Reactions of Aryldiazonium Salts and Arylazo Alkyl Ethers. 5. General Acid Catalysis of the Ionization of *anti*-Arylazo Methyl Ethers in Methanol[1a]

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The ionization of *anti*-arylazo alkyl ethers in alcoholic solvents is shown to be subject to general acid catalysis when the reaction is carried out in buffered solutions of aliphatic carboxylic acids and their salts. The reaction is also subject to ionic-strength effects and common-ion rate depressions. For the 3- and 4-cyano compounds there is evidence for complex formation between the cyano group and methoxide ion. In the case of the 2-cyano substituted compound no complex formation is detected, but a significant steric acceleration of the ionization is observed.

Introduction

Previous studies on the reactions of aryldiazonium salts in basic alcoholic solvents have shown that initially on mixing the syn ether is the predominant product[1b,2] but that it is unstable and is rapidly converted into a mixture of the anti ether and the dediazoniation product.[3,4] It is then possible to look at reactions of the anti ether thus generated in situ and to compare rates with reactions carried out by using synthetic samples of *anti*-arylazo alkyl ethers.[4] Of interest here is the rate of ionization of the *anti*-arylazo alkyl ether to free diazonium and alkoxide ions (k_{-1A}, Scheme I).

Previous studies have shown that the rate of ionization of the anti ether is accelerated by electron-donating substituents on the aromatic ring,[4,5] by decreasing the basicity of the alkoxide ion (OMe > OEt > *i*-PrO)[4] and by solvents of greater ion-solvating power (MeOH > EtOH).[4,6] In addition, it has been observed that on acidification of a solution containing either *syn*- or *anti*-arylazo alkyl ethers, ionization to free diazonium and alkoxide ions is very rapid. It was decided to investigate this acid catalysis of the ionization reaction initially with a view to distinguishing between specific and general catalysis[7,8] and hence to determine the role played by the proton in the catalysis.

General acid catalysis has recently been reported for several related reactions which involve alkoxide ion leaving groups. These include the decomposition of Meisenheimer complexes,[9,10] the hydrolysis of acetals of benzaldehydes,[11,12] and ortho ester hydrolysis.[13]

It was decided to also look at the magnitude of the salt effects on this ionization in the absence of acid catalysis.

Scheme I

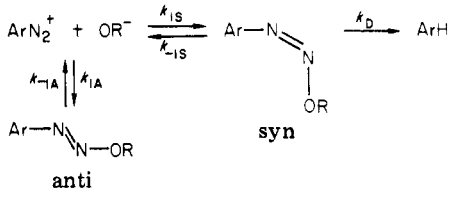

Table I. Acetic Acid Catalysis of the Ionization of Substituted *anti*-Phenylazo Methyl Ethers in Methanol at 30.0 °C[a]

substituent	$10^4 k_{cat}$,[b] L mol^{-1} s^{-1}	10^4 × intercept,[c] s^{-1}	SD/rms	*r*
4-NO_2	12.3	6.42 (5.04)	0.005	0.999
4-CN	26.1	12.3 (11.4)	0.017	0.987
2,4-Cl_2	85.3	32.1 (24.0)	0.011	0.998
2,4-Cl_2	85.0[d]	31.1 (24.0)	0.000	1.000
4-CF_3	49.0	33.7 (28.3)[e]	0.008	0.994
3-Cl	193	104 (89)	0.007	0.999
3-CF_3	63.0	33.9 (27.7)	0.003	1.000
2-Cl	498	216 (184)	0.000	1.000
2-Me-4-NO_2	130	75.8 (59.3)	0.007	0.997

[a] Ionic strength 0.6 M ($NaClO_4$), α-naphthol 0.01–0.05 M, [HA]/[NaA] = 5.0, [HA] = 0.05–0.30 M. [b] Slope of plot of k_{-1A} vs. [HA]. [c] Intercept of plot of k_{-1A} vs. [HA]. This corresponds to the uncatalyzed rate. Uncatalyzed rate using 0.1 M NaOMe, 0.5 M $NaClO_4$, and 0.01 M α-naphthol in parentheses. [d] [HA]/[NaA] = 8.0, [HA] = 0.08–0.32 M. [e] Uncatalyzed rate using 0.02 M NaOMe, 0.01 α-naphthol, and 0.58 M $NaClO_4$ is 31.9 × 10^{-4} s^{-1}.

Reactions in which ions are produced in the rate-determining step are expected to be catalyzed by added salts, e.g., $NaClO_4$ (ionic-strength effect), and to be hindered by addition of the leaving group, in this case methoxide ion, if the ionization is reversible (common-ion effect).[7b]

Results

Rate constants for the ionization of substituted *anti*-arylazo methyl ethers in the presence of acetic acid buffers in methanol at 30.0 °C are given in Table I. Rate constants have been obtained at several different concentrations of a 5:1 buffer (HAc/NaAc) for each *anti*-arylazo methyl ether. Under these conditions, i.e., constant buffer ratio and hence constant pH, an increase in ionization rate is observed as the concentration of acetic acid is increased at constant ionic strength.[14] This is consistent with

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pounds. It was thought that this extra catalysis may be of steric origin and for this reason the 2-methyl-4-nitro compound was studied. In this case, the point lay on the Hammett plot for the catalyzed reaction, using the "σ value" calculated from the uncatalyzed reaction. Thus the additional catalysis for the 2-chloro and 2,4-dichloro compounds is not of steric origin since the 2-methyl-4-nitro compound behaved normally. We suggest that the extra catalysis for the 2-chloro and the 2,4-dichloro compounds may arise from some favorable interaction between the dipolar ortho substituent and the catalyzing acid. Such an interaction would be absent in the case of the nonpolar methyl group.

A Brønsted plot for the catalysis of the ionization of *anti*-(*p*-(trifluoromethyl)phenyl)azo methyl ether by various carboxylic acids is shown in Figure 2. The plot shows some scatter of points, but this may be due to some doubt about the pK values of some of the acids in methanol. The Brønsted α value (0.32) suggests little proton transfer in the rate-determining transition state.[8] It will be of interest to determine how the Brønsted value changes for different substituted arylazo methyl ethers and for different nucleofuges.

Surprisingly, there was not much difference in the extent of acetic acid catalysis of the ionization of the methyl and ethyl ethers of the 4-nitro compound in ethanol. It was anticipated that catalysis would be greater for the more strongly basic nucleofuge (OEt),[19] but this was not found. Possibly the extent of catalysis is not great enough to differentiate between the two nucleofuges. The extent of acetic acid catalysis for the methyl ether of the 4-nitro compound, however, is sensitive to the solvent. Catalysis in ethanol (k_{cat}/k_{uncat} = 9.3) is greater than in methanol (2.4). Thus the nature of the medium in which the reaction is carried out seems to have more effect on the magnitude of catalysis than does variation of either the substituent on the aromatic ring or the nucleofuge. Acetic acid catalysis of the ionization of the methyl ether of the 4-nitro compound in methanol, however, is not affected by varying the concentration of added salt ($NaClO_4$). The extent of catalysis at 0.6 M ionic strength (1.92) is within experimental error of that at 0.3 M ionic strength (1.98). This observation argues against the catalysis being due to a specific salt effect.[20]

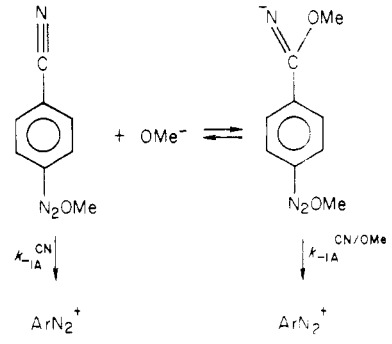
Attempts to measure the rate of ionization of *anti*-(4-(trifluoromethyl)phenyl)azo methyl ether in the presence of 0.001 M HCl/methanol were unsuccessful because the rate of coupling of the diazonium ion formed during ionization was slow and hence the rate measured in this case reflected the rate of coupling rather than the rate of ionization. The same problem was encountered in the presence of 5:1 buffers of trichloroacetic acid, pK_a = 4.98[15b] (pH 4.3),[15] but for 5:1 buffers of dichloroacetic acid (pK_a = 6.4)[16] (pH 5.7),[15] coupling was shown to be instantaneous and the observed rate actually was the rate of ionization. Thus we were unable to determine k_{H^+} directly. Using a pK_a value of $(MeOH_2)^+$ = −1.4 and assuming that the point for H^+ lies on the Brønsted line, we may derive a value of k_{H^+} (36 L mol^{-1} s^{-1}). This is much smaller than the value required for 10% reaction via free H^+ catalysis (3×10^5) and consequently explains why the $k_{H^+}[H^+]$ term in eq 1 is negligible.

2. Ionic-Strength Effects. Reactions in which charge is produced in the rate-determining transition state, e.g., uncatalyzed ionization of arylazo alkyl ethers (Scheme I, k_{-1S} or k_{-1A}), react faster if the ionic strength of the medium is increased.[7c] Increasing the concentration of added $NaClO_4$ in the reaction solution resulted in rate accelerations in all cases (Table IV). Further it was found that within the range of $NaClO_4$ concentrations studied (0–0.5 M) the rate constant was linearly related (eq 3) to the concentration of $NaClO_4$ as found by Winstein for some S_N1 reactions.[21,22] The b values ranged from 1.47 for the

$$k_{salt} = k_0(1 + b[salt]) \quad (3)$$

4-cyano compound to 2.03 for the 4-nitro compound. These are rather small b values but in general b values are smaller in more polar solvents. For example, the salt effect of $LiClO_4$ on the solvolysis of 2-phenethyltosylate in ethanol (b = 3.0) is less than in acetic acid (b = 14).[22]

Scheme III



3. Common-Ion Effects. In S_N1 reactions, where ionization is reversible, it is possible to observe a rate retardation if the common ion is added to the reaction mixture. Ionization of substituted arylazo methyl ethers in methanol shows this common-ion effect superimposed upon a common-salt effect when NaOMe is added to the reaction mixture (Table V). For the 4-nitro, 4-trifluoromethyl, and 2,4-dichloro compounds, the observed rate of ionization decreased as [NaOMe] was increased. Surprisingly, the 4-cyano compound showed the reverse effect. A possible explanation for the increase in rate of ionization of the 4-cyano compound as the [NaOMe] was increased is available from the work of Miller on S_NAr reactions of cyano-substituted chloronitrobenzenes.[23] Miller found that in basic methanolic solution the cyano group reacted with methoxide ion to form an imido ester group which has a reduced electron-withdrawing power (cf. Scheme III). This manifests itself in reduced rates of S_NAr reactions,[23] but since ionization of arylazo alkyl ethers is hindered by electron withdrawal the rate of ionization should increase for the imido ester (i.e., $k_{-1A}^{CN/OMe} > k_{-1A}^{CN}$). Thus as the concentration of NaOMe is increased, the equilibrium in Scheme III is displaced to the right and a rate increase is observed. We would predict that the same behavior should be shown for the 3-cyano compound and indeed it is (Table V). Furthermore, we would predict that if the equilibrium is displaced completely by addition of NaOMe, then further addition of NaOMe should cause a normal common-ion decrease in rate. This prediction is also borne out for the 3-cyano compound at [NaOMe] above 1.2 M. Finally, since Miller could find no evidence of imido ester formation for 2-cyano substituted compounds,[24] we would predict

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Table III. Effect of Ionic Strength, Solvent, and Nucleofuge on Acetic Acid Catalysis of the Ionization of *anti*-(4-Nitrophenyl)azo Alkyl Ethers in Alcoholic Solvents at 30.0 °C[a]

alkyl ether	solvent	ionic strength	$10^4 k_{cat}$,[b] L mol^{-1} s^{-1}	10^4 × intercept,[c] s^{-1}	SD/rms	r
methyl	MeOH	0.6	12.3	6.42 (5.04)	0.005	0.999
methyl	MeOH	0.3	8.87	4.49 (3.65)	0.004	0.999
methyl[d]	EtOH	0.3	6.31	0.95 (0.68)	0.004	1.000
ethyl[d]	EtOH	0.3	1.83	0.32 (0.23)	0.023	0.994

[a] α-Naphthol = 0.01–0.05 M, [HA]/[NaA] = 5.0, [HA] = 0.05–0.20 M. [b] Slope of plot of k_{-1A} vs. [HA]. [c] Intercept of plot of k_{-1A} vs. [HA]. This corresponds to the uncatalyzed rate. Uncatalyzed rate using 0.10 M NaOMe, 0.01 M α-naphthol, and $NaClO_4$, as required, in parentheses. [d] Alkyl ethers prepared externally.

Table IV. Effect of Added $NaClO_4$ on Rate of Ionization of Some Substituted *anti*-Arylazo Methyl Ethers in Methanol at 30.0 °C[a]

	$10^4 k_{-1A}$, s^{-1}			
[$NaClO_4$], M	4-NO_2	4-CN	4-CF_3	2,4-Cl_2
0	2.75	7.01	16.0	14.1
0.125	3.34	7.96	19.2	16
0.25	4.01	9.21	22.3	18.7
0.375	4.51	10.1	25.6	21.8
0.50	5.04	11.4	28.3	24.0
Winstein *b* value[b]	2.03	1.47	1.82	1.77

[a] Using 0.1 M NaOMe, 0.01 M α-naphthol. [b] References 21, 22.

Table V. Effect of Added NaOMe on Rate of Ionization of Some Substituted *anti*-Arylazo Methyl Ethers in Methanol at 30.0 °C[a]

[NaOMe], M	$10^4 k_{-1A}$, s^{-1}					
	2-CN	3-CN	4-CN	4-NO_2	4-CF_3	2,4-Cl_2
0.1	2440	8.77	7.01	2.75	16.0	14.2
0.2	2025	9.78	7.47	2.53	15.1	13.0
0.3	1510	11.2	8.40	2.40	13.7	11.9
0.4	1200	13.4	9.28	2.30	13.4	11.1
0.5		14.9	10.2	2.19	12.9	9.78
0.6	823	15.9	11.4	2.09	11.6	9.21
0.8		17.8				
0.9						6.97
1.0		19.2				
1.2		19.4				5.05
1.5		16.7				3.81
1.8		12.6				2.64

[a] Using 0.01 M α-naphthol.

9.12–9.4.[18] Interestingly, for all of the acids, with the exception of dichloroacetic, the intercept rate is constant within experimental error, and this is further evidence that the $k_{H^+}[H^+]$ term in eq 1 is negligible.

The effects of ionic strength, solvent, and nucleofuge on both the uncatalyzed ionization and acetic acid catalyzed ionization of *anti*-(4-nitrophenyl)azo alkyl ethers are shown in Table III. Interestingly, the change of solvent (MeOH to EtOH) causes a large decrease in the rate of uncatalyzed ionization of the methyl ether (k_{EtOH}/k_{MeOH} = 0.18) whereas the rate of catalyzed ionization is much less affected (k_{EtOH}/k_{MeOH} = 0.71). Thus the catalysis is much greater in the less polar solvent ethanol (k_{cat}/k_{uncat} = 9.3) than in methanol (2.4). However, changing the nucleofuge from methoxide to ethoxide ion has only a small effect on the ratio k_{cat}/k_{uncat} (9.3, OMe, and 8.0, OEt).

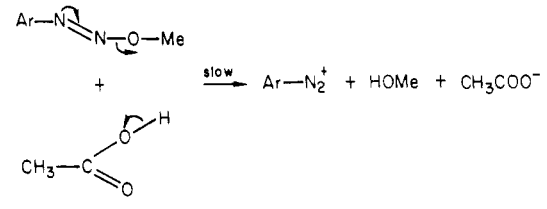
The effect of added $NaClO_4$ on the rate of ionization of some substituted *anti*-arylazo methyl ethers in methanol is given in Table IV. In each case, the rate of ionization is increased as the concentration of $NaClO_4$ is increased. The effect of added NaOMe on the rate of ionization of some substituted *anti*-arylazo methyl ethers in methanol is given in Table V. For the 2-CN, 4-NO_2, 4-CF_3, and 2,4-Cl_2 compounds, the rate decreases as the [NaOMe] is increased, while for the 3-CN and 4-CN compounds the rate initially increases up to a maximum (at 1.2 M NaOMe for the 3-CN compound) and then decreases.

Table VI. Kinetic Data and Activation Parameters for the Ionization of *anti*-(4-Nitrophenyl)azo Methyl Ether in Methanol[a]

T, K	$10^4 k_{-1A}$, s^{-1}
273[b]	0.10[c]
293	1.03
303.1	2.78
314.4	8.82

[a] Using 0.1 M NaOMe and 0.01 M α-naphthol. [b] Calculated from E_a = 18.4 kcal; ΔS^*_{298} = −16.0 cal mol^{-1} K^{-1}. [c] Cf. k_{-1S} = 0.98 s^{-1}; ref 6.

Scheme II



Rate constants at several temperatures and activation parameters for the ionization of *anti*-(4-nitrophenyl)azo methyl ether in methanol are given in Table VI. A rate constant is calculated at 0 °C and this is compared to the rate of ionization of the corresponding syn ether under the same conditions.

Discussion

1. Acid Catalysis. The observation of general acid catalysis in the ionization of *anti*-arylazo methyl ethers indicates that proton transfer occurs in the rate-determining step. A possible mechanism that is consistent with this observation is shown in Scheme II.

A synchronous process is favored in related reactions, e.g., the breakdown of Meisenheimer complexes,[9] ortho ester hydrolysis,[13] and the hydrolysis of acetals of benzaldehydes.[12] Further work is underway to establish the above mechanism for this reaction. Hammett plots for uncatalyzed and acetic acid catalyzed ionization of substituted *anti*-arylazo methyl ethers are shown in Figure 1.

The ρ values for the uncatalyzed (−3.06) and catalyzed (−3.06) reactions are identical and this suggests equal catalysis for each of the diazonium salts. The exceptions to this are the 2-Cl and 2,4-Cl_2 compounds for which the points lie above the Hammett plot, indicating greater catalysis than for the 4-NO_2, 4-CF_3, 4-CN, and 3-Cl com-

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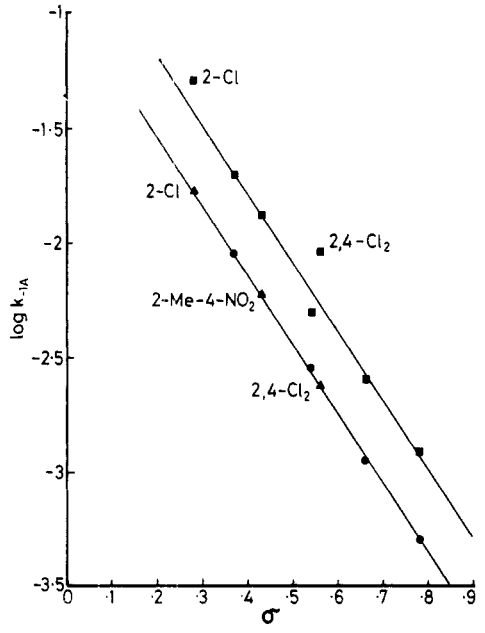

Figure 1. Hammett plots for the uncatalyzed (●) and acetic acid catalyzed (■) ionization of a series of *anti*-arylazo methyl ethers in methanol at 30.0 °C. For ortho-substituted compounds, σ values were derived from the Hammett plot for uncatalyzed ionization and are designated by ▲.

general acid catalysis of the ionization reaction and leads to a kinetic equation (eq 1). Rate constants for buffer

$$k_{obsd} = k_{uncat} + k_{H^+}[H^+] + k_{cat}[HAc] \quad (1)$$

catalysis, k_{cat}, were determined from the slope of plots of k_{obsd} vs. [HAc] at constant pH. For the 2,4-dichloro compound, ionization rates were measured by using both a 5:1 and an 8:1 buffer (HAc/NaAc). The catalytic rate constants obtained were within experimental error and plots of k_{obsd} vs. [HAc] were coincident with the same intercept. This suggests that the $k_{H^+}[H^+]$ term of eq 1 is negligible, and eq 1 can be simplified to eq 2.

$$k_{obsd} = k_{uncat} + k_{cat}[HAc] \quad (2)$$

Thus from a plot of k_{obsd} vs. [HAc] we obtain both the catalytic rate constant, k_{cat} (from the slope), and the uncatalyzed rate constant, k_{uncat} (from the intercept). One reason why the $k_{H^+}[H^+]$ term is negligible may be that since the pH is high (8.9)[15] the concentration of free hydrogen ion is very low (1.26×10^{-9} M) and hence the term $k_{H^+}[H^+]$ is small.

Hammett treatment of the data (Figure 1) for the 4-NO_2, 4-CN, 4-CF_3, and 3-Cl compounds vs. σ gave good straight lines $\rho_{uncat} = -3.06$, correlation coefficient = 1.000, SD = 0.015, $f = 0.004$; $\rho_{cat} = -3.06$, correlation coefficient = 0.984, SD = 0.105, $f = 0.041$. σ values for the ortho substituents, viz., 2,4-Cl_2 (0.56), 2-Cl (0.27), and 2-Me-4-NO_2 (0.43), were calculated from the uncatalyzed rates by using the Hammett plot and were used in the plot of the catalyzed rate constants.

(14) The concept of constant ionic strength in methanol is clouded because of the problem of different salts having different dissociation constants. To minimize this problem we have used high acid/salt ratios (5:1) which result in low sodium carboxylate concentrations (0.01–0.04 M). The variation of the concentration of the added salt to maintain a constant "ionic strength" is thus minimized (0.56–0.59 M).

(15) Approximate pH values were calculated by assuming aqueous solution methodology, i.e., pH = pK_a + log ([salt]/[acid]), without any allowance for variation of activity coefficients or dielectric constant in methanol. Since the contribution of the $k_{H^+}[H^+]$ term in eq 1 is negligible, these approximate pH values have not been used in calculations and thus do not detract from our conclusions.

Table II. Acid Catalysis of the Ionization of *anti*-(4-(Trifluoromethyl)phenyl)azo Methyl Ether in Methanol at 30.0 °C[a]

acid[b]	$10^4 k_{cat}$,[c] L mol^{-1} s^{-1}	10^4 × intercept,[d] s^{-1}	SD/rms	r
acetic (9.6)[e]	49.0	33.7 (31.9)[f]	0.008	0.994
benzoic (9.1)[e]	100	34.2	0.003	1.000
3-chloropropionic (9.1)[g]	118	33.0	0.006	0.999
2-chloropropionic (8.06)[g]	219	32.3	0.010	0.999
chloroacetic (7.7)[e]	239	34.2	0.007	1.000
2,3-dichloropropionic (7.5)[g]	296	36.0	0.001	1.000
dichloroacetic (6.4)[e]	637	39.8	0.003	1.000

[a] Ionic strength = 0.6 M ($NaClO_4$), α-naphthol = 0.01–0.05 M, [HX]/[NaX] = 5.0, [HA] = 0.05–0.20 M. [b] pK_a in parentheses. [c] Slope of plot of k_{-1A} vs. [HA]. [d] Intercept of plot of k_{-1A} vs. [HA]. This corresponds to the uncatalyzed rate. [e] Reference 16. [f] Uncatalyzed rate using 0.02 M NaOMe, 0.01 M α-naphthol, and 0.5 M $NaClO_4$. [g] Reference 17.

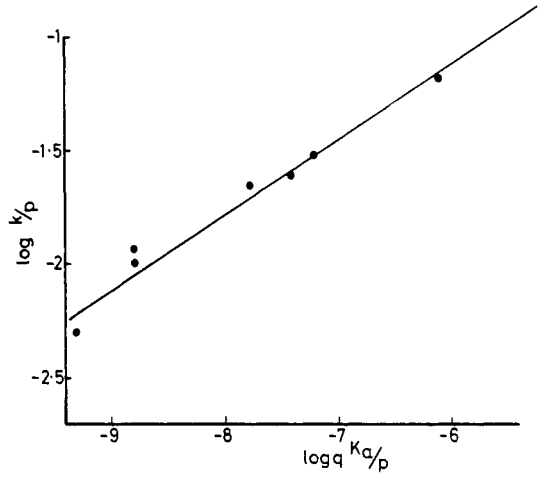

Figure 2. Brønsted plot for the acid-catalyzed ionization of *anti*-(4-(trifluoromethyl)phenyl)azo methyl ether in methanol at 30.0 °C.

In all cases the intercept rate, from the plot of k_{obsd} vs. [HAc], which is a measure of the uncatalyzed rate of ionization, was larger than the experimental uncatalyzed rate. This is because the experimental uncatalyzed rate was measured in the presence of NaOMe whereas the intercept rate is calculated in the absence of NaOMe. As shown later (Table V), added NaOMe causes a reduction of the rate of ionization for most compounds studied.

Rate constants for the ionization of *anti*-(4-(trifluoromethyl)phenyl)azo methyl ether in the presence of a number of different buffers are given in Table II. It can be seen that the stronger the acid, the larger the rate constant for general acid catalysis. A Brønsted plot for this compound had $\alpha = 0.32$ (correlation coefficient 0.981, SD = 0.077, $f = 0.036$) (Figure 2). This is not a particularly good correlation, but this may arise from the doubt about the pK_a of these acids in methanol. For example, the pK_a of chloroacetic acid is quoted as 7.7[16] and 7.96[17] while the quoted pK_a for benzoic acid ranges from

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(17) C. Moreau, *Bull. Soc. Chim. Fr.*, 31 (1968).

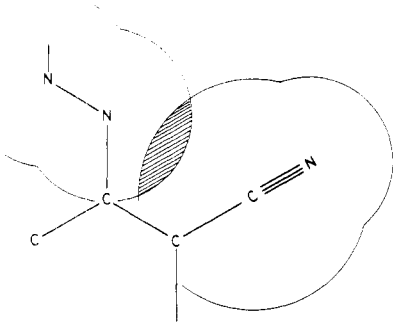


Figure 3. Diagrammatic representation of steric clashing in *anti*-(2-cyanophenyl)azo methyl ether.

a normal common-ion effect for the 2-cyano compound and this also is observed (Table V). The absence of imido ester formation for 2-cyano substituted compounds is explained by the unfavorable loss of coplanarity if the imido ester group is formed.[24]

The observation of common-ion rate retardation is explained by the reversion of some of the free diazonium and alkoxide ions (or the solvent-separated ion pair) to the anti ether. Now we know that the diazonium salt partitions strongly in favor of the syn ether in reaction with methoxide ion,[1b] but formation of the syn ether would not affect the observed rate of ionization since it reionizes much faster than the initial anti ether. The rate of ionization of the anti ether of the 4-nitro compound at 0 °C can be calculated from the activation parameters (Table VI) ($k_{-1A} = 1 \times 10^{-5}$ s^{-1}). The rate of ionization of the corresponding syn ether under these conditions[6] is 0.98 s^{-1} and thus the syn ether ionizes 10^5 times faster than the anti ether. Thus the common-ion rate retardation cannot be due to syn ether formation but must be due to anti ether formation. But since the syn–anti partitioning factor for the diazonium ion in methanol is large (>200),[6] there must be considerable syn ether formation which is not detectable kinetically as well as the kinetically detectable anti ether formation.

4. Steric Effects. An interesting feature of Table V is the comparison in rate for the 2-cyano and the 4-cyano compounds. At 0.1 M NaOMe, the 2-cyano compound reacts almost 350 times faster than the 4-cyano compound. On the basis of electronic effects, one would expect that the greater inductive electron-withdrawing effect of the 2-cyano group would result in slower reaction than for the 4-cyano compound. The much faster reaction for the 2-cyano compound is probably the result of steric acceleration of the ionization.[6] Such steric acceleration by ortho halogen and ortho nitro substituents has been reported,[6] but the magnitude of the effect for these compounds is much smaller. In fact for the nitro compounds the rates of ionization of the ortho and para compounds are similar.[6] Consideration of bond lengths, bond angles, and van der Waals radii shows that for the 2-cyano compound (Figure 3) there is considerable overlap between the α nitrogen of the azo ether group and the carbon of the cyano group. This interaction cannot be relieved by rotation about the bond between the aromatic carbon and the cyano group since the cyano group is cylindrical. In the case of the 2-nitro compound (Figure 4), overlap between the α nitrogen of the azo ether group and the nitrogen of the nitro group is small, but interaction between the α nitrogen and the oxygen of the nitro group is significant. In this case, however, this interaction can be relieved by rotation about the bond between the aromatic carbon and the nitro group. A small rotation would be sufficient to remove this steric interaction and this would not be sufficient to destroy the resonance effect of the nitro group since that requires a twist of 60–70°.[25] Thus the steric acceleration is greater for the 2-cyano compound than for the apparently more bulky 2-nitro compound.

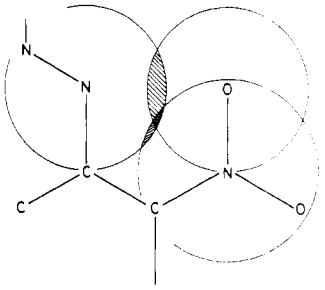
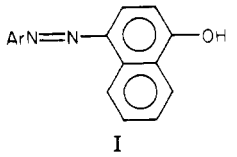


Figure 4. Diagrammatic representation of steric clashing in *anti*-(2-nitrophenyl)azo methyl ether if the nitro group is coplanar with the benzene ring.

Experimental Section

Aryl diazonium salts were prepared by diazotization of the corresponding anilines.[4] Methyl and ethyl (*p*-nitrophenyl)azo ethers were prepared as described previously.[4] Methanol and ethanol were dried by distillation from the corresponding magnesium alkoxide.[26] Sodium perchlorate monohydrate (UNILAB-98%) was dried by heating in an oven at 80 °C for at least 3 days. 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. Carboxylic acid solutions were prepared freshly for each kinetic run and were titrated against sodium methoxide before and after each run to check for any esterification. There was no significant esterification in any case in the time required for a kinetic run.

Kinetic Measurements. A. Acid Catalysis. A stock solution of the required diazonium salt was prepared by dissolving the salt (0.005 g) in 100 mL of dry methanol to which 5 mL of 0.01 M toluenesulfonic acid (prepared from anhydrous toluenesulfonic acid) was added. Sodium methoxide solution was then added to a 5-mL aliquot of the diazonium salt solution to generate the *anti*-arylazo methyl ether in situ. Excess carboxylic acid solution was then added to prepare a 5:1 buffer solution (acid–salt). The required amount of sodium perchlorate solution was then added to make the ionic strength the required level (0.3 or 0.6 M).[14] Finally, α-naphthol solution was added. The solutions were diluted to 50 mL, thoroughly shaken, and then transferred to a cuvette which was placed in the thermostatted cell holder of a Varian Associates 635 UV–vis spectrophotometer. All of the solutions were temperature equilibrated to 30 °C before mixing to minimize the time required for temperature equilibration in the cuvette. The reaction was followed by monitoring the rate of production of azo dye I by UV–vis spectrophotometry.



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B. Ionic-Strength Variation. Sodium methoxide solution (10 mL, 0.5 M) was added to a 5-mL aliquot of the diazonium salt solution to generate the *anti*-arylazo methyl ether in situ. The required amount of sodium perchlorate was added and then α-naphthol solution was added. After dilution to 50 mL and mixing, the solution was transferred to the cuvette which was placed in the UV–vis spectrophotometer.

(24) R. L. Heppolette, J. Miller, and V. A. Williams, *J. Am. Chem. Soc.*, 78, 1975 (1956).

(25) B. M. Wepster, personal communication.

(26) A. I. Vogel, "A Textbook of Practical Organic Chemistry", 3rd ed., Longmans Green & Co., New York, 1961, p 169.

C. Common-Ion Studies. The required amount of sodium methoxide solution was added to a 5-mL aliquot of the diazonium salt solution to generate the *anti*-arylazo methyl ether in situ. α-Naphthol solution was then added and the solution was then diluted to 50 mL with methanol. The reaction was followed by UV–vis spectrophotometry. For the 2-cyano compound, a stopped-flow technique was required.[5] One syringe of the stopped-flow apparatus contained the α-naphthol solution which was equilibrated to 30 °C in the drive syringe of the stopped-flow apparatus. Solutions of the diazonium salt and sodium methoxide were equilibrated to 30 °C in an external thermostat bath. These solutions were mixed and rapidly added to the other syringe of the stopped-flow apparatus which was then triggered. Three reactions were carried out for each concentration of NaOMe, and the rate constant was calculated from the mean value of the half-life for the three runs.

Registry No. *anti*-4-Nitrophenylazo methyl ether, 16020-14-7; *anti*-4-cyanophenylazo methyl ether, 58692-51-6; *anti*-2,4-dichlorophenylazo methyl ether, 73396-56-2; *anti*-4-(trifluoromethyl)-phenylazo methyl ether, 58692-53-8; *anti*-3-chlorophenylazo methyl ether, 58692-55-0; *anti*-3-(trifluoromethyl)phenylazo methyl ether, 58692-54-9; *anti*-2-chlorophenylazo methyl ether, 58692-57-2; *anti*-2-methyl-4-nitrophenylazo methyl ether, 73396-57-3.

Heterogeneous Catalytic Racemization of 4,4′-Disubstituted 1,1′-Binaphthyls by Active Carbons and by Modified Carbon Catalysts

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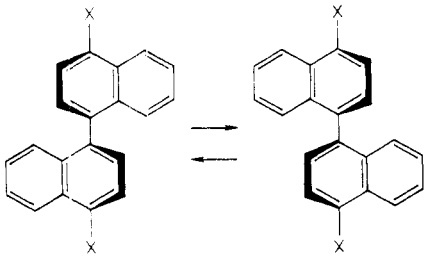
The racemization of four 4,4′-disubstituted 1,1′-binaphthyls is heterogeneously catalyzed by active carbon or carbon black suspended in chloroform solutions. In the presence of 1 mg/mL of Norit SG1 in chloroform the observed first-order rate constants for racemization of 0.025 M substrate were increased over the uncatalyzed rate constants by factors of 2.9, 6.7, 8.3, 8.1, and 14 for disubstituents NH_2, CH_3, Br, NO_2, and H, respectively. The rates of uncatalyzed racemization of these binaphthyls are electronically influenced by the para substituents (giving a Hammett ρ of −0.88) and the catalyzed racemization rates show a similar but slightly decreased substituent effect (ρ = −0.57). However, a small steric effect is indicated for the catalyzed reaction since all substituted compounds are less sensitive to catalysis than is 1,1′-binaphthyl itself. Bromination or chlorination of a carbon black results in increased catalytic activity, and potassium–graphite intercalate is an effective, but irratic, racemization agent. An electron-accepting binaphthyl molecule, loosely bound on electron-donor sites of the graphitic basal planes of carbon catalysts, is suggested as an intermediate complex in the catalyzed racemization.

The chiral aromatic hydrocarbon 1,1′-binaphthyl (1, X = H) is sufficiently restricted in rotation around the central bond so that its racemization proceeds only slowly near room temperature in solution.[1] However, the rate of loss of optical activity is dramatically increased by the presence of various active carbons and by industrial carbon blacks.



(*R*)-1,1′-binaphthyl (*S*)-1,1′-binaphthyl

1, X = H; 2, X = NH_2; 3, X = CH_3; 4, X = Br; 5, X = NO_2

The kinetic characteristics of this heterogeneous reaction fit a rate relationship involving adsorption to form a catalyst–binaphthyl surface complex,[3] and an attractive possibility for this complex is a flattened binaphthyl molecule adsorbed on the basal planes of the graphitic carbon surfaces. Such a racemization mechanism would involve a close and simultaneous approach of both naphthalene rings of binaphthyl to the planar surface, and this specific interaction might therefore be greatly hindered, if not prevented, by the steric effect of *any* substituent such as, for example, the 4,4′-disubstituents of compounds **2–5** with X equal to NH_2, CH_3, Br, and NO_2, respectively.

The work reported was begun with the intention of establishing whether or not the observed catalyzed racemization of binaphthyl could be more generally observed with some of its derivatives. It was then extended to determine what effect a variety of different substituents would have on the rates of both the catalyzed and the uncatalyzed racemizations. With a study of substituent effects we hoped to characterize the polarity of the binaphthyl molecule bound to the carbon surface and also to define the electronic and steric sensitivity of the active sites on carbon.

In addition, we have also investigated a variety of other carbon-derived catalysts to determine their ability to racemize binaphthyl. From previous studies the most catalytically active carbons are those with the greater surface areas of less organized character, and it is possible that the racemization takes place not on graphitic planar areas but on disorganized edge sites.[3] The functional groups (i.e., largely oxygen-containing groups)[4] that are present on the edges of the graphitic planes may be involved. To help establish the location and nature of the active sites we have also determined the catalytic efficiency that modified carbons (produced by oxidation, reduction, halogenation,

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(2) R. E. Pincock, W. M. Johnson, K. R. Wilson, and J. Haywood-Farmer, *J. Am. Chem. Soc.*, **95**, 6477 (1973).
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(4) J. B. Donnet and A. Voet, "Carbon Black: Physics, Chemistry, and Elastomer Reinforcement", Marcel Dekker, New York, 1976, Chapter 4.

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