Acidity of Hydrocarbons. XXXVII. The Brønsted Correlation and Hydrogen Isotope Exchange Kinetics of Fluorenes, Benzfluorenes, and Indene with Methanolic Sodium Methoxide[1]

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Abstract: Kinetic results are reported for tritium exchange of several hydrocarbons related to fluorene with methanolic sodium methoxide. The second-order rate constant for fluorene increases with NaOMe concentration and a comparison with H_- results is presented. Primary isotope effects are high and indicate the absence of significant amounts of internal return. k_H, k_D, and k_T are interrelated for 9-phenylfluorene and 9-methylfluorene. The secondary isotope effect for exchange of fluorene-*9,9-d*$_2$ is 15%. Tritium exchange rates given as 10^4k_2 (M^{-1} sec^{-1}) at 45°, ΔH^* (kcal/mol), and ΔS^* (eu) are, respectively, 1,12-*o*-phenylene-7,12-dihydropleiadene, 5630, 17.13, −5.99; 9-phenyl-3,4-benzfluorene, 1030, . . ., . . .; 9-phenylfluorene, 173, 21.30, 0.20; 3,4-benzfluorene, 90.3, 20.95, −2.20; indene, 50.0, 20.29, −5.43; 1,2-benzfluorene, 31.9, 18.49, −11.98; 4,5-methylenephenanthrene, 6.85, 23.66, 1.21; fluorene, 3.95, 23.26, −1.16; 2,3-benzfluorene, 2.15, . . ., ... These rates give a linear Brønsted plot with pK's derived from cesium cyclohexylamide with a slope, α, of 0.37. No curvature is detectable in this correlation. The significance of the value of α is discussed.

For the past several years we have undertaken a systematic survey of rates of deuterium and tritium exchange of relatively acidic hydrocarbons with methanolic sodium methoxide for comparison with relative equilibrium pK values determined in cyclohexylamine.[3] The hydrocarbons studied are those which lead to highly conjugated carbanions; that is, fluorenes, polyarylmethanes, etc. In this paper, we discuss the results with the more reactive group of hydrocarbons: fluorene and some 9-substituted fluorenes, indene, and several benzfluorenes. These compounds have in common a cyclopentadiene nucleus which confers relatively high acidity on the hydrocarbons such that hydrogen isotope exchange kinetics can be followed conveniently with methanolic sodium methoxide. In the paper we treat the kinetic form of the reaction with a detailed study of fluorene, consider primary and secondary isotope effects, examine the question of internal return by comparing primary deuterium and tritium isotope effects with two 9-substituted fluorenes, and discuss the reactivities of the entire range of these hydrocarbons in terms of a Brønsted correlation with pK values.

Results and Discussion

Sodium Methoxide Kinetics with Fluorene. At the time this work was begun some years ago there were several reports of exchange reactivities of fluorene: Shatenshtein and Zvyagintseva[4] reported rates in ND_3, $ND_2C_2H_4ND_2$, $ND_2C_2H_4OD$, and NaOEt–EtOD, other authors[5] gave additional data in ethanol, Dessy, *et al.*,[6] reported some results in aqueous dimethylformamide, and Andreades[7] contributed one run in methanolic sodium methoxide. None of these studies has the scope and detail of the present investigation. More recently, Cram and his research group have reported important kinetic and stereochemical studies of fluorene and derivatives[8-10] that complement the present work.

In order to compare a range of hydrocarbons over a variety of conditions, it was important to determine the exact kinetic order of methanol as a function of concentration. In an early phase of this work we examined the rate of loss of deuterium from fluorene-*9-d* using ir spectroscopy. Much of this work was of unsatisfactory precision and is not discussed here.[11] In subsequent work low voltage mass spectrometry was used for the deuterium analyses and extensive kinetic results were obtained for tritium exchange reactivities.

These experiments were carried out by treating fluorene-*9-t* with methanolic sodium methoxide under controlled conditions; aliquots were isolated periodically and analyzed for tritium by liquid scintillation counting. These tritium results are summarized in Table I. Note that many individual investigators contributed experimental results. This system was used as small undergraduate research programs and for training students in exchange kinetics. As a result the rate constants are of variable quality but have a precision gen-

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[1] Supported in part by Grant No. GM-12855 of the National Institutes of Health, U. S. Public Health Service, Grant No. 6125X of the National Science Foundation, and Grant No. 1761-C of the Petroleum Research Fund, American Chemical Society. Some preliminary results were reported previously in A. Streitwieser, Jr., A. P. Marchand, and A. H. Pudjaatmaka, *J. Amer. Chem. Soc.*, **89**, 693 (1969), at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., 1968, Division of Petroleum Chemistry, Abstracts, p A7, and in A. Streitwieser, Jr., and J. H. Hammons, *Progr. Phys. Org. Chem.*, 3, 41 (1965).

[2] (a) A. I. D. Fellow, 1961–1965; (b) National Institutes of Health Predoctoral Fellow, 1968–1970; (c) National Science Foundation Postdoctoral Fellow, 1966–1967.

[3] (a) A. Streitwieser, Jr., J. H. Hammons, E. Ciuffarin, and J. I. Brauman, *J. Amer. Chem. Soc.*, **89**, 59 (1967); (b) A. Streitwieser, Jr., E. Ciuffarin, and J. H. Hammons, *ibid.*, **89**, 63 (1967).

[4] A. I. Shatenshtein and E. N. Zvyagintseva, *Proc. Acad. Sci. USSR, Phys. Chem.*, 117, 781 (1957).

[5] M. Avramoff and Y. Sprinzak, *J. Amer. Chem. Soc.*, **82**, 4953 (1960); N. N. Zatzepina, A. W. Kirova, and J. F. Tupizin, *Org. Reactiv. (USSR)*, **5**, 70 (1968).

[6] R. E. Dessy, Y. Okuzumi, and A. Chen, *J. Amer. Chem. Soc.*, **84**, 2899 (1962).

[7] S. Andreades, *ibid.*, **86**, 2003 (1964).

[8] D. J. Cram and L. Gosser, *ibid.*, **85**, 3890 (1963); **86**, 2950 (1964).

[9] W. T. Ford, E. W. Graham, and D. J. Cram, *ibid.*, **89**, 689, 690, 4661 (1967).

[10] D. J. Cram and W. D. Kollmeyer, *ibid.*, **90**, 1791 (1968).

[11] A. H. Pudjaatmaka, Dissertation, University of California, Berkeley, 1966.

Table I. Protodetritiation of Fluorene-*9-t* with Methanolic NaOMe

Run[a]	Temp, °C	[NaOMe], M[b]	$10^5 k_1$,[b] sec^{-1}	$10^4 k_2$,[c] $M^{-1}\,\mathrm{sec}^{-1}$
HMN1	25.2	0.202	0.720 ± 0.009	0.346
PHO1	24.9	0.515	2.00 ± 0.03	0.392
DR1	25.0	0.592	2.45 ± 0.03	0.414
WKCC1	25.0	0.795	3.71 ± 0.07	0.467
HY1	25.1	1.241	7.81 ± 0.15	0.626
PHO4	24.9	1.928	19.0 ± 0.2	0.992
HY2	25.1	2.93	54.7 ± 1.0	1.86
PHO5	24.9	4.16	193 ± 3	4.67
PHO2[d]	24.9	0.0932	0.247 ± 0.007	0.266
PHO3[e]	24.9	0.195	0.692 ± 0.005	0.356
WKCC1	26.0	0.0569	0.212 ± 0.001	0.324
WKCC2	26.0	0.1342	0.515 ± 0.003	0.334
WKCC3	26.0	0.313	1.30 ± 0.03	0.360
WKCC4	26.0	0.616	2.86 ± 0.03	0.404
AHP51	44.9	0.0633	2.50 ± 0.05	3.98
AHP52	44.9	0.0783	3.10 ± 0.33	4.00
AHP53	45.0	0.1563	6.27 ± 0.06	4.01
RIS1	45.0	0.283	12.2 ± 0.4	4.32
RAM3	44.6	0.351	14.7 ± 0.6	4.35
AHP55	45.0	0.355	15.7 ± 0.2	4.43
APM1	45.0	0.381	16.7 ± 0.2	4.39
JSW1	45.0	0.467	20.6 ± 0.2	4.41
SB2	44.6	0.479	19.1 ± 0.3	4.19
RAM4	44.6	0.676	29.9 ± 3.0	4.60
SB3	44.6	1.678	120 ± 1	7.44
HMN3	70.1	0.0438	26.1 ± 0.3	59.5
MLB2	80.0	0.0174	30.3 ± 0.5	174
MLB3[f]	80.0	0.0158	29.1 ± 0.5	184

[a] APM = A. P. Marchand, PHO = P. H. Owens, WKCC = W. K. C. Chu, AHP = A. H. Pudjaatmaka, RAM = R. A. MacQuarrie, SB = S. Bryant, HMN = H. M. Niemeyer, DR = D. Reuben, HY = H. Yip, RIS = R. I. Sadayasu, JSW = J. S. Wright, MLB = M. L. Brokaw. [b] At the temperature indicated. [c] At the nearest rounded temperature: 25°, 45°, 70°, 80°. [d] 0.90 M in $NaClO_4$. [e] 1.0 M in H_2O. [f] Tritiodeprotonation with methanol-*t*.

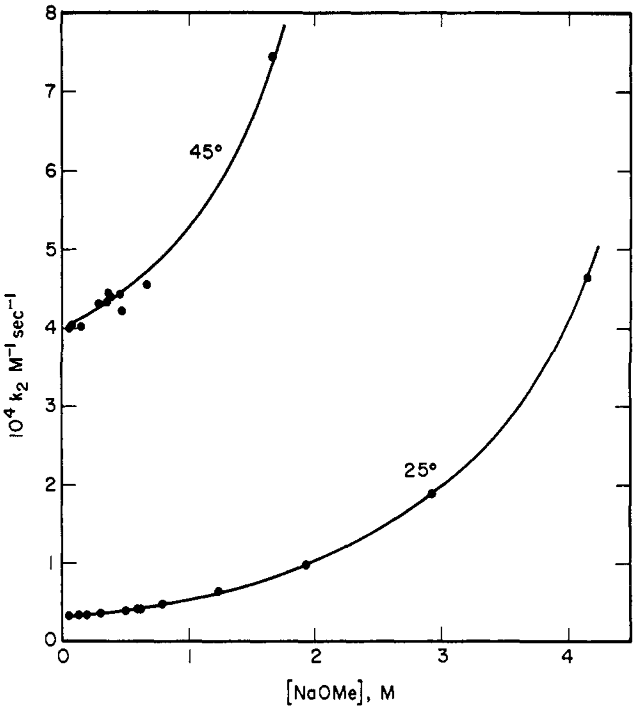

Figure 1. Pseudo-first-order protodetritiation rates of fluorene-*9-t* as a function of sodium methoxide concentration at two temperatures.

erally of 1–3%. All of the original data have been reworked using the LSKIN1 program.[12] In general, data were obtained over several half-lives and infinities were taken for complete reaction. The substrate concentrations used (generally 0.02–0.1 M) and the molecular weight of methanol are such that at equilibrium a negligible amount of isotope remains in the hydrocarbon; thus a simple pseudo-first-order kinetics treatment suffices. The experimental first-order rate constant was converted to the second-order rate constant by dividing by the concentration of sodium methoxide *at the temperature of the run;* that is, the sodium methoxide concentration was corrected for solvent expansion. The actual k_2 values listed in Table I have been further adjusted, using Arrhenius parameters discussed below, to the nearest simple temperature, 25°, 45°, 70°, and 80°, for convenience in comparisons.

The extensive data for protodetritiation at 25° and 45° in Table I show that second-order rate constants are not constant but increase with increasing sodium methoxide concentration. At low methoxide concentrations ($<\sim 1\ M$) the dependence is approximately linear and can be represented as a "salt effect" according to eq 1.[13] This approach leads to the results in Table II. This method of treating the data puts high demands on accuracy and there is some scatter. Nevertheless, the "salt effect" diminishes substantially with temperature. If the salt coefficient b is treated as an activity coefficient, log b is expected to be inversely proportional to the absolute temperature. To test this assumption, an approximate value of b was derived from 9-phenylfluorene (PhFl) data to be discussed below. Using the b values from fluorene at 25 and 45°, the resulting k_2^0 values for PhFl at these temperatures were extrapolated to a k_2^0 value at 0° using the Arrhenius equation. The experimental rate constants at this temperature fit reasonably well to the value, b = 1.2, expected from the proportionality of log b with $1/T$. Results from such a plot were used for the data at other temperatures discussed below. The effect becomes quite small at higher temperatures.

$$k_2 = k_2^0[1 + b(\mathrm{NaOMe})] \qquad (1)$$

Table II. Sodium Methoxide "Salt Effect"

Temp, °C	$10^4 k_2^0$, $M^{-1}\,\mathrm{sec}^{-1}$	b, M^{-1}	Corr coeff
25	0.314 ± 0.003	0.49 ± 0.03	0.99
45	3.95 ± 0.05	0.23 ± 0.04	0.96
0		1.2[a]	

[a] See text.

However, Figure 1 shows that both at 25 and 45° the linear dependence of k_2 on methoxide concentration holds only over a short range. The strongly curved dependence is reminiscent of H_- behavior and suggests a comparison of the rate constants with the H_- values of methanolic sodium methoxide solutions. A plot of log k_1 *vs.* the H_- function of Bowden[14] based on amine

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[12] D. F. DeTar and C. E. DeTar in "Computer Programs for Chemistry," D. F. DeTar, Ed., Vol. 1, W. A. Benjamin, New York, N. Y., 1968, p 126. We are indebted to Miss R. I. Sadayasu for these calculations.

[13] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2763 (1956).

[14] K. Bowden, *Chem. Rev.*, 66, 119 (1966); see also R. A. M. O'Ferrall and J. H. Ridd, *J. Chem. Soc.*, 5030 (1963).

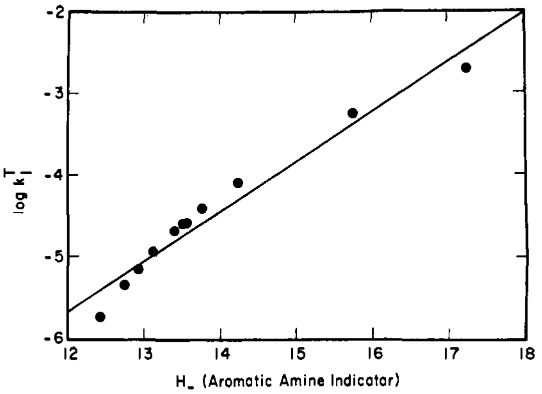

Figure 2. Pseudo-first-order protodetritiation rates of fluorene-*9-t* as a function of Bowden's H_- values based on aromatic amine indicators. The straight line shown is the best least squares correlation of all of the points and is shown only for reference in order to demonstrate the curvature of the points.

indicators gives a slope of 0.61 and a correlation coefficient of 0.979 (Figure 2). However, this superficial analysis hides the distinct curvature of the points. This H_- function does not really adequately represent the present reaction nor is there any real reason why it should. It is now a commonplace that H_- functions depend on the nature of the indicators used. The H_- scale for methanolic sodium methoxide of Rochester[15] is derived from phenols and is different from the Bowden scale. With both scales the present results give an initial slope close to unity and curve sharply to lower slopes. Similar curvature has been demonstrated for the methanolysis of chloroform.[16] In both reactions the transition states clearly have a different activity coefficient dependence on medium than do the indicator anions used to define the H_- scales. In both reactions the transition states incorporate methoxide ion whose solvation is probably more similar to reactant methoxide ion than is solvation of the indicator ions.

It is possible to define a new H_- scale based on our exchange rates at 25°. With the scale defined by the two analytical expressions in eq 2 and 3, log k_1 for tritium

$$H_M = 15.75 + \log[9.53M_{NaOMe} + 4.7M_{NaOMe}{}^2] \quad (2)$$

for $M_{NaOMe} \leqslant 0.733$

$$H_M = 17.426 + 1.649[\log M_{NaOMe}] + 1.425\,[\log M_{NaOMe}]^2 \quad (3)$$

exchange at 25° gives a straight line of slope unity.

Note that we have followed Rochester in presenting an H_- scale based on methanol as the standard state, *i.e.*, H_M.[15] Equation 2 derives directly from eq 1 with the provision that at $M_{NaOMe} = 0.1$, H_M is equal to the Rochester value, 15.75. Equation 3 was derived by fitting the higher points to the best least squares fit parabola with the constraint that the derivatives of the two equations be equal at the point of intersection (at $M_{NaOMe} = 0.733$). For comparison with the H_- scale of Bowden,[14] 3.09 units should be subtracted from values derived from eq 2 or 3.

Finally, the two runs in Table I with addends require comment. The addition of 1 *M* water (run PHO 3) gave $k_2 = 3.56 \times 10^{-5}\ M^{-1}\ sec^{-1}$ compared to the value of 3.44×10^{-5} calculated from eq 1 and Table II. Clearly, even a substantial amount of water has little effect on the rate, undoubtedly because water and methanol have comparable acidities. Traces of water are unimportant in this exchange reaction. A possible ordinary salt effect was studied with run PHO 2 which contained 0.90 *M* sodium perchlorate. The value of k_2 obtained, $2.66 \times 10^{-5}\ M^{-1}\ sec^{-1}$, is only slightly lower than the value expected from eq 1 and Table II of 3.28×10^{5}. The reaction has a small negative salt effect, perhaps because charge is being dissipated at the transition state. However, it is clear that the "salt effect" described above with sodium methoxide is of a different kind.

Activation Parameters. We assume that the second-order rate data in Table I at 70 and 80° require essentially no "salt effect" correction. These data, together with the k_2 results in Table II extrapolated to zero NaOMe concentration, give the following weighted activation parameters using the ACTENG program:[17] $\Delta H^* = 23.26 \pm 0.04$ kcal/mol; $\Delta S^* = -1.16 \pm 0.11$ eu. These values give rate constants compared to experiment in Table III. Values are given at several temperatures to facilitate later comparison of relative rates.

Table III. Protodetritiation of Fluorene-*9-t*

Temp, °C	$10^4 k_2^0$, M^{-1} sec^{-1} Exptl	Calcd[a]
0		0.0078
25	0.314 ± 0.003	0.314
45	3.95 ± 0.05	3.95
70	59.5 ± 0.7	61.9
80	179 ± 5	167
100		1033

[a] $\Delta H^* = 23.26$ kcal/mol, $\Delta S^* = -1.16$ eu.

Reaction Mechanism and Primary Isotope Effect. The near-zero entropy of activation found for fluorene (Table III) for a second-order reaction can probably best be rationalized as a solvation change. The loss of three translational degrees of freedom in going from two molecules to the transition state is compensated by the effective replacement of one methanol solvating methoxide ion by a hydrocarbon molecule. However, note that these activation parameters differ substantially from those found by Cram and Kollmeyer[10] for exchange of fluorene with KOMe in 75% MeOD–25% DMSO-d_6: $\Delta H^* = 16.7$ kcal/mol, $\Delta S^* = -10.8$ eu.

The nature of the bonding to the hydrogen being transferred was studied by the primary isotope effect; in many runs both deuterium and tritium loss were followed from fluorene-*9-d(t)*. These results are summarized in Table IV. The values show a small but real temperature dependence and give the following isotope activation parameters: $\Delta\Delta H^* = -0.59 \pm 0.03$ kcal/mol and $\Delta\Delta S^* = -0.37 \pm 0.08$ eu. Note that the enthalpy difference corresponds almost exactly to the zero point energy difference for bond stretching of C–D com-

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[15] C. H. Rochester, *J. Chem. Soc.*, 676 (1965); *Quart. Rev., Chem. Soc.*, 20, 511 (1966); "Acidity Functions," Academic Press, New York, N. Y., 1970, Chapter 7. An H_- scale based on methanol as the standard state is about three units higher than the H_- scale and is symbolized as H_M by Rochester.

[16] R. A. M. O'Ferrall and J. H. Ridd, *J. Chem. Soc.*, 5035 (1963).

[17] D. F. DeTar, "Computer Programs for Chemistry," Vol. III, W. A. Benjamin, New York, N. Y., 1969, p 6.

Table IV. Primary Isotope Effect

Run no.	Temp, °C	k_D/k_T	
		Exptl	Calcd [a]
WKCC2	25	2.21 ± 0.12	2.25
WKCC4		2.14 ± 0.12	
HMN1		2.20 ± 0.04	
RAM3	45	2.0 ± 0.3	2.11
RAM4		2.4 ± 0.3	
APM1		2.21 ± 0.05	
AHP52		2.03 ± 0.22	
AHP53		2.01 ± 0.13	
AHP55		2.23 ± 0.08	
HMN2	70	2.17 ± 0.05	1.97
HMN3		1.90 ± 0.04	
MLB2	80	1.81 ± 0.04	1.93

[a] $\Delta\Delta H^{\ddagger}$ −0.59 kcal; $\Delta\Delta S^{\ddagger}$ −0.37 eu.

Table V. Exchange Kinetics in Methanol

Run no.	Temp, °C	[NaOMe], *M*	$10^5k_1^T$, sec^{-1}	$10^5k_2^{0T}$,[a] M^{-1} sec^{-1}	$10^5k_1^D$, sec^{-1}	k_D/k_T
9-Phenylfluorene						
WBH1[b]	0.0	0.646	6.10 ± 0.42	5.32 ± 0.37		
WBH2[b]	0.0	0.598	6.36 ± 0.20	6.19 ± 0.19		
WBH11[b]	25.02	0.281	52.5 ± 1.1	164 ± 3		
WBH12[b]	25.02	0.225	43.1 ± 1.7	173 ± 7		
WBH37	25.02	0.0121	2.15 ± 0.13	177 ± 11	4.76 ± 0.17	2.54 ± 0.11[c]
TK14	25.0	0.012	2.09 ± 0.16	173 ± 13	5.14 ± 0.04	2.46 ± 0.20
AHP71[b]	44.9	0.00749	12.8 ± 0.3	1706 ± 40		
AHP72[b]	44.9	0.01243	21.3 ± 0.8	1709 ± 64		
WBH35	45.8	0.0119	22.1 ± 0.5	1852 ± 42	53.1 ± 2.4	2.28 ± 0.08[c]
9-Methylfluorene						
PR2	44.7	0.321	3.35 ± 0.06	9.72 ± 0.17	7.58 ± 0.10	2.26 ± 0.12
PR4	44.7	0.380	3.92 ± 0.07	9.49 ± 0.17	9.01 ± 0.08	2.29 ± 0.11
RAM5	44.6	0.582	6.91 ± 0.3	10.5 ± 0.5	17.3 ± 0.7	2.5 ± 0.2
AHP124	45.0	0.0427			1.08 ± 0.04	
AHP125	45.0	0.154			4.09 ± 0.09	
AHP77	44.96	0.0382	0.408 ± 0.006	10.6 ± 0.2		

[a] At the temperature indicated. [b] Tritiodeprotonation in methanol-*t*. [c] Determined from a log–log plot of loss of D *vs.* loss of T rather than from the ratio of rate constants.

pared to C–T. This normal temperature coefficient and the relatively high value of the primary isotope effect suggest substantial C–H bond breaking at the transition state.

Tritium, deuterium, and hydrogen isotope effects are interrelated by eq 4. In the familiar Swain–Schaad

$$\frac{k_{H}}{k_D} = \left(\frac{k_D}{k_T}\right)^x \tag{4}$$

$$\frac{k_H}{k_T} = \left(\frac{k_D}{k_T}\right)^{x+1} = \left(\frac{k_H}{k_D}\right)^{(x+1)/x}$$

treatment,[18] $x = 2.26$, by the assumptions that all of the isotope effects are in the zero-point energies and that reduced masses can be approximated by the masses of the hydrogen isotopes. If the latter assumption is relaxed and reduced masses are calculated for ^{12}C–L bonds, a better reproduction is obtained for the deuterium isotope effects on vibrational frequencies and $x = 2.344$. The k_D/k_T value for fluorene at 25°, 2.25, converts to $k_H/k_D = 6.3$ or 6.7, using $x = 2.26$ and 2.344, respectively. This value for the primary isotope effect in fluorene is in the normal high range indicative of substantial proton transfer at the transition state. Moreover, this high value indicates that internal return (k_{-I} in eq 5) cannot be significant.[19,20] k_{II} as a diffusion-type

$$RH + {}^-OMe \underset{k_{-I}}{\overset{k_I}{\rightleftharpoons}} R^- \text{ H-OMe} \xrightarrow{k_{II}} \text{exchange} \tag{5}$$

$$k_{\text{exptl}} = \frac{k_I k_{II}}{k_{-I} + k_{II}} \tag{6}$$

of step is expected to have a negligible isotope effect whereas that for k_{-I} is substantially equal to that for k_I. If $k_{-I} \gg k_{II}$, abnormally small primary isotope effects result and have been found for several reactions.[21] Moreover, the denominator of eq 6 has two terms of differing isotope effect, and if both terms are significant, k_{exptl} cannot give a normal interrelationship between H, D, and T transfer.[22] This interrelationship was studied experimentally by comparing k_D/k_T in MeOH with k_H/k_T in MeOD. To avoid complications by secondary isotope effects (*vide infra*), it is necessary to use a tertiary system. Our results with 9-phenylfluorene (PhFl) and 9-methylfluorene (MeFl) are summarized in Tables V and VI. In the reaction of RH(T) in MeOD, the rate of formation of RD gives k_H in this solvent. There is a solvent isotope effect that is obtained by comparing k_T in MeOH with that in MeOD; the more extensive data for 9-methylfluorene at 45° gives $k_2^{0T}(\text{MeOD})/k_2^{0T}(\text{MeOH}) = 2.2$.

With the assumption that the solvent isotope effect on the primary isotope effect is negligible, we determine x experimentally from

$$(k_H/k_T)_{\text{MeOD}} = (k_D/k_T)_{\text{MeOH}}{}^{x+1} \tag{7}$$

The results in Tables V and VI give $x = 2.0 \pm 0.2$ for PhFl at 25° and MeFl at 45°, in close agreement with theory. We conclude that internal return is not important for the exchange of fluorenyl systems in methanolic NaOMe. This conclusion agrees with the elegant

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[18] C. G. Swain, E. C. Stivers, J. F. Reuwer, Jr., and L. J. Schaad, *J. Amer. Chem. Soc.*, **80**, 5885 (1958).

[19] D. J. Cram, C. A. Kingsbury, and B. Rickborn, *ibid.*, **83**, 3688 (1961).

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

[21] For two examples, see J. E. Hofmann, A. Schriesheim, and R. E. Nichols, *Tetrahedron Lett.*, 1745 (1965); A. Streitwieser, Jr., J. A. Hudson, and F. Mares, *J. Amer. Chem. Soc.*, **90**, 648 (1968).

[22] This approach was suggested independently by J. M. Motes and H. M. Walborsky, *ibid.*, **92**, 3697 (1970), although their specific application involves the erroneous assumption that the rate of replacement of H by D is equal to replacement by T.

Table VI. Exchange Kinetics in Methanol-*d*

Run no.	Temp, °C	[NaOMe], *M*	$10^5 k_1^T$, sec^{-1}	$10^5 k_2^{0T}$,[a] M^{-1} sec^{-1}	$10^5 k_1^H$, sec^{-1}	k_H/k_T
9-Phenylfluorene						
WBH36	45.8	0.0155	51.0 ± 0.7	3280 ± 45		
WBH39[b]	25.0	0.1	31.7 ± 1.0		510 ± 10	16.1 ± 0.6
TK13	25.0	0.01	3.15 ± 0.11		50.1 ± 1.0	15.9 ± 0.6
9-Methylfluorene						
PR5	44.7	0.143	3.59 ± 0.05	21.4 ± 0.3	42.7 ± 0.3	11.9 ± 0.3
AHP78	44.9	0.196	5.13 ± 0.4	25.0 ± 2.0		
AHP128	45.0	0.155	3.53 ± 0.06	22.0 ± 0.4		

[a] k_2^0 at the temperature indicated. [b] Rate of D incorporation and T loss was followed for RH (T) in MeOD.

stereochemical experiments of Ford, Graham, and Cram[9] with 9-methylfluorene-2-(*N*,*N*-dimethyl)carboxamide in methanolic KOMe which demonstrated only a small amount of net inversion of configuration due entirely to "isoinversion," an inversion of configuration without exchange, a form of internal return. The further analysis of the present isotope effects is deferred to the following paper in which the method of experimental comparison of hydrogen isotope effects is applied to triarylmethanes.[23]

Secondary Isotope Effect. The secondary isotope effect was measured from the protodedeuteration of fluorene-*9,9-d*$_2$. The D_2, D_1, and D_0 contents were measured by low voltage mass spectrometry as a function of time. The experimental data for run AHP-148 are summarized in Table VII. The pseudo-first-order rate constant for loss of D_2 was obtained directly in the usual manner from the D_2 mole fraction data: $k_1(D_2) = 2.62 \times 10^{-4}$ sec^{-1}. The D_1 rate is more difficult to determine since D_1 is formed from exchange of D_2 and in turn exchanges to give D_0

$$D_2 \xrightarrow{k(D_2)} D_1 \xrightarrow{k(D_1)} D_0 \qquad (8)$$

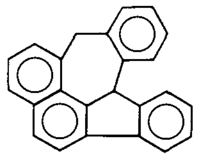
Treatment of the data in Table VII by the graphical integration method described previously[24] gives $k_1(D_1) = 1.54 \times 10^{-4}$ sec^{-1}. The secondary isotope effect given as $^1/_2 k_1(D_2)/k_1(D_1) = 0.85$. Two other runs involved fewer kinetic points and are probably somewhat less accurate but gave the comparable ratios, 0.91 and 0.89. These values agree excellently with the value, 0.85 per deuterium, obtained for the exchange of toluene-α,α,α-d_3 with lithium cyclohexylamide;[24] however, this result has limited significance at the present time in the absence of suitable analogies of secondary isotope effects in carbanions known to be planar. That is, an isotope effect of the direction found could result from a pyramidal or a planar carbanion and does not, at this time, provide any real information about the configuration of the central carbon atom at the transition state.

Table VII. Secondary Deuterium Isotope Effect

Time, sec	Mole fractions[a] D_2	D_1	D_0
985	0.677	0.285	0.039
4,565	0.274	0.462	0.266
8,197	0.106	0.390	0.504
11,786	0.042	0.272	0.686
15,393	0.011	0.191	0.798
18,908	0.007	0.115	0.878

[a] Run AHP 148: 0.195 *M* NaOMe at 45.0°.

Reactivities of Related Hydrocarbons. Using similar kinetic techniques, tritium exchange rates were determined for a number of benzfluorenyl hydrocarbons. The simple benzfluorenes, 1,2-benzfluorene (1,2-BF; 11H-benz[*a*]fluorene), 2,3-benzfluorene (2,3-BF; 11H-benz[*b*]fluorene), 3,4-benzfluorene (3,4-BF; 7H-benz[*c*]fluorene), and 4,5-methylenephenanthrene (4,5-MP; 4H-benz[*def*]fluorene), have been described previously.[8] 1,12-*o*-Phenylene-7,12-dihydropleiadene (PDP, I) was

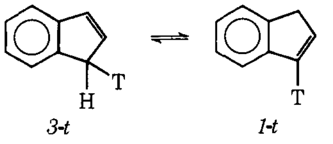


I

the generous gift of Professor Lansbury.[25] 9-Phenyl-3,4-benzfluorene (9-Ph-3,4BF; 7-phenyl-7H-benz[*c*]fluorene) has been reported.[26]

Tritium exchange kinetics were obtained either by tritiodeprotonation using MeOH-*t* or by preparing the labeled hydrocarbon and following the rate of protodetritiation. Results are summarized in Table VIII.

Of these compounds, only for indene and derivatives have kinetic studies been reported previously.[27] Indene-*3-t* was prepared by treating indene with butyllithium and quenching with tritiated water. Because of the high k_H/k_T isotope effect demonstrated for related compounds (*vide supra*), we assume that the equilibrium (9) is set up rapidly relative to the rate of tritium exchange



(9)

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Table VIII. Exchange Rates of Benzfluorenes and Indene

Compound	Run[a]	Temp, °C	[NaOMe], M	$10^5k_1^T$, sec^{-1}	$10^5k_2^{0T}$
PDP, I	MLB2	24.99	0.0135	119 ± 3	8760 ± 221
	MLB3	25.18	0.00934	80.0 ± 4.8	8530 ± 512
	MLB5	44.53	0.00967	523 ± 18	54000 ± 1900
9-Ph-3,4-BF	WKCC6[b]	24.98	0.00398	6.30 ± 0.08	1580 ± 20
3,4-BF	WBH9	0.00	0.298	1.34 ± 0.07	3.31 ± 0.17
	WBH10	0.00	0.448	2.38 ± 0.13	3.46 ± 0.19
	WBH7	25.02	0.162	15.3 ± 0.3	87.5 ± 1.7
	WBH8	25.02	0.157	14.7 ±0.2	86.9 ± 1.2
	APH61	44.9	0.0382	34.5 ± 0.7	895 ± 18
	AHP62	44.9	0.0387	34.6 ± 2.0	886 ± 51
	APH63	44.9	0.0443	43.0 ± 1.0	961 ± 22
Indene	TK3	25.0	0.0712	2.64 ± 0.06[c]	53.7 ± 1.2[c]
	TK5	25.0	0.0712	2.71 ± 0.04[c]	55.2 ± 0.8[c]
	TK4	25.0	0.0695	23.5 ± 0.4[c]	550 ± 9[c]
1,2-BF	WBH5	25.02	0.290	14.3 ± 0.2	43.2 ± 0.6
	WBH6	25.02	0.329	15.7 ± 0.3	41.1 ± 0.8
	AHP57	44.9	0.0668	21.5 ± 1.0	317 ± 15
	AHP58	44.9	0.0829	26.6 ± 0.8	315 ± 9
4,5-MP	TLK6	25.0	0.406	2.50 ± 0.16	5.14 ± 0.33
	AHP64	44.9	0.0660	4.51 ± 0.04	67.3 ± 0.6
	AHP65	44.9	0.0668	4.76 ± 0.09	70.2 ± 1.3
	WBH14	59.50	0.0922	34.2 ± 3.0	366 ± 32
	WBH17	59.34	0.0889	31.6 ± 3.0	351 ± 33
2,3-BF	AHP59	44.9	0.106	2.32 ± 0.05	21.4 ± 0.5
	AHP60	44.9	0.0699	1.50 ± 0.05	21.1 ± 0.7

[a] WBH = W. B. Hollyhead; TLK = T. L. Kruger; for others, see Table I. [b] For D loss, $k_I^D = (15.6 \pm 0.3) \times 10^{-5}$ sec^{-1}; $k_D/k_T = 2.48 \pm 0.06$. [c] k_1^T is given as the direct experimental rate constant derived from LSKIN. k_2^{0T} has been increased by $^3/_2$ to correct for equilibration to indene-*1-t*.

Table IX. Summary of Results

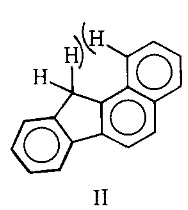
Hydrocarbon	pK[a]	$10^4k_2^{0T}$ (45°) M^{-1} sec^{-1}	ΔH^*, kcal/mol	ΔS^*, eu
PDP, I	15.39[b]	5630	17.13 ± 0.12	−5.99 ± 0.39
9-Ph-3,4-BF	15.68[b]	1030[c]		
9-PhFl	18.49	173	21.30 ± 0.04	0.20 ± 0.12
3,4-BF	19.75	90.3	20.95 ± 0.04	−2.20 ± 0.12
Indene	19.93	50.0	20.29 ± 0.12	−5.43 ± 0.38
1,2-BF	20.35	31.9	18.49 ± 0.09	−11.98 ± 0.31
4,5-MP	22.93	6.85	23.66 ± 0.70	1.21 ± 0.22
Fluorene	23.04	3.95	23.26 ± 0.04	−1.16 ± 0.11
2,3-BF	23.47	2.15		

[a] Derived from Cs ion pairs in cyclohexylamine; ref 3b. Values are on a per hydrogen basis corrected for statistical effects. [b] Unpublished results of W. B. Hollyhead. [c] Extrapolated from 25° using the same activation energy as PDP.

Except for secondary isotope effects which we will neglect for the present purposes, two-thirds of the indene-*t* at any time is present as *3-t* and one-third as the relatively inert *1-t* isomer. Thus, the experimental rate constants for loss of tritium are multiplied by $^3/_2$ in order to obtain the k_T appropriate for the *3-t* isomer.

In Table VIII the results summarized include the NaOMe concentration at the temperature of the run and the experimental pseudo-first-order rate constant for loss of tritium, k_1^T, as determined by the LSKIN1 program. These values are converted to second-order rate constants extrapolated to zero NaOMe concentration by the use of eq 1 and the values of b given in Table II. For other temperatures, log b was assumed to be proportional to $1/T$ (*vide supra*).

For most of these compounds, data were obtained at more than one temperature so that activation parameters could be determined. These are summarized in Table IX together with the standard deviations as given by the ACTENG program.[17] Note that the entropies of activation generally hover in the region of −2 eu and that the reactivities are determined primarily by ΔH^*. The largest deviation from this generalization is that of 1,2-benzfluorene in which the reactive hydrogen may be perturbed by steric rate effects, II.



II

Brønsted Correlation and Reaction Mechanism. Assignments of pK values have been made for all of these hydrocarbons and are summarized in Table IX on a per-hydrogen basis—that is, corrected for statistical effects. These pK's were derived from pK differences given from the cesium ion pair equilibria in cyclohexylamine.[3b] However, for highly delocalized carb-

$$\mathrm{RH + R'^{-}Cs^{+} \rightleftharpoons R^{-}Cs^{+} + R'H}$$

anions of this fluorenyl type such acidity differences are now available in several solvents and show a

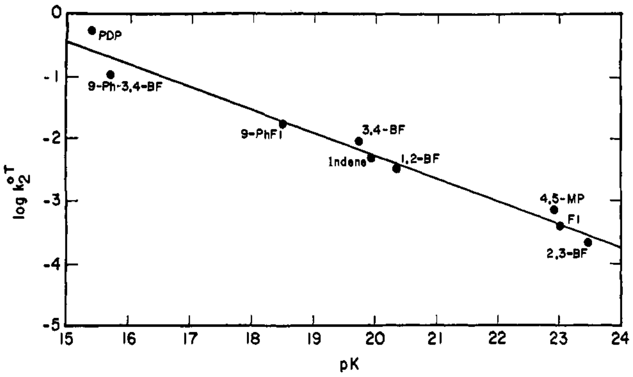


Figure 3. Brønsted plot of protodetritiation reactivities of fluorenyl hydrocarbons and pK's derived from ion pair equilibria of cesium salts in cyclohexylamine. The least squares line shown is log k_2^{0T} = 5.1085 ± 0.47 − (0.3690 ± 0.024)pK with r = 0.986 and the standard deviation of fit = 0.201.

remarkable consistency both for ion pairs and for free anions.[3,28,29] This constancy is undoubtedly the result of extensive charge delocalization in these highly conjugated carbanions such that specific solvent effects and hydrogen bonding are minimized. Furthermore, several of these hydrocarbons have had their pK values determined by the H_- method,[29,30] in which the standard state is the dilute aqueous solution. Thus, the values given in Table IX refer to aqueous solution pK's. However, the H_- method is known to have important limitations because of important solvation differences between hydrocarbon carbanions and the indicator anions used to define the H_- scales.[29b,30d] Consequently, the absolute magnitudes of the pK's in Table IX may be in doubt by one to two units but the relative values should be reasonably accurate.

Furthermore, to compare proton transfer rates with proton transfer equilibria in a typical Brønsted correlation, data should pertain to the same solvent; hence, in the present case we would require pK values for methanol solution, not water! The few data available indicate that such pK's would be about six units higher than those given in Table IX.[29b,31] *All of the hydrocarbons discussed in this study are orders of magnitude less acidic than methanol in methanol.* Nevertheless, the constancy of ΔpK values in various solvent systems for hydrocarbons of the present type suggests strongly that ΔpK values in Table IX are accurate and may be applied to methanol solution. In short, the hydrogen isotope exchange reaction in methanol involves an anionic transition state and an essentially free carbanion intermediate whereas the pK values used are derived from ion-pair equilibria extrapolated to free ions in water; but the Brønsted correlation actually involves relative rates and ΔpK's so that a direct correlation is rational. Such a Brønsted plot is shown in Figure 3 with the data summarized in Table IX for tritium exchange rates at 45° and pK values. The least squares slope corresponds to a Brønsted α of 0.369 ± 0.024 (r = 0.986, standard deviation of fit = 0.200), a value somewhat on the low side. If kinetic data at 25° were used, the same temperature as the pK values, α would be increased by only 7%. The second noteworthy feature is that the plot shows no suggestion of curvature despite a pK range of eight units; the scatter about the least squares line in Figure 3 appears to be random. Linearity was further checked by fitting the data to the best least squares second-order equation in pK to give the result, log k = 5.921 − 0.454 pK + 0.00218(pK),[2] with a standard deviation of fit = 0.176. This approach makes high demands on precision, of course, but we note that the standard deviation of fit is hardly better when a second adjustable parameter is included; that is, the deviation from linearity is essentially random. Furthermore, the slope given by the quadratic equation is 0.389 at pK = 15 and 0.345 at pK = 25, exactly the wrong direction according to theory. This result of a completely linear correlation with nine points differs from that of Cram and Kollmeyer,[10] who found some curvature in a Bronsted plot of five points for deuterium exchange rates in 75% MeOD–25% DMSO-d_6 that, moreover, included only fluorene among the present group, the other compounds being polyarylmethanes. Accordingly, their result will be discussed in the following paper.[23]

The linearity of Figure 3 suggests strongly a relative constancy of proton transfer mechanism over this range of structures. This suggestion is reinforced by the relative constancy of ΔS^* values for these compounds (*vide supra*) and by the primary isotope effects: at 25° k_D/k_T is 2.48 for 9-Ph-3,4-BF (Table VIII), 2.50 for 9-PhFl (Table V), and 2.25 for Fl (Table IV); these compounds cover almost the full range of acidities in this group. These high isotope effects indicate that proton transfer has reached the "symmetrical" stage at the transition state; that is, the force constants from hydrogen to carbon and to oxygen are approximately the same.[32] The proton being transferred undoubtedly fills one coordination site on the displacing methoxide ion, a site made available by the loss of one hydrogen-bonding solvent. In the resulting reaction

$$\text{R—H} + \text{MeO}^- \cdots \text{HOMe} \longrightarrow (\text{R}\cdots\text{H}\cdots\text{OMe})^- + \text{HOMe}$$

the overall entropy change is approximately zero and agrees with the ΔS^* values found. This loss of one hydrogen-bonding solvent is also consistent with the direction found (*vide supra*) for the solvent isotope effect, k(MeOD) > k(MeOH).

Geometrical symmetry does not necessarily imply charge symmetry at the transition state. For such information we look to the Bronsted α. Caution is clearly necessary in interpreting α values in view of the demonstration of Bordwell, *et al.*,[33] of "impossible" α-values of >1 and <0. However, these cases are always those in which inductive substituents can have a different field effect interaction with the electron distribution in the product anion than in the transition state; in particular, a dipolar substituent close to the reacting carbon could well have a greater electrostatic interaction with the substantial charge at this carbon and on the at-

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(29) Recently reviewed by (a) H. Fischer and D. Rewicki, *Progr. Org. Chem.*, 7, 116 (1968); (b) C. D. Ritchie in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, p 219.

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(31) C. J. Chang, unpublished results.

(32) F. H. Westheimer, *Chem. Rev.*, 61, 265 (1961); see also R. P. Bell, *Discuss. Faraday Soc.*, **39**, 16 (1966).

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tacking base than with the charge in a delocalized product anion where the charge may be effectively farther away.[34] However, when the mechanism of charge stabilization is exclusively delocalization, we suggest that the Brønsted α value is a valid measure of the amount of charge being delocalized. In the present case, the compounds chosen are such that relative acidity is due almost entirely to charge delocalization in the carbanions. Given the limitations of real compounds it is impossible to isolate completely a single interaction mechanism and even in the compounds chosen, there is undoubtedly some "inductive" effect of different π-carbons and phenyl substituents but these effects are clearly of a lower order of magnitude than delocalization in these structures. We shall show, for example, in a subsequent publication that a Brønsted α derived in the same manner for substituted fluorenes has a substantially different—and higher—value. According to the above postulate only 37% charge delocalization has occurred in these π-systems compared with the equilibrium carbanions. This relatively low value further suggests that the central carbon atom has not achieved coplanarity at the transition state and may be substantially pyramidal. A highly pyramidal central carbon for these systems implies the corollary that such is the case for other rate-determining carbanion systems as well; the application of this corollary to other such systems is under active current study.

Experimental Section

9-Labeled Fluorenes. Fluorene is readily metalated with butyllithium; however, direct quenching of 9-fluorenyllithium with D_2O gives variable and substantial amounts (over 20% in one experiment) of fluorene-*9-d*$_2$. Thus, fluorenyllithium was converted to the Grignard reagent before quenching. A typical procedure is as follows. To a stirred solution of 7.5 g (0.045 mol) of fluorene in ether was added dropwise 35 ml of 1.5 *M* butyllithium in hexane. The resulting solution was added dropwise to a stirred mixture of magnesium bromide in ether prepared from 20 g (0.100 mol) of ethylene bromide and 2.92 g (0.12 g-atom) of magnesium powder. The mixture was stirred at reflux for 2 hr, cooled to room temperature, and quenched with 2 ml of D_2O. Normal work-up and recrystallization from ethanol gave 6.4 g (84%) of fluorene-*9-d*, mp 115°.

Fluorene-*9-d,t* was prepared by adding a few drops of tritiated water before the final quench with D_2O. A sample used for many of the kinetic runs had mp 115–116°, 83% deuterim, and a specific activity of 3.1×10^7 dpm/mmol.

Fluorene-*9-d*$_2$ was prepared by refluxing a solution of 8.5 g of fluorene in dry dimethoxyethane with 50 ml of 0.5 *M* KOD in D_2O for 2 days.

Other Hydrocarbons. 9-Phenylfluorene was prepared by reaction of phenylmagnesium bromide with fluorenone and reduction of the 9-phenylfluoren-9-ol by hydrogenolysis over 5% Pd/C with a few drops of perchloric acid or by refluxing with formic acid, mp 145–146° (lit.[35] mp 145°).

9-Methylfluorene was prepared in an analogous manner with methylmagnesium iodide followed by hydrogenolysis, mp 44–45° (lit.[36] mp 45–46°).

1,2-Benzfluorene was purchased from Dr. Theodore Schuchardt and recrystallized from acetic acid, mp 186–187.5° (lit.[37] mp 185.4–186°).

2,3-Benzfluorene was purchased from K & K Lab., Inc., and recrystallized from ligroin, mp 206–208° (lit. mp 204–206°,[38] 208–209).[39]

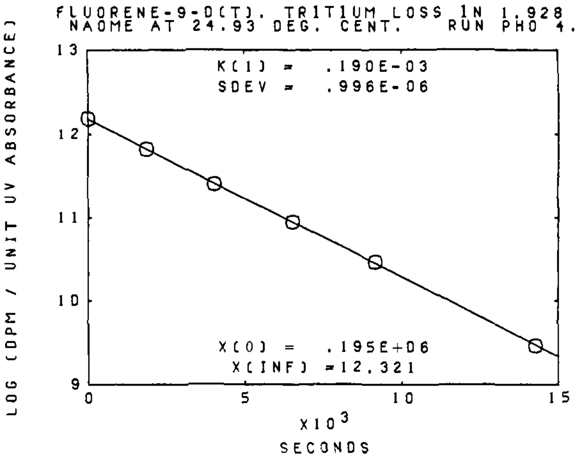

Figure 4. CalComp plot of kinetic run PHO 4.

3,4-Benzfluorene was purchased from Dr. Theodore Schuchardt and recrystallized from ethanol, mp 123–124° (lit.[40] mp 124–125°).

4,5-Methylenephenanthrene was purchased from K & K Lab., Inc., and purified by recrystallization of the picric acid complex (mp 167–168°, lit.[41] mp 166°) from 95% ethanol. The hydrocarbon was regenerated with ammonia and recrystallized from 95% ethanol, mp 115–116° (lit.[42] mp 114.3–115.3°).

9-Phenyl-3,4-benzfluorene was prepared by a modification of the method of Ullmann and Mouraviev–Vinigradov:[26] methyl 2-naphthoate was treated with phenyllithium in ether to give diphenyl-2-naphthylcarbinol which on refluxing with a mixture of glacial acetic acid and hydrochloric acid gave the hydrocarbon which was recrystallized from methanol, mp 140–141° (lit.[26] mp 137°). Infrared, ultraviolet, and mass spectra and the analysis were consistent with the assigned structure.

Labeled materials were generally prepared by treatment with butyllithium and quenching with D_2O or tritiated water. Being liquid, indene required special handling. Commercial indene was vacuum distilled under argon to give product giving a single peak on glpc. Hexane was removed from butyllithium in a vacuum system and replaced by ether. Purified indene was slowly syringed in under nitrogen and the mixture was stirred overnight. Tritiated water was syringed in under nitrogen and the product was vacuum distilled and stored in a freezer before use. Because of the tracer amounts of tritium used, the product is an indene-*t*, although because of reaction of indene with indenyllithium during the quenching process, the compound may be 1- and 3-labelled. We would expeet, for example, that an attempt to use this procedure for deuterated material would produce multiply deuterated product as in the case of fluorene above. In practice, the compound will equilibrate rapidly to a mixture of indene-*1-t* and indene-*3-t* during thee kintic runs.

Kinetics. Many individuals contributed kinetic runs on fluorene exchange and the detailed procedures varied somewhat. However, this exchange reaction is unexceptional and only the following typical procedure is given. A known solution of fluorene-*9-d,t* in dry methanol contained in a flask fitted with a serum cup was allowed to equilibrate in a thermostat. An aliquot of a known solution of sodium methoxide in methanol, similarly equilibrated, was syringed in. Aliquots were removed at intervals, quenched with HCl, and extracted with CCl_4 or spectrograde cyclohexane. Efforts were taken to keep the kinetic solution under nitrogen by filling a syringe with nitrogen and injecting it prior to removing a kinetic aliquot. Carbon tetrachloride solutions were evaporated and the solid was weighed out for preparation of the scintillation solution in toluene. The cyclohexane solutions were assayed by uv and diluten with scintillation solution. These solutions were counted on a Nuclear-Chicago Mark I liquid scintillation counter.[43] The kinetic solution remaining at infinity was allowed to cool to

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(34) A similar explanation has been derived independently by A. J. Kresge, *J. Amer. Chem. Soc.*, **92**, 3210 (1970).

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(39) C. Graebe, *Justus Liebigs Ann. Chem.*, **254**, 265 (1889).

(40) J. W. Cook, A. Dansi, C. L. Hewett, J. Iball, W. V. Mayneord, and E. Roe, *J. Chem. Soc.*, 1319 (1935).

(41) O. Kruber, *Ber. Deut. Chem. Ges.*, **67**, 1000 (1934).

(42) W. E. Bachmann and J. C. Sheehan, *J. Amer. Chem. Soc.*, **63**, 204 (1941).

(43) Purchased with a gift from the E. I. DuPont de Nemours Co.

room temperature and aliquots were removed with calibrated pipets and titrated with standard HCl. The resulting base concentration was corrected to the kinetic temperature using published data on the change of density of methanol with temperature.[44]

Deuterium content was determined by infrared in the earlier runs. The C–D stretching band at 2170 cm^{-1} gave a linear plot of absorbance *vs.* concentration. In later runs, low voltage mass spectrometry was used. Also in later runs the bath temperature was calibrated with a quartz thermometer. Kinetic runs at 70° and above made use of aliquots in sealed glass tubes in place of the serum-capped flask.

Kinetic data were treated as pseudo-first order using the LSKIN1 program[12] and were plotted with a CalComp plotter. A typical example is given in Figure 4.

Similar procedures were used for the exchange kinetics of the other compounds; however, reaction was too fast for these techniques for some compounds. An example is given for run MLB 5 with PDP at 44.53°: A bifurcated reactor[45] contained a solution of PDP in MeOH-*t* in one leg and NaOMe in MeOH in the other, and was pressured with nitrogen. After temperature equilibration, the contents were mixed and aliquots were ejected into dilute HCl. The entire run was recorded with verbal notes on a tape recorder from which the times of each aliquot could be obtained later.

In the case of indene, the liquid hydrocarbon was isolated by concentration of the organic extract and glpc separation (25% Apiezon on Chromosorb W). Samples were injected into scintillation counting solution with a syringe fitted with a Chaney adaptor.

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[44] J. Timmermanns, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, New York, N. Y., 1950, pp 303–304.

[45] A. Streitwieser, Jr., and W. C. Langworthy, *J. Amer. Chem. Soc.*, **85**, 1757 (1963); A. Streitwieser, Jr., R. G. Lawler, and C. Perrin, *ibid.*, **87**, 5383 (1965).

Acidity of Hydrocarbons. XXXVIII. Kinetic Acidity and Brønsted Correlation of Di- and Triarylmethanes with Methanolic Sodium Methoxide[1]

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Abstract: Exchange rates and isotope effects are reported for polyarylmethanes in methanolic sodium methoxide. Tritium exchange rates given as 10^7k_2 (M^{-1} sec^{-1} at 100°), ΔH^* (kcal/mol), and ΔS^* (eu) are, respectively, 10-phenyl-9,9-dimethyldihydroanthracene (PDDA), 533, 27.80, −4.05; *p*-biphenylyldiphenylmethane (BDM), 42.7, 28.88, −6.14; *p*-dibiphenylylmethane (DBM), 30.5, 30.20, −3.33; triphenylmethane (TPM), 13.8, 32.28, 0.70; diphenylmethane (DPM), 1.65, 33.80, 0.56. Kinetic primary isotope effects are relatively small; k_D/k_T at 100° are PDDA, 1.64; TPM, 1.34; DPM, 1.52. These reduced isotope effects are shown to result from internal return by interrelating H, D, and T exchange with TPM. These five hydrocarbons give an excellent Brønsted acidity correlation with a line of $\alpha = 0.46$ (at 100°) that shows no sign of curvature. The correlation is different in slope and displaced from the similar linear Brønsted correlation demonstrated previously for fluorene-type hydrocarbons. The significance of this difference is discussed.

Only a few studies have been reported of kinetic acidities of di- and triarylmethanes. Shatenshtein[3] has results in liquid ammonia and some amines and Ebel and Ritterbusch[4] have more extensive data for deuterium and tritium exchange with lithium *N*-methylanilide in methylaniline. Some preliminary reports have been made of our own studies with lithium cyclohexylamide in cyclohexylamine[5] but complete results will be published shortly. Kollmeyer and Cram[6] have demonstrated a Brønsted correlation for deuterium exchange reactivity of di- and triarylmethanes in 75% MeOD–25% DMSO-d_6. Their results are discussed below together with a related study by Zatzepina, Kirova, and Tupizin[7] in EtOD. In the present study we present exchange reactivities of five compounds, 10-phenyl-9,9-dimethyldihydroanthracene (PDDA), *p*-biphenylyldiphenylmethane (BDM), triphenylmethane (TPM), di-*p*-biphenylylmethane (DBM), and diphenylmethane (DPM), with methanolic sodium methoxide for comparison with a related study of more acidic fluorene derivatives.[8]

The preparation of PDDA has been presented earlier.[9] The other compounds are well-known materials. The labeled compounds were prepared generally by metallation with butyllithium and quenching with D_2O containing tritium. Kinetic treatment of such compounds gave infinity values corresponding to relatively high isotope content presumably on the rings. This

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