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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[1] This research was supported in part by Grant No. 12855 of the National Institutes of Health, U. S. Public Health Service. A preliminary report of some of this work was presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., 1968, Abstracts of Petroleum Division, p A7.

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

[3] Reviewed in A. I. Shatenshtein, *Advan. Phys. Org. Chem.*, **1**, 155 (1963).

[4] H. F. Ebel and G. Ritterbusch, *Justus Liebigs Ann. Chem.*, **704**, 15 (1967).

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

[7] N. N. Zatzepina, A. W. Kirova, and J. F. Tupizin, *Org. Reactiv. (USSR)*, **5**, 70 (1968).

[8] A. Streitwieser, Jr., W. B. Hollyhead, A. H. Pudjaatmaka, P. H. Owens, T. L. Kruger, P. A. Rubenstein, R. A. MacQuarrie, M. L. Brokaw, W. K. C. Chu, and H. M. Niemeyer, *J. Amer. Chem. Soc.*, **93**, 5088 (1971).

[9] A. Streitwieser, Jr., J. H. Hammons, E. Ciuffarin, and J. I. Brauman, *ibid.*, **89**, 59 (1967).

Table I. Values of b Used

Temp, °C	b^a
45	0.23
100	0.046
118	0.03
134	0.022
150	0.015

[a] Log b is assumed to be proportional to $1/T$.

Table II. Tritium Exchange Rates with NaOMe–MeOH

Hydrocarbon	Run no.[a]	Temp, °C	[NaOMe], M^b	$10^5k_1^{\mathrm{T}}$, sec^{-1}	$10^5k_2^{0\mathrm{T}}$, M^{-1} sec^{-1}
PDDA	AHP129[c]	45.0	0.228	0.00172 ± 0.00020	0.00717 ± 0.00083
	AHP130[c]	45.0	0.248	0.00191 ± 0.00020	0.00729 ± 0.00076
	AHP131[c]	50.1	0.223	0.0031 ± 0.0007	0.0133 ± 0.0030
	WBH42	99.79	0.0955	0.481 ± 0.007	5.01 ± 0.07
	WBH43	99.79	0.0982	0.512 ± 0.007	5.19 ± 0.07
	WBH40	118.12	0.232	7.64 ± 0.05	32.7 ± 0.2
	WBH41	118.12	0.236	7.66 ± 0.03	32.2 ± 0.1
BDM	CJC1	97.6	0.119	0.903 ± 0.0030[d]	0.755 ± 0.025[d]
	CJC2	148.1	0.101	9.5 ± 0.4[d]	94 ± 4[d]
TPM	GS1	97.7	0.1968	0.0204 ± 0.0014	0.103 ± 0.007
	GS2	97.7	0.2098	0.0210 ± 0.0008	0.099 ± 0.004
	GS3	97.7	0.1891	0.0440 ± 0.012[d]	0.231 ± 0.006[d]
	GS4	97.7	0.1710	0.0399 ± 0.0008[d]	0.232 ± 0.005[d]
	AHP134	99.0	0.357	0.0484 ± 0.002	0.133 ± 0.001
	AHP135	99.0	0.191	0.0263 ± 0.0010	0.136 ± 0.005
	WBH21	128.95	0.722	1.98 ± 0.03	2.70 ± 0.04
	TLK9	144.2	0.700	13.0 ± 0.2	18.4 ± 0.3
DBM	CJC3	153.8	0.181	10.6 ± 0.2	58.4 ± 1.0
	CJC4	134.1	0.189	1.87 ± 0.03	9.85 ± 0.15
DPM	AHP136	99.0	0.378	0.00579 ± 0.00040	0.0151 ± 0.0010
	WHB38	118.32	0.433	0.0631 ± 0.0018	0.144 ± 0.004
	WBH34	147.27	0.413	1.32 ± 0.04	3.18 ± 0.10
	TLK11	147.3	0.504	1.64 ± 0.03	3.23 ± 0.06

[a] AHP = A. H. Pudjaatmaka; WBH = W. B. Hollyhead; CJC = C. J. Chang; GS = G. Sonnichsen; TLK = T. L. Kruger. [b] At temperature of run. [c] Tritiodeprotonation in MeOH-*t*. [d] Loss of tritium in MeOD–NaOMe.

Table III. Primary Isotope Effects in Methanol

Hydrocarbon	Run	Temp, °C	$10^5k_1^{\mathrm{D}}$, sec^{-1}	$k_{\mathrm{D}}/k_{\mathrm{T}}$	Average $k_{\mathrm{D}}/k_{\mathrm{T}}$ at 100°
PDDA	WBH42	99.79	0.855 ± 0.032	1.71 ± 0.03[a]	1.64
	WBH43	99.79	0.825 ± 0.017	1.56 ± 0.04[a]	
TPM	GS1	97.7	0.0269 ± 0.0003	1.32 ± 0.10	1.34
	GS2	97.7	0.0286 ± 0.0014	1.36 ± 0.09	
	WBH13	98.8 ± 0.4	0.0657 ± 0.015	1.32 ± 0.05[a]	
	TLK8	98.9 ± 0.6	0.0466 ± 0.0017[b]	1.35 ± 0.05[a]	
DPM	WBH38	118.32	0.0955 ± 0.0020	1.47 ± 0.02	1.52[c]
	WBH34	147.27	1.78 ± 0.02	1.42 ± 0.06	
	TLK11	147.3 ± 0.2	2.19 ± 0.04	1.34 ± 0.04	

[a] From a direct plot of log $(D_0 - D_t)$ *vs.* log $(T_0 - T_t)$. [b] Value for k_{T}. [c] Extrapolated from results shown at higher temperature assuming the same temperature dependence found for fluorene (ref 8).

point was confirmed by oxidation in some cases. For example, a sample of deuterated and tritated diphenylmethane, prepared in this manner, on oxidation with chromium trioxide in acetic acid gave benzophenone that retained 7.5% of the original tritium and 4.8% of the original deuterium. Such ring labeling can be reduced by converting the lithium derivative to the Grignard reagent by treatment with magnesium bromide in ether (from ethylene bromide and magnesium) before quenching.[8]

At temperatures near the boiling point of methanol, kinetic measurements were made with aliquots of kinetic solution in sealed tubes. At higher temperatures, a specially constructed but straightforward stainless steel reactor was used. This reactor contained a tube inside, connected to a needle valve such that, when the valve was opened, the vapor pressure of methanol caused ejection of a kinetic aliquot. Under the conditions used only a negligible amount of the methanol is in the vapor phase and, for reasonable values of the volume of activation, there is no significant change in rate constant due to pressure.

The pseudo-first-order rate constants were converted to second-order rate constants by dividing by the sodium methoxide concentration at the temperature of the run and were corrected to zero sodium methoxide concentration with the "salt effect" equation[8]

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

Values of b were derived from previous work and are summarized in Table I. The kinetic results for tritium exchange are summarized in Table II.

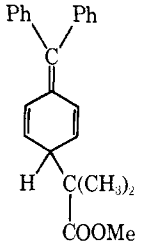
Primary Isotope Effect and Reaction Mechanism. Because of the importance of primary isotope effects in monitoring proton transfer reactions, several values were determined and are summarized in Table III.

Table IV. Primary Isotope Effects in Methanol-*d*

Hydrocarbon	Run	Temp, °C	[NaOMe], M	$10^6 k_I^T$, sec^{-1}	k_H/k_T
TPM	GS3	97.7	0.189	0.0770 ± 0.0015	1.75 ± 0.07
	GS4	97.7	0.171	0.0712 ± 0.0012	1.79 ± 0.05
BDM	CJC1	97.6 ± 0.2	0.119	0.280 ± 0.004	3.10 ± 0.10
	CJC2	148.1 ± 0.2	0.101	32.2 ± 1.0	3.38 ± 0.17

The striking feature about these results is that they are all comparatively small. The average values at 100° are all substantially less than k_D/k_T for fluorene at the same temperature, 1.84.[10] Such low values may result from an unsymmetrical transition state or from the incursion of substantial internal return or both.

Some internal return is expected. In a beautiful set of experiments, Cram, *et al.*,[11] showed that the rearrangement of I to II with NaOMe in DOMe is 46–7% intramolecular. Since the triarylmethyl anion implicated is similar to that in our exchange reaction, we must anticipate a comparable amount of internal return.



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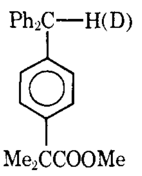

II

In order to determine the amount of internal return taking place under the present exchange conditions for TPM itself, we make use of the interrelationship between hydrogen, deuterium, and tritium isotope effects.

For an internal return mechanism

$$\text{R—D} \underset{k_{-I}^D}{\overset{k_I^D}{\rightleftarrows}} \text{R}^-, \text{DOMe} \xrightarrow{k_{II}^D} \text{exchange} \tag{2}$$

$$k_{\text{exptl}}^D = \frac{k_I^D k_{II}^D}{k_{-I}^D + k_{II}^D} \tag{3}$$

If k_{II} has a substantially different isotope effect from k_I and k_{-I}, k_{exptl} will not show a normal interrelationship between proton, deuterium, and tritium rates. Actually, k_{II} represents a diffusion type of step and is expected to have essentially no isotope effect; thus, we assume $k_{II}^H = k_{II}^D = k_{II}^T$. From eq 3, an experimental isotope effect is given by

$$\frac{k_{\text{exptl}}^T}{k_{\text{exptl}}^H} = \frac{k_I^T(k_{-I}^H + k_{II})}{k_I^H(k_{-I}^T + k_{II})} \tag{4}$$

set

$$a^T = k_{-I}^T/k_{II} \tag{5}$$

and introduce the equilibrium constants

$$K = k_I/k_{-I} \tag{6}$$

We then derive

$$\frac{k_I^T}{k_I^H} = \frac{k_{\text{exptl}}^T}{k_{\text{exptl}}^H} + a^T(k_{\text{exptl}}^T/k_{\text{exptl}}^H - K_T/K_H) \tag{7}$$

Similarly, for deuterium–tritium isotope effects

$$\frac{k_I^T}{k_I^D} = \frac{k_{\text{exptl}}^T}{k_{\text{exptl}}^D} + a^T(k_{\text{exptl}}^T/k_{\text{exptl}}^D - K_T/K_D) \tag{8}$$

The isotope effects for the primary step are related by eq 9

$$k_I^T/k_I^H = (k_I^T/k_I^D)^y \tag{9}$$

in which y is given as 3.26 by the Swain–Schaad treatment[12] and is 3.344 by our related treatment.[8] To solve eq 8 and 9 for the internal return ratio, a^T, we now need values for the experimental isotope effects and the equilibrium constants.

It can be shown readily that the assumption that k_{II} has no isotope effect implies that

$$K_T/K_H = K_T' \tag{10}$$

for the equilibrium

$$\text{RT} + \text{MeOH} \overset{K_T'}{\rightleftarrows} \text{RH} + \text{MeOT} \tag{11}$$

Since this equilibrium isotope effect is determined almost entirely by zero point energy differences for vibrations and librations between products and reactants, K_T' is expected to be essentially the same for all of our hydrocarbons. K_T' was measured for 9-phenylfluorene (PhFl) by determining the amount of tritium incorporation at equilibrium from MeOT containing NaOMe. This hydrocarbon was picked simply because its exchange rate is relatively fast and equilibrium measurements could be made conveniently at several temperatures. Results are summarized in Table V. Note that there is a small equilibrium isotope effect in the expected direction: O–H involves somewhat higher vibration frequencies and zero point energies than C–H. The values in the last column of Table V are based on the value at 25° and the temperature coefficient expected if

Table V. Equilibrium Isotope Effect for 9-Phenylfluorene

Temp, °C	K_T' [a]	Av K_T' [b]	Calcd K_T' [c]
0	1.35 ± 0.15, 1.25 ± 0.04	1.30 ± 0.07	1.35
25	1.21 ± 0.11, 1.35 ± 0.03, 1.42 ± 0.04, 1.30 ± 0.07, 1.30 ± 0.03, 1.31 ± 0.03, 1.34 ± 0.07	1.32 ± 0.05	(1.32)
50	1.33 ± 0.07, 1.23 ± 0.04, (1.60 ± 0.08),[d] 1.27	1.28 ± 0.05	1.29
100			1.23

[a] K_T' = [MeOT][RH]/[MeOH][RT]. [b] Errors given as $[\Sigma(x_i - \bar{x})^2/(N - 1)]^{1/2}$. [c] Calculated from the value at 25° assuming that only zero point energies are important. [d] Omitted from average.

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(10) Extrapolated from Table IV, ref 8.

(11) D. J. Cram, F. Willey, H. P. Fischer, H. M. Relles, and D. A. Scott, *J. Amer. Chem. Soc.*, **88**, 2759 (1966).

(12) C. G. Swain, E. C. Stivers, J. F. Reuwer, Jr., and L. J. Schaad, *ibid.*, **80**, 5885 (1958).

Table VI. Internal Return from Isotope Effects

	TPM, 97.7°	9-Phenylfluorene,[a] 25°	9-Methylfluorene,[a] 45°
$k_{\text{exptl}}^{\text{D}}/k_{\text{exptl}}^{\text{T}}$	1.34 ± 0.03	2.50 ± 0.1	2.30 ± 0.1
$k_{\text{exptl}}^{\text{H}}/k_{\text{exptl}}^{\text{T}}$	1.77 ± 0.05	16.0 ± 0.5	11.9 ± 0.3
a^{T}	0.66 ± 0.04	0.016 ± 0.006	0.024 ± 0.022
$k_{\text{I}}^{\text{D}}/k_{\text{I}}^{\text{T}}$	$1.85\ {}^{+\ 0.3}_{-\ 0.2}$	$2.54\ {}^{+\ 0.2}_{-\ 0.1}$	$2.38\ {}^{+\ 0.6}_{-\ 0.2}$

[a] See ref 8.

the isotope effect results only from zero point energy differences.

The experimental interrelationships between k_{H}, k_{D}, and k_{T} were obtained by comparing $k_{\text{D}}/k_{\text{T}}$ in MeOH (Table III) with $k_{\text{H}}/k_{\text{T}}$ obtained in MeOD (Table IV). We assume that the solvent isotope effect on the primary kinetic isotope effect is negligible. This is a significant assumption because it implies that k_{II} in MeOH is the same as k_{II} in MeOD or that a^{T} has no solvent isotope effect. This assumption is undoubtedly the weakest part of the present treatment but it is a necessary one. This assumption is different from that given above in eq 10 and 11 because tritium is a tracer isotope in the common solvent, MeOH, whereas the macroscopic isotope, deuterium, changes the properties of the solvent.

Continuing with these assumptions, we derive eq 12

$$A + (A - B)a^{\text{T}} = [1 - (B^{1/y} - 1)a^{\text{T}}]^{y} \qquad (12)$$

in which A and B are now the experimentally determined quantities

$$A = (k_{\text{exptl}}^{\text{D}}/k_{\text{exptl}}^{\text{T}})^{y}/(k_{\text{exptl}}^{\text{H}}/k_{\text{exptl}}^{\text{T}}) \qquad (13)$$

$$B = (k_{\text{exptl}}^{\text{D}}/k_{\text{exptl}}^{\text{T}})^{y}K_{\text{T}}' \qquad (14)$$

From the data in Tables III, IV, and V, and y = 3.344, we find a^{T} = 0.66 ± 0.04 for triphenylmethane at 97.7° (Table VI). This substantial amount of internal return is of the same order of magnitude as that obtained by Cram (*vide supra*). With this value we can now correct for internal return and find the isotope effect for the primary step: $k_{\text{I}}^{\text{D}}/k_{\text{I}}^{\text{T}}$ = 1.85. This value is the same, within experimental error, as that of fluorene at 100°, 1.84 (*vide supra*).

Moreover, a direct comparison can now be made to fluorene derivatives. We showed previously[8] that H, D, and T exchange for PhFl and 9-methylfluorene (MeFl) agreed approximately with expectations from a Swain–Schaad type of treatment, indicating that internal return was of minor significance. We now reverse the logic and use the above treatment with y = 3.344 to deduce a^{T} for these compounds. The isotope effects reported previously yield a^{T} values of 0.016 ± 0.006 for PhFl at 25° and 0.024 ± 0.022 for MeFl at 45° (Table VI). These small amounts of internal return have virtually no effect on the conclusions reached earlier.[8] Note especially that the derived primary isotope effects for the proton transfer step hardly differ from the experimental values. Moreover, these isotope effects, $k_{\text{I}}^{\text{D}}/k_{\text{I}}^{\text{T}}$, both extrapolate to 2.08 at 100° using the experimental temperature dependence found for fluorene. This value is hardly greater than that found for TPM. The corresponding $k_{\text{H}}/k_{\text{D}}$ values are 5.6 and 4.2, respectively, for PhFl and TPM at 100°, certainly quite normal values for proton transfers. The combined experimental errors are not small and these numbers could actually be the same. Nevertheless, the important and remarkable conclusion emerges that these isotope effects differ little considering the 13 pK unit difference in acidity of these hydrocarbons. This small effect does not agree with contemporary thought that changes in equilibrium acidity will produce continuous changes in transition state structure for related compounds as reflected in primary isotope effects. Our results do agree with the recent experimental work of Bordwell and Boyle[13] who found comparatively small changes in isotope effects for proton exchange of a wide range of nitroalkanes.

If we now assume that $k_{\text{I}}^{\text{D}}/k_{\text{I}}^{\text{T}}$ is constant at 1.85 along this series, the experimental $k^{\text{D}}/k^{\text{T}}$ alone can be used in eq 8 to derive a^{T}. Values derived in this way are summarized in Table VII. The value so derived for TPM, of course, is the same as that obtained above. The values for internal return for PDDA, BDM, and DPM are smaller. Smaller values for PDDA and BDM may be expected because the carbanions are more stable; the $k_{-\text{I}}$ step is thus slower and the solvent exchange step may compete more effectively. However, the smaller a^{T} for DPM is not expected. This result is a direct consequence, of course, of the stronger experimental primary isotope effect found for DPM compared to TPM. If the conclusion is sustained by further work, it would mean that the k_{II} step is not a constant for the series; this step could well be different for secondary and tertiary systems.

Brønsted Correlation. The rate data in Table II were used to obtain activation parameters with the ACTENG program.[14] The results are summarized in Table VIII. The pK values listed are those derived from cesium cyclohexylamide (CsCHA) equilibria.[15] The meaning of such numbers was discussed earlier;[8] although the absolute pK values are of limited significance when applied to methanol solution, the relative pK values have precision of about ±0.1 unit and have fundamental significance. The enthalpies of activation show a monotonic trend with pK. The en-

Table VII. Internal Return from Experimental $k_{\text{D}}/k_{\text{T}}$[a]

Compd	a^{T} (100°)
PDDA	0.15
BDM	0.21[b]
TPM	0.66
DPM	0.28

[a] The $k_{\text{D}}/k_{\text{T}}$ values used are listed in Table III. [b] Calculated from $(k_{\text{H}}/k_{\text{T}})_{\text{exptl}}$ in MeOD, Table IV.

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(13) F. G. Bordwell and W. J. Boyle, Jr., *J. Amer. Chem. Soc.*, **93**, 512 (1971).

(14) D. F. DeTar, "Computer Programs for Chemistry," Vol. III, W. A. Benjamin, New York, N. Y., 1969, p 6.

(15) A. Streitwieser, Jr., E. Ciuffarin, and J. H. Hammons, *J. Amer. Chem. Soc.*, **89**, 63 (1967).

Table VIII. Summary of Kinetic Results and Activation Parameters for Tritium Exchange

Hydrocarbon	pK^a	ΔH^*, kcal/mol	ΔS^*, eu	$10^7 k_2^{0T}$, M^{-1} sec^{-1}, 100°	$10^{10} k_2^{0T}$, M^{-1} sec^{-1}, 45°
PDDA	28.04	27.80 ± 0.03	−4.05 ± 0.08	533	698
BDM	30.20	28.88	-6.14^b	42.7^b	43.9^b
DBM	30.86	30.20	−3.33	30.5	22.8
TPM	31.48	32.28 ± 0.06	0.70 ± 0.17	13.8	6.41
DPM	33.45^c	33.80 ± 0.08	0.56 ± 0.19	1.65	0.543

[a] pK per position with CsCHA. [b] For MeOH derived from MeOD with a rate factor of 2.29. [c] This value is slightly different from that reported previously, 33.4,[15] because of a change in the extinction coefficient of diphenylmethylcesium [G. Häfelinger and A. Streitwieser, Jr., *Chem. Ber.*, **101**, 657 (1968)].

tropies of activation show no simple progression or constancy but these activation parameters are based on limited data and this feature of the entropies may reflect experimental error.

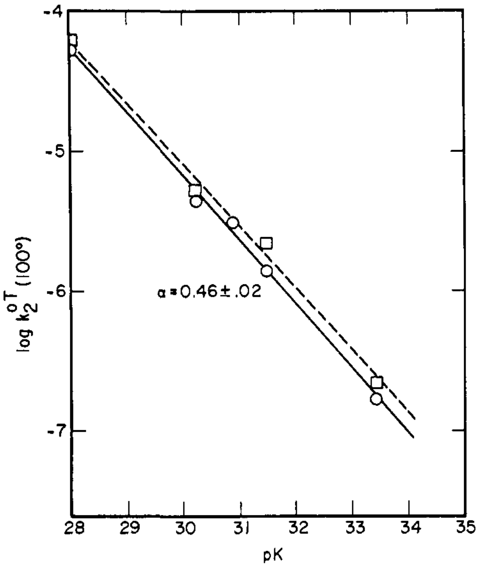

Figure 1. Brønsted plot of log k_2^{0T} at 100° *vs.* CsCHA pK's (circles). The straight line is log $k = -0.460\text{p}K + 8.599$ (r = 0.998, standard deviation of fit = 0.066). Squares refer to k_I rates (correction for internal return).

From the activation parameters a set of reactivities was derived at 100° and summarized in Table VIII. BDM was measured only in MeOD but a value could be extrapolated to MeOH using the ratio k_2^{0T}(MeOD)/k_2^{0T}(MeOH) found for TPM, 2.29, by direct measurement in the two solvents. Note that this ratio is close to the value, 2.2, reported in the previous paper[8] for 9-methylfluorene at 45°.

These compounds form a closely related set and, accordingly, a Brønsted plot of the rates at 100° *vs.* the CsCHA pK's gives an excellent straight line with slope, $\alpha = 0.460 \pm 0.017$ (r = 0.998, Figure 1). This set does combine secondary and tertiary hydrogens but no apparent difference is evident that could be ascribed to any steric hindrance. Furthermore, over a range of 6 pK units, no curvature at all is discernible. This point was confirmed by least squares fitting of the data to a second-order polynomial in pK; the coefficient of the square term is small and of the wrong sign. The corresponding slope at pK = 28 is 0.463; that at pK = 33.5 is 0.456.

The slope corresponds to typical Brønsted correlations that have α of about 0.5. We may ask about the effect of internal return on the slope. If the amount of internal return were the same for each compound in this series, no change in slope would result; but the analysis in the preceding section indicated that internal return is not constant for the series. The a^T values in Table VII were used to plot log k_I^T *vs.* pK (squares and dotted line in Figure 1). On a logarithm scale, the inclusion of modest amounts of internal return clearly has but little effect; the slope is changed only to 0.45.

We next compare the Brønsted correlation for the present group of compounds with that determined previously[8] for fluorene-type hydrocarbons. For this purpose, the present rates were extrapolated to 45° using the Eyring equation and the activation parameters in Table VIII. The resulting Brønsted correlation is highly linear with little apparent loss in quality despite the long temperature extrapolation (Figure 2). The new slope, 0.578 ± 0.021 (r = 0.998), is higher than at 100°, as expected, but still in a "normal" range. What is most remarkable, however, is that this Brønsted correlation is totally irreconcilable with that of the fluorenes also reproduced in Figure 2. Both correlations are linear over long ranges with no sign of curvature, they have substantially different slopes, and they are displaced from each other.

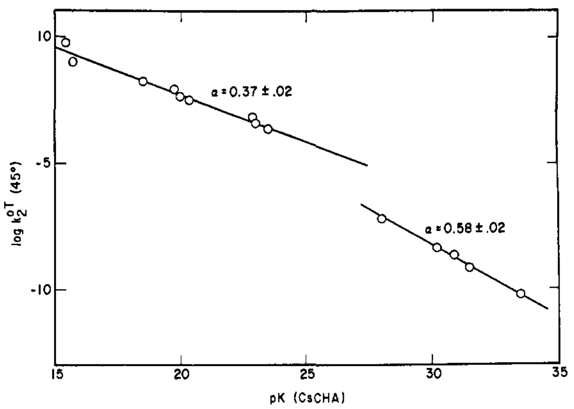

Figure 2. Brønsted correlation of log k_2^{0T} at 45° *vs.* CsCHA pK's for fluorenes (upper line) compared to polyarylmethanes (lower line).

We may ask whether this difference results from internal return. At the lower temperature, methanol is more highly structured by hydrogen bonding and internal return is probably greater. The actual k_I rates would then be higher than the k_{exptl} which are actually plotted. Nevertheless, to "lift" the polyarylmethane line to join the fluorenes line would require a^T values of almost two powers of ten. Such a temperature coefficient for internal return would be indeed remarkable, and we would still be left with a different slope. The two lines are too linear and the slopes too different (0.37 and 0.58) to actually represent a continuous curve.

Another possibility is that the scale of pK's is incorrect. The relative pK's used are based on ion pair equilibria with cesium cations in CHA with the assumption that relative ionic pK's in methanol will have comparable magnitudes. If the methanol pK's for polyarylmethanes were actually ∼6 units more positive than those of the fluorene group, one could make more of an argument that Figure 2 shows two segments of a continuous curve. But this case cannot be sustained. The relative pK's in DMSO for TPM and DPM compared to fluorenes are similar to those in CHA and no important solvent effect is expected for such large delocalized carbanions.[16]

We are left with a simple and direct alternative; namely, that the two groups of compounds are indeed different and exchange by different mechanisms. The two groups of compounds do indeed have an important obvious difference. The polyarylmethyl anions are carbanions in which negative charge is delocalized into attached aryl rings. The fluorene-type systems are characterized by a central cyclopentadienyl anion moiety that introduces an additional aromatic stability. We might expect that for a given degree of proton transfer, the fluorenyl systems would delocalize charge more effectively than the polyarylmethyl systems. Such an effect could require less charge transfer at the transition state for fluorenes with a consequent lower α and a faster rate for a given equilibrium acidity.

The demonstration that polyarylmethanes and fluorenes are not part of the same Brønsted family in methanol–methoxide has extensive repercussions. In the past, the common relationship has been *assumed* and important conclusions were based on this assumption. Ritchie and Uschold have reported a curved Brønsted relationship in methanol[17] but the "curve" is based largely on the single point for TPM compared with several fluorene derivatives. Similarly, Cram and Kollmeyer[6] reported a curved Brønsted correlation for fluorene and for polyarylmethanes in 75% MeOD–25% DMSO-d_6. Actually, the four polyarylmethanes form an excellent straight line in their plot; the "curve" is due almost entirely to the point for fluorene. Our results suggest that the Cram–Kollmeyer results should be interpreted as two linear Brønsted correlations with the fluorene line represented by a single point.

Zatzepina, *et al.*,[7] have reported deuterium exchange rates for fluorene, DPM, and TPM in EtO^-–EtOD. They *assumed* a three-point linear Brønsted correlation and used the exchange rates of a variety of heterocyclic compounds with this same Brønsted line to estimate the pK values. The present results emphasize that their pK values assigned to the heterocyclic compounds have only the most qualitative significance.

Many of the conclusions in these older researches must now be reevaluated. One final remark needs emphasis. There is no doubt that over a sufficiently wide range, Brønsted correlations must be curved. What has been demonstrated in this and the previous paper[8] is that for hydrocarbons with delocalized anions in methanol, Brønsted correlations are accurately linear over substantial pK ranges; thus, the pK range required for the observation of curvature in this system is large indeed—larger than most previous estimates. We are far from diffusion-controlled reactions at either extreme. For example, the experimental primary isotope effect for diphenylmethane is far from unity. This means that the reverse reaction has a significant isotope effect and, even for this hydrocarbon, the reaction of the carbanion with methanol is not diffusion controlled. The long linear range of the Brønsted correlations in the present systems contrasts markedly with the systems observed by Eigen[18] in which the Brønsted slope changes completely from 0 to 1 over as little as 6 pK units. Eigen's systems were invariably hydrogen-bonded compounds in aqueous solution in which proton transfers occur within a hydrogen-bonded encounter complex with relatively little molecular reorganization. Hydrogen bonding is not important with highly delocalized carbanions and proton transfer in such systems requires substantial molecular reorganization. Much more activation is required for such proton transfers, and it can be shown[19] that an increased Brønsted range is a direct consequence of such higher activation requirements.

Experimental Section

Labeled Hydrocarbons. Di-*p*-biphenylylmethane was prepared by allowing *p*-biphenylyllithium (*p*-bromobiphenyl and butyllithium in ether)[20] to react with ethyl formate. The carbinol, mp 153–155° (lit.[21] mp 151°), was hydrogenolyzed by refluxing in glacial acetic acid with zinc and 5% Pd/C. The product was recrystallized from MeOH, mp 164–165° (lit. mp 159°,[22] 162°[23]).

p-Biphenylyldiphenylmethane was prepared[24] by reaction of *p*-biphenylyllithium with benzophenone. The resulting carbinol, mp 136–138° (lit.[25] mp 136.4–137.2°), was hydrogenolyzed with hydrogen and 10% Pd/C in glacial acetic acid containing a few drops of perchloric acid. The hydrocarbon was recrystallized from ethanol, mp 113.5–114.5° (lit.[26] 111–112°).

The hydrocarbons were generally labeled by treatment with butyllithium in ether and quenching with tritiated water or D_2O. This procedure incorporates some isotope into the aromatic rings; the amount was determined by infinity measurements in the exchange kinetics or by oxidation to triarylcarbinol or diaryl ketone.

Kinetics. Kinetic solutions were made up with methanolic sodium methoxide in sealed tubes or in a stainless steel reactor from which aliquots could be withdrawn periodically. Thermostated baths were calibrated with a Hewlett-Packard quartz thermometer which was in turn standardized with ice–water. Kinetic aliquots were quenched with hydrochloric acid and the mixture was extracted with pentane or isooctane. The washed and dried extracts were evaporated and a portion of the solid hydrocarbon was used for low voltage mass spectrometric determination of deuterium. A weighed portion was also used for preparation of the liquid scintillation solution for tritium counting. Alternatively, a portion was dissolved in cyclohexane and assayed by uv spec-

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troscopy. In the case of diphenylmethane, the liquid hydrocarbon was isolated by concentration of the extract and glpc separation (25% Apiezon on Chromosorb W).

The base concentration was determined by quenching kinetic aliquots at various times with water and titrating with standard HCl. The resulting base concentration was corrected to kinetic temperature with the density–temperature tables of Timmermans.[27]

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The Basic Strength of Carbazole. An Estimate of the Nitrogen Basicity of Pyrrole and Indole[1]

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Abstract: The protonation of *N*-methylcarbazole in strong acids was found to occur on nitrogen, as evidenced by changes in its nmr spectrum, and to be accompanied by the disappearance of strong absorption of ultraviolet light at 235 mm. Similar spectral changes occur with other carbazole bases; these were used, in conjunction with standard indicator methods, to determine extents of protonation of carbazole and eight of its derivatives. The acidity dependencies of these protonation reactions fall, on the whole, into categories expected for secondary and tertiary amines, but slopes of plots of log I *vs.* H_0 show enough individual variation to give a set of individually extrapolated pK_a's inconsistent with expected substituent effects. Half-protonation points, $(H_0)_{I=1}$, on the other hand, correlate very well with Hammett σ constants; these $(H_0)_{I=1}$ values were therefore used to estimate basicities by a method which gives carbazole itself a pK_a of about -6. This provides an upper limit for the basic strength of the nitrogen atom in the related heteroaromatics pyrrole and indole, substances in which equilibrium protonation occurs preferentially on carbon and for which nitrogen basicity is not directly measurable.

The N-heteroaromatics pyrrole and indole are unusual in that they undergo equilibrium protonation on carbon in preference to nitrogen and display their basic properties only in concentrated acid solution.[5,6] The nitrogen atom in these substances must therefore be very weakly basic indeed. It is not possible, of course, to measure this property of these systems directly, but it might be estimated in the following way. Under equilibrium conditions, pyrrole undergoes preferential protonation on an α-carbon atom,[5a,7] but indole protonates on β-carbon,[6b] thus trading off an additional resonance form for undisturbed conjugation in its benzene ring. This suggests that the next higher benzolog, carbazole, in which the second side of the pyrrole ring is blocked as the first is in indole, might protonate on nitrogen; determination of the gross basicity of carbazole would then furnish an estimate of nitrogen basicity in the pyrrole system.

With this objective in mind, we undertook to determine the site of protonation and the basic strength of carbazole. In the sole previous report on this subject, the pK_a of carbazole itself was estimated only as < -1, and the site of protonation was not established.[8]

Results and Discussion

Protonation of carbazole occurs in very strong acids (*e.g.*, half-protonation at $\sim$8.5 M sulfuric acid), as evidenced by the reversible change in the ultraviolet spectrum. The principal band in the ultraviolet spectrum of the fully protonated carbazole (Figure 1) closely resembles that of fluorene (λ_{max} 262 mm, log ϵ_{max} 4.30 M^{-1} cm^{-1})[9] in both wavelength and intensity, suggesting that protonation occurs on nitrogen. Confirmation of nitrogen as the site of protonation was established from the nmr spectra of *N*-methylcarbazole in strong acids. In a mixture of trifluoroacetic acid and sulfuric acid the nmr spectrum consists of a complex multiplet in the aromatic proton region and a singlet some 4 ppm further upfield. Since these bands have the relative areas of 8–3, they can be attributed to the aromatic ring protons and those of the *N*-methyl group, respectively. In fluorosulfonic acid at 30° the methyl-group peak appears as a doublet, $J = 6$ Hz, demonstrating that protonation occurs on nitrogen. No splitting is observed in the weaker acid because of fast proton exchange, which also accounts for the absence of an observable signal for this proton in both cases.

The intense ultraviolet absorption band of the basic form of carbazole at 235 nm, $\epsilon > 10^4$, which disappears upon protonation, is especially suited to quantitative

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