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Changes in Transition State Structure for Protonation of Aryldiazomethanes in Aqueous Solutions

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Rate constants are reported for the decay of a series of aryldiazomethanes in aqueous media, 4% acetonitrile, 25 °C, ionic strength 0.2 M ($NaClO_4$). Plots of the log of k_o, the buffer independent first-order rate constant for decay, against pH that range from pH 2 to 13 are biphasic. At the low pH end the value of log k_o decreases with increasing pH with a unit slope, whereas at the high pH end the value of log k_o is pH independent. The solvent deuterium isotope effect for the pH independent reaction of the 4-methoxyphenyldiazomethane is $k_o^{H_2O}/k_o^{D_2O} = 4.5 \pm 0.1$. On the basis of the isotope effect it is concluded that the mechanism of the pH independent reaction of aryldiazomethanes is identical with that deduced previously for the acid-catalyzed reaction and involves rate-limiting protonation by H_2O. The value of ϱ for the hydrogen ion catalyzed reaction is $\varrho_{k_H} = -1.14$ while that for the water-catalyzed reaction is $\varrho_{k_{H2O}} = -2.01$. Catalysis of decomposition by four oxygen acid buffers was examined for three aryldiazomethanes. The slopes, α, of the linear Bronsted plots for catalysis change as a function of the substituent in the benzene ring, yielding the "cross interaction coefficient" $\delta\alpha/\delta\sigma = 0.15$. There is a corresponding change in the ϱ values for sensitivity of the log of k_{HA}, the rate constant for catalysis by a particular catalyst, to the substituent in the benzene ring, $-\delta\varrho/\delta pK_{HA} = 0.15$. These data establish that there are changes in the structure of the transition state for the proton transfer reactions of monoaryldiazomethanes. Examination of a similar range of data obtained by others for the decomposition of diaryldiazomethanes in 80% DMSO/20% H_2O indicates two important contrasts: first, cross interaction coefficients in those cases are not significantly different from zero, and second, the Bronsted plots for these latter reactions show strong curvature. The differences between mono- and diaryldiazomethanes are rationalized as being due to a difference in orientation, relative to the orthogonal axes of a reaction coordinate diagram, of the reaction coordinates at the two transition states. The orientation in the case of the monoaryldiazomethanes is more diagonal while the orientation in the case of the diaryldiazomethanes is more parallel to the O−H bond cleavage axis.

Introduction

Proton transfer involving carbon acids and bases is a reaction that has been the subject of extensive investigation. Because of the elementary nature of this reaction many studies have sought to characterize what factors can effect changes in the structure of its transition state. In spite of the large number of studies, there are presently few uncontested examples of changes in transition state structure with reactant structure for proton transfer involving carbon acids and bases, as has been concisely summarized recently.[1] Some unvarnished examples of changes in transition state structure for these types of reactions have recently been reported for the base-catalyzed formation of ylides from sulfonium,[1] phosphonium,[2] and thiazolium cations.[3]

The studies of the Kreevoy group on the protonation of diazoalkanes[4−6] provide additional examples of changes in transition state structure with reactant structure. The Bronsted plots, plots of log k for protonation against acid catalyst pKa, are strongly curved with limiting slopes (α) of ~0.9 and 0.1−0.2 in the cases of reactions of phenyldiazomethanes with carboxylic acids and phenols in 80% DMSO/20% water[4] and diazoacetate with either carboxylic acids and phenols[5] or substituted *tert*-ammonium ions,[6] in both cases in water. This behavior was ascribed to a Hammond effect in which the transition state becomes more reactant-like with respect to the catalyst-hydron bond cleavage with increasing catalyst acidity. The catalysts used were sufficiently homogeneous, and the changes in α were sufficiently large, so that it seems unlikely that the curvature can be alternatively and completely explained by differences in the requirements for desolvation of catalysts at different extremes of the plots.[7]

Our laboratory has an interest in the fundamental properties of diazoalkanes and their conjugate acids, diazonium ions, as these may be reactive intermediates in the mutagenicity, carcinogenicity, and cancer chemotherapeutic activity of a large class of compounds that posess the *N*-alkyl-*N*-nitroso functionality.[8] We have had occasion to carry out a study of the decomposition of a series of aryldiazomethanes in aqueous media. Previous studies by others have established that the rate-limiting step in this reaction involves proton transfer.[9,10] The

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present paper establishes that there are changes in the structure of the transition state for this reaction with changes in the structure of the reactants. However, the nature of the changes observed for the monoarlydiazomethanes studied here is fundamentally different from that observed by Kreevoy in the case of the diaryldiazomethanes. It is concluded that the differences in the nature of the changes in transition state structure for reactions of mono- compared to diaryldiazomethanes lie in the differing orientations of the reaction coordinates at the transition states for these two reactions.

Experimental Section

Synthesis. All aryldiazomethanes were prepared by the vacuum pyrolysis method of Creary[11] and used for kinetics without further purification. All compounds were stable for at least 2 weeks when stored in sealed, Teflon-capped vials, under solid carbon dioxide. Compounds synthesized were as follows: 4−Methoxyphenyldiazomethane: ^{1}H NMR (DMSO-d_6) 6.88 (4 H, d), 5.63 (1 H, s), 3.71 (3 H, s); UV (MeCN, CaH_2-dried) $\lambda_{max} = 279$ nm. Phenyldiazomethane: ^{1}H NMR (DMSO-d_6) 7.28 (2 H, t), 6.96 (3 H, q), 5.69 (1 H, s); UV (MeCN, CaH_2-dried) $\lambda_{max} = 280$ nm. 3-Chlorophenyldiazomethane: ^{1}H NMR (DMSO-d_6) 7.28 (1 H, t), 7.01 (2 H, d), 6.91 (1 H, d), 5.76 (1 H, s); UV (MeCN, CaH_2-dried) $\lambda_{max} = 284$ nm. 3,5-Dichlorophenyldiazomethane: ^{1}H NMR (DMSO-d_6) 7.12 (1 H, s), 7.00 (2 H, s), 5.79 (1 H, s); UV (MeCN, CaH_2-dried) $\lambda_{max} = 290$ nm. 3,5-Bis(Trifluoromethyl)phenyldiazomethane: ^{1}H NMR (DMSO-d_6) 7.52 (2 H, s), 7.49 (1 H, s), 6.01 (1 H, s); UV (MeCN, CaH_2-dried) $\lambda_{max} = 291$ nm.

Kinetics. Decomposition reactions of phenyldiazomethanes were monitored at wavelengths between 279 and 291 nm using either a Milton Roy 1001+ or an Applied Photophysics DX17.MV stopped-flow spectrophotometer at 25 °C. Reactions were initiated by mixing one part of the dry acetonitrile solution containing aryldiazomethane into 25 parts of aqueous buffer (ionic strength = 0.20 M, maintained with $NaClO_4$). The rate constant k_{obsd} was obtained from the first-order decay of absorbance that was monitored for between 3 and 7 half-lives. The rate constant k_o , the buffer independent rate constant for decomposition of the aryldiazomethane, was obtained by extrapolating the linear buffer dilution plots of k_{obsd} against buffer concentration to the *y* intercept. Experiments were carried out to determine the solvent deuterium isotope effect for decomposition of 4-methoxyphenyldiazomethane in D_2O (min 99.6% D) at 0.005, 0.020, and 0.050 M NaOD.

Results

The decay of substituted phenyldiazomethanes in aqueous media (4% acetonitrile, ionic strength 0.2 M $NaClO_4$) was observed by standard and stopped-flow spectrophotometry at 279−291 nm for between 3 and 7 half-lives. Analysis of the decay curves yielded constants, k_{obsd}, which gave good agreement with a single exponential process over the observation period. The rate constants, k_o, for buffer independent processes were determined by extrapolation, to a buffer concentration of zero, of plots of k_{obsd} against buffer concentration for a given buffer ratio. Buffers used included methoxyacetic, acetic, morpholinopropanesulfonic, cyclohexylethanesulfonic, and cacodylic acids as well as hexafluoro-2-propanol, triethanolammonium, and ethylenediamine (1$^+$) cations. Unbuffered solutions of $HClO_4$ and NaOH were used at extremes of the pH range. Strong buffer catalysis of the reactions necessitated the use of buffer concentrations in the millimolar range in some cases in order to obtain accurate extrapolations to the intercept. The values of pH of such weakly buffered solutions varied less than 0.1 units over the entire buffer concentration range in 75 of 77 such experiments. The change in k_o as a function of pH is indicated in Figure 1 for several monoaryldiazomethanes. In the case of 3,5-dichlorophenyldiazomethane, in the intermediate region of pH studied, catalysis was so strong that the determination of accurate intercept values was problematic. The same was true for 3,5-bis(trifluoromethyl)phenyldiazomethane, and in addition in this case, reactions in dilute hydroxide gave irreproducible rate constants, presumably due to the onset of other thermal and/or photochemical decomposition pathways.

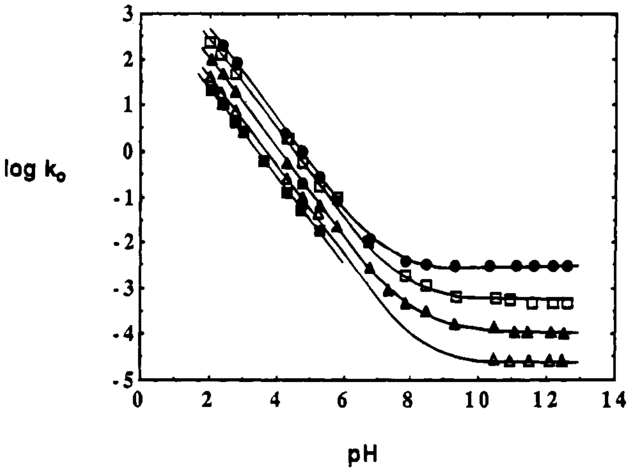

Figure 1. Plots of log of k_o, the buffer independent rate constants for decomposition of monoaryldiazomethanes, as a function pH. Reactions carried out at 25 °C in aqueous media, 4% acetonitrile, ionic strength 0.2 M ($NaClO_4$). Symbols: ●, 4-CH_3O−; □ , unsubstituted; ▲, 3-Cl−; △, 3,5-$(Cl)_2$−; ■, 3,5-$(CF_3)_2$−.

The solvent deuterium isotope effect, $k_o^{H_2O}/k_o^{D_2O} = 4.5 \pm 0.1$, was determined for 4-methoxyphenyldiazomethane in 0.005, 0.02, and 0.05 M sodium lyoxide solutions.

Catalysis of the decomposition of some of the phenyldiazomethanes by four oxygen acids was studied in detail. The slopes of plots, referred to above, of k_{obsd} against buffer concentration for a particular buffer ratio were taken as the values of the observed second order rate constants, k^o_{HA}, for catalysis. The catalytic constants, k_{HA}, for a given acid were obtained as the intercept, at 100% buffer acid, of the linear plots of k^o_{HA} against "percent buffer acid". The values of k_{HA} are summarized in Table 1.

Discussion

Overview. The profiles of log of k_o, the buffer independent rate constant for decay, against pKa in Figure 1 indicate that there are two kinetic terms involved in the buffer independent decay of phenyldiazomethanes in the pH range studied: a hydrogen ion dependent term, k_H, and a pH independent term, k_{H_2O}, as indicated in eq 1. The hydrogen ion dependent term was previously

$$k_o = k_H[H^+] + k_{H_2O} \qquad (1)$$

studied in 60% dioxane/40% water,[9,10] but the pH independent term has not, to our knowledge, been previously identified for aryldiazomethanes. Good fits to eq 1 are indicated by the solid lines in Figure 1 using values for

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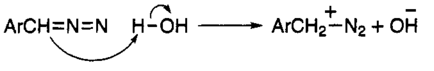
[11] Creary, X. *J. Am. Chem. Soc.* **1980**, *102*, 1611. Closs, G. L.; Moss, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 4042

Table 1. Summary of Rate Constants for the Decomposition of Substituted Phenyldiazomethanes in Aqueous Media, 25 °C, Ionic Strength 0.2 M ($NaClO_4$), 4% Acetonitrile

			$10^{-2}k_{HA}$ (M^{-1} s^{-1})			
substituent	$10^3k_{H_2O}$ (s^{-1})	$10^{-4}k_H$ (M^{-1} s^{-1})	$CH_3OCH_2CO_2H$	CH_3CO_2H	$(CH_3)_2AsO_2H$	$(CF_3)_2CHOH$
4-CH_3O–	3.1	4.9	75	14	4.8	0.077
H–	0.59	3.6				
3-Cl–	0.13	1.3	11	2.1	0.52	0.0038
3,5-$(Cl)_2$–	0.025	0.49				
3,5-$(CF_3)_2$–		0.21	1.9	0.37	0.057	0.000 19

the constants k_H and k_{H_2O} that are summarized in Table 1. The ϱ values for the two reactions are $\varrho_{k_{H+}} = -1.14$ and $\varrho_{k_{H2O}} = -2.01$. A value of $\varrho_{k_{H+}} = -2.0$ in 60% dioxane/40% H_2O was previously reported.[9]

The dominant kinetic term in basic media is k_{H_2O} so that the solvent deuterium isotope effect of $k_0^{H_2O}/k_0^{D_2O} = 4.5 \pm 0.1$ that was determined for the decomposition of the (4-methoxyphenyl)diazomethane in lyoxide solutions indicates that the mechanism for this term in the rate law involves rate-limiting proton transfer, as in eq 2. It can be shown that the observed solvent isotope effect contains a large primary isotope effect component, indicative of rate-limiting proton transfer, in spite of the fact that there may be significant secondary isotope effect contributions to the observed effect.[12] The secondary effects may arise due to the formation of the lyoxide ion in the rate-limiting step and the likelihood that the zero point energy differences between H and D are quite different in the product diazonium ion compared to the reactant water molecule. An analysis of the maximal secondary effects expected sets a lower limit on the primary component of the observed effect of $k^p_{H_2O}/k^p_{D_2O} > 2.2$. Values near this limit are sufficiently different from a value of 1 so as to require the conclusion that proton transfer is rate-limiting as indicated in the mechanism of eq 2. This mechanism is identical with that deduced for the k_H term (eq 1) and for the previously observed general acid-catalyzed decomposition of mono-[9,10] and diphenyldiazomethanes[4] in partly aqueous media.


(2)

The conclusion that the rate-limiting step for both solvent acid species, H^+ and H_2O, involves proton transfer predicts that general acid catalysis should be observed, and this has been reported previously for mono-[9,10] and diaryldiazomethanes.[4] The observation is confirmed here in the case of oxygen acid catalysis of the three aryldiazomethanes studied (Table 1).

Changes in Transition State Structure. The Bronsted plots for general acid catalysis of the decay of monoaryldiazomethanes are presented in Figure 2 (solid points) and clearly exhibit a decrease in the slope α with increasing reactivity of the carbon base. The slope decreases with decreasing electron-withdrawing properties of the substituents from α = 0.65 (± 0.03, $r^2 = 0.996$), for 3,5-$(CF_3)_2$, to α = 0.56 (± 0.03, $r^2 = 0.994$), for 3-Cl, to α = 0.48 (± 0.03, $r^2 = 0.991$) for 4-CH_3O–. The decrease in α for catalysis by oxygen acids with increasing carbon base reactivity is consistent with a change in transition state structure of the Hammond type.

The change in transition state structure is due to the existence of a "cross interaction" in which a change in substituent at the carbon base affects the sensitivity to changes in substituent in the oxygen acid moiety, as described by Jencks and others.[18] The "cross interaction"

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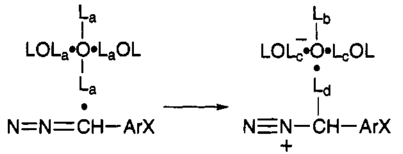
(12) The observed isotope effect can be described as the product of primary and secondary components as indicated in eq 3, where the superscript p indicates a primary effect

$$k_{H_2O}/k_{D_2O} = (k^p{}_{H_2O}/k^p{}_{D_2O})(k^s{}_{H_2O}/k^s{}_{D_2O}) \qquad (3)$$

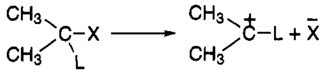
while the superscript s indicates a secondary effect. The maximal secondary effects are predicted for a very product-like transition state that is depicted in eq 4


(4)

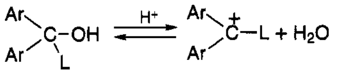
in which the product-like hydroxide ion is hydrogen bonded to two water molecules and the diazonium ion is fully formed. The fractionation factor expression[13a] for the secondary isotope effect is indicated in eq 5,

$$k^s{}_{H_2O}/k^s{}_{D_2O} = (\phi_a)^4/(\phi_c{}^2\phi_b\phi_d) \qquad (5)$$

where the fractionation factors labeled ϕ_a-ϕ_d represent those for the hydrogen atoms identically labeled in the diagram above. Values for the fractionation factors ϕ_a-ϕ_c can be taken from the literature as $\phi_a = 1$,[13] $\phi_c = 0.7$,[14] $\phi_b = 1.15$,[14] and a value for $\phi_d = 0.86$ is deduced below. This yields a maximal value of $k^s{}_{H_2O}/k^s{}_{D_2O} = 2.06$ and thus a minimal value of $k^p{}_{H_2O}/k^p{}_{D_2O} = 2.18$, using eq 3, and $k_{H_2O}/k_{D_2O} = 4.5$. The value of $\phi_d = 0.86$ is deduced in the following way. Williams has calculated the equilibrium isotope effect due to α-deuterium substitution in the process in eq 6


(6)

for different leaving groups X.[15] For X = F, OH, or OH_2^+, the calculated value of $K_H/K_D = 1.32 \pm 0.01$ is consistent with the effect ($K_H/K_D = 1.35$) observed in the alcohol–cation equilibrium of benzhydrols in acidic media,[16] eq 7.


(7)

For X = N_2^+, the calculated value of $K_H/K_D = 1.03$ indicates that there is little difference in the zero point energy difference between H and D in the diazonium ion compared to the carbocation. This conclusion is qualitatively in accord with the conclusions of Glaser based on ab initio calculations that the carbon framework in diazonium ions is carbocation-like.[17] Thus, a fractionation factor for the α-hydrogen of a carbocation, ϕ_{C^+}, is nearly equal to the fractionation factor for the hydrogen α to a diazonium ion, ϕ_d. A value for the fractionation factor for the hydrogen α to the cationic carbon, $\phi_{C^+} = 0.86$, may be calculated from the isotope effect on benzhydryl cation formation, the fractionation factor expression for the observed isotope effect in this reaction in eq 8,

$$K_H/K_D = 1.35 = \phi_{CL}/\phi_{C^+} \qquad (8)$$

and the value for the fractionation factor of the α-hydrogen in the secondary alcohol of $\phi_{CL} = 1.16$.[13b] And, on the basis of the above observation, i.e., $\phi_{C^+} = \phi_d$, then $\phi_d = 0.86$.

(13) (a) Schowen, R. L. *Prog. Phys. Org. Chem.* **1972**, *9*, 275. (b) Cleland, W. W. *Methods Enzymol.* **1980**, *64*, 104.

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(16) Mocek, M. M.; Stewart, R. *Can. J. Chem.* **1963**, *41*, 1641.

(17) Glaser, R.; Choy, G. S.-C.; Hall, K. M. *J. Am. Chem. Soc.* **1991**, *113*, 1109. Glaser, R.; Choy, G. S.-C.; Horan, C. J. *J. Org. Chem.* **1992**, *57*, 995.

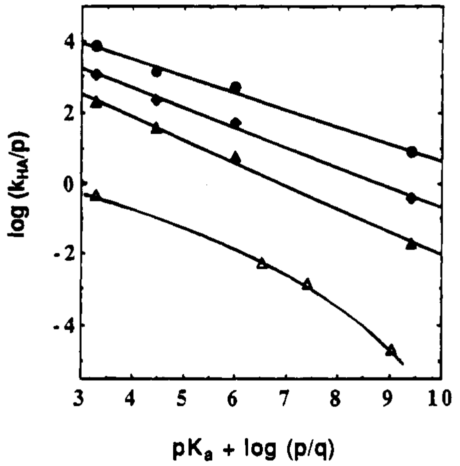

Figure 2. Bronsted plots for general acid catalyzed decomposition of aryldiazomethanes by oxygen acids. Reactions of monoaryldiazomethanes (solid symbols) studied at 25 °C in aqueous media, 4% acetonitrile, ionic strength 0.2 M ($NaClO_4$): ●, 4-CH_3O−; ◆, 3-Cl−; ▲, 3,5-$(CF_3)_2$−. Data for the reaction of diphenyldiazomethane △ in 80% DMSO/20% H_2O with dichloroacetic and acetic acids, pentafluorophenol and 3,4,5-trichlorophenol (ref 4).

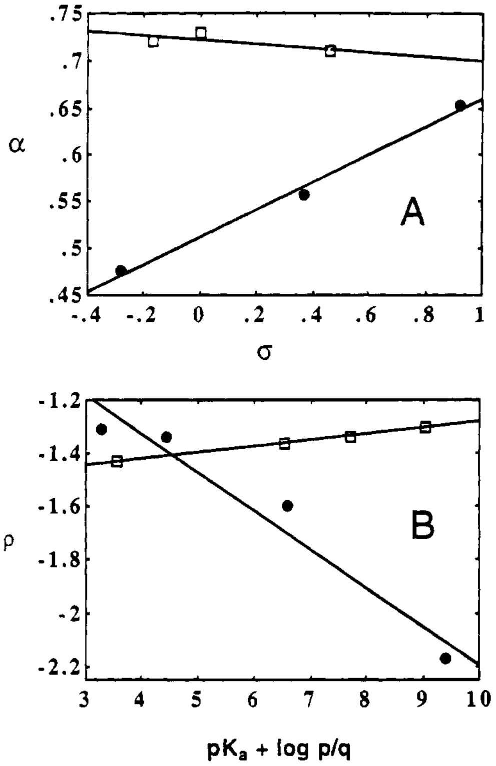

Figure 3. Changes in transition state structure for protonation of aryldiazomethanes. A. Plot of Bronsted α aqainst σ for monoaryldiazomethanes (solid symbols) and diaryldiazomethanes (open symbols). The data for diaryldiazomethanes are for the bis-*p*-Cl, unsubstituted, and *p*-CH_3 compounds (ref 4). B. Plot of Hammet ϱ against statistically corrected oxygen acid p*K*a for monoaryldiazomethanes (solid symbols) and diaryldiazomethanes (open symbols). Reaction conditions for monoaryldiazomethanes as in Figure 2. Data for the diaryldiazomethanes under the same conditions and with the same acid catalysts as in Figure 2.

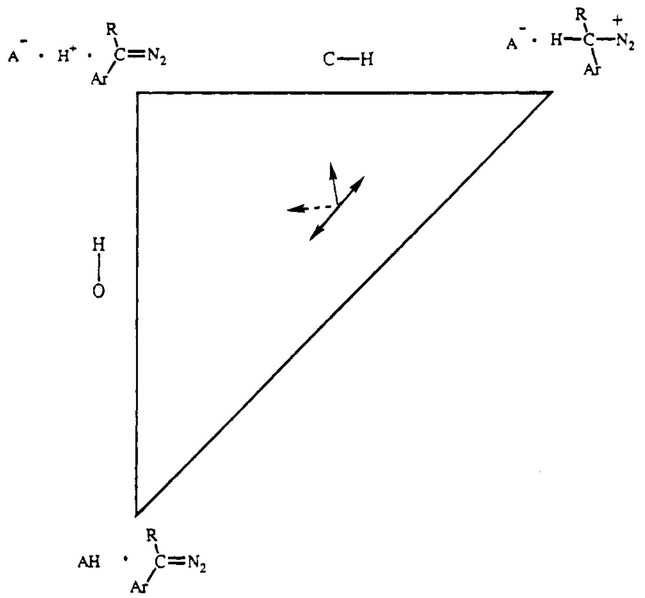

Figure 4. Two-dimensional reaction coordinate diagram for protonation of monoaryldiazomethanes. The diagonal orientation of the reaction coordinate at the transition state is indicated by observed changes in transtion state that are indicated by the solid and dashed single headed arrows, as described in the text.

is more clearly illustrated in the plot of α against σ, as in Figure 3A (solid points), in which the value of the slope of the line represents the value of the cross interaction coefficent $\delta\alpha/\delta\sigma = 0.15$ ($r^2 = 0.992$) and is a measure of the substituent interactions across the molecular framework of the transition state. The cross interaction coefficient is a second derivative of log k_{HA}, $\delta(\delta \log k_{HA}/\delta pK_{HA})/\delta\sigma$. As consequence of the fact that second partial derviatives commute,[18] $\delta(\delta \log k_{HA}/\delta pK_{HA})/\delta\sigma = -\delta(\delta \log k_{HA}/\delta\sigma)/\delta pK_{HA} = -\delta\varrho/\delta pK_{HA}$, an equivalent sensitivity of the value of -ϱ to changes in catalyst p*K*a is predicted. This is confirmed in the plot of Figure 3B (solid points) in which the negative of the slope of the plot of ϱ against catalyst p*K*a is $-\delta\varrho/\delta pK_{HA} = 0.15$ ($r^2 = 0.95$).

The observation of a significant cross interaction requires that the reaction coordinate at the transition state has a substantial diagonal character as indicated qualitatively in the reaction coordinate diagram in Figure 4 for monoaryldiazomethanes where the double headed arrow represents the position and orientation of the transition state.[19] The vertical axis indicates progress toward O−H bond cleavage in the oxygen acid while the horizontal axis indicates progress toward C−H bond formation. The position of the transition state with respect to the vertical axis is roughly determined by the average value of α observed in the present study, $\alpha_{obs} = 0.55$, after correcting, by +0.09, for a contribution to the observed α due to the dependence on catalyst p*K*a of the equilibrium desolvation of the catalyst that is required to form the encounter complex, as suggested by Murray and Jencks.[1] In Figure 4 the position of the transition state relative to the horizontal axis is rather more arbitrary because the limiting value of ϱ for the equilibrium formation of the diazonium ion is unknown. The value of ϱ for the log of the equilibrium constant for formation of benzylammonium ions from benzylamines and H$^+$ is $\varrho = -1.06$[20] so that the average value of ϱ =

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(18) Jencks, D. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 7948.

(19) The essential point is the significant diagonal orientation, the uncertainty with regard to exact position is empasized.

(20) Blackwell, L. F.; Fischer, A.; Miller, I. J.; Topsom, R. D.; Vaughan, J. *J. Chem. Soc.* **1964**, 3588.

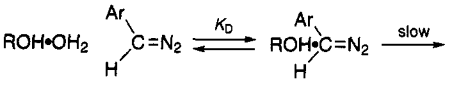
−1.6 observed here indicates that the aryl substituents experience a significant buildup of positive charge in the transition state. However, the sensitivity to substituents in diazonium ion forming reactions may be considerably larger than in the equilibrium protonation of benzylamines due to the carbocationic nature of diazonium ions that is indicated by the recent ab initio calculations of Glaser.[17]

The diagonal orientation of the transition state in Figure 4, for protonation of monoaryldiazomethanes, is qualitatively consistent with the observed cross interactions. An increase in σ, increase in electron-withdrawing power of the aryl substituent, raises the right corner of the diagram relative to the left edge. The resultant movement, indicated by the solid single-headed arrow in Figure 4, of the transition state with respect to the vertical axis, is toward the top and left edges and this movement precipitates a transition state that is later with respect to O−H bond breaking. Thus, a commensurately larger value of Bronsted α with increasing σ is predicted for the resultant transition state, and this is as observed in Figure 3A. The predicted movement of the transition state upon increasing the acidity of the oxygen acid catalyst is such that the value of ϱ should become less negative—as indicated by the dashed single-headed arrow in Figure 4. This is in qualitative accord with the experimental data plotted in Figure 3B (solid points).

Change in Orientation of the Transition State. The substantial cross interactions reported here for the protonation of monoaryldiazomethanes by oxygen acids in water (4% acetonitrile) contrast with what has been reported for the reaction of diaryldiazomethanes with oxygen acids in 80%DMSO/20% H_2O.[4] Figures 3A,B (open symbols) illustrates that the cross interaction coefficients $\delta\alpha/\delta\sigma$ (Figure 3A) and $\delta\varrho/\delta pKa$ (Figure 3B) for diaryldiazomethanes have values that are nearly zero, perhaps non-zero but of opposite sign in Figure 3B, in contrast to monoaryldiazomethanes. The absence of marked cross interactions indicates that the orientation of the transition state is likely fundamentally different in the case of diaryldiazomethanes.

Further contrast between the mono- and diaryldiazomethanes is found in the fact that the Bronsted plots for protonation of diaryldiazomethanes exhibit marked curvature whereas those for protonation of monoaryldiazomethanes exhibit little or no curvature. In the original study,[4] the Bronsted plot for protonation of diphenyldiazomethane was composed of 13 carboxylic acids and phenols and spanned ~9 p*K*a units. A change in Bronsted slope from ~1 to ~0.2 as the catalyst p*K*a changed from 10 to 2 was indicated for the reaction of diphenyldiazomethane. The curvature in the Bronsted plot for protonation of diphenyldiazomethane is evident in Figure 2 (open symbols). The plot includes a subset of points from the original study in order to indicate that a difference in curvature for di- versus monoaryldiazomethanes can be detected with the smaller number of catalysts used in the present study. Curvature similar to that in the case of diphenyldiazomethane is obvious in the Bronsted plots (not shown) for the 4-CH_3−, the 4-Cl−, and the 4,4′-bis(dichlorodiphenyl)diazomethanes using the limited number of catalysts plotted in Figure 2.[4] The data for protonation of monoaryldiazomethanes (Figure 2, solid points) could also be fit to a curve; however, the curve would be noticeably shallower than that for protonation of diphenyldiazomethane (Figure 2, open symbols), and the deviations from a simple straight line are small and not consistent with curvature and possibly systematic—for a given catalyst there is a similar small deviation for each monoaryldiazomethane studied.

The difference in *curvature* of the Bronsted plots for protonation of mono- and diaryldiazomethanes is not likely to be due to differences in solvents between the two studies—aqueous 4% acetonitrile in the former and 80% DMSO/20% H_2O in the latter. The protonation of carbon bases is generally direct,[21,22] and this requires the equilibrium desolvation of the oxygen acid, ROH, prior to proton transfer, as in eq 9. That the dependence of



$$\mathrm{ROH{\bullet}OH_2}\quad \mathrm{(Ar)(H)C{=}N_2} \overset{K_D}{\rightleftharpoons} \mathrm{ROH{\bullet}C(Ar)(H){=}N_2} \xrightarrow{\text{slow}} \qquad (9)$$

the equilibrium constant K_D upon p*K*a of the acid can affect the absolute value of the observed Bronsted exponent is well documented.[23] The values of the Bronsted exponents might therefore be expected to change with a change to the less polar solvent if there is a larger dependence of K_D upon the p*K*a of the acid in the less polar solvent. However, the explanation that *curvature* is induced by a change to the somewhat less polar solvent, 80% DMSO/20% H_2O, requires the assertion that, upon change to the less polar solvent , there is a *change* in the dependence of K_D on acid p*K*a *with changing acid* pK_a. Such changes indeed explain the curvature in Bronsted-type plots for base catalysis or substitution reactions that include a wide range of oxyanion catalysts/nucleophiles.[2,7,24-26] In these cases the curvature is apparent with the more strongly basic oxyanions that are strongly solvated. Such effects are likely to be smaller and insufficient to explain the curvature observed in the protonation of diaryldiazomethanes by neutral oxygen acids. Direct evidence that is consistent with this claim is the linear dependence upon p*K*a of the free energy of transfer of phenols[1] and enthalpy of transfer of pyridinium ions[27] from the gas phase to water. Such plots would be curved if there were a change in the dependence of free energies or enthalpies of transfer upon changing phenol or pyridinium ion p*K*a. Additionally, the curvature in the Bronsted plots for decomposition of diazoacetate in water[5,6] indicates that curvature is not unique to the less polar solvents.

In concurrence with the conclusions of the previous study,[4] the large curvature in the Bronsted plot for protonation of diaryldiazomethanes is due, at least in part, to a change in transition state structure with catalyst p*K*a in which the transition state becomes earlier with respect to O−H bond cleavage as oxygen acid

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strength increases—a classical Hammond effect. This Hammond effect is described by a non-zero, positive, "direct interaction coefficient", $= \delta\alpha/\delta pKa$, in which a change in substituent in the oxygen acid effects a change in the extent of oxygen acid bond cleavage in the transition state. This contrasts with the monoaryldiazomethanes for which the essentially linear Bronsted plots indicate that $\delta\alpha/\delta pKa \approx 0$.

Both the appearence of direct interaction coefficients and the disappearence of measurable cross interaction coefficients are expected if the reaction coordinate at the transition state for protonation of diaryldiazomethanes is more parallel, relative to that for the monoaryldiazomethanes, to the O−H bond-breaking axis of the reaction coordinate. The direct interaction coefficients for O−H bond cleavage are expected to be larger for a transition state that is oriented more parallel to the axis of O−H bond cleavage because the perpendicular and parallel movements of the transition state that is diagonally oriented tend to cancel movement along the O−H bond axis.[18] Likewise, the lack of coupling between C−H bond formation and O−H bond cleavage in a transition state that is more paralell to one axis, as suggested in the case of diaryldiazomethanes, is manifest in the negligibly small cross interaction coeficients for this reaction.

The change from a transition state that is more diagonally oriented in the case of aryldiazomethanes to one that is oriented more paralell to the O−H bond cleavage axis, upon substitution of an arene ring for a hydrogen, may not be unexpected. Arene ring substitution stabilizes the left side of the diagram in Figure 4 by conjugation and destabilizes the right corner inductively. If the curvature of the surface that is perpendicular to the reaction coordinate at the transition state is sufficiently shallow, there could be substantial movement toward the left edge of the diagram with this perturbation. As the edge of the diagram is approached, the orientation of the transition state inevitably becomes more paralell to the vertical axis. This type of reorientation, an "edge effect", similarly accounts for the change from general base catalyzed to uncatalyzed hydration of carbocations with decreasing stability of the cation.[28]

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Supplementary Material Available: Sample plots of k_{obsd} against buffer concentration and plots of the observed second-order rate constant for catalysis against fraction of buffer acid (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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