(nmr method) was used. The optical rotation of thermally quenched aliquots was measured at 25° and 356 mμ. In runs 5 and 6, (−)-I-*h* with $[\alpha]^{25}_{546}$ −5.7° (*c* 2.5, chloroform) and mp 98–101° was used. The optical rotation of thermally quenched aliquots was measured at 35° and 356 mμ. The higher temperature in the latter case was required to prevent crystallization of the substrate in the polarimeter tube. The use of shorter wavelength in both cases afforded higher valued observed rotations.

Exchange Runs and Isotopic Analyses. Runs 1 and 2 employed racemic VI-*h* with mp 78–79°. Thermally quenched aliquots were poured into 20 ml each of pentane and 1% (weight by weight) aqueous sodium chloride, washed with the salt solution and pure water, and then dried over anhydrous calcium chloride. The pentane layer was filtered through a glass wool plug, reduced in volume to *ca.* 3 ml, placed in a preweighed vial (±0.1 mg), and then stored in a vacuum desiccator at 1 mm or less overnight. The weight of substrate was determined by reweighing the vials. Errors were minimized by zeroing the balance before weighing every vial. To each vial was added 0.100 ml of carbon tetrachloride just prior to the infrared deuterium analysis which made use of the doublet CD band at 2100 and 2120 cm^{-1}. Absorbances were measured at both bands with the following instrument settings: scale 5×, slit program 2×, gain 5, attenuator speed 600, suppression 8, scan speed 32 min, and source current 0.30 amp. A calibration curve of absorbance/milligram *vs.* mole % exchangeable protium was constructed for both bands. The analyses of kinetic points were obtained by comparison to these curves. The average value was then used. The two values were normally within ±2% protium of each other. Analytical spectra for the calibration curves and kinetic points were measured during the same session.

Electrophilic Substitution at Saturated Carbon. XXXVI. Correlations between Rates of Potassium Methoxide Catalyzed Hydrogen–Deuterium Exchange Reactions of Carbon Acids and H_-[1]

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Abstract: Rate constants for isotopic exchange of triphenylmethane and diphenylmethane and racemization of (−)-4-biphenylylmethoxyphenylmethane and (+)-4-biphenylylmethoxyphenyldeuteriomethane in methanol-O-*d*–dimethyl sulfoxide-d_6 (75:25, by volume) catalyzed by potassium methoxide were measured. Increases in the apparent kinetic molecularity of the catalyst and observed second-order rate constants were noted as the catalyst concentration was raised. The rate data correlated with the reported thermodynamic behavior of methanolic potassium methoxide solutions as measured by the acidity function, H_-. The theoretical basis and qualitative limitations of such rate correlations with H_- are discussed. In an alternative treatment, the kinetic data were fitted to a rate equation of the form, rate = k_2(RH)(B) + k_3(RH)(B)^2, where RH is the substrate, and B is the base. The two kinetic components were interpreted in terms of free carbanions and potassium carbanide ion pairs as reaction intermediates.

Correlations between acidity functions[2a] and rates of acid-catalyzed reactions[2b,3] have been extensively investigated. Although basic media have been less studied, data on the H_- acidity function for 29 basic solvent systems have been summarized.[4] This function measures the relative ability of a given solution to ionize a weak acid. A few reports on correlations between H_- and rates of base-catalyzed reactions have appeared in the literature, all but one[5] of which involve reactions in which base-catalyzed breaking of C–H bonds are involved.[6]

The present study reports results of potassium methoxide catalyzed isotopic exchanges of triphenylmethane (I) and diphenylmethane (II), and exchanges and racemizations of 4-biphenylylmethoxyphenylmethane (III-*h*(*d*), in deuterated methanol-O-*d*–dimethyl-d_6 sulfoxide. The pseudo-first-order rate constants for these reactions were empirically related to an H_- scale for methanolic potassium methoxide solutions. The kinetic data were also fitted to rate equations which possess terms both first and second order in base.

Methods and Results

Starting Materials and Media. Compounds (−)-III-*h* and (+)-III-*d* were available from another study.[7] Base titer determinations were routinely performed with an acidic titrant composed of benzoic acid dissolved in methanol–dimethyl sulfoxide (75:25, by volume). Comparison of a base concentration determination by this method with one made by potentiometric titration gave a negligible difference. In representative cases for every compound, the base titer was determined at the beginning and end of the kinetic run. With either long periods of time or high temperatures, noticeable decreases were detected. Typically, the decrease was less than 1%, and in the worst kinetic

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[1] This research was sponsored by the U. S. Army Research Office, Durham, N. C. The authors extend their thanks.

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[6] (a) M. F. L. Allison, C. Bumford, and J. H. Ridd, *Chem. Ind.* (London), 718 (1958); (b) R. A. More O'Ferrall and J. H. Ridd, *J. Chem. Soc.*, 5030, 5035 (1963); (c) R. Stewart, J. P. O'Donnell, D. J. Cram, and B. Rickborn, *Tetrahedron*, **18**, 917 (1962); (d) M. Anbar, M. Bobtelsky, D. Samuel, B. Silver, and G. Yagil, *J. Am. Chem. Soc.*, **85**, 2380 (1963).

[7] W. D. Kollmeyer and D. J. Cram, *ibid.*, **90**, 1779 (1968).

Table I. Hydrogen–Deuterium Exchange Rates for Diphenylmethane in Methanol-O-*d*-Dimethyl Sulfoxide-d_6 (75:25)[a] Catalyzed by Potassium Methoxide

Run	Temp,[b] °C	Half-lives followed	No. of points	Substrates concn, *M*	Base concn, *M*	$k_1^{obsd} \times 10^6$, sec^{-1},[c] %	$k_2^{obsd} \times 10^5$, l./mol sec,[d] %
1	105	2.16	8	0.188	0.692	27.1 ± 3.0	3.91 ± 4.0
2	105	1.16	7	0.187	0.387	10.6 ± 5.1	2.73 ± 6.1
3	105	1.39	8	0.191	0.188	3.80 ± 2.8	2.02 ± 3.8
4	105	1.53	8	0.185	0.592	21.8 ± 2.2	3.68 ± 3.2
5[e]	105	1.52	8	0.192	0.679	28.1 ± 1.1	4.14 ± 2.1
6[f]	105	0.95	6	0.186	0.291	8.36 ± 3.4	2.97 ± 4.4
7	105	1.87	8	0.0343	0.304	7.48 ± 2.7	2.46 ± 3.7
8	105	1.65	8	0.234	0.869	40.7 ± 3.1	4.68 ± 4.1
9	125	1.19	6	0.193	0.576	172 ± 2.2	29.8 ± 3.2
10	125	1.80	8	0.187	0.412	100 ± 3.4	24.3 ± 4.4
11	125	1.78	7	0.182	0.248	50.6 ± 3.1	20.4 ± 4.1
12	125	2.00	8	0.183	0.170	34.7 ± 2.7	20.4 ± 3.7
13	125	1.41	7	0.187	0.642	171 ± 4.4	26.6 ± 5.4
14	125	1.18	7	0.184	0.114	23.1 ± 2.1	20.2 ± 3.1
15	125	1.90	7	0.187	0.695	226 ± 2.6	32.5 ± 3.6

[a] Per cent by volume at room temperature before mixing. [b] 105 = 105.60 ± 0.05°, 125 = 125.60 ± 0.05°. [c] Observed pseudo-first-order rate constants; k_1's and standard deviations obtained *via* a "least-squares" computer program. [d] Observed second-order rate constant; $k_2 = k_1$/base concentration; 1.0% added to standard deviations to account for errors in base concentrations. [e] Solution was 0.320 *M* in potassium iodide. [f] Solution was 0.738 *M* in potassium iodide.

Table II. Hydrogen–Deuterium Exchange Rates for Triphenylmethane in Methanol-O-*d*-Dimethyl Sulfoxide-d_6 (75:25)[a] Catalyzed by Potassium Methoxide

Run	Temp,[b] °C	Half-lives followed	No. of points	Substrate concn, *M*	Base concn, *M*	$k_1^{obsd} \times 10^5$, sec^{-1},[c] %	$k_2^{obsd} \times 10^4$, l./mol sec,[d] %
16	100	1.04	7	0.123	0.203	2.84 ± 1.7	1.40 ± 2.7
17	100	1.26	7	0.123	0.415	6.90 ± 2.2	1.66 ± 3.2
18	100	1.46	7	0.123	0.297	4.71 ± 0.8	1.59 ± 1.8
19	100	1.54	7	0.123	0.106	1.41 ± 2.1	1.33 ± 3.1
20	120	1.80	6	0.122	0.109	12.0 ± 2.7	11.0 ± 3.7
21	120	1.70	7	0.120	0.413	56.0 ± 2.2	13.5 ± 3.2
22	120	1.89	7	0.121	0.296	36.3 ± 1.8	12.2 ± 2.8
23	120	2.42	7	0.122	0.198	23.3 ± 1.0	11.8 ± 2.0

[a] Per cent by volume at room temperature before mixing. [b] 100° = 100.60 ± 0.05°, 120° = 120.60 ± 0.05°. [c] Observed pseudo-first-order rate constant; k_1's and standard deviations obtained *via* a "least-squares" computer program. [d] Observed second-order rate constant; $k_2 = k_1$/base concentration; 1.0% added to standard deviations to account for errors in base concentrations.

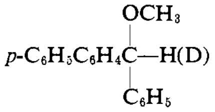
run (3 of Table I) was about 3%. For this reason runs at base concentrations of less than 0.1 *M* were not generally feasible.

$(C_6H_5)_3C\text{-}H$

I

$(C_6H_5)_2CH_2$

II



$p\text{-}C_6H_5C_6H_4\underset{C_6H_5}{\overset{OCH_3}{C}}\text{—}H(D)$

III

All of the kinetic experiments were performed in 3:1 methanol-O-*d*-dimethyl-d_6 sulfoxide (by volume), which corresponds to a mole per cent ratio of 84.1:15.9. All runs were made under conditions such that the concentration of exchangeable deuterium in the solvent was at least 100 times greater than the concentration of exchangeable hydrogen in the substrate. Dimethyl-d_6 sulfoxide was considered part of the solvent-deuterium pool. The protio compound readily undergoes isotopic exchange in deuterium oxide with sodium deuterioxide at much lower temperature (25°)[8] than those of the present study.

Because freshly opened ampoules that had been heated above 100° possessed a foul odor,[6c] a kinetic solution containing diphenylmethane was sealed in ampoules and held at 135°. The contents were quenched and analyzed[9] at timed intervals (see Experimental Section). The results indicated negligible decomposition in the kinetic runs.

Isotopic Analyses. Pseudo-first-order rate constants were measured and calculated as described previously.[7] Hydrogen–deuterium analyses for triphenylmethane utilized a reported infrared method.[10] Diphenylmethane analysis involved an nmr peak integration method in which the signal of the aromatic protons was compared to that of the exchangeable benzylic position. A detailed description of the nmr method is described elsewhere[11] in connection with similar analysis of fluorene.

Exchange and Racemization Data. The results of isotopic exchange of diphenylmethane and triphenylmethane are listed in Tables I and II. Table III contains the results of isotopic exchange and racemization of 4-biphenylylmethoxyphenylmethane. The striking feature of the results is the increase in second-order rate constants with base concentration. Logarithmic plots of pseudo-first-order rate constants *vs.* potassium methoxide concentration also demonstrate the increase of apparent base order with base concentration (Figure 1). The apparent base order ranges from 1.01 to 1.45

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(8) E. C. Buncel, E. A. Symons, and A. W. Zabel, *Chem. Commun.*, 173 (1965).

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(10) V. Franzen and C. Mertz, *Ber.*, **93**, 2819 (1960).

(11) D. J. Cram and W. D. Kollmeyer, *J. Am. Chem. Soc.*, **90**, 1791 (1968).

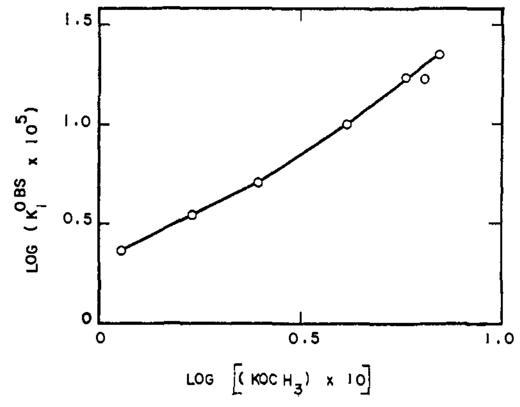

Figure 1. Kinetic order in potassium methoxide for diphenylmethane exchangers at 125.60°; initial slope = 1.01; final slope = 1.45.

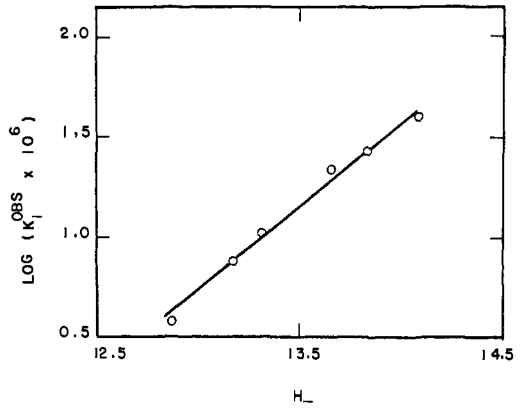

Figure 2. A correlation of diphenylmethane exchange rate constants with H_- at 105.60°; slope = 0.85.

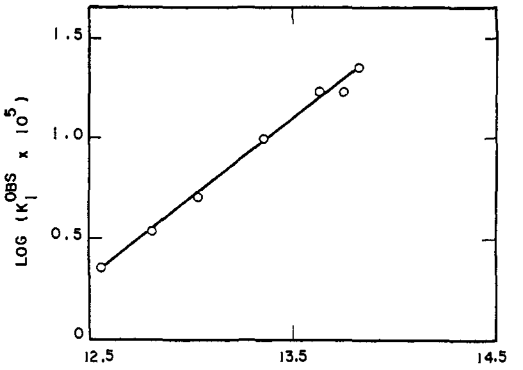

Figure 3. A correlation of diphenylmethane exchange rate constants with H_- at 125.60°; slope = 0.78.

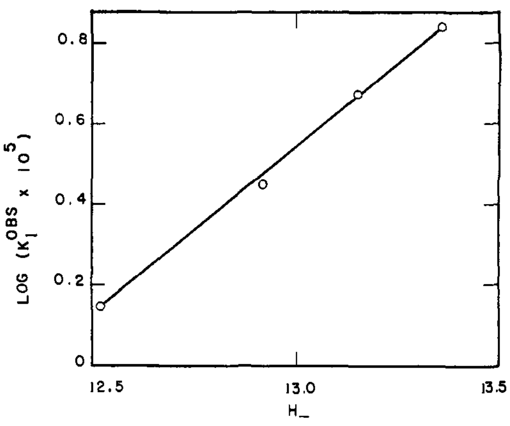

Figure 4. A correlation of triphenylmethane exchange rate constants with H_- at 100.60°; slope = 0.82.

as base concentration varies from 0.114 to 0.695 *M* for the isotopic exchange of diphenylmethane at 126°.

Acidity Function Correlation. Logarithms of pseudo-first-order rate constants from this work were plotted against H_- values for various concentrations of potassium methoxide in methanol taken from Bowden's review.[4] Values for intermediate concentrations were interpolated from a plot of the logarithm of potassium methoxide concentration *vs.* H_-. To avoid a slight inconsistency caused by overlapping data from different sources, values between 0.1 and 0.2 *M* base were obtained by extrapolation of data at 0.2 and 0.4 *M*. The resulting linear plots are shown in Figures 2–6.

Table III. Hydrogen–Deuterium Exchange Rates and Racemization Rates for 4-Biphenylylmethoxyphenylmethane (III-*h* or III-*d*) in Methanol-O-*d*–Dimethyl Sulfoxide-d_6 (75:25)[a] Catalyzed by Potassium Methoxide at 126°[b]

	——Substrate——		Base		
Run	Kind	Concn, *M*	concn, *M*	$k_1^{obsd} \times 10^5$, sec^{-1},[c] %	$k_2^{obsd} \times 10^5$, l./mol sec,[d] %
24	(−)-III-*h*	0.0737	0.792	10.2 ± 2.8	12.9 ± 3.8
25	(−)-III-*h*	0.0611	0.419	3.46 ± 4.0	8.27 ± 5.0
26	(−)-III-*h*	0.0611	0.230	1.38 ± 3.2	5.99 ± 4.2
27	(−)-III-*h*	0.0618	0.601	5.87 ± 2.4	9.77 ± 3.4
28[e]	(−)-III-*h*	0.0618	0.601	6.21 ± 4.4	10.3 ± 5.4
29	(−)-III-*h*	0.0614	0.781	9.07 ± 2.1	11.6 ± 3.1
30[e]	(−)-III-*h*	0.0614	0.781	10.3 ± 3.0	13.2 ± 4.0
31	(+)-III-*d*[f]	0.0920	0.995	5.94 ± 4.2	5.97 ± 5.2
32	(+)-III-*d*[f]	0.0915	0.805	4.17 ± 2.1	5.17 ± 3.1
33	(+)-III-*d*[f]	0.0919	0.690	2.81 ± 2.2	4.08 ± 3.2
34	(+)-III-*d*[f]	0.0919	0.587	2.34 ± 1.9	3.98 ± 2.9
35	(+)-III-*d*[f]	0.0909	0.440	1.40 ± 2.0	3.18 ± 3.0

[a] Per cent by volume at room temperature before mixing. [b] 126° = 125.60 ± 0.05°. [c] Observed pseudo-first-order rate constants and standard deviations obtained *via* a "least-squares" computer program. [d] Observed second-order rate constants; $k_2 = k_1$/base concentration; 1.0% added to standard deviations to account for errors in base concentrations. [e] Exchange runs; all other runs are for racemization. [f] (+)-III-*d* was 98.0% deuterated.

The isotopic exchange of tritiated fluorene in methanol with sodium methoxide also exhibits kinetic behavior similar to that observed in this work.[12] The kinetic behavior was reported in terms of eq 1.[12]

$$\text{rate} = [3.68 + 2.3(\text{NaOCH}_3)] \times (\text{fluorene})(\text{NaOCH}_3)10^{-4} \qquad (1)$$

Pseudo-first-order rate constants were calculated from this expression and plotted against H_- values as before. The H_- values were for sodium methoxide solutions as given in Bowden's review.[4] The plot is linear up to about 1 *M* base and is shown in Figure 7.

Rate Equations. The results of this work were fitted to rate eq 2 (similar to eq 1). In this case (RH) is the concentration of substrate which has exchangeable protium, and (B) is the stoichiometric concentration of potassium methoxide which was determined by titra-

$$\text{rate} = k_2(\text{RH})(\text{B}) + k_3(\text{RH})(\text{B})^2 \qquad (2)$$

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(12) A. Streitwieser, Jr., J. I. Brauman, J. H. Hammons, and A. H. Pudjaatmaka, *J. Am. Chem. Soc.*, 87, 384 (1965).

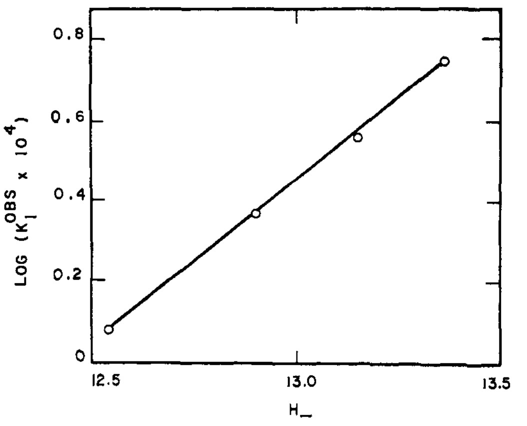

Figure 5. A correlation of triphenylmethane exchange rate constants with H_- at 120.60°; slope = 0.82.

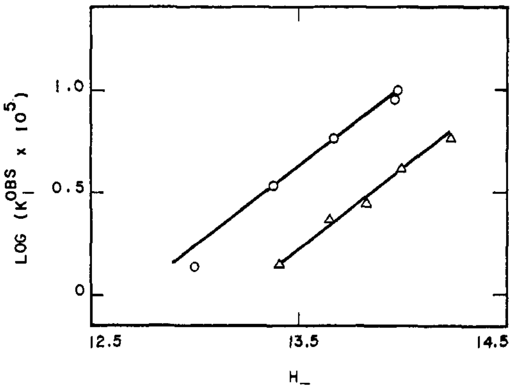

Figure 6. A correlation of 4-biphenylylmethoxyphenylmethane, III-*h*(*d*), racemization rate constants with H_- at 125.60°: ○ = (−)-III-*h*; △ = (+)-III-*d*; both slopes = 0.80.

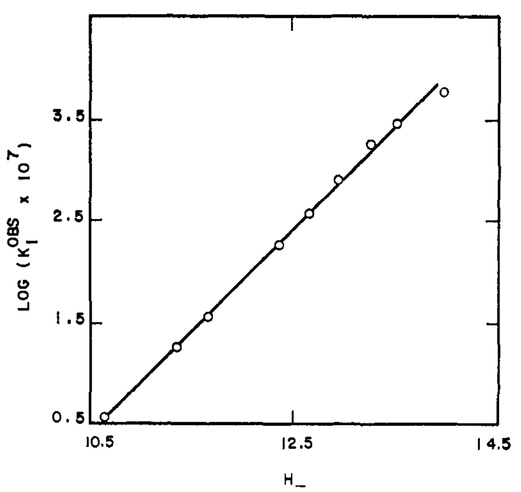

Figure 7. A correlation of reported fluorene exchange rate constants with H_- at 44.9°; slope = 0.98.

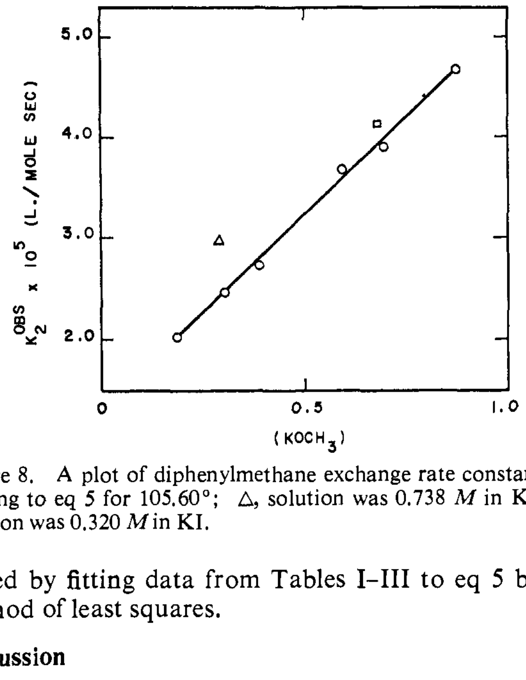

Figure 8. A plot of diphenylmethane exchange rate constants according to eq 5 for 105.60°; △, solution was 0.738 *M* in KI; □, solution was 0.320 *M* in KI.

tion. Adherence to this expression was determined in the following manner. Pseudo-first-order rate constants (eq 3) obtained over a range of base concentrations were converted into the corresponding observed second-order rate constants (eq 4) which were plotted against the base concentration. Combination of eq 2 and 4 gives 5. The intercept of the plot provided k_2

$$\text{rate} = k_1^{\text{obsd}}(\text{RH}) \qquad (3)$$

$$\text{rate} = k_2^{\text{obsd}}(\text{RH})(\text{B}) \qquad (4)$$

$$k_2^{\text{obsd}} = k_2 + k_3(\text{B}) \qquad (5)$$

and the slope k_3. Figure 8 records an example of one of the plots. Table IV gives values of k_2 and k_3 obtained by fitting data from Tables I–III to eq 5 by the method of least squares.

Table IV. Second- and Third-Order Rate Constants[a] for Hydrogen–Deuterium Exchange and Racemization in Methanol-O-*d*-Dimethyl Sulfoxide-d_6 (75:25)[b] Catalyzed by Potassium Methoxide

Compd	Temp, °C	$k_2 \times 10^5$, l./mol sec,[a] %	$k_3 \times 10^5$, l.^{2}/mol^2 sec, %
I[c]	100.60	11.9 ± 4.2	11.7 ± 15.4
I[c]	120.60	101 ± 2.6	80.9 ± 8.8
II[c]	105.60	1.27 ± 5.0	3.92 ± 2.9
II[c]	125.60	16.3 ± 6.4	22.5 ± 10.8
(−)-III-*h*[d]	125.60	3.43 ± 19.5	11.1 ± 10.0
(+)-III-*d*[d]	125.60	0.877 ± 43.4	5.10 ± 10.4

[a] k_2 and k_3 are derived from data in Tables I, II, and III fitted to eq 5 by the method of least squares. [b] Per cent by volume at room temperature before mixing. [c] Exchange substrates. [d] Racemization substrates.

Discussion

Correlation between Kinetic Results and H_-. The basis of a linear relationship between H_- and the logarithm of the pseudo-first-order rate constant for a base-catalyzed reaction can be derived in a manner similar to previously reported equations for acid-catalyzed reactions.[2,3] A treatment for aqueous alkaline solutions has also been reported.[6d] However, that study deals with the state of solvation of aqueous hydroxide ion and the concentration of "free water." In contrast, our derivation deals with the solvation of all species and the activity of the solvent.

The following discussion is in terms of a methanol solution which contains methoxide. However, the results can be generalized to any basic solution of a lyate ion in the appropriate hydroxylic solvent. According to More O'Ferrall and Ridd[6b] one can write eq 6 for the acidity function H_- of a basic methanolic solution in which an indicator acid AH can ionize

$$\text{AH} + \text{CH}_3\text{O}^- \rightleftharpoons \text{A}^- + \text{CH}_3\text{OH}$$

$$H_- = \log(\text{CH}_3\text{O}^-) + pK_{\text{CH}_3\text{OH}} + \log\frac{\gamma_{\text{AH}}\gamma_{\text{CH}_3\text{O}^-}}{\gamma_{\text{A}^-}} - \log a_{\text{CH}_3\text{OH}} \qquad (6)$$

where γ's are the activity coefficients of AH, CH_3O^-, and A^-, and a_{CH_3OH} is the activity of the solvent. In a kinetic process which involves another similar acid, RH, in a basic methanol solution, two mechanisms are treated. If ionization is the rate-determining step, rate eq 7 applies. In eq 7, $\gamma_\ddagger$ is the activity coefficient

$$RH + CH_3O^- \xrightarrow[k_a]{\text{slow}} R^- + CH_3OH \xrightarrow{\text{fast}} \text{product}$$

$$\text{rate} = k_a(RH)(CH_3O^-)\gamma_{RH}\gamma_{CH_3O^-}/\gamma_\ddagger \tag{7}$$

of the transition state which leads to formation of the anion R^-. The logarithm of the observed pseudo-first-order rate constant is given by eq 8 which, when combined with eq 6, gives 9. Equation 9 is set in terms

$$\log k_1^{\text{obsd}} = \log k_a + \log (CH_3O^-) + \log (\gamma_{RH}\gamma_{CH_3O^-}\gamma/_\ddagger) \tag{8}$$

$$\log k_1^{\text{obsd}} = H_- + \log k_a - pK_{CH_3OH} + \log (\gamma_{RH}\gamma_{A^-}/\gamma_{AH}\gamma_\ddagger) + \log a_{CH_3OH} \tag{9}$$

of formal species and not the actual solvated species which exist in solution. Grunwald has shown how the activity coefficients of the two are related.[13] For example, if M^+ is the formal species and $M(CH_3OH)_n{}^+$ is the actual cation in solution, eq 10 applies. Combination of eq 10 and eq 9 gives a relationship cast in

$$M^+ + nCH_3OH \rightleftarrows M(CH_3OH)_n{}^+ \tag{10}$$

$$\gamma_{M^+} = [\gamma_{M(CH_3OH)_n{}^+}]a_{CH_3OH}{}^{-n}$$

terms of the actual solvated species. The result, eq 11, is the analog of Bunnett's expression for acid-catalyzed reactions.[3] His conventions for the solvation numbers of the various species are retained.

$$\log k_1^{\text{obsd}} = H_- + \log k_a - pK_{CH_3OH} + \log \left[\frac{\gamma_{RH(CH_3OH)_s}\gamma_{A^-(CH_3OH)_a}}{\gamma_{AH(CH_3OH)_b}\gamma_{\ddagger(CH_3OH)_t}}\right] + [(t - s) - (a - b) + 1] \log a_{CH_3OH} \tag{11}$$

Solvation no.	Species
a	A^-, indicator anion
b	AH, indicator acid
p	R^-, substrate
s	RH, substrate
t	‡, transition state

If the base-catalyzed reaction involves a rapid pre-equilibrium followed by a rate-limiting reaction with solvent, then a similar treatment yields eq 12. The transition states in eq 11 and 12 are not the same, although the two equations greatly resemble one another.

$$RH + {}^-OCH_3 \overset{K_e}{\rightleftarrows} R^- + HOCH_3 \xrightarrow[\text{slow}]{k_b} \text{product}$$

$$\log k_1^{\text{obsd}} = H_- + \log K_e k_b - pK_{CH_3OH} + \log \left[\frac{\gamma_{RH(CH_3OH)_s}\gamma_{A^-(CH_3OH)_a}}{\gamma_{AH(CH_3OH)_b}\gamma_{\ddagger(CH_3OH)_t}}\right] + [(t - s) - (a - b) + 1] \log a_{CH_3OH} \tag{12}$$

A number of good approximations reduce either eq 11 or 12 to eq 13, which correlates our experimental data. If the indicator acids (AH) used to generate the

$$\log k_1^{\text{obsd}} = H_- + \text{constant} \tag{13}$$

H_- scale and the kinetic substrates RH behave similarly with respect to medium changes, and likewise for the transition state species and indicator anion, then the activity coefficient term is a constant. This assumption has been made for acid-catalyzed reactions with considerable success.[2,3] A possible reservation is that the H_- values used here derive from nitrate diphenylamines and anilines.[14] Thus, the H_- data reflect the sensitivity of nitrogen rather than carbon acids to a changing medium. In one case where carbon acids were used as indicators, the pK_a values were essentially the same as those calculated from H_- values measured with nitrogen acids[4,15] in ethanolic dimethyl sulfoxide. However, in aqueous dimethyl sulfoxide[16] and less in methanolic dimethyl sulfoxide,[17] nitrogen and carbon acids show somewhat different response to medium changes. Such differences might account for curvature and nonunit slope in plots of eq 13.

If the activity of the solvent does not change drastically with base concentration, and if the coefficient of $\log a_{CH_3OH}$ is sufficiently small, then this entire term may be approximated as zero over a wide range of base concentration. The activity of methanol ranges from unity to *ca.* 0.92 as potassium methoxide concentration varies from 0 to 1 *M*.[18] Hence, $\log a_{CH_3OH}$ varies from 0 to −0.04 over the same concentration range. No valid estimate can be made of the value of the coefficient $[(t - s) - (a - b) + 1]$. It is assumed to be sufficiently small so that the entire logarithmic term is effectively zero. The terms $\log k_a$, $\log K_e k_b$, and pK_{CH_3OH} are true constants invariant with medium changes. This fact coupled with the above approximations allow all of the terms of eq 11 and 12 except H_- and $\log k_1^{\text{obsd}}$ to be gathered into a single constant, and eq 13 results. Thus, a justification has been obtained for the observed linear correlation between rate constants and H_-.

The H_- and kinetic data refer to different temperatures, 25 and 100°, respectively. The slopes of $\log k_1^{\text{obsd}}$ *vs.* H_- plots of Figures 2 and 3 decrease slightly with an increase of temperature (the slopes of Figures 5 and 6 do not). A similar observation has been made in the acid-catalyzed inversion of sucrose which exhibits fine k_1^{obsd} *vs.* H_0 plots whose slopes decrease from 1.29 at 0° to 0.89 to 50°.[19]

The kinetic data of the present work were obtained in a medium 84 mol % in methanol-O-*d* and 16 mol % in dimethyl-d_6 sulfoxide, whereas the H_- scale was obtained in methanol, and yet eq 13 provides a reasonable correlation of the data. Apparently, the H_- scale follows a trend similar to that in pure methanol. The data of Figure 7 taken from Streitwieser, *et al.*,[12] was gathered in methanol at 45°, whereas the H_- scale refers to 25°. The fact that the slope in Figure 7 is close to unity (0.98) suggests that the deviation of the slopes of Figures 2–6 might have been closer to unity had methanol been the solvent and had the tempera-

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[13] Equation 22 and ref 14 in J. F. Bunnett, *J. Am. Chem. Soc.*, **83**, 4973 (1961).

[14] R. Schaal and G. Lambert, *J. Chim. Phys.*, **59**, 1151, 1164, 1170 (1962).

[15] K. Bowden and R. Stewart, *Tetrahedron*, 21, 261 (1965).

[16] E. C. Steiner and J. D. Starkey, *J. Am. Chem. Soc.*, **89**, 2751 (1967).

[17] C. D. Ritchie and R. E. Uschold, *ibid.*, **89**, 2752 (1967).

[18] E. C. Steiner, J. D. Starkey, J. M. Tralmer, and R. O. Trucks, 153rd National Meeting of the American Chemical Society, April 1967, Miami Beach, Fla., Abstracts, Q33.

[19] Calculated from data of P. M. Leininger and M. Kilpatrick, *J. Am. Chem. Soc.*, 60, 1268, 2891 (1938).

tures been closer to 25°. The fact that the Streitwieser data obey eq 13 so well and provide a slope of unity indicates that the nitrogen indicator acids used to determine H_- behaved similarly to fluorene in methanol.

Mechanisms of Isotopic Exchange Reactions. The reasonable correlation of the kinetic data by eq 2 implies at least two mechanisms for isotopic exchange, one of which is first order and the other second order in base. A possible mechanism is as follows.

At the concentrations employed, it is assumed that potassium methoxide is largely dissociated so that both potassium and methoxide ion concentrations are effectively equal to the stoichiometric base concentration (B) which is determined by titration. It is further assumed that the rate of formation and dissociation of potassium methoxide ion pairs is much faster than rates of ionization of the carbon acids. Application of these assumptions to eq 2 produces eq 14–16. Equation 16 suggests that carbanion arises from two distinctly different transition states, one of which involves substrate and methoxide ion, and the other substrate, methoxide ion, and potassium ion. From the several ways of bringing together substrate, potassium ion, and methoxide, the most reasonable is to have ion-paired (contact or solvent-separated) potassium methoxide react with carbon acid. The mechanism is formulated in Chart I. Whether or not intermediates A and B interconvert faster than they go to products is unclear.

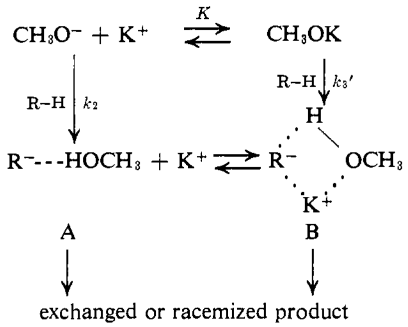
$$\mathrm{CH_3O^- + K^+ \overset{K}{\rightleftharpoons} CH_3OK} \quad \text{or with } K \text{ small}$$

$$(\mathrm{CH_3OK}) = K(\mathrm{CH_3O^-})(\mathrm{K^+}) \approx K(\mathrm{B})^2 \text{ and } k_3 = k_3'K \quad (14)$$

$$\text{rate} = k_2(\mathrm{RH})(\mathrm{CH_3O^-}) + k_3'(\mathrm{RH})(\mathrm{CH_3OK}) \quad (15)$$

$$\text{rate} = k_2(\mathrm{RH})(\mathrm{CH_3O^-}) + k_3(\mathrm{RH})(\mathrm{CH_3O^-})(\mathrm{K^+}) \quad (16)$$

Chart I



Unfortunately, the state of ionization of methanolic potassium methoxide has not been studied above 10^{-3} M.[20] Sodium ethoxide in ethanol appears to be considerably associated even at low base concentrations.[21] For example, at 24° a 0.0125 M solution is 73.5% dissociated and at 1.00 M, 22.1% dissociated. Potassium methoxide in methanol–dimethyl sulfoxide is expected to be considerably more dissociated.

Precedents for mechanistic utilization of both associated and unassociated forms of metal alkoxides are found in aliphatic nucleophilic substitution.[21,22] Of more immediate interest is Acree's observation that ethoxide ions and associated sodium ethoxide were about equally effective at epimerizing menthone in ethanol.[21,22b]

Equation 16 indicates that addition of potassium iodide as a common ion salt should increase the rate of isotopic exchange. Thus, in the exchange of diphenylmethane in runs 5 and 6 (Table I), the solutions were 0.320 and 0.738 M in potassium iodide, respectively. Equation 16 predicted rate increases by factors of 1.32 and 2.40 in the values of k_2^{obsd} in the two runs. Rate increases for k_2^{obsd} by factors of 1.06 and 1.34 were actually observed. These results are thought to be inconclusive as a mechanistic probe since added potassium iodide could well lower the energy of the reactant ground state *via* a thermodynamic salt effect, and thus produce a smaller than expected rate enhancement.

The data treatments inherent in eq 2 and 13 are not necessarily mutually exclusive. Thus, changes in chemical activities could well reflect both the existence of species such as potassium methoxide, substrate anions, and indicator anions as mixtures of associated and dissociated forms and the variation of composition of these mixtures with the medium.

Stereochemistry of Exchange. Rate constants for runs 27 and 28 and for runs 29 and 30 (Table III) provide values of $k_e/k_\alpha = 1.06 \pm 0.05$ and 1.13 ± 0.04, respectively, where k_e is the rate constant for isotopic exchange and k_α that for racemization of (−)-III-*h* in deuterated solvent at 126°. The small increase of this ratio with base concentration may point to a small mechanistic component in which associated ions provide exchange with retention of configuration.[7]

Isotope Effects. Figure 6 contains plots of log k_1^{obsd} for racemization for both (−)-III-*h* and (+)-III-*d* against H_-. The slopes of the lines for the two substrates are almost the same for the two isotopic species, and therefore the isotope effect for racemization, $(k_H/k_D)_\alpha = 2.5$, does not change much over a base concentration change from 0.23 to 0.995 M. The proximity of k_e/k_α values to unity suggests that $(k_H/k_D)_\alpha \sim (k_H/k_D)_e \sim 2.5$. The observed isotope effect for racemization corresponds to a value of about 3.4 at 25°,[23] and compares with a value of 2.7 observed with the same compounds in *t*-butyl alcohol-O-*d* with potassium *t*-butoxide at 116°.[7] The significance of this value for the isotope effect will be discussed in the next paper of this series.[11]

Experimental Section

General Comments. Deuterium analyses by the combustion and falling-drop method were performed by J. Nemeth of Urbana, Ill. Melting points were taken on a Mel-Temp melting point block and are uncorrected, as are the boiling points. Infrared spectra for deuterium analyses were obtained with a Perkin-Elmer 421 spectrophotometer; all others were recorded on a Beckman IR-5 spectrophotometer. Nuclear magnetic resonance (nmr) spectra and integrations were obtained with a Varian A-60 instrument with tetramethylsilane as an internal standard. Optical rotations were measured with a Perkin-Elmer 141 polarimeter and a 1-dm thermostated cell. All kinetic solutions were prepared in a dry-box filled with purified nitrogen.

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Carbon Acids. Diphenylmethane (I), mp 25–27°, and triphenylmethane (III), mp 92.5–94° (after recrystallization from methanol), were obtained from Matheson Coleman and Bell. The preparation of optically active and deuterated 4-biphenylylmethoxyphenylmethane (III) has been reported.[7] Triphenyldeuteriomethane, needed as a standard for infrared analyses (see below), was prepared by quenching an ethereal solution of triphenylmethylsodium with deuterium oxide.[10] The product, mp 92–92.5°, contained 82.4% of one atom of deuterium by combustion and falling-drop method. An infrared spectrum of the material in carbon tetrachloride showed a C–D band at 2120 cm^{-1} as reported.[10]

Solvents. Methanol-O-*d* was prepared by hydrolysis of dimethyl carbonate with 99.8% deuterium oxide.[24] Various preparations contained 99% of one atom of deuterium per molecule or better (combustion and falling drop). Dimethyl-d_6 sulfoxide was prepared by a series of facile exchanges with deuterium oxide.[8,25] A representative exchange and final purification are given here.

A mixture of 281 g of 42% deuterium oxide, 328 g of dimethyl sulfoxide, and 4.5 g of sodium hydroxide was mixed, allowed to stand at 25° for 12 hr, and then heated at 80–100° for 2 hr. The exchanged water was removed by careful distillation through a 70-cm silvered and vacuum-jacketed column at 38° (45 mm). In this manner, dimethyl sulfoxide was exchanged seven times with increasingly enriched water samples, the last of which involved 99.8% deuterium oxide. After the last exchange, the distillation column was replaced with a 65-cm spinning-band column. After a small forerun of about 20 ml, 312 g (88%) of product was collected over Linde 4A Molecular Sieve at 86–87° (20 mm). This material was 98.6% deuterated (combustion and falling-drop method). An additional exchange raised the deuterium content to 98.8%. During all exchanges, the materials were protected from the atmosphere. All deuterated solvents were stored in a drybox in a tightly stoppered flask.

Base Titers. Freshly sliced potassium metal was dissolved in chilled methanol-O-*d* under a blanket of dry nitrogen. The *ca.* 1 *N* basic solution was tightly stoppered and stored in a drybox. This material was used to prepare standard solutions. Potassium methoxide normality was determined by a modification of a reported procedure.[26]

An experiment which demonstrated the validity of this modification is described. The 0.100 *N* acidic titrant was prepared by dissolving a weighed amount of primary standard grade benzoic acid in three volumes of methanol and one volume of dimethyl sulfoxide. A potassium methoxide solution of similar solvent composition was prepared. A 10.00-ml aliquot of the basic mixture was titrated and the end point was simultaneously observed colorimetrically (thymol blue indicator) and potentiometrically (Beckman Model H2 glass electrode pH meter). The colorimetric end point, blue to yellow, differed from the potentiometric end point by 0.56%. The calculated normality of the basic solution was 0.0535 *N*. The thymol blue indicator was used in all subsequent determinations and was prepared by dissolving 0.3 g in 100 ml of methanol.

Deuterium Analyses of Diphenylmethane. The deuterium content at the benzylic position was determined from the nmr integration ratio of aromatic protons to benzylic protons. Each ratio was calculated from the average of ten or more integrations of each peak. Recovered diphenylmethane samples, *ca.* 50–60 mg, were melted and placed neat into capillary tubes which were then inserted into a normal nmr tube. The analyses for a kinetic run were all obtained at the same session without intervening adjustments of the spectrometer.

Deuterium Analyses of Triphenylmethane. Purified kinetic samples were analyzed according to a known procedure which made use of an infrared CD band at 2120 cm^{-1}.[10] Infrared solutions used *ca.* 40 mg of purified substrate dissolved in 0.200 ml of spectral grade carbon tetrachloride. The pertinent instrument settings for absorbance measurements were as follows: scale 5×, slit program 2×, gain 5, attenuator speed 350, suppression 3.5, scan speed 32 min, and source current 0.30 amp. Analytical spectra for the calibration curve and kinetic points were always obtained during the same session.

Deuterium Analyses of 4-Biphenylylmethoxyphenylmethane. The procedure has been reported.[7]

General Procedure for Exchange and Racemization Runs. All exchange and racemization runs were carried out in a solvent which consisted of three parts by volume of potassium methoxide in methanol-O-*d* and one part of dimethyl-d_6 sulfoxide. All kinetic solutions were prepared in a drybox by the addition of the appropriate volumes of each solvent to a weighed amount of substrate. The basic methanol-O-*d* was obtained by dilution of a *ca.* 1 *N* stock solution. In some cases rapid dissolution of the substrate was facilitated by use of a hot plate. In these instances, the solution was kept in a tightly stoppered flask to avoid solvent evaporational losses. A syringe was used to place aliquots in ampoules which had been cleaned as described previously.[7] Aliquots were also taken at this time for base titer determinations as described above. The ampoules were stoppered with rubber septum caps, passed out of the drybox, and sealed under vacuum except where noted. For safety reasons, heavy-walled ampoules were used. At timed intervals ampoules were removed from the thermostated rate bath and thermally quenched in ice–water unless otherwise noted. The work-up and purification of aliquots for each compound are described below.

Triphenylmethane Exchange Runs. A typical experiment, run 18, was prepared from 0.5999 g of substrate, 15.00 ml of basic methanol-O-*d*, and 5.00 ml of dimethyl-d_6 sulfoxide. Each ampoule contained *ca.* 2 ml. In runs 16–19 the solutions were made up to initially contain *ca.* 25% triphenyldeuteriomethane. In runs 20–23 the ampoules were allowed to equilibrate for a sufficient length of time so that the first point was *ca.* 25% exchanged. The analytical error would have been excessively large for samples which were less than 25% exchanged. The aliquots were each cooled and shaken with 15 ml of pure pentane and 1 *N* hydrochloric acid. The organic layer was washed twice with water, dried, and evaporated. The recovered material was recrystallized from 0.75 ml of methanol. The weighed sample, *ca.* 40 mg, was then dissolved in 0.200 ml of carbon tetrachloride and analyzed by infrared.

Diphenylmethane Exchange Runs. A typical experiment, run 8, was prepared from 0.7866 g of substrate, 15.00 ml of basic methanol-O-*d*, and 5.00 ml of dimethyl-d_6 sulfoxide. Each ampoule contained 2 ml. The aliquots were worked up in the manner described for triphenylmethane. The oily mixture of recovered substrate was frozen; residual pentane was pumped off under vacuum. The substrate was melted, placed neat into a capillary melting point tube, and then analyzed by nmr.

4-Biphenylylmethoxyphenylmethane Exchange and Racemization Runs. A typical experiment, run 27, was prepared from 0.2035 g of protio substrate with $[\alpha]^{25}_{546}$ $-5.7°$ (*c* 2.5, chloroform), dissolved in 9.00 ml of basic methanol-O-*d* and 3.00 ml of dimethyl-d_6 sulfoxide. Each ampoule contained *ca.* 1.1 ml. The optical rotations of thermally quenched aliquots were measured at 25° and 356 mμ. In runs 31–35, racemization of 98.0% deuterated substrate with $[\alpha]^{25}_{546}$ $+3.3°$ (*c* 2,5, chloroform) was measured. In runs 28 and 29, and in runs 30 and 31, both exchange and racemization rates were determined simultaneously. In these cases, the aliquot was retrieved from the polarimeter cell, worked up, and isotopically analyzed as described previously.[7]

Control on Dimethyl-d_6 Sulfoxide Decomposition in Kinetic Runs. A stock solution of perchloric acid in glacial acetic acid was prepared according to Streuli.[9] The acid solution was standardized against potassium hydrogen phthalate according to Seaman and Allan.[27] A sample of Baker Analyzed Reagent dimethyl sulfoxide with a stated purity of 99.9% by weight was analyzed by a slight modification of Streuli's procedure;[9] the end point was detected with crystal violet indicator instead of by a potentiometric method. The correct end point was the first appearance of yellow color from the previously green solution. Triplicate analyses gave a mean value of 99.9 ± 0.3% by weight for the purity of the dimethyl sulfoxide.

A typical kinetic solution of 0.620 g of diphenylmethane in 15.00 ml of basic methanol-O-*d* and 5.00 ml of dimethyl-d_6 sulfoxide was prepared, sealed in ampoules, and placed in a 135° bath. The initial base concentration was 0.0475 *N*. At timed intervals ampoules were thermally quenched, and an aliquot was taken to determine the base titer. A weighed amount of the ampoule's contents, 350–450 mg, was diluted to 100.0 ml with acetic anhydride. Three 25.00-ml aliquots were pipetted into separate 125-ml flasks. To each 25.00-ml aliquot there was added an additional *ca.* 30 ml of acetic anhydride before titrating with perchloric acid. Each titration was corrected for the amount of potassium methoxide present. The results of this experiment are recorded in Table V.

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Table V. Solvent Decomposition in Methanol-O-d-Dimethyl Sulfoxide-d_6 (75:25)[a] Solutions Which Contain Potassium Methoxide at 135°

Time, hr	Wt %[b] dimethyl-d_6 sulfoxide	Potassium methoxide concn, M
0.0	31.9 ± 0.2	0.0475
24.0	31.8 ± 0.1	0.0095
52.5	31.6 ± 0.1	0.0000
89.3	31.6 ± 0.1	0.0000
91.7	30.9 ± 0.1	0.0000

[a] Per cent by volume at room temperature before mixing. [b] Mean value of triplicate analyses with the indicated standard deviation.

Control on Isotopic Fractionation during Crystallization. A mixture of 31.2 mg of triphenylmethane and 172.1 mg of triphenyldeuteriomethane (82.4% of one atom of deuterium) was dissolved in carbon tetrachloride, divided into two equal aliquots, and evaporated to dryness. Residual solvent was removed *in vacuo*. One aliquot was recrystallized from methanol. The recrystallized and untreated samples were weighed and dissolved in 0.200 ml of carbon tetrachloride. The infrared absorbance at 2020 cm^{-1} was measured. Recrystallized and untreated triphenylmethane samples gave values of 4.96 and 4.89, respectively, for (absorbance × 10^3/mg of sample). Estimated maximum errors of ±0.2 mg in sample weights at ±0.5% in absorbances indicate that these values are identical with experimental error. Hence, isotopic fractionation did not occur to any measurable extent.

Electrophilic Substitution at Saturated Carbon. XXXVII. A Kinetic–Thermodynamic Acidity Correlation of Carbon Acids[1]

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Abstract: Rate constants and activation parameters for potassium methoxide catalyzed exchange of fluorene, 9-phenylxanthene, 4-biphenylyldiphenylmethane, triphenylmethane, and diphenylmethane with methanol-O-d-dimethyl-d_6 sulfoxide (75:25 by volume) were measured and extrapolated to 75°. These kinetic acidities varied by a rate factor of *ca.* 10^7 and were correlated by the Brønsted relationship with reported thermodynamic acid dissociation constants that varied by a factor of about 10^{10}. Substrate kinetic isotope effects for racemization of 2-(N,N-dimethylcarboxamido)-9-methylfluorene (k_H/k_D = 6.75 at 25°) and 4-biphenylylmethoxyphenylmethane (k_H/k_D = 2.5 at 126°) in the same medium were also measured. The curvature in the Brønsted plot coupled with the variation of the kinetic isotope effect and changes in activation parameters with pK_a of the carbon acids are interpreted in terms of changes in mechanism that occur for the isotopic exchange reaction as the ΔpK_a's (pK_a of carbon acid − pK_a of methanol) change.

Thermodynamic and kinetic acidity characteristics of carbon acids have been reviewed to 1965.[2] Since that time Streitwieser,[3] working in cyclohexylamine, and Steiner,[4] Bowden and Stewart,[5] and Ritchie,[6] working in dimethyl sulfoxide, have developed a large body of thermodynamic acidity data for carbon acids in the 11–32 pK_a range. The extensive work of Shatenshtein and coworkers on both kinetic and thermodynamic acidity in liquid ammonia–potassium amide has been reviewed in English.[7] Much of the work of Streitwieser and coworkers on both thermodynamic and kinetic acidity has been reviewed,[8] as has the kinetic work of Cram and coworkers.[2]

A number of authors have correlated thermodynamic and kinetic acidities of carbon acids with Brønsted relationships. The classic attempt at correlation was published by Pearson and Dillon who treated carbon acids in the pK_a range of 5–20.[9] Bell and coworkers have studied Brønsted relationships in depth.[10] Shatenshtein correlated isotopic exchange rates of carbon acids in liquid ammonia with their pK_a's in ether.[7] This is the only study to date which involved correlation of thermodynamic and kinetic acidities of carbon acids in the pK_a range of 20–30. More recently Shatenshtein observed good Hammett σ–ρ plots for isotopic exchanges at the *ortho* and *meta* positions of monosubstituted benzenes.[11] Dessy and coworkers[12] correlated the rates of exchange of carbon acids in dimethylformamide-deuterium oxide with pK_a values in other solvents. Streitwieser and coworkers reported a Brønsted relationship for the exchange of a series of substituted tritiated fluorenes in methanol.[3a] Streitwieser and coworkers also obtained good Hammett σ–ρ plots for

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(1) This research was sponsored by the U. S. Army Research Office, Durham, N. C. The authors extend their thanks.

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