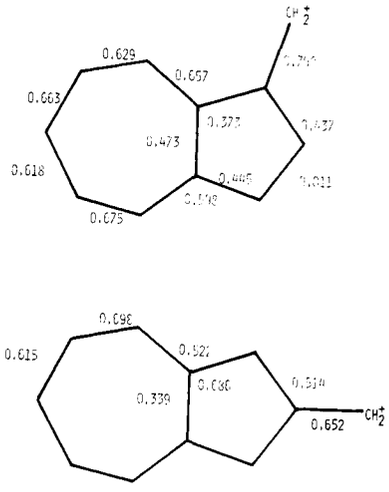

Figure 8. π-Bond orders of the planar 2-azulylmethyl cation (bottom) and the planar 1-azulylmethyl cation (top).

onset of a fundamental change in the nature of the π system. At this point, the molecule is probably best described as beginning to resemble contiguous tropylium and butadienic subsystems.

The general correspondence between the experimentally derived and theoretical results suggests that variations in ^{13}C NMR chemical shifts in azulenes can serve as an index of π-electron-density redistribution effected by substituents. Nonetheless, the lack of a complete correspondence does signal caution in their interpretation. Subject to this caveat, however, our observations are consistent with a variety of data on the kinetic and equilibrium behavior of azulene systems.

Our CNDO calculations indicate that 1-substituted azulenes should be much more efficient at stabilizing an adjacent positive charge than 2-substituted ones. Consistent with expectation, McDonald and Richmond have reported that 2-(1-azulyl)ethyl arenesulfonates undergo acetolysis via the ethyleneazulenium ion approximately 2000 times faster than the corresponding 2-(2-azulyl)ethyl arenesulfonates.[8]

Our observation that attachment of a substituent to the 1-position of azulene affects primarily the 5- and 7-positions is also consistent with the report that the acid-weakening effect of methyl substitution on the pK_a of 1-azuloic acid is greatest at positions 5 and 7 and considerably weaker at C-3, C-4, C-6, and C-8.[21]

The 3-position in 1-azuloic acid exhibits behavior intermediate between a meta and a para position,[21] again consistent with the ^{13}C NMR spectral results. Table VIII compares the values of ρ_I and ρ_R for 1-substituted azulenes with those for C-3 and C-4 of 1-substituted naphthalenes. Interestingly, ρ_R is moderately large and positive, as expected for a para-like position, while ρ_I is negative, as expected for a meta-like position (although much larger in magnitude). The relative insensitivity of C-3 to substitution thus appears to be due partly to cancellation of inductive and resonance effects.

Table VIII. Comparison of Regression Parameters of 1-Substituted Azulene 3-Positions with 1-Substituted Naphthalene 3- and 4-Positions

series	position	ρ_I	ρ_R
1-X-azulene	3	−1.46	+4.48
1-X-naphthalene	3	−1.80	−1.63
1-X-naphthalene	4	+5.92	+19.98

Experimental Section

All compounds were prepared by literature procedures[22] and had physical constants consistent with those reported in the literature. Product identity was also checked by proton NMR spectroscopy.

NMR spectra were recorded on one of three different instruments: Bruker WH-90 spectrometers (Brandeis University and University of Lodz, Poland) or a Bruker HFX-270 spectrometer (Florida State University). Samples were dissolved in acetone-d_6 (ca. 1 M solutions in 10-mm tubes) containing a small amount of Me_4Si.

Dual parameter fits were performed on a PDP-11 computer by using the statistical analysis program COSAP.

CNDO calculations were performed by using the program CNINDO (program no. 141, Quantum Chemistry Program Exchange) on an IBM 370/145 computer, using the electron-diffraction geometry for azulene reported by Bastiansen.[23]

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Registry No. Azulene, 275-51-4; 1-methylazulene, 769-31-3; 1-chloroazulene, 23306-02-7; 1-acetylazulene, 7206-57-7; 1-nitroazulene, 7206-56-6; 1,3-dibromoazulene, 14658-95-8; 1,3-diacetylazulene, 10487-55-5; 2-methoxyazulene, 36044-37-8; 2-methylazulene, 769-86-8; 2-chloroazulene, 36044-31-2; 2-cyanoazulene, 58081-28-0; 2-iodoazulene, 36044-41-4; 1-azulylmethyl cation, 73274-81-4; 2-azulylmethyl cation, 73274-82-5.

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(23) Bastiansen, O. *Acta Chem. Scand.* **1966**, *20*, 1319.

Basic Methanolysis of *N*-Aryl-*N*-phenylbenzamides

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The mechanism of basic methanolysis of a series of *N*-aryl-*N*-phenylbenzamides in methanol and in 80% Me_2SO–methanol has been studied. Comparison of Hammett ρ values with results in the literature suggest that in methanol the rate-determining step is solvent-assisted C–N bond breaking while in 80% Me_2SO–methanol the rate-determining step is methoxide attack. The mechanism of basic methanolysis in a given case is shown to depend both on the relative basicity of methoxide ion and the arylamine anion and on steric effects in the intermediate complex.

The mechanism of basic methanolysis of anilides is finely balanced, with several possible rate-determining steps (Scheme I).[1] The rate-determining step in any particular case is governed by the relative rates of loss of

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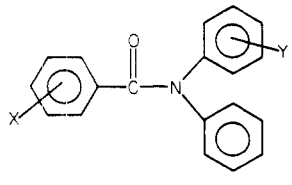
amine (k_2) and methoxide ion (k_{-1}) from the intermediate complex (I).

With very poor amine leaving groups $k_2 \ll k_{-1}$, and a slow protonation of the amine function (k_3) in the intermediate is necessary before C–N bond breaking (k_4, fast) can occur (mechanism A).[2,3] For better amine leaving groups the rate-determining step is solvent-assisted C–N bond breaking (k_2) (mechanism B). In the extreme case where the amine is a better leaving group than methoxide ion ($k_2 > k_{-1}$), the rate-determining step becomes bond forming (k_1) (mechanism C).[1,4,5]

The mechanism or combination of mechanisms that applies in a given series depends upon the identity of R (H or methyl),[1] the nature of R′ (methyl, trifluoromethyl, or aryl),[2,6] and the solvent (methanol or Me_2SO–methanol).[4] Of particular interest here is the possible occurrence of mechanism C. In methanol as solvent it has been suggested that mechanism C applies only for tertiary amides (R = methyl) in which the aromatic ring contains a nitro group at the para position, as a result of the combination of both steric and electronic effects.[1] In 80% Me_2SO–methanol the occurrence of mechanism C is more common, and it has been reported for *N*-aryl-*N*-methylbenzamides which contain substituents of equal or greater electron-withdrawing power than *p*-bromo.[4] The wider occurrence of mechanism C in 80% Me_2SO–methanol has been explained by the dramatic increase in basicity of methoxide ion on transfer from methanol to 80% Me_2SO–methanol (greater than 4 pK_a units)[7] and the expected much smaller increase, if any, in basicity of the larger amine anions.[8] This results in a large decrease in k_{-1} and a smaller decrease in k_2 (i.e., k_2/k_{-1} increases).

The occurrence of mechanism C should also be favored by a decrease in the basicity of the amine leaving group, and for this reason we have now looked at the basic methanolysis of a series of substituted *N*-aryl-*N*-phenylbenzamides (II). It is known that diphenylamines are



II

stronger acids (as indicated by smaller pK_{HA} values) than the corresponding anilines, and consequently their conjugate bases should be better nucleofuges than those of the corresponding anilines. Stirling[9] has looked at the relationship between the nucleofugality of nucleofuges and their basicity, as measured by the pK_{HA} values of their conjugate acids. While there is no general correlation of nucleofugality with pK_{HA} over a wide range of nucleofuges,[9] within a series of nucleofuges of the same type, small variations of structure do result in a correlation between the pK_{HA} and the nucleofugality.[9,10] Thus, we might expect a good correlation between the pK_{HA} of various anilines and the nucleofugality of the corresponding aniline anions.

One of the probes used to study the mechanism of basic methanolysis in a particular case is the use of Hammett plots of substituent effects on rate for a series of anilides substituted on the aromatic ring. It has been found that the Hammett ρ value depends on the mechanism of reaction.[2,4-6] Typically in methanol, mechanism A is characterized by a very small ρ value ($\sim$0) while mechanism B ($\rho \approx 3$) and mechanism C (ρ = 1.2–1.7) have substantial

Scheme I

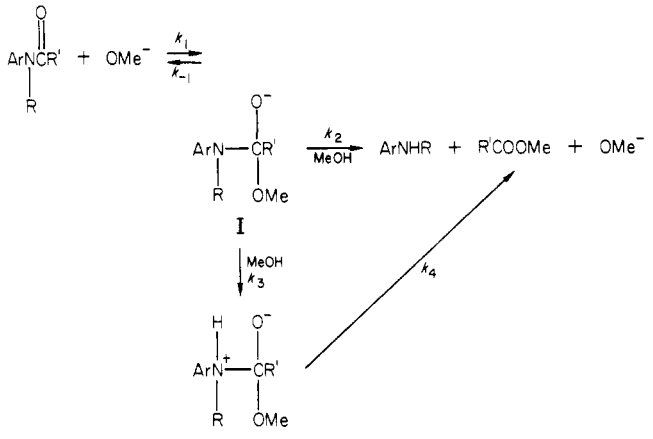


Table I. Rate Data for the Basic Methanolysis of $XC_6H_4CON(C_6H_5)C_6H_4Y$ in Methanol at 373 K and in 80% Me_2SO–Methanol at 303 K[a]

	X	Y	analyt λ, nm	10^4k_2, M^{-1} s^{-1} MeOH[b]	80% Me_2SO–MeOH[c]
a	4-NO_2	H	284	661 (636)[d]	
b	3-NO_2	H	284	654	
c	4-Cl	H	284	67.9	
d	H	H	284	16.9[e] (17.1)[d]	41.4
e	4-CH_3	H	284	10.3	
f	4-OCH_3	H	284	8.15	
g	H	*f*	283	9050 (9240)[d]	11000
h	H	4-NO_2	390	5070[g] (5050)[h]	15200[i]
i	H	3-NO_2	274	1490 (1370)[d]	2210
j	H	4-CO_2CH_3	323	679 (674)[d]	987
k	H	3-Cl	285	241	358
l	H	4-Cl	289	113 (116)[d]	200
m	H	3-CH_3	285	11.1 (11.4)[d]	27.1
n	H	4-CH_3	290		22.9
o	H	4-OCH_3	284	5.5	
p	H	4-NH_2	295		3.44

[a] Rate of amine production at wavelength indicated. [b] $[NaOCH_3]$ = 0.002–0.08 M. [c] $[NaOCH_3]$ = 0.002–0.05 M. [d] Rate of amide loss at 245 nm. [e] 4.28 (358 K), 60.6 (389 K); E_a = 23.7 kcal mol^{-1}; ΔS^*_{298} = −9.8 eu. [f] 4-$[C_6H_5CON(C_6H_5)C_5H_4N]$. [g] 41.1 (303 K), 764 (342 K), 2090 (358 K); E_a = 15.5 kcal mol^{-1}; ΔS^*_{298} = −20 eu. [h] Rate of amide loss at 320 nm. [i] Followed at 500 nm due to ionization of the amine in Me_2SO-methanol.

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(4) T. J. Broxton, L. W. Deady, and Y. T. Pang, *Tetrahedron Lett.*, 2799 (1975).
(5) G. M. Blackburn and J. D. Plackett, *J. Chem. Soc., Perkin Trans. 2*, 1366 (1972).
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ρ values. Thus, a Hammett plot for a series of substituted anilides typically shows nonlinearity if more than one mechanism is applicable throughout the series. A change from mechanism A to mechanism B is characterized by upward curvature of the Hammett plot,[2,3] while a change from mechanism B to mechanism C results in downward curvature.[4]

Results

Rate constants for the basic methanolysis of substituted *N*-aryl-*N*-phenylbenzamides (II) in methanol and in 80% Me_2SO–methanol are given in Table I. Results obtained by monitoring the rate of production of amine at the wavelength indicated were within experimental error of those obtained by following the rate of loss of amide.

Rate constants in methanol for compounds substituted in the acid ring (i.e., X) correlate well with σ (ρ = 1.95, r = 0.996, sd = 0.091, f = 0.031). Rate constants for compounds substituted on the amine ring (i.e., Y) correlate well with σ (ρ = 2.82, r = 0.993, sd = 0.150, f = 0.067) in methanol, but in 80% Me_2SO–methanol correlation with σ^- (ρ = 1.98, r = 0.995, sd = 0.124, f = 0.057) is significantly better than with σ (ρ = 2.41, r = 0.981, sd = 0.252, f = 0.116).

For compound IIh, it was found that the amine product absorbed at 390 nm in methanol but at 500 nm in 80% Me_2SO–methanol. This is explained by the ionization of the N–H of the amine in Me_2SO–methanol (see below). It was found that on acidification of the product solution, the wavelength of maximum absorbance for the amine product shifted to 403 nm.

Discussion

(a) Mechanistic Conclusions. (i) Reaction in Methanol. The Hammett ρ value for substituents in the amine ring (ρ_Y = 2.82) suggests that reaction occurs via solvent-assisted bond breaking (mechanism B). Surprisingly, however, correlation with σ is better than with σ^-. This is the first example for which the rate of basic methanolysis of a series of anilides correlates better with σ than with σ^-. Previous results, even where reaction by mechanism C is involved, have all correlated better with σ^-.[4,6] A possible explanation for the correlation with σ is suggested after inspection of space-filling molecular models (Courtauld) of the reactant and the intermediate complex. In the intermediate complex, overlap of the p orbitals on the nitrogen atom and in the aromatic rings attached to the nitrogen is not possible because the aromatic rings are not coplanar with the nitrogen atom, because of severe steric clashing. In fact, in the most stable conformation, the p orbitals of the aromatic rings are orthogonal to that on the nitrogen atom, and through conjugation with a para electron-withdrawing substituent on the aromatic ring is not possible. Hence correlation with σ^- is not observed.

(ii) Reaction in 80% Me_2SO–Methanol. Comparison of the Hammett ρ value obtained for the reaction in 80% Me_2SO–methanol (ρ_Y = 1.98) with the results previously obtained for the *N*-aryl-*N*-methylbenzamides in 80% Me_2SO–methanol[4] (ρ_Y = 2.3 for mechanism C and ρ_Y = 5.4 for mechanism B) suggests that for the *N*-phenyl compounds reaction occurs by mechanism C throughout the series.

Surprisingly, in contrast to the situation in methanol, the Hammett treatment for the basic methanolysis of the *N*-aryl-*N*-phenylbenzamides in 80% Me_2SO–methanol correlates better with σ^- than with σ. The operation of mechanism C in this solvent means that bond forming is the rate-determining step. Inspection of space-filling molecular models of the reactant show that clashing is less severe than in the intermediate complex, and it is possible to achieve coplanarity between one of the aromatic rings attached to the nitrogen atom and the nitrogen atom itself, provided that the other ring is orthogonal. Thus, through conjugation with a para substituent is possible, and correlation with σ^- is reasonable. Correlation with σ^- has previously been observed for the basic methanolysis of amides by mechanism C[4,5] whereas the hydrolysis of esters, which also occurs by a mechanism analogous to mechanism C, requires the use of σ for a good correlation.

Table II. pK_{HA} Values for Substituted Anilines and Diphenylamines[a]

aniline	pK_{HA}	diphenylamine	pK_{HA}
4-NO_2	18.91	4-NO_2	15.67[b]
4-NO_2-*N*-Me	18.49	3-NO_2	19.53
3,5-Cl_2	23.59	3-Cl	20.73
3-CN	24.64	4-Cl	21.33
3-Cl	25.63	H	22.44
H	27	4-Me	22.95
		4-OMe	23.22

[a] Reference 11. [b] pK_{HA} for methanol = 15.5 (water) and 17.7 (2-propanol).[7]

(b) Factors Affecting Mechanism. Any rationalization of the overall mechanistic pattern observed for the basic methanolysis of anilides must explain the operation of mechanisms A and B for substituted acetanilides, mechanism B for benzanilides, with the possible exception of *N*-methyl-*N*-4-nitrophenylbenzamide for which mechanism C has been proposed,[1] and mechanism B for the *N*-aryl-*N*-phenylbenzamides. In Me_2SO–methanol, however, *N*-methylbenzanilides react by mechanism B (4′-methyl to 4′-bromo) or by mechanism C (4′-bromo to 4′-nitro) whereas the *N*-aryl-*N*-phenylbenzamides react by mechanism C throughout.

We now attempt to rationalize these mechanistic changes by recourse to the basicity of the nucleofuges and also to steric effects in the intermediate complex.

(i) Basicity of Nucleofuge. As mentioned at the beginning, some indication of the basicity of a nucleofuge is obtained from the pK_{HA} value of the conjugate acid. The pK_{HA} values for some substituted anilines and diphenylamines in Me_2SO–water are given in Table II.[11] These pK_{HA} values are in Me_2SO–water mixtures ranging from 23 to 99 mol % Me_2SO, and Stewart makes the assumption that the pK_{HA} values are independent of the solvent, which may be reasonable since large anions such as those of aniline and diphenylamine are not considered to be hydrated extensively.[11] Reported values[7] of the pK_{HA} for methanol range from 15.5 (in water) to 17.7 (in 2-propanol), so at face value it would appear, on the basis of these pK_{HA} values, that methoxide ion should be a better leaving group from the intermediate I than all of the amine anions with the exception of the anion of 4-nitrodiphenylamine.

However, a word of caution is warranted here because we are assuming that the basicity of these anions to hydrogen, as measured by pK_{HA} values, is equal to their carbon basicity which governs their nucleofugality from the intermediate complex. Furthermore, it has been reported[12,13] that amines are better leaving groups from tetrahedral intermediates than oxygen anions of comparable basicity by factors ranging from 10^4 to 10^6, depending on the systems being studied. Thus, it is not reasonable

(11) D. Dolman and R. Stewart, *Can. J. Chem.*, **45**, 911 (1967).
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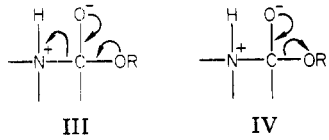
to deduce orders of nucleofugality for different classes of nucleofuge directly from simple pK_{HA} values.

Further insight into this problem can be obtained from ionization studies of the relevant amines in solutions containing sodium methoxide. Studies on 4-nitrodiphenylamine in methanolic sodium methoxide solution showed no detectable ionization of the amine (UV–vis spectral studies). However, in 80% Me_2SO–methanol ionization was detectable (visible spectral shift from 403 nm for the un-ionized amine to 500 nm for the ionized amine), and 50% ionization was observed for 2.16×10^{-3} M sodium methoxide with 5.4×10^{-5} M amine. This leads to a difference of 1.9 pK units for the pK_{HA} of methanol and 4-nitrodiphenylamine. From Table II the pK_{HA} value for 4-nitrodiphenylamine is 15.67, and thus a calculated value for methanol is 13.8 (in 80% Me_2SO–methanol).

For the *N*-methylbenzanilides in 80% Me_2SO–methanol the mechanistic change (from B to C) occurs for the 4-bromo compound. We can estimate a value for the pK_{HA} of 4-bromo-*N*-methylaniline from the data in Table II provided we make some assumptions. First we must assume that the pK_{HA}'s for the 4-bromo- and 4-chloroanilines are similar, second that pK_{HA}'s differences between 4-chloro- and 3-chloroanilines are the same as for the corresponding diphenylamines (0.60 units), and finally that the contribution by the *N*-methyl group for the 4-bromo-*N*-methylaniline is the same as that for the 4-nitro-*N*-methylaniline (−0.4 units). Applying these assumptions, we arrive at a pK_{HA} value for the 4-bromo-*N*-methylaniline of 25.63 + 0.60 − 0.40 = 25.8. Thus, although the calculated pK_{HA} value for methanol in 80% Me_2SO–methanol is 13.8, the amine nucleofuge is lost more rapidly than methoxide ion from the intermediate complex (i.e., mechanism C) until the pK_{HA} of the amine reaches 25.8. Above this value methoxide ion is lost more rapidly from the intermediate complex, and mechanism B applies. The change from mechanism C to mechanism B thus occurs for amines of pK_{HA} = 25.8; i.e., equal rates of loss of methoxide ion and amine anion occur for $\Delta pK_{HA} = pK_{HA}^{amine} - pK_{HA}^{MeOH} = 12$.

Conversely, Jencks[14] has shown that in ester aminolysis, for oxygen anions and amines of equal basicity, amines are better leaving groups by a factor of 10^5. One of the reasons proposed to explain this difference in rate is that amine expulsion (III) is assisted by electron donation from the

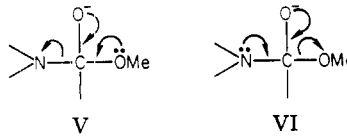


III

IV

alcohol oxygen atom. No such assistance is available for oxygen expulsion (IV) since the nitrogen is quaternary and does not have a free lone pair.

In the methanolysis of amines, however, amine expulsion (V) is assisted by electron donation from the methoxy oxygen atom and alkoxide expulsion (VI) is assisted by



V

VI

electron donation from the nitrogen atom, which in this case carries a lone pair. Thus, in the methanolysis of amides, for oxygen anions and amines of equal basicity, we would predict that the difference in rate of loss of amine and oxygen anions would be less than 10^5.

For the *N*-aryl-*N*-phenylbenzamides mechanism C operates throughout the series in 80% Me_2SO–methanol and this is in line with the above calculations. The pK_{HA} values of the amine nucleofuges range from 15.67 (4-nitro) to 22.4 (hydrogen), and thus reaction by mechanism C is reasonable for all compounds studied.

In methanol as solvent, we have to consider the effect on our pK_{HA} values of changing the solvent from 80% Me_2SO–methanol. The basicity of methoxide ion, being a small anion of high charge density, is dramatically increased on transfer from methanol to 80% Me_2SO–methanol.[15] The solvent activity coefficient for transfer of methoxide ion from methanol[15] to 80% Me_2SO–methanol is 4.0, and this is a measure of the difference of solvation of methoxide ion in methanol and in the dipolar aprotic solvent. Acidity function measurements (H_-) also show the effect of this solvation difference on the basicity of methoxide ion in methanol (H_- = 12.23) and in 80% Me_2SO–methanol (H_- = 16.80). Thus, the change of solvent results in a change of 4.5 units in the basicity of methoxide ion. The calculated pK_{HA} value for methanol in 80% Me_2SO–methanol is 13.8, and thus in methanol the calculated pK_{HA} for methanol is 9.3.

We assume that the basicities of the large anions of aniline and diphenylamine are not changed by the solvent transfer, and this is reasonable since these anions are not considered to be extensively solvated by protic solvents.[11] In addition, large anions have been shown to have small solvent activity coefficients for transfer from protic to dipolar aprotic solvents.[15] In some cases large anions are actually better solvated by the aprotic solvent.[15]

Allowing for differences in nucleofugality between amines and oxygen anions, we would expect a mechanistic change (from B to C) in methanol if the pK_{HA} of the amine is less than 21.3 (i.e., 9.3 + 12.0). For the benzanilides this only applies for the 4-nitro compounds, but for the *N*-aryl-*N*-phenylbenzamides it applies to compounds with electron-withdrawing substituents equal to or better than 4-chloro. However, no mechanistic change is apparent for the *N*-aryl-*N*-phenylbenzamides in methanol so some other factor must be operating to stop the change from mechanism B to mechanism C occurring in methanol.

(ii) Steric Effects. On inspection of space-filling molecular models of the intermediate complex for the methanolysis of the *N*-aryl-*N*-phenylbenzamides it becomes apparent that the intermediate is very crowded. This results in it being unlikely that a solvent molecule would be able to approach the intermediate close enough to provide solvent assistance to carbon–nitrogen bond breaking. In fact, the nitrogen atom is very effectively buried in the intermediate complex as a result of the combined effects of the methoxide, the carbonyl oxygen, and the aryl rings attached to the nitrogen. On the other hand, the oxygen of the methoxide is exposed to the solvent and can benefit from solvent assistance in the carbon–oxygen bond-breaking process, i.e., k_{-1}.

Let us now consider the consequences of these steric effects both in methanol and in 80% Me_2SO–methanol. In 80% Me_2SO–methanol neither step, i.e., k_{-1} or k_2, would receive much solvent assistance because the methanol is tightly bound by the Me_2SO. Thus, the steric effect would not be of great importance in 80% Me_2SO–methanol. In methanol, however, solvent assistance is of more importance, and, consequently, the steric effects are manifested

(14) N. Gravitz and W. P. Jencks, *J. Am. Chem. Soc.*, **96**, 499 (1974).

(15) R. Alexander, E. C. F. Ko, A. J. Parker, and T. J. Broxton, *J. Am. Chem. Soc.*, **90**, 5049 (1968).

in this solvent. Carbon–oxygen bond breaking (k_{-1}) would thus experience solvent assistance, but carbon–nitrogen bond breaking (k_2) would not. This results in the continued operation of mechanism B after the changeover to mechanism C is expected as observed in the basic methanolysis of *N*-aryl-*N*-phenylbenzamides.

Let us now consider the steric requirements of reaction by each of the different mechanisms. In mechanism A the methanol must approach the nitrogen in the intermediate complex before any stretching of the carbon–nitrogen bond. Thus, this mechanism has the greatest steric requirements, and it only occurs in cases where the solvent molecule may approach the nitrogen atom in the intermediate complex. This may well explain why mechanism A is observed for the basic methanolysis of substituted acetanilides but not for benzanilides. Molecular models show that the methanol cannot closely approach the nitrogen atom in the complex for the benzanilides unless there is some stretching of the carbon–nitrogen bond. In the case of reaction by mechanism B, the solvent molecule assists the carbon–nitrogen bond breaking process. The extent of assistance depends on when the solvent molecule can interact with the nitrogen atom in the complex, i.e., how much bond breaking is necessary before the solvent can interact with the nitrogen atom in the intermediate complex. The more bond breaking that has occurred before the solvent can interact with the nitrogen atom in the complex the smaller will be the steric requirements of the reaction but also the smaller the solvent assistance. The logical extension of this idea is the later changeover to mechanism C that would be expected from basicity considerations, e.g., the *N*-aryl-*N*-phenylbenzamides in methanol. Finally, reaction by mechanism C involves rate-determining attack of methoxide ion so this mechanism has the least steric requirements of all.

Experimental Section

Compounds. Benzoylations of the commercially available amines were carried out by using benzoyl chloride (or the substituted benzoyl chloride) in pyridine.[16] The following compounds, pure according to TLC analysis, were prepared by this method: *N*,*N*-diphenylbenzamide, mp 179–180 °C (lit.[17] mp 180–181 °C); *N*-4-nitrophenyl-*N*-phenylbenzamide, mp 130–130.5 °C (lit.[18] mp 129 °C); *N*-3-methylphenyl-*N*-phenylbenzamide, mp 105–105.5 °C (lit.[19] mp 104–106 °C); *N*-4-methoxyphenyl-*N*-phenylbenzamide, mp 120.5–121 °C (lit.[20] mp 121 °C); *N*-3-chlorophenyl-*N*-phenylbenzamide, mp 99.5–100 °C (lit.[20] mp 101–102 °C); 4-chloro-*N*,*N*-diphenylbenzamide, mp 135.5–136 °C (lit.[20] mp 136–137.5 °C); 4-methoxy-*N*,*N*-diphenylbenzamide, mp 139.5–140 °C (lit.[20] mp 139–140 °C); 4-methyl-*N*,*N*-diphenylbenzamide, mp 152–152.5 °C (lit.[20] mp 152 °C); 4-nitro-*N*,*N*-diphenylbenzamide, mp 157–157.5 °C (lit.[20] mp 156–157 °C); 3-nitro-*N*,*N*-diphenylbenzamide, mp 116.5–117.5 °C (lit.[21] mp 118 °C).

N-(4-aminophenyl)-*N*-phenylbenzamide [mp 186–187 °C (Anal. Calcd for $C_{19}H_{16}N_2O$: mol wt 288.1263. Found: mol wt 288.1260 by high-resolution mass spectrometry)] was prepared by the catalytic reduction (H_2/Pd) of the corresponding nitro compound.

The remaining amides were prepared by the Chapman rearrangement[22] by heating the aryl *N*-phenylbenzimidate[23] in a sealed tube at 250–300 °C. The following compounds, pure by TLC analysis, were prepared by this method: *N*-4-chlorophenyl-*N*-phenylbenzamide, mp 109–109.5 °C (lit.[17] mp 110 °C); *N*-4-methylphenyl-*N*-phenylbenzamide, mp 96.5–97.5 °C (lit.[24] mp 96–97 °C); *N*-[4-(carbomethoxy)phenyl]-*N*-phenylbenzamide, mp 113–113.5 °C (lit.[25] mp 112–114 °C); *N*-phenyl-*N*-4-pyridinylbenzamide, mp 165–167 °C (Anal. Calcd for $C_{18}H_{14}N_2O$: mol wt 274.1106. Found: mol wt 274.1106 by high-resolution mass spectrometry); *N*-(3-nitrophenyl)-*N*-phenylbenzamide, oil (Anal. Calcd for $C_{19}H_{14}N_2O_3$: mol wt 318.1004. Found: mol wt 318.0997 by high-resolution mass spectrometry).

Solvents. Methanol was dried by treatment with magnesium methoxide.[26] Sodium methoxide solutions were prepared by dissolving clean dry sodium metal in dry methanol. The solution was standardized by titration against hydrochloric acid with bromocresol green as indicator.

Dry Me_2SO was prepared by the method of Hirst et al.[27] All operations involving the dry Me_2SO were carried out in a glovebag under dry nitrogen.

Rate Measurements. Rate measurements were carried out in methanol ([NaOMe] = 0.002–0.08 M) or in 80% Me_2SO–methanol ([NaOMe] = 0.002–0.05 M) under pseudo-first-order conditions.[1] All compounds were studied at more than one base concentration within the above limits, and second-order rate constants agreed to within 4%. The analytical wavelengths and the species monitored are given in Table I.

Product Study. Product analysis was carried out for the reaction of *N*-(4-nitrophenyl)-*N*-phenylbenzamide. TLC analysis on silica gel indicated the presence of two products. After separation, these products were shown by TLC and IR spectra to be 4-nitrodiphenylamine and methyl benzoate. The infinity UV spectrum from a kinetic run matched that of an authentic product mixture.

Registry No. *N*,*N*-Diphenylbenzamide, 4051-56-3; *N*-(4-nitrophenyl)-*N*-phenylbenzamide, 73333-79-6; *N*-(3-methylphenyl)-*N*-phenylbenzamide, 73333-80-9; *N*-(4-methoxyphenyl)-*N*-phenylbenzamide, 73333-81-0; *N*-(3-chlorophenyl)-*N*-phenylbenzamide, 73347-61-2; 4-chloro-*N*,*N*-diphenylbenzamide, 15732-27-1; 4-methoxy-*N*,*N*-diphenylbenzamide, 16034-40-5; 4-methyl-*N*,*N*-diphenylbenzamide, 40686-26-8; 4-nitro-*N*,*N*-diphenylbenzamide, 20971-31-7; 3-nitro-*N*,*N*-diphenylbenzamide, 73333-82-1; *N*-(4-aminophenyl)-*N*-phenylbenzamide, 73333-83-2; *N*-(4-chlorophenyl)-*N*-phenylbenzamide, 23938-23-0; *N*-(4-methylphenyl)-*N*-phenylbenzamide, 21397-40-0; *N*-[4-(carbomethoxy)phenyl]-*N*-phenylbenzamide, 73347-62-3; *N*-phenyl-*N*-(4-pyridinyl)benzamide, 73333-84-3; *N*-(3-nitrophenyl)-*N*-phenylbenzamide, 73333-85-4.

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