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Cation Effects on the Equilibrium Acidity of Carbon Acids in Methanol

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Abstract: The ratio $[A^-]/[AH]$ where AH is a carbon acid was examined in methanol at various concentrations of potassium and tetramethylammonium methoxides. The carbon acids were 9-cyanofluorene, 9-carbomethoxyfluorene, *N*-fluorenylidenefluoren-9-amine, 1,3-diphenylindene, and *N*-methyl-*N*-phenylfluorene-9-carboxamide. All of these compounds with the exception of 9-cyanofluorene were more completely ionized by tetramethylammonium methoxide than by potassium methoxide but none showed as great a sensitivity to this change in cation as did the previously studied fluoradene system. Within the series, the value of [MOMe] at which cation differentiation was observed varied with carbanion (A^-) structure. It is concluded that carbanion–cation interaction can be an important stabilizing influence in methanol but that the magnitude of this effect varies considerably with carbanion structure. An interpretation is made in terms of a competition between hydrogen bonding and ion pairing which is sensitive to charge delocalization in A^-.

Several investigations have shown that the equilibrium basicity of methoxide at high concentrations is a function of concentration.[1] Streitwieser[1d] has pointed out that the empirical acidity functions used to correlate the effective basicity of methoxide ion with its concentration are dependent to some extent on the indicator acid used to establish the function. In other terms, for the ratio $\gamma_{A^-}/\gamma_{AH}\gamma_{MeO^-}$ where the γ are activity coefficients, the effect of methoxide concentration on γ_{A^-} cannot be ignored. Schaal and Lambert[1a] have also shown that different acidity functions are obtained using different methoxide salts (K^+, Na^+, Li^+) with potassium methoxide being an effectively stronger base for the indicators of their study. More precisely, $\gamma_{A^-}/\gamma_{AH}\gamma_{MeO^-}$ is also dependent on the nature of the cation present.

This dependence on [MOMe] and on M also extends to kinetic acidity measurements. Cram and co-workers[2] noted a kinetic order of 1.09 for the KOMe-catalyzed racemization of 2-methyl-3-phenylpropionitrile. More O'Ferrall and Ridd[3] showed that, in the NaOMe-promoted methanolysis of chloroform, the second-order rate constant varied with [NaOMe]. The order in [NaOMe] can be calculated as 1.3 over the same concentration range as Cram's study (below 0.6 M). The temperature was 60 °C in the latter study and 85 °C in the former. A particularly interesting feature of the More O'Ferrall and Ridd study was the progressive disappearance of this excess order in methoxide when the substrate was changed from chloroform to 1-phenylethyl chloride and then to 1-chloro-3,3-dimethylbutane. Clearly, the change in [MOMe] cannot be viewed as affecting only γ_{MeO^-}. The effect on γ_{A^-} or $\gamma^{\ddagger}$ must also be considered.

More recently, we have shown that the kinetic basicity of methoxide ion in methanol is affected by both [MOMe] and M in its reaction with 9-methoxyfluorene.[4] The apparent kinetic order in methoxide for concentrations below 1 M was 1.5 for KOMe and 1.4 for NaOMe at 30 °C. Data for LiOMe and Me_4NOMe were also provided and showed clearly that the kinetic basicity of methoxide ion in methanol is cation dependent with the basicity order being $Me_4NOMe > KOMe > NaOMe > LiOMe$.

The discovery of cation-dependent changes in the visible spectrum of fluoradenide ion, FD^-, in methanol[5] tends to support arguments[2,6] that the effects described above should be interpreted in terms of ion pairing. When FD^- is produced by treating fluoradene (FDH) with either Me_4NOMe or CsOMe,[5b] its visible spectrum shows a double maximum characteristic of contact ion pairs.[7] (For comparison, KO-*t*-Bu in *t*-BuOH also produces the double maximum.) We also observed[5b] that the equilibrium basicity of Me_4NOMe toward FDH is greater than that of potassium methoxide by a factor of 20–25 between 0.1 and 1 M. It seemed important to establish whether the tendency to form ion pairs could be observed for other carbanions or whether we had happened upon a unique system. To do this we tried to select carbon acids of differing structure which were sufficiently similar to fluoradene in acidity that ionization could be measured under the conditions of our previous study. We chose five compounds and examined both spectra and extent of ionization for KOMe and Me_4NOMe solutions in methanol.

Results

9-Cyanofluorene (CFH) is essentially completely ionized at $[MeO^-]$ greater than 0.03 M. The carbanion, CF^-, absorbs in the visible region at 410 nm with ϵ_{max} 2120.[8] The shape of the spectrum and the λ_{max} are unaffected by changes in [MOMe] or by changing M from K to Me_4N. As it was also found that the spectral characteristics of this carbanion are not affected by using potassium *tert*-butoxide in *tert*-butyl alcohol for its generation, it is clearly not possible to use visible spectroscopy to determine ion pairing in this case.

We also investigated the dependence of $[CF^-]/[CFH]$ on

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Table I. Concentration Equilibrium Constant Values for the Anion Formation Reaction of 9-Cyanofluorene with Potassium Methoxide and Tetramethylammonium Methoxide Solutions[a]

M	$[\mathrm{MOMe}] \times 10^3$,[b] M	$[\mathrm{CFH}]_0$,[b] 10^4M	absorbance[c]	$[\mathrm{CF}^-]$, 10^4M	$K_c = [\mathrm{CF}^-]/[\mathrm{CFH}][\mathrm{MeO}^-]$
K	3.82	9.76	1.33	6.27	563
	7.45	9.52	1.61	7.59	588
	10.9	9.30	1.69	7.97	593
	14.2	9.09	1.71	8.07	591
	17.4	8.89	1.70	8.02	555
	26.1	8.33	1.65	7.78	559
	31.3	8.00	1.59	7.50	491
Me_4N	2.23	9.76	1.00	4.72	533
	4.35	9.52	1.38	6.51	585
	9.31	9.09	1.58	7.45	530
	11.9	8.69	1.61	7.59	619
	15.3	8.33	1.57	7.41	553
	18.3	8.00	1.55	7.31	603

[a] In methanol at approximately 25 °C. [b] Initial concentration. [c] Obtained using a 1-cm cell.

Table II. Concentration Equilibrium Constant Values for the Anion Formation Reaction of 9-Carbomethoxyfluorene with Potassium Methoxide and Tetramethylammonium Methoxide Solutions[a]

M	$[\mathrm{MOMe}]$,[b] M	$[\mathrm{CMFH}]_0$,[b] 10^4M	absorbance[c]	$[\mathrm{CMF}^-]$, 10^4M	$K_c = [\mathrm{CMF}^-]/[\mathrm{CMFH}][\mathrm{MeO}^-]$
K	0.0192	8.89	0.865	1.87	14.0
	0.0340	8.00	1.33	2.87	16.6
	0.0464	7.27	1.49	3.23	17.4
	0.0567	6.67	1.55	3.35	17.9
	0.0585	4.90	1.11	2.40	16.5
	0.114	4.79	1.47	3.17	17.2
	0.167	4.67	1.62	3.50	17.9
	0.218	4.57	1.67	3.61	17.3
	0.267	4.47	1.69	3.65	16.7
	0.313	4.37	1.72	3.71	18.0
Me_4N	0.001 27	9.82	0.115	0.248	20.8
	0.002 51	9.76	0.220	0.475	21.0
	0.004 90	9.52	0.415	0.896	21.6
	0.0114	8.89	0.900	1.94	24.9
	0.0206	8.00	1.33	2.87	27.5
	0.0251	9.76	1.98	4.28	31.7
	0.0275	7.27	1.47	3.17	28.4
	0.0421	5.48	1.42	3.07	30.5
	0.0538	4.90	1.40	3.02	30.0
	0.0562	5.41	1.57	3.39	30.0
	0.0788	4.79	1.57	3.39	30.9
	0.0812	5.26	1.72	3.71	29.6
	0.1021	4.68	1.64	3.54	30.5

[a-c] See notes for Table I.

[MOMe]. Within the limits of experimental accuracy, we found that the concentration equilibrium constant, $K_c = [\mathrm{CF}^-]/[\mathrm{CFH}][\mathrm{MeO}^-]$, was independent of [MOMe] and unaffected by changing from M = K to M = Me_4N. The data are listed in Table I. Although it seemed unlikely that a significant cation dependence would develop between 0.03 M, the highest concentration at which K_c for CFH could be measured, and 0.06 M, the lowest concentration at which K_c for FDH was available, we were unable to make comparisons in a common concentration range.

9-Carbomethoxyfluorene (CMFH) was chosen in an attempt to obtain data at higher [MOMe]. The pK_a of CMFH in Me_2SO is 10.3 whereas that of CFH is 8.4.[9] The carbanion, CMF^-, absorbs at 388 nm, with ϵ_{max} 4630 in methanol.[10] Again the spectra obtained at different [MOMe] and with different M were identical. Data for K_c vs. [MOMe] were recorded as described for CFH and are reported in Table II. It will be noted that with KOMe there is little or no change in K_c between 0.02 and 0.3 M. Using Me_4NOMe, K_c is also essentially unaffected by [MOMe]. However, there is a small but reproducible difference between the data obtained with the two different cations. Me_4NOMe produces more ionization than KOMe at the same concentration by a factor which ranges from 1.5 to 2.0. This relationship extends at least to [MOMe] = 0.1 M and probably to 0.3 M. This range overlaps significantly with that in which data for FDH are available. It is clear that $[\mathrm{FD}^-]/[\mathrm{FDH}]$ is much more sensitive to [MOMe] and M than is $[\mathrm{CMF}^-]/[\mathrm{CMFH}]$.

***N*-Methyl-*N*-phenylfluorene-9-carboxamide (CAFH)** was chosen to allow examination of a 9-substituted fluorene at higher [MOMe]. We initially tried *N*,*N*-dimethylfluorene-9-carboxamide but it was found to be insufficiently acidic. CAFH itself was too weakly acidic to allow determination of ϵ_{max} in methanol. We therefore added Me_2SO and determined ϵ_{max} ~22 000 at 66% v/v Me_2SO-MeOH. With the more acid carbon acids described above, addition of Me_2SO did not change ϵ_{max}. In methanol, λ_{max} is 420 nm. The data in Table III show that the value of K_c increases by a factor of 2 as [KOMe] is raised from 0.24 to 1.4 M. There is a larger change in K_c for a smaller range of [Me_4NOMe]. The effective ba-

Table III. Equilibrium Measurements for the Anion Formation Reactions of *N*-Methyl-*N*-phenylfluorene-9-carboxamide with Potassium Methoxide and Tetramethylammonium Methoxide[a]

M	[MOMe],[b] M	$[CAFH]_0$,[b] 10^4M	absorbance[c]	$[CAF^-]$, 10^5M	$K_c = [CAF^-]/[CAFH][MeO^-]$ ($\times 10^2$)
K	0.240	8.02	0.080	0.364	1.90
	0.400	6.69	0.110	0.500	1.89
	0.514	5.73	0.130	0.591	2.03
	0.600	5.01	0.140	0.636	2.14
	0.600	3.76	0.110	0.500	2.25
	0.960	3.01	0.160	0.727	2.58
	1.20	2.51	0.200	0.909	3.13
	1.37	2.15	0.235	1.07	3.82
Me_4N	0.281	3.76	0.140	0.636	6.12
	0.452	3.01	0.250	1.14	8.71
	0.565	2.51	0.325	1.48	11.1
	0.642	2.15	0.390	1.77	14.0
	0.706	1.88	0.420	1.91	16.0
	0.753	1.67	0.440	2.00	18.1

[a-c] See notes for Table I.

Table IV. Equilibrium Measurements for the Anion Formation Reaction of *N*-Fluorenylidenefluoren-9-amine with Potassium Methoxide and Tetramethylammonium Methoxide Solutions[a]

M	[MOMe], M	$[FAFH]_0$,[b] 10^4M	absorbance[c]	$[FAF^-]$, 10^5M	$K_c = [FAF^-]/[FAFH][MeO^-]$ ($\times 10^2$)
K	0.0045	9.80	0.005	0.09	4.53
	0.012	9.43	0.020	0.075	6.6
	0.019	9.09	0.031	0.116	6.7
	0.026	8.77	0.039	0.146	6.4
	0.052	9.76	0.113	0.423	8.4
	0.100	9.52	0.240	0.900	9.5
	0.146	9.30	0.350	1.31	9.8
	0.204	9.03	0.485	1.82	10.1
	0.246	8.83	0.590	2.21	10.4
	0.233	8.89	0.620	2.32	11.5
	0.300	8.57	0.865	3.24	13.1
	0.420	8.00	1.25	4.68	14.8
	0.442	7.89	1.35	5.06	15.5
	0.525	7.50	1.65	6.18	17.1
	0.600	7.14	1.89	7.08	18.3
NMe_4	0.0020	9.76	0.005	0.019	9.7
	0.0050	9.52	0.007	0.026	5.5
	0.0069	9.30	0.012	0.045	7.0
	0.0089	9.02	0.015	0.056	7.0
	0.011	8.89	0.019	0.071	7.3
	0.015	8.51	0.032	0.120	9.4
	0.016	8.33	0.038	0.142	10.7
	0.020	8.00	0.048	0.180	11.3
	0.0469	9.52	0.275	1.03	23.3
	0.0896	9.09	0.725	2.72	34.4
	0.129	8.69	1.30	4.87	46.0
	0.141	8.57	1.63	6.10	54.4

[a-c] See notes for Table I.

sicity of Me_4NOMe is greater than that of KOMe at 0.25 M by a factor of 3 and this ratio increases with increasing [MOMe]. The cation effect on K_c, while appreciable in this range of [MOMe], is much less than that for fluoradene and the threshold [MOMe] for its onset is apparently higher. No cation-dependent spectral changes were observed in these experiments. Whether CFH and CMFH would respond similarly in this [MOMe] range cannot be determined with present experimental techniques.

N-Fluorenylidenefluoren-9-amine (FAFH) was chosen to represent fluorenyl systems in which there is no appreciable distribution of charge to a heteroatom. The visible absorption maximum for the carbanion, FAF^-, occurred at 635 nm with ϵ_{max} 26 700.[11]

As expected, the threshold [MOMe] at which K_c became significantly cation dependent was lower than that for the fluorenes with carbonyl-containing 9 substituents. This can be seen in Table IV. In spite of this greater sensitivity to the nature of M, the spectra of both KOMe- and Me_4NOMe-produced carbanions were identical throughout the range of concentrations described in Table IV. The effect on K_c of changing from K to Me_4N was also much less than that observed for FDH at corresponding concentrations.

1,3-Diphenylindene (DPIH) produced the only carbanion in this study (besides FD^-) which had different visible spectra in KOMe and Me_4NOMe. The spectrum in KOMe is shown in Figure 1. There is a broad maximum at ca. 350 nm with a shoulder at ca. 410 nm. Figure 2 shows that, with Me_4NOMe as base, particularly at high [Me_4NOMe], DPI^- shows two distinct peaks with the long-wavelength peak red shifted by ca. 10 nm. It may also be seen in Figure 2 that the spectra at low [Me_4NOMe] are more similar to the KOMe spectrum

Table V. Equilibrium Measurements for the Anion Formation Reaction of 1,3-Diphenylindene with Potassium and Tetramethylammonium Methoxide Solutions[a]

M	[MOMe],[b] M	$[DPIH]_0$,[b] 10^4M	absorbance[c]	$[DPI^-]$, 10^6M	$K_c = [DPI^-]/[DPIH][MeO^-]$ ($\times 10^2$)
K	0.700	4.90	0.100	5.52	1.63
	0.900	4.20	0.125	6.91	1.86
	1.05	3.67	0.155	8.56	2.27
	1.17	3.27	0.180	9.94	2.68
	1.34	2.67	0.225	12.4	3.63
NMe_4	0.197	5.88	0.130	7.18	6.27
	0.198	6.31	0.115	6.35	5.13
	0.269	5.34	0.205	11.3	8.04
	0.328	4.90	0.230	12.7	8.11
	0.330	5.26	0.260	14.4	8.53
	0.423	4.20	0.423	23.4	13.9
	0.424	4.51	0.390	21.5	11.8
	0.495	3.95	0.460	25.4	13.9
	0.550	3.51	0.485	26.8	15.0
	0.594	3.16	0.495	27.3	15.9

[a-c] See notes for Table I.

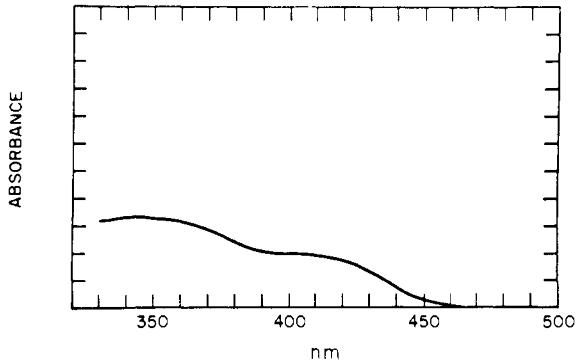

Figure 1. UV-visible spectrum of DPI^- formed from DPIH and 1.8 M KOMe.

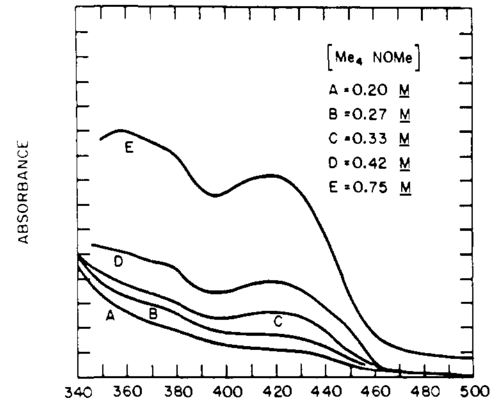

Figure 2. UV-visible spectrum of DPI^- formed from Me_4NOMe and DPIH. Spectra were not all run at same [DPIH].

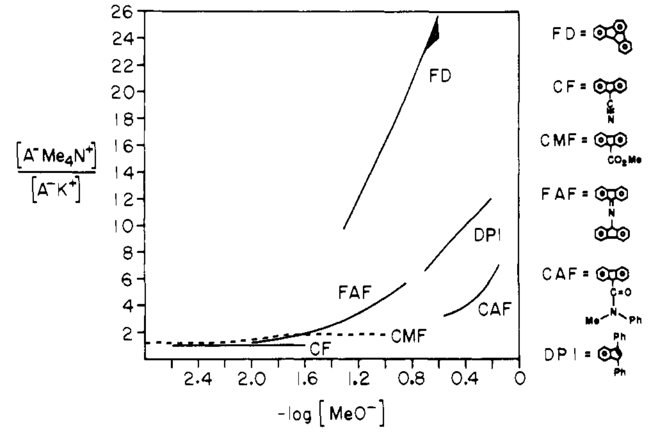

Figure 3. Relative amounts of anion formation from carbon acids as a function of cation at constant $[MeO^-]$ and [AH].

suggesting that at low [MOMe] the environments of the DPI^- ions are more similar. We determined ϵ_{max} 18 100 for the long-wavelength band of DPI^- in Me_2SO-methanol[1d] and, assuming that ϵ_{max} would be relatively unaffected by M, assembled the data in Table V.

Unfortunately the data in Table V do not allow a straightforward comparison of K_c for DPIH with KOMe and Me_4NOMe because of the difficulty of getting consistent data below [KOMe] = 0.7 M. However, the fact that $K_c = 0.16$ at $[Me_4NOMe] = 0.6$ and increases with increasing $[Me_4NOMe]$ clearly shows a minimum factor of 10 for the cation effect on K_c at this [MOMe]. An extrapolative method for comparison will be described in the next section. It appears that DPI^-, in addition to being the only system which shows cation-dependent spectral changes, also shows the largest cation effect on K_c in this concentration range (excluding FD^-). It seems possible that FAF^- would show a comparable effect on K_c, but this was not measurable in the same concentration range.

It is interesting to compare our data for KOMe and DPIH with that reported by Streitwieser for NaOMe and DPIH.[1d] Within the relatively limited range covered by our data, it is found that the equilibrium acidity of DPIH is roughly a factor of 5 greater in KOMe solution than in NaOMe solution.[12] Although we have no data for NaOMe with FDH, there appears to be a sizable difference between KOMe and LiOMe.[13]

Summary and Conclusions

In order to allow a visual assimilation of the data discussed above, we offer the plot of Figure 3. The line segments were obtained by plotting K_c or log K_c against [MOMe] for each M and drawing a least-squares line or a smooth curve through the data points. K_c for Me_4NOMe was then divided by K_c for KOMe to give the values termed $[A^-Me_4N^+]/[A^-K^+]$ and plotted in Figure 3 vs. $[MeO^-]$. In the case of DPIH, for which the data for the two cations did not overlap, it was found that a plot of log K_c vs. [KOMe] was linear over the range of our data. Because Streitwieser had previously shown[1d] that log K_c vs. [NaOMe] was linear over a much wider concentration range, we decided to extrapolate the KOMe values necessary to calculate K_c ratios through the range of our Me_4NOMe data assuming that log K_c vs. [KOMe] would remain linear. There is no theoretical basis for this assumption, and it is clear that there must eventually be some curvature at low [KOMe] in order that the intercept at [KOMe] = 0 may be the same as the pK_a value extrapolated by Streitwieser. If this curvature becomes manifest above 0.2 M it will cause an upward shift in the low [MOMe] section of the DPI curve in Figure 3. For this reason and because of other, relatively minor assumptions made in preparing Figure 3, no necessary significance should be assigned to the *shapes* of the curves. It will also be noted that the data for FDH in our previous paper,[1b] if treated in the same manner as the other systems in this work, shows a leveling and downward turn at [MOMe] above 0.2 M. We are unwilling at the present time to ascribe any significance to this trend partly because there is no obvious physical explanation and partly because FDH is more than 50% ionized in the range of [Me_4NOMe] in question, making K_c determination relatively inaccurate.

The important features of Figure 3 are as follows. Firstly, it clearly shows that, even in this protic, polar medium, counterions have a significant effect on the apparent acidity of carbon acids, with the larger cation producing the highest acidity. This change in anion stability need not be reflected in its visible spectrum. The second and most important revelation of the present work is that this effect is strongly dependent on the carbon acid under consideration. The carbon acids of this study can be grouped into those which form enolates (CMFH, CAFH, and the aza version, CFH), those which form allyl anions (FAFH and DPIH), and the unique system FDH. With a willing imagination, reflections of these family relationships can be found in Figure 3, with enolate ion stability being least perturbed by the cation change, and the most extensively delocalized fluoradenide ion being most affected. Implicit in this analysis is the prediction that enolate ions lacking the additional delocalization of the fluorenyl system would experience less stabilization by large cations. Anions with only one simple resonance form would be least affected. Unfortunately we have no examples from these categories to offer.

Why is this effect observed? At least in the case of FD^-, the answer is stabilization by ion pairing.[5] But why should the more localized ions not be equally affected? Ion pairing is clearly stabilizing for localized anions even in polar solvents such as Me_2SO.[14] The key to this problem is that hydrogen bonding is an even more powerful stabilizing influence on localized ions.[14,15] This should lessen the ion-pairing interaction with enolate-type anions. It will be noted that the effect of changing K to Me_4N is noticeable even for enolate ions particularly at high concentrations of MOMe. Thus anion and cation interact, but the statistically favored species are probably well insulated from each other by their solvation spheres. For delocalized ions, both hydrogen bonding and contact ion pairing with cations capable of coordinative bonding should be minimized by the expected tendency of these interactions to localize charge in the carbanion. The energetic benefit of the bonding interaction would be offset by the destabilization of the anion. As a result, the presence of a large, weakly solvated cation such as tetramethylammonium ion can substantially lower the energy of a delocalized carbanion such as FD^- by providing the benefits of Coulombic neutralization without the penalties of charge localization.[16]

An unanswered question arising from this study is that of the nature of the association between the delocalized systems (e.g., FD^-) and K^+ in methanol. That an interaction exists is indicated by the increase in K_c with [MeOK]. Contact ion pairing is ruled out by the absence of a spectral change. It has, however, been suggested that this carbanion is hydrogen bonded when prepared with KOMe in MeOH because its spectrum differs from that of the free ion.[7] The fact that the Cs salt exhibits an ion-pair spectrum[5b] suggests that the free-energy difference between the FD^-K^+ contact ion pair and the species actually present in KOMe–MeOH is not large. A solvent-separated ion pair or a series of spectrally indistinguishable solvent-separated ion pairs would seem to be a viable hypothesis. It should be possible for hydrogen bonding to occur between FD^- and cation-coordinated methanol molecules. The interaction would be a weak one and would allow for a gradual transition to hydrogen-bonded free ions at low [KOMe].

Experimental Section

9-Cyanofluorene was prepared by the method of Wislicenus and Waldmüller.[17]

***N*-Fluorenylidenefluoren-9-amine** was prepared using the method of Schönberg and Singer.[18]

1,3-Diphenylindene was the generous gift of Professor L. M. Tolbert.

9-Carbomethoxyfluorene was prepared by the method of Bordwell.[19]

***N*-Methyl-*N*-phenylfluorene-9-carboxamide.** Fluorene-9-carboxylic acid[20] (2.0 g, 9.5 mmol) was treated with 4 mL of thionyl chloride and the mixture warmed in a water bath until a clear solution was obtained. The excess thionyl chloride was then removed by rotary evaporation and codistillation with dry benzene. The residue was treated with 2 mL of freshly distilled *N*-methylaniline in 20 mL of dry benzene and the mixture allowed to stand for 1 h. The benzene was removed and the product taken up in $CHCl_3$. The $CHCl_3$ solution was washed successively with aqueous $NaCO_3$ solution, dilute aqueous HCl solution, and water and was dried over anhydrous $MgSO_4$. Evaporation of the $CHCl_3$ and recrystallization from toluene gave the product: mp 210–213 °C; 67%; NMR ($CDCl_3$) δ 3.0 (s, 3 H), 4.6 (s, 1 H), 6.6–7 (m, 13 H); IR (KBr) 1630, 1350 cm^{-1}; MS *m/e* 299 (calcd for $C_{21}H_{17}NO$, 299), 165 (100%), 134, 77. Anal. Calcd for $C_{21}H_{17}NO$: C, 84.24; H, 5.72; N, 4.68. Found: C, 84.51; H, 5.69; N, 4.46.

Solvents, solutions, and procedures have been described previously.[5b]

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