090 computer. Analysis of this system by the previous, approximate technique would have required several hours of computation.

Acidity of Hydrocarbons. XVIII. Exchange Reactions of Polycyclic Aromatic Protons with Lithium Cyclohexylamide¹

A. Streitwieser, Jr., and R. G. Lawler²

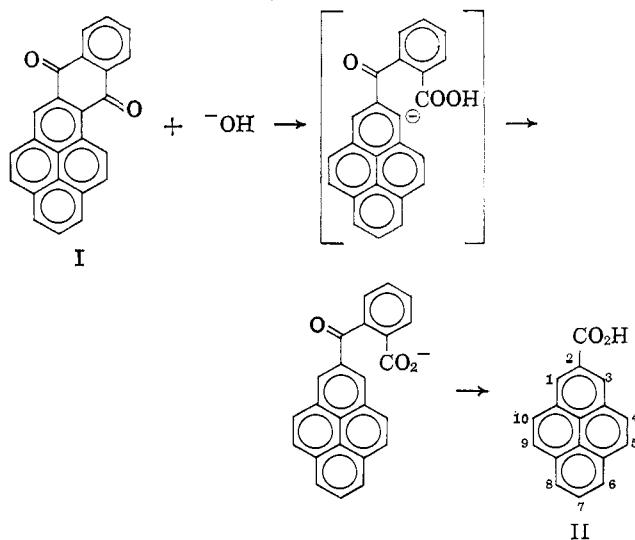
Contribution from the Department of Chemistry, University of California, Berkeley, California. Received July 19, 1965

Relative rates of deuterium or tritium exchange with lithium cyclohexylamide were determined for various positions in benzene, naphthalene, phenanthrene, anthracene, and pyrene and have been found to span a relative rate range of almost 50-fold. The effect of structure on these rates is considered in terms of carbene resonance structures and molecular orbital polarizabilities, but the best correlation is with an inductive effect model based on a simple classical picture.

The relative acidities of polycyclic aromatic hydrocarbons are of interest for several reasons. They provide a structural variation of π -electrons in a reaction in which conjugation may not be important. The possible applications of molecular orbital theory in such cases requires exploration. Such a series also provides a further test of a possible relationship between hydrocarbon acidities and amine basicities.

Indications of the relative acidities of different positions in polycyclic aromatic hydrocarbons have come from several sources. The cleavage of nonenolizable ketones with sodium amide to give an amide and a hydrocarbon³ appears to go through carbanion inter-

mediates and provides useful inferences. Phenyl alkyl ketones give only benzene and the aliphatic amide; hence, phenyl anions are deduced to be more stable than alkyl anions. Unfortunately, this method has apparently not been applied to different polycyclic hydrocarbons. Isolated examples of KOH fusions are of value; for example, this reaction with 1,2-phthaloylpyrene (I) gives mostly pyrene-2-carboxylic acid⁴ (II)



(1) (a) This work was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Grants No. 62-175 and 64-554; (b) part XVII: A. Streitwieser, Jr., R. G. Lawler, and C. Perrin, *J. Am. Chem. Soc.*, **87**, 5383 (1965); (c) a preliminary communication was published in A. Streitwieser, Jr., and R. G. Lawler, *J. Am. Chem. Soc.*, **85**, 2854 (1963).

(2) National Science Foundation Predoctoral Fellow, 1960-1963; Eastman Kodak Science Award in Chemistry, 1962-1963.

(3) A. Haller and E. Bauer, *Compt. rend.*, **148**, 127 (1909); K. E. Hamlin and A. W. Weston, *Org. Reactions*, **9**, 1 (1957).

(4) H. Vollmann, H. Becker, M. Corell, and H. Streeck, *Ann.*, **531**, 1 (1937).

indicating that a pyrenyl anion is more stable than a phenyl anion.

Metalation experiments are more direct and several studies are available. The principal problems in interpretation derive from the question of rate vs. equilibrium control of the reaction and experimental error in analyzing product mixtures, particularly in the older literature. Phenyllithium metalates dibenzothiophene more readily than does 1-naphthyllithium⁵; thus, naphthalene is a stronger acid than benzene.⁶ Metalation of naphthalene with butyllithium in ether followed by carbonation gives a ratio of α - to β -naphthalene-carboxylic acids of 2.5,⁷ indicating that the α -position is more acidic than the β . Similar treatment of pyrene gives the following relative amounts of metalation: 1-, 1.0; 2-, 0.2; and 4-, 2.0.⁸ The 4-position is indicated as the most acidic in the pyrene molecule. In these results, there are only qualitative indications of the relative reactivities of different hydrocarbons.

Huisgen, *et al.*,⁹ have applied an interesting technique in obtaining relative rates of dehydrobromination of bromoarenes with lithium piperidide to give aryne intermediates. These rates appear to be measures of the rates of removal of the hydrogen adjacent to the bromine. Some of the relative rates found are: bromobenzene, 1.0; 1-bromonaphthalene, 6.8; 2-bromonaphthalene, 11.6; 9-bromophenanthrene, 39; and 1-bromopyrene, 6.8. The ratio of α - to β -hydrogens in naphthalene, 1.7, agrees qualitatively with the metalation results.

A related method depends on the product distribution of reaction of aryne intermediates. This procedure must be employed with caution because of possible steric influences and because the reaction is assumed to be a nucleophilic attack on the triple bond; nevertheless, Huisgen and Zirngibl¹⁰ have found that 1-halonnaphthalenes react with a variety of bases to give 2:1 ratios of β - to α -substituted products in agreement with the foregoing indications that the α -naphthyl position is more acidic than the β .

Finally, we consider the base-catalyzed exchange of aryl hydrogens—a traditional measure of kinetic acidity. The extensive studies by Shatenshtein¹¹ as well as the more limited measurements of Hall, Piccolini, and Roberts¹² on protodeuteration rates of substituted benzenes with potassium amide in liquid ammonia provide evidence that these kinetic acidities are valid measures of relative thermodynamic acidities. For example, the rates for a variety of *ortho* substituents correlate reasonably well with σ_I to give $\rho_I = 11$,¹¹ a rather high value.

Prior to our study, the only exchange rates available for polycyclic aromatic hydrocarbons are those of Shatenshtein for naphthalene and biphenyl,^{11,13} sum-

marized in Table II. The relative rates, benzene, 1.0, α -naphthyl, 9.3, and β -naphthyl, 4.2, show that the α -position is about twice as reactive as the β , in qualitative agreement with the other indications of relative acidities in naphthalene. In similar exchange studies with lithium cyclohexylamide (LiCHA) in cyclohexylamine (CHA), we found the following relative rates: α -naphthyl, 6.5 and β -naphthyl, 4.1.^{1b} The good agreement between these results and other criteria for relative acidities prompted a more extensive kinetic study of other polycyclic aromatic hydrocarbons.

Experimental Section

The procedures used are largely the same as in the preceding papers.^{1b}

Materials. The deuterated and tritiated arenes were prepared in general by treatment of the corresponding bromoarene with butyllithium in ether followed by quenching with D₂O or with tritium-enriched H₂O or D₂O in a manner similar to that described in the preceding paper.^{1b}

Phenanthrene-9-*d* from 9-bromophenanthrene (Aldrich Chemical Co.) had m.p. 100–101° (lit.¹⁴ m.p. 100.7–101°) and absorption at 2260 with a reference band at 1943 cm.⁻¹.

Anthracene-9-*d,t* from 9-bromoanthracene (Aldrich) was chromatographed on alumina and recrystallized from toluene to give blue fluorescent platelets, m.p. 218–219° (lit.¹⁵ 216.2–216.4°), 1.6×10^6 d.p.m./mmole, with C–D absorption at 2256 and a reference band at 1942 cm.⁻¹. The infrared spectra were run on 0.4 mole % solutions in CCl₄ with a Perkin-Elmer 421 instrument at 5 \times scale expansion.

Biphenyl-4-*d* from 4-bromobiphenyl (Aldrich) was distilled and recrystallized from aqueous methanol to give m.p. 69.9–70.1° (lit.¹⁶ m.p. 70.5°) and a C–D band at 2282 with a reference band at 1800 cm.⁻¹.

Biphenyl-2-*d* from 2-bromobiphenyl (Aldrich) had m.p. 69–69.7° and a C–D band at 2300 with a reference band at 1840 cm.⁻¹.

Commercially available 3-bromobiphenyl was not free of isomers and was prepared from *m*-bromoaniline (Eastman) by the method of Gomberg and Bachmann.¹⁷ The product, b.p. 138° (3 mm.), n_D^{20} 1.6414 (lit.¹⁸ b.p. 169–173° (17 mm.), n_D^{20} 1.6411), was converted to biphenyl-3-*d*, m.p. 69.5–70.5°, C–D doublet at 2260 and 2290 with reference bands at 1950 and 1885 cm.⁻¹.

1-Chloroanthraquinone (Matheson) was reduced with zinc dust and ammonia to give 1-chloroanthracene¹⁹ which was converted to the Grignard reagent in refluxing tetrahydrofuran and quenched with tritiated water. The product was diluted with anthracene. Three successive recrystallizations from toluene gave product with the specific activities of 6.29×10^6 , 5.30×10^6 , and 5.30×10^6 d.p.m./mmole, respectively. The final product of blue fluorescent plates had m.p. 215.8–216.8°.

chkina, and A. I. Shatenshtein, *Zh. Fiz. Khim.*, **34**, 587 (1960); A. I. Shatenshtein and E. Z. Izrailevich, *ibid.*, **28**, 3 (1954).

(14) L. F. Fieser, M. Fieser, and E. B. Hershberg, *J. Am. Chem. Soc.*, **58**, 1463 (1936).

(15) G. P. Baxter and A. H. Hale, *ibid.*, **59**, 506 (1937).

(16) W. Lautsch, *Z. physik. Chem.*, **B1**, 115 (1928).

(17) M. Gomberg and W. E. Bachmann, *J. Am. Chem. Soc.*, **46**, 2339 (1924).

(18) C. S. Marvel, E. Ginsberg, and M. B. Mueller, *ibid.*, **61**, 77 (1939).

(19) O. Fischer and H. Ziegler, *J. prakt. Chem.*, **86**, 289 (1912).

(5) A. L. Jacoby, *Iowa State Coll., J. Sci.*, **13**, 70 (1938).

(6) This argument is weak: *cf.* R. Waack and P. West, *J. Am. Chem. Soc.*, **86**, 4494 (1964).

(7) H. Gilman and R. L. Bebb, *ibid.*, **61**, 109 (1939).

(8) A. Berg, *Acta. Chem. Scand.*, **10**, 1362 (1956).

(9) R. Huisgen, W. Mack, K. Herbig, N. Ott, and E. Anneser, *Chem. Ber.*, **93**, 412 (1960).

(10) R. Huisgen and L. Zirngibl, *ibid.*, **91**, 1438, 2375 (1958).

(11) (a) A. I. Shatenshtein, *Tetrahedron*, **18**, 95 (1962); (b) *Advan. Phys. Org. Chem.*, **1**, 155 (1963).

(12) G. E. Hail, R. Piccolini, and J. D. Roberts, *J. Am. Chem. Soc.*, **77**, 4540 (1955); *cf.* also G. E. Hall, E. M. Libby, and E. L. James, *J. Org. Chem.*, **28**, 311 (1963).

(13) E. N. Yurygina, P. P. Alkhanov, E. Z. Izrailevich, P. N. Mano-

Table I. Exchange Rates of RD(T) with LiCHA in CHA at 49.9°

Run no.	R	[Hydrocarbon], mole/l.	[LiCHA], ^a mole/l.	10 ⁷ k _D , sec. ⁻¹	10 ⁴ k _{2D} , ^b l. mole ⁻¹ sec. ⁻¹	10 ⁷ k _T , sec. ⁻¹	10 ⁴ k _{2T} , ^b l. mole ⁻¹ sec. ⁻¹
33	2-Biphenyl	0.15	0.066	6.56 ± 0.38	1.28		
32	3-Biphenyl	0.15	0.061	19.9 ± 0.1	3.96		
21	4-Biphenyl	0.18	0.052	11.9 ± 0.4	2.49		
18	9-Phenanthryl	0.11	0.035	81.5 ± 7.5	19.3		
20	9-Phenanthryl	0.13	0.057	99.5 ± 3.4	19.3		
13	9-Anthracyl	0.028	0.055	184 ^c ± 41	38		
14	9-Anthracyl	0.027	0.067	270 ^c ± 30	53		
15	9-Anthracyl	0.027	0.061	170 ^c ± 20	34		
23	9-Anthracyl	0.027	0.067	300 ^c ± 18	58	254 ± 29	49
35	1-Pyrenyl	0.017	0.061	145 ± 5	28.7	119 ± 3	23.9
36	1-Pyrenyl	0.0078	0.061			104 ± 2	20.7
42	2-Pyrenyl	0.0078	0.060			94.5 ± 2.0	19.0
44	2-Pyrenyl	0.0078	0.060			90.4 ± 0.6	18.1
38	4-Pyrenyl	0.0078	0.058			142 ± 3	28.8
40	4-Pyrenyl	0.0078	0.061			137 ± 4	27.3
39	1-Anthracyl	0.0082	0.062			50.0 ± 1.1	9.95
41	1-Anthracyl	0.0084	0.061			47.1 ± 1.1	9.59

^a Formal concentration. ^b Model 2; *cf.* ref. 1b. ^c Because of limited solubility, these rates were followed by n.m.r. and are less precise than the infrared measurements.

Pyrene-1-*d*,*t*, -2-*t*, and -4-*t* were described previously.²⁰

Kinetics. The kinetic procedures used were similar to those with naphthalene in the preceding paper.^{1b} About six or seven points were taken in each kinetic run. The tritium analyses of the solid hydrocarbons were carried out using a Nuclear-Chicago Model 723 ambient temperature liquid scintillation counter. Experimental results were converted to rate constants with Perrin's computer program.^{1b} The results are summarized in Table I. These rates differ slightly from those reported in the preliminary communication^{1c} in which a more approximate method was used to derive the rate constants.

Discussion

The rate constants summarized in Table I generally have a probable error of less than 5% based on the reproducibility observed. The most serious error is that for anthracene-9-*d* for which solubility problems produce a larger error. The primary isotope effects, k_D/k_T , for 9-anthracene, 1.2 ± 0.15 , and 1-pyrene, 1.2 ± 0.05 , are somewhat smaller than those for benzene, 1.6, and 1-naphthalene, 1.7.^{1b} Use of the SSRS equation^{21,22} converts $k_D/k_T = 1.2$ to $k_H/k_D = 1.5$. These are low values indeed for primary kinetic isotope effects. Nevertheless, the arguments concerning mechanism developed for benzene and naphthalene pertain as well to these polycyclic hydrocarbons and it seems likely that the same mechanism applies, namely, a rate-determining proton transfer to LiCHA yielding the aryllithium as an intermediate. This conclusion is based heavily on analogy and on the over-all consistency of the results; the low primary isotope effect presents a concern that will require additional work for a complete understanding.

The hydrocarbons used in the present study were generally stable to the reaction conditions. Solutions

(20) A. Streitwieser, Jr., R. G. Lawler, and D. Schwaab, *J. Org. Chem.*, **30**, 1470 (1965).

(21) C. G. Swain, E. C. Stivers, J. F. Reuwer, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, **80**, 5885 (1958).

(22) A. Streitwieser, Jr., W. C. Langworthy, and D. E. Van Sickle, *ibid.*, **84**, 251 (1962).

remained colorless and the hydrocarbons were recovered unchanged except for proton exchange. Anthracene is an exception. After several hours a blue color developed that was shown to signify the radical anion. After long reaction times, some anthraquinone could be isolated. This phenomenon was studied in considerable detail and the results will be published separately. However, the important conclusion is that this reaction appears to be independent of the proton exchange process; for anthracene, proton exchange is faster than radical anion formation by about two orders of magnitude. We attempted to include fluoranthene in the present study but in this case a wine color developed rapidly after mixing the reagents and the solution had the spectrum of the fluoranthene radical anion. From this solution 3-(*N*-cyclohexyl)aminofluoranthene could be isolated in 24% yield.

A control experiment was required to evaluate the possible role of radical anion formation on proton exchange. Anthracene radical anion was shown to be in mobile equilibrium with anthracene and dihydroanthracene; dihydroanthracene is expected to exchange rapidly with solvent and LiCHA. Hence, such an equilibrium provides another mode of exchange of a 9-proton. The control run was carried out with 0.027 *M* anthracene-9-*d*,*t* and 0.25 *M* toluene- α -*d* with 0.043 *M* LiCHA (0.037 *M* after formation of radical anion) and 0.0029 *M* 9,10-dihydroanthracene. Dihydroanthracene, anthracene, and LiCHA react immediately to give anthracene radical anion. The rate constants for hydrogen exchange obtained for anthracene are: $k_{D_{\text{expt}}}$, 1.2×10^{-3} sec.⁻¹; $k_{T_{\text{expt}}}$, 1.3×10^{-3} sec.⁻¹; that is, the presence of 0.006 *M* anthracene radical anion gave a 40-fold rate increase for proton exchange and an inverse isotope effect, k_D/k_T , which is probably experimentally indistinguishable from unity. Thus, if exchange *via* the radical anion were significant for our kinetic experiments, the exchange reaction would exhibit an induction period, nonfirst-order kinetics and no isotope effect. The excellent first-order behavior observed and the small but real isotope effect found demonstrate that the proton exchange rates measured for anthracene are not augmented

importantly by this additional mechanism. It is also noteworthy that the rate of exchange of the toluene- α - d in the above system, $k_2 = 1.6 \times 10^{-2}$ l. mole $^{-1}$ sec. $^{-1}$, does not differ seriously from the normal rate with LiCHA, $k_2 = 1.9 \times 10^{-2}$ l. mole $^{-1}$ sec. $^{-1}$.²³

We are primarily concerned with the effect of structure on the relative rates of exchange. Because of the decrease in primary isotope effect from benzene ($k_D/k_T = 1.6$)^{1b} to 1-pyrene and 9-anthracene ($k_D/k_T = 1.2$) the choice of k_D or k_T rates will make a difference in the values of the derived relative rates. We choose benzene- d as the standard and compare relative k_D rates because many of these quantities have been determined directly and because deuterium lies between hydrogen and tritium such that relative k_D rates are a type of mean of the corresponding k_H and k_T values. In the summary of relative rates in Table II, the 1-anthracene and the pyrene values were derived from the experimental k_T values assuming $k_D/k_T = 1.2$.

Table II. Relative Exchange Rates of ArD

Ar	LiCHA at 49.9°	KNH ₂ at 25° ^a	$\pi_{r,r}$	$\Sigma 1/r$, Å $^{-1}$
Benzene	1.0	1.00	0.398	2.616
2-Biphenyl	1.2	4.7		4.302
3-Biphenyl	3.7	3.3	0.396	3.831
4-Biphenyl	2.3	2.9	0.411	3.707
1-Naphthalene	6.5 ^b	9.7	0.443	3.809
2-Naphthalene	4.1	4.4	0.405	3.531
9-Phenanthrene	17.9		0.442	4.724
1-Anthracene	10.9		0.454	4.515
9-Anthracene	45 ^b		0.526	5.002
1-Pyrene	24.9		0.466	4.952
2-Pyrene	20.9		0.395	4.662
4-Pyrene	31.3		0.445	5.129

^a See ref. 11b. ^b Weighted average.

The comparison of our results with those of Shatenshtein shows a qualitative similarity. Our lower value for *o*-biphenyl probably reflects some steric hindrance. Furthermore, the exchange rates for the pyrene positions show the same relative order, $4 > 1 > 2$, as metalation experiments (*vide supra*).

The over-all pattern shows a substantial effect of structure on reactivity. The relative rates for this group of polycyclic aromatic hydrocarbons covers a log relative rate range of about 1.5. The relative rates of exchange of deuteriomethylarenes over this same group of aromatic hydrocarbons covered a log range of 2.²⁴ The latter series involves arylmethyl anions, and reactivity differences are generally explicable with normal resonance structures which show the distribution of charge around the π -electron system. By comparison, the arenes also show a rather large reactivity range and we next inquire whether these reactivity changes find a ready explanation with our physical organic chemical concepts.

Carbene Resonance Structures and Molecular Orbital Polarizability. In a phenyl anion, the lone-pair electrons are orthogonal to the π -system and normal resonance structures do not apply. However, the presence

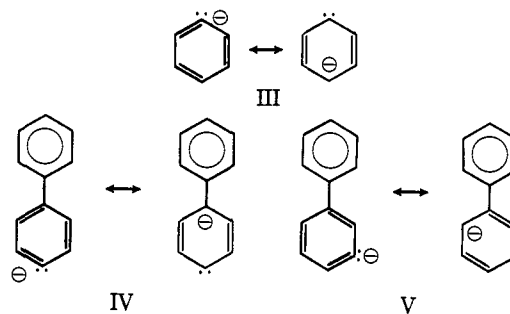
(23) A. Streitwieser, Jr., R. A. Caldwell, M. R. Granger, and P. M. Laughton, *J. Phys. Chem.*, **68**, 2916 (1964).

(24) A. Streitwieser, Jr., and W. C. Langworthy, *J. Am. Chem. Soc.*, **85**, 1757 (1963).

of this charge could lead to a polarization of the π -electrons as shown in the "carbene-resonance" structure (III). However, if such resonance structures were important we would expect the *para* position of biphenyl, in which the anionic charge can conjugate with the second ring (IV) to be more acidic than the *meta* position for which such conjugation is not possible (V).

This concept can be applied to other polycyclic aromatic hydrocarbons in a straightforward way but does not provide a satisfactory rationalization of the experimental results; for example, the pyrene 1-position is predicted on this basis to be far more reactive than the 2-position. We conclude that such carbene resonance structures are not a dominating factor in determining the relative stabilities of the transition states.

Resonance structures such as III are the valence-bond counterpart of the molecular orbital polarizabilities (π). Shatenshtein has suggested that the



reactivities of arenes can be explained by relative polarizabilities.^{11b} In applying molecular orbital theory we consider that the negative charge makes the associated aromatic carbon less electronegative; that is, the Coulomb integral α is made more positive. The effect of this change on the π -energy, E_π , is given as eq. 1 and 2 in which the usual symbols in HMO theory are

$$\delta E_\pi = \frac{\partial E_\pi}{\partial \alpha_r} \delta \alpha_r + \frac{1}{2} \frac{\partial^2 E_\pi}{\partial \alpha_r^2} \delta \alpha_r^2 + \dots \quad (1)$$

$$= q_r \delta \alpha_r + \frac{1}{2} \pi_{r,r} \delta \alpha_r^2 + \dots \quad (2)$$

used: $\pi_{r,r}$ is the atom-atom polarizability.²⁵ Since q_r is unity for all positions of alternant hydrocarbons, the variations in energy come from the second or polarizability term in the expansion. That is, according to simple molecular orbital theory, the effect of structure on the π -electron energy for a change in effective electronegativity of a carbon atom (r), as in the change from C-H to C $^-$, is proportional to $\pi_{r,r}$ to the second degree of approximation. Table II includes a tabulation of appropriate $\pi_{r,r}$ values; the plot of log relative rate vs. $\pi_{r,r}$ shown in Figure 1 shows no reasonable correlation. The pyrene positions, for example, have comparable experimental reactivities but have $\pi_{r,r}$ values varying over a wide range. This application of molecular orbital theory leads to the same conclusion as did the consideration of π -electron carbene resonance structures, namely, that the observed relative rates are not the result of a perturbation of the π -electron system. This unexpected result prompts a second look at eq. 2—since the first term in the expansion is the same for all of the hydrocarbons studied,

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

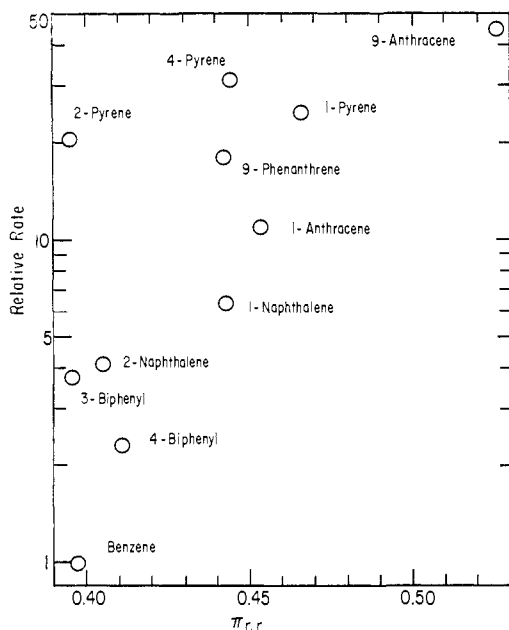


Figure 1. Comparison of relative exchange rates of ArD-LiCHA with corresponding self-atom polarizabilities, $\pi_{r,r}$.

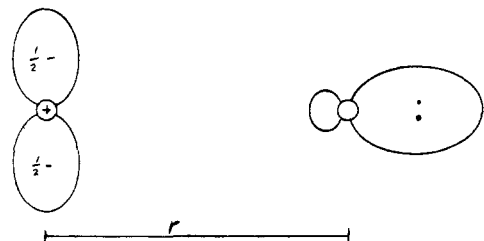


Figure 2. Classical model of the interaction of a lone pair with a p-electron as an electrostatic attraction of a negative charge with a quadrupole in which the distance is approximated by r .

there should be no change to the first approximation. The large structural effects actually observed must come from some other source.

Inductive Effects. Shatenshtein's correlation of exchange rates of *ortho* hydrogens with σ_I of the substituent (*vide supra*) suggests that inductive effects may also be important in our system. Phenyl rings are electron attracting and the inductive effect could well be greater in the *meta* position than in the *para*, in agreement with our results. In a simple model for this inductive effect, the attraction of a negative charge toward the nucleus of an aromatic ring carbon is not completely screened by the associated p-electron since this electron is, on the average, more distant, (Figure 2). The classical model is that of the electrostatic interaction between a charge and a quadrupole—the electrostatic energy varies as $1/r$ for small r and $1/r^3$ for large r . On the basis of this suggestive model we tried a field effect function defined as

$$F_i = \sum_j 1/r_{ij} \quad (3)$$

in which r_{ij} is the distance between the reacting carbon, i , and each remaining aromatic carbon, j . This function is tabulated in Table II for the hydrocarbons studied and a plot of log relative rate vs. F_i is given in Figure 3. This simple model gives a rather good account of the

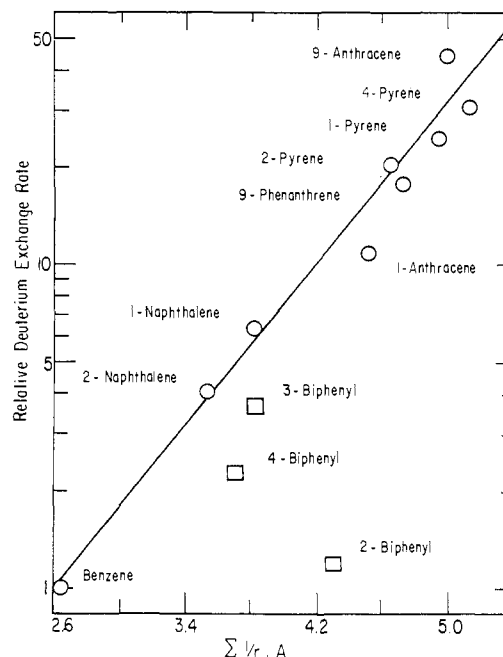


Figure 3. Correlation of exchange rates with the field effect function, F_i .

experimental results. The biphenyls deviate as might be expected—the second ring is not coplanar with the first and screening of the nuclei in the second ring by the π -electrons is more effective than in a planar system. In deriving numerical values for F_i , for simplicity we assumed regular hexagons for the aromatic rings with sides having the benzene bond length, 1.397 Å. The character of the correlation should not change appreciably with a relaxing of this assumption. A more significant change derives from the use of k_D rather than k_T ; the latter relative rates give an equally good correlation^{1c} but with a slightly different slope.

The success of this correlation suggests strongly that the observed rate variations result from inductive field effects. Such inductive effects have long been derived from substituent effects on the acidities of acetic acids. A few pK values are known for arylacetic acids: phenyl, 4.312²⁶; α -naphthyl, 4.236²⁷; and β -naphthyl, 4.256.²⁷ These values plotted against either the log relative rate of the exchange reaction or against the F_i function give straight lines but three points hardly serve as a satisfactory test. Nevertheless, since the pK values of substituted acetic acids do correlate well with the σ_I or σ^* functions,²⁸ we can derive the following σ_I values from the pK data and the fall-off factor of 2.8 per methylene group: phenyl, 0.326; α -naphthyl, 0.382; and β -naphthyl, 0.367. The LiCHA k_D exchange rates then give $\rho_I = 14.7$. From these values and F_i , σ_I values can be calculated for other polycyclic aromatic hydrocarbons. The generality of the F_i function has also been indicated by Acton and Berliner²⁹ who have shown its usefulness in correlating hydrolysis rates of some arylacetic esters.

(26) J. F. J. Dippy and F. R. Williams, *J. Chem. Soc.*, 161 (1934).

(27) J. F. J. Dippy, S. R. C. Hughes, and J. W. Laxton, *ibid.*, 4102 (1954).

(28) For reviews see R. A. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13; and C. D. Ritchie and W. F. Sanger, *Progr. Phys. Org. Chem.*, 2, 323 (1964).

(29) N. Acton and E. Berliner, *J. Am. Chem. Soc.*, 86, 3312 (1964).

Further Molecular Orbital Considerations. The F_i correlation is actually embarrassingly good since the $1/r$ dependence for the electrostatic interaction of a charge and a quadrupole holds only for distances small compared to the length of the quadrupole. In the present case the distances used are larger than the average distance of a π -electron from its associated carbon and something closer to a $1/r^3$ dependence should be better. Yet, functions similar to F_i but using $1/r^2$ or $1/r^3$ are less successful. Hence, we tested a molecular orbital model based on the Pariser-Parr-Pople SCF method.³⁰ Applied to the lone-pair orbital of the aryl anion, considering a single configuration and neglecting the interaction with other σ -bonding electrons, we have a one-element matrix (eq. 4) in which α , q , and γ are the Coulomb integral,

$$H_{rr} = \alpha + 1/2q\gamma + \sum_s (s:rr) \quad (4)$$

electron density, and Coulomb repulsion integral for the lone-pair orbital, and $(s:rr)$ is the penetration integral between an electron in the lone-pair orbital and each neutral carbon atom, s , in the aromatic skeleton. Only the penetration integral term varies as the ring structure is changed; that is, the penetration integral is the quantum mechanical equivalent of the classical electrostatic energy considered above.

Calculations were made³¹ for an electron pair in a C_{sp^2} -orbital with neutral carbon atoms in the plane defined by the two p-orbitals using tables of penetration integrals compiled by Simmons.³² The derived values of $(C:rr)$ for the hydrocarbons studied are summarized in Table III. It is clear that there is little variation in this term for the different hydrocarbons. This is a consequence of the fall-off of the penetration integrals to values close to zero for distances larger than a few Ångströms. Consequently, this approach does not account for the observed correlation and we are left without a satisfactory theoretical explanation.

Table III. Penetration Integral Term for Aryl Anions

Anion	(C:rr), e.v.
Phenyl	5.060
1-Naphthyl	5.081
2-Naphthyl	5.060
1-Anthryl	5.081
2-Anthryl	5.060
9-Anthryl	5.102
9-Phenanthryl	5.081
1-Pyrenyl	5.081
2-Pyrenyl	5.060
4-Pyrenyl	5.081

The large inductive effect of aromatic rings is also not incorporated into simple HMO methods and can have important consequences. An example is the HMO correlation of arylmethane exchange rates which we presented earlier.³³ The correlation was used to de-

(30) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953); J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(31) We are indebted to Mr. H. Rabitz for carrying through these calculations.

(32) We are indebted to Dr. H. E. Simmons for supplying tables as a function of distance of $(C:2s2s)$, $(C:2p\sigma2p\sigma)$, and $(C:2p\pi2p\pi)$. Slater orbitals were used with the effective nuclear charge = 1.625.

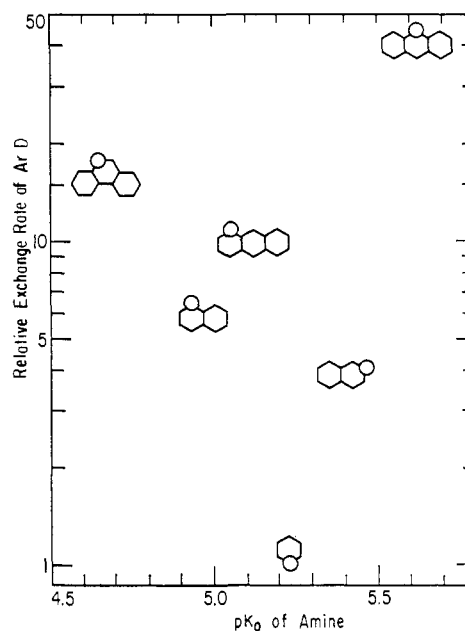


Figure 4. Comparison of ArD-LiCHA exchange rates with basicities of the corresponding heterocyclic amines.

rive a series of pK values of hydrocarbons which was shown later to be seriously in error.³⁴ In the application of this method it was assumed that the increase in rate from toluene to a polycyclic methylarene was due only to the greater resonance stabilization of the polycyclic arylmethyl anion. It is now apparent that the greater inductive effect of the polycyclic systems is also an important contributing factor. Introduction of this factor would tend to reduce the slope of the HMO correlation and compress the resulting pK scale in agreement with the direct experimental results.

Basicities of Amines. The acidity of a phenyl hydrogen bears a formal resemblance to the acidity of the ammonium salt of the corresponding heterocyclic base (see eq. 5 and 6). It is of interest to compare our exchange rates with the pK values of corresponding amines. Values for six such amines are available and are summarized in Table IV. A plot of our log relative

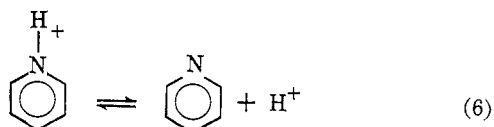
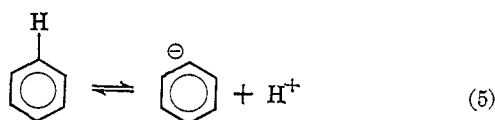
Table IV

Heterocyclic base	pK_a^a	Relative exchange rate of corresponding hydrocarbon
Pyridine	5.23	1.0
Quinoline	4.93	6.5
Isoquinoline	5.46	4.1
Phenanthridine	4.65	17.9
Acridine	5.62	45
6,7-Benzoquinoline	5.05	10.9

^a A. Albert, R. Goldacre, and J. Phillips, *J. Chem. Soc.*, 2240 (1948); A. Albert and J. N. Phillips, *ibid.*, 1294 (1956).

(33) A. Streitwieser, Jr., W. C. Langworthy, and J. I. Brauman, *J. Am. Chem. Soc.*, **85**, 1761 (1963).

(34) A. Streitwieser, Jr., J. I. Brauman, J. H. Hammons, and A. H. Pudjattmaka, *ibid.*, **87**, 384 (1965).



rates against these pK values in Figure 4 shows no semblance of a correlation. It seems clear that dif-

ferent factors are involved in the effect of structure on these two systems. It may be noted incidentally that the simple MO argument in eq. 2 can be applied as well to the amine basicities but the values in Table IV also do not correlate with $\pi_{\tau,r}$. Daudel³⁵ has shown recently that advanced MO theories provide little improvement over this simple method but that the introduction of a solvation energy term does help to explain the variations in amine basicities.

(35) R. Daudel, *Tetrahedron Suppl.*, **2**, 351 (1963).

Acidity of Hydrocarbons. XIX. Kinetics and Mechanism of Exchange of Benzene and *sec*-Butylbenzene with Cesium Cyclohexylamide¹

A. Streitwieser, Jr., and R. A. Caldwell²

Contribution from the Department of Chemistry, University of California, Berkeley, California. Received July 19, 1965

Proton exchange of benzene-*t* with cesium cyclohexylamide (CsCHA) is first order each in hydrocarbon and in CsCHA ion pairs. The second-order rate constants are 3300 times faster than the comparable rate constants with lithium cyclohexylamide and the reaction has a high primary isotope effect ($k_D/k_T = 2.5$). The α -position of 2-phenylbutane has a k_T 0.38 that of benzene-*t* and each replacement of an α -hydrogen by hydrogen occurs with complete racemization. The reaction mechanism appears to be a rate-determining proton transfer to a cesium cyclohexylamide ion pair giving an organocesium as a definite intermediate which reacts with solvent by the microscopic reverse process.

Introduction

An extensive and continuing study of hydrocarbon acidities, as determined by rates of proton exchange reactions in cyclohexylamine with lithium cyclohexylamide (LiCHA) as catalyst, has been carried out in these laboratories.³ The mechanisms of the exchange reactions with LiCHA have been studied in considerable detail and the observed rate constants apparently are useful measures of relative carbanion stabilities. Benzylic,⁴ arylmethyl,⁵ phenylalkyl,⁶ and aryl^{1b} anions have been studied in this manner. However, the exchange rate of benzene-*d* or -*t* itself is inconveniently slow with LiCHA and application to still less reactive hydrocarbons would be difficult.

(1) (a) This work was supported in part by grants from the Petroleum Research Fund of the American Chemical Society; (b) paper XVIII: A. Streitwieser, Jr., and R. G. Lawler, *J. Am. Chem. Soc.*, **87**, 5388 (1965).

(2) National Science Foundation Predoctoral Cooperative Fellow, 1962-1964.

(3) See ref. 1b and preceding papers in this series.

(4) A. Streitwieser, Jr., and W. C. Langworthy, *J. Am. Chem. Soc.*, **85**, 1757 (1963).

(5) A. Streitwieser, Jr., and H. F. Koch, *ibid.*, **86**, 404 (1964).

(6) A. Streitwieser, Jr., and D. E. Van Sickle, *ibid.*, **84**, 249 (1962).

In preliminary experiments⁷ we found that cesium cyclohexylamide (CsCHA) gave exchange several orders of magnitude faster than LiCHA. These observations led to the present study of the kinetics and mechanism of exchange with CsCHA of benzene-*d,t* and 2-phenylbutane-2-*d,t*.

Experimental Section

Benzene-*d,t* was described earlier.⁸

2-Phenylbutane. Addition of phenylmagnesium bromide to 2-butanone afforded 2-phenyl-2-butanol, b.p. 91° (8 mm.) (lit.⁹ b.p. 97° (15 mm.)). The lithium salt of this alcohol was prepared in dry benzene with butyllithium. Addition of methyl *p*-toluenesulfonate to the benzene solution and refluxing for 2 days afforded 2-phenyl-2-methoxybutane, b.p. 84-89° (10 mm.). Cleavage with sodium-potassium alloy (78% potassium, from MSA Research Corp.) in ether and quenching with tritiated D₂O afforded 2-phenylbutane-2-*d,t*, b.p. 77-78° (25 mm.).

(-)-2-Phenylbutane was prepared following Cram.¹⁰

Kinetic Procedures. The general procedures were patterned after those used for LiCHA with changes as noted.

A. Preparation of Cesium Cyclohexylamide Solutions. Metallic cesium was obtained from MSA Research Corp. in sealed ampoules. The ampoules were broken under vacuum in a reactor designed for that purpose. The cesium was then allowed to react with cyclohexylamine, which was bulb-to-bulb distilled from LiCHA into the reactor. Reaction of 1 g. of cesium with 25 ml. of cyclohexylamine at about 60° required about 1 day. A piece of platinum wire

(7) Unpublished results of W. M. Padgett, II, H. F. Koch, and R. G. Lawler.

(8) Paper XVII: A. Streitwieser, Jr., R. G. Lawler, and C. Perrin, *J. Am. Chem. Soc.*, **87**, 5383 (1965).

(9) K. T. Serijan and P. H. Wise, *ibid.*, **74**, 365 (1952).

(10) D. J. Cram, *ibid.*, **74**, 2137 (1952).