

ACID-CATALYZED HYDROLYSIS OF PHENYLDIAZOACETIC ACID. EFFECT OF AN α -DIAZO GROUP ON CARBOXYLIC ACID ACIDITY

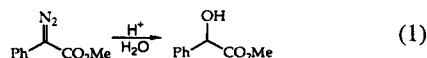
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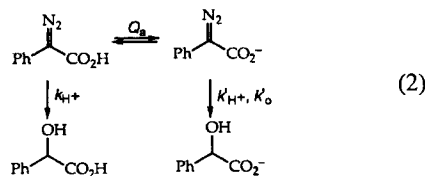
Rates of acid-catalysed hydrolysis of phenyldiazoacetic acid were measured in aqueous solution at 25 °C across the entire acidity range $pC_H^+ = 1-13$. The reaction was found to occur through both the non-ionized and ionized forms of the substrate, with the ionized form reacting faster by a factor of 650. Appreciable solvent isotope effects in the normal direction ($k_H/k_D > 1$) and the occurrence of general acid analysis show that hydrolysis occurs by rate-determining proton transfer to the diazocarbon atom of the substrate. Analysis of the rate profile for the reaction provides an estimate of the acidity constant of phenyldiazoacetic acid, $pK_a = 3.70$, which is apparently the first determination of the acid strength of an α -diazocarboxylic acid. Comparison of this result with the pK_a of phenylacetic acid shows the diazo group to have a mild ($4\times$) acid-strengthening effect, whose modest magnitude is attributed to opposing resonance and polar effects.

INTRODUCTION

The acid-catalyzed hydrolysis of aliphatic diazo compounds is a much-studied reaction that has figured prominently in the development of modern ideas on acid-base catalysis.¹ A recent report from this laboratory² provided rate constants for the acid-catalyzed hydrolysis of methyl phenyldiazoacetate [equation (1)]. We have now



followed up that investigation with a detailed study of the acid-catalyzed hydrolysis of phenyldiazoacetic acid itself. This substrate undergoes reaction through both its non-ionized carboxylic acid and its ionized carboxylate ion forms [equation (2)], and



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analysis of the rate data has produced an estimate of the acidity constant of the acid. α -Diazocarboxylic acids generally undergo hydrolysis very readily at acidities where their acidity constants can be determined, and this lability appears to have precluded any previous measurement of the acidity constant of such a substance.

EXPERIMENTAL

Materials. Methyl phenyldiazoacetate was prepared by lead tetraacetate oxidation of the hydrazone of methyl phenylglyoxylate.³ This substance was converted into the potassium salt of phenyldiazoacetic acid by saponification in 2 M KOH. A mixture of 1 g of the ester and 5 mL of 2 M aqueous KOH, protected against light, was stirred for 3 days until the initially two-phase system became homogeneous. The resulting solution was then extracted with diethyl ether to remove unreacted ester and the water layer was evaporated to dryness under vacuum at room temperature. The residue so obtained contained unreacted KOH in addition to the desired potassium phenyldiazoacetate. These two substances were separated by extracting this residue with acetone, evaporating the solvent from the acetone solution, extracting the new residue with acetonitrile

and evaporating the solvent from the acetonitrile solution. This gave the product as yellow-red crystals. Stock solutions for use in the kinetic measurements were made by dissolving this salt in acetonitrile.

Kinetic measurements were also carried out using stock solutions in which saponification had been carried out directly without isolating the carboxylate salt. It was found that saponification of methyl phenyldiazoacetate is complete after 40 h in aqueous 0.1 M NaOH at room temperature. Although phenyldiazoacetic acid is hydrolyzed rapidly in acid solutions, it is stable in base and these aqueous stock solutions could be kept for several days.

All other materials were of the best available commercial grades.

Kinetics. Rates of hydrolysis of phenyldiazoacetic acid were determined spectroscopically by monitoring the decrease in strong absorbance of the diazo acid at 280 nm. Measurements were made with Cary 118 and 2200 spectrometers whose cell compart-

ments were thermostated at $25.0 \pm 0.05^\circ\text{C}$. The rate data fitted the first-order rate law well, and observed first-order rate constants were obtained by non-linear least-squares fitting of an exponential function.

RESULTS

The hydrolysis of phenyldiazoacetic acid is expected to give the corresponding hydroxy compound, mandelic acid, as the reaction product. This was confirmed in the present study by the observation that the UV spectra of spent reaction mixtures were identical with those of authentic samples of mandelic acid measured under the same conditions.

Rates of hydrolysis of phenyldiazoacetic acid were determined in aqueous solutions of perchloric acid, hydrochloric acid and sodium hydroxide, and aqueous buffer solutions of formic acid, acetic acid, cacodylic acid, biphosphate ion and tris(hydroxymethyl)methylammonium ion. The data are summarized in Tables 1 and 2.

Table 1. Rate data for the hydrolysis of phenyldiazoacetic acid in aqueous perchloric acid solutions at 25°C^a

H_2O		D_2O	
[Acid]/ 10^{-2} M	$k_{\text{obs}}/10^{-2} \text{ s}^{-1}$	[Acid]/ 10^{-2} M	$k_{\text{obs}}/10^{-2} \text{ s}^{-1}$
0.0120	2.10, 1.81, 2.10	0.0100 ^c	0.356, 0.349
0.0144	2.03, 2.06	0.0300 ^c	0.4881, 0.486
0.0254	3.20, 3.03	0.0600	0.603, 0.606
0.0323	3.57	0.180	0.768, 0.773
0.0464	4.26, 4.18, 4.04	0.600 ^c	0.898, 0.863
0.0674	4.83, 4.74	0.980	0.889, 0.888
0.0800	5.30, 5.16, 6.12	3.90	1.32, 1.16
0.194	5.74, 5.82	5.98	1.30, 1.30
0.404	6.34, 6.54, 6.60	7.98	1.58, 1.56
0.614	6.78, 6.81	9.98	1.89, 1.88
0.824	6.39, 6.35, 6.28	20.0 ^c	3.04, 2.91
1.00	8.00, 8.24	41.3 ^c	5.47, 5.55
1.04	6.63, 6.47, 6.57		
2.08	7.24, 7.12		
4.18	7.89, 7.82		
6.28	8.62, 8.55		
8.38	9.16, 9.16		
10.0	10.7, 10.6		
10.5	9.89		
20.4	13.6, 13.3		
30.6	16.9, 16.7		
40.8	21.4, 21.8, 22.2		
51.0	24.3, 24.6		
0.100 ^b	0.000189		
5.00 ^b	0.000186		
10.00 ^b	0.000187		

^a Ionic strength = 0.10 M (NaClO_4), except at [acid] > 0.10 M where ionic strength = [acid].

^b NaOH solutions; concentrations are [NaOH].

^c DCl solutions

Table 2. Rate data for the hydrolysis of phenyldiazoacetic acid in aqueous buffer solutions at 25 °C^a

H ₂ O		D ₂ O	
[Buffer]/10 ⁻² M	<i>k</i> _{obs} /10 ⁻² s ⁻¹	[Buffer]/10 ⁻² M	<i>k</i> _{obs} /10 ⁻² s ⁻¹
HCO ₂ H; [HA]/[A ⁻] = 1.00; [H ⁺] = 2.80 × 10 ⁻⁴ M:		HCO ₂ D; [DA]/[A ⁻] = 1.00; [D ⁺] = 9.82 × 10 ⁻⁵ M:	
4.00	8.78, 8.54, 8.41, 8.57	4.00	1.72, 1.56, 1.63
6.00	12.3, 11.8	8.00	2.64, 2.82
8.00	14.4, 13.8, 13.1, 14.0, 13.9	12.0	3.54, 3.55, 3.91
1.20	19.1, 19.1, 25.5, 25.7	16.0	5.19, 5.14, 5.19
<i>k</i> _{obs} /s ⁻¹ = (3.04 ± 0.31) × 10 ⁻² + (1.38 ± 0.03)[buffer]		<i>k</i> _{obs} /s ⁻¹ = (4.14 ± 1.39) × 10 ⁻³ + (2.89 ± 0.12) × 10 ⁻¹ [buffer]	
CH ₃ CO ₂ H; [HA]/[A ⁻] = 3.00; [H ⁺] = 8.16 × 10 ⁻⁵ M:		CH ₃ CO ₂ D; [DA]/[A ⁻] = 1.00; [D ⁺] = 8.32 × 10 ⁻⁶ M:	
0.800	2.18, 2.22, 2.22	1.00	0.216, 0.199
1.60	3.07, 3.05, 3.10	1.50	0.271, 0.265
4.00	5.07, 5.26, 5.51	2.50	0.387, 0.383
8.00	8.64, 9.00, 9.36	5.00	0.688, 0.686
<i>k</i> _{obs} /s ⁻¹ = (1.52 ± 0.09) × 10 ⁻² + (9.37 ± 0.20) × 10 ⁻¹ [buffer]		7.50	0.964, 0.964
CH ₃ CO ₂ H; [HA]/[A ⁻] = 1.00; [H ⁺] = 2.72 × 10 ⁻⁵ M:		12.0	1.44, 1.43
1.00	1.20, 1.19	16.0	1.82, 1.84
1.50	1.54, 1.53	<i>k</i> _{obs} /s ⁻¹ = (1.19 ± 0.10) × 10 ⁻³ + (1.09 ± 0.01) × 10 ⁻¹ [buffer]	
2.00	1.68, 1.68		
4.0	3.22, 2.99		
8.00	5.64, 5.89		
12.0	8.62, 8.54		
16.0	10.6, 10.9		
<i>k</i> _{obs} /s ⁻¹ = (5.19 ± 0.70) × 10 ⁻³ + (6.51 ± 0.08) × 10 ⁻¹ [buffer]			
CH ₃ CO ₂ H; [HA]/[A ⁻] = 0.333; [H ⁺] = 9.06 × 10 ⁻⁶ M:			
0.500	0.431		
1.00	0.633		
2.00	1.09		
3.50	1.82		
5.00	2.56		
<i>k</i> _{obs} /s ⁻¹ = (1.66 ± 0.19) × 10 ⁻³ + (4.78 ± 0.07) × 10 ⁻¹ [buffer]			
(CH ₃) ₂ AsO ₂ H; [HA]/[A ⁻] = 4.00; [H ⁺] = 3.28 × 10 ⁻⁶ M:			
2.00	0.543, 0.586		
4.00	1.04, 1.09		
6.00	1.55, 1.54, 1.57		
<i>k</i> _{obs} /s ⁻¹ = (7.13 ± 2.24) × 10 ⁻⁴ + (2.47 ± 0.05) × 10 ⁻¹ [buffer]			
H ₂ PO ₄ ⁻ ; [HA ⁻]/[A ⁻] = 1.00; [H ⁺] = 1.66 × 10 ⁻⁷ M:			
0.250	0.0247, 0.0245		
0.500	0.0443, 0.0446		
0.700	0.0619, 0.0623		
1.00	0.0861, 0.0859		
1.20	0.105, 0.0106		
1.50	0.121, 0.124		
<i>k</i> _{obs} /s ⁻¹ = (5.61 ± 1.55) × 10 ⁻⁵ + (7.97 ± 0.15) × 10 ⁻² [buffer]			
(CH ₂ OH) ₃ CNH ₃ ⁺ ; [HA ⁺]/[A] = 1.00; [H ⁺] = 8.20 × 10 ⁻⁹ M:			
2.00	0.00130		
3.00	0.00167		
4.00	0.00224, 0.00221		
8.00	0.00382, 0.00394		
<i>k</i> _{obs} /s ⁻¹ = (4.50 ± 0.62) × 10 ⁻⁶ + (4.31 ± 0.12) × 10 ⁻⁴ [buffer]			

^a Ionic strength = 0.10 M (NaClO₄).

The measurements in buffers were performed using series of solutions of constant buffer ratio but varying buffer concentration, with ionic strength maintained at 0.10 M; this served to hold hydrogen ion concentrations constant throughout a given solution series. As is illustrated in Figure 1, observed first-order rate constants increased linearly with increasing buffer concentration, in accord with the rate law shown as equation (3).

$$k_{obs} = a + k_{cat}[\text{buffer}] \quad (3)$$

Linear least-squares analysis produced values of intercepts at zero buffer concentration, a , and buffer catalytic coefficients, k_{cat} ; these are also listed in Table 2.

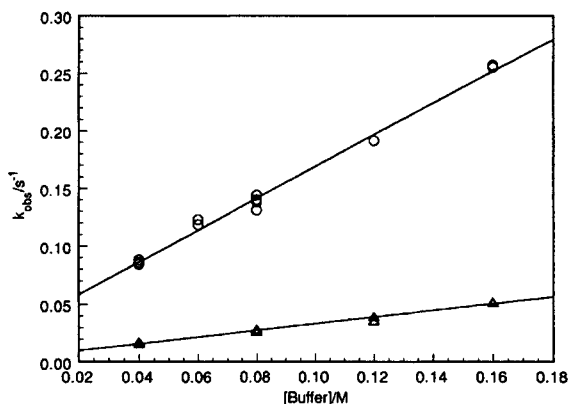


Figure 1. Relationship between buffer concentration and observed first-order rate constants for the hydrolysis of phenyldiazoacetic acid in aqueous formic acid buffer solutions at 25 °C. (O), H₂O; (Δ), D₂O; buffer ratio = 1.00 in each case

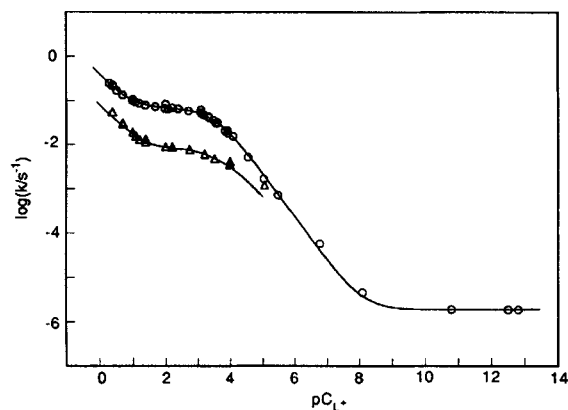


Figure 2. Rate profiles for the hydrolysis of phenyldiazoacetic acid in aqueous solution at 25 °C; (O), H₂O, (Δ), D₂O. L⁺ represents either H⁺ or D⁺

These intercepts, together with rate constants measured in perchloric acid, hydrochloric acid and sodium hydroxide solutions were used to construct the rate profiles shown in Figure 2. Hydrogen ion concentrations of the buffer solutions needed for this purpose were calculated using literature pK_a values for formic,⁴ acetic⁵ and cacodylic⁶ acids and biphosphate⁷ and tris(hydroxymethyl)methylammonium⁸ ions, plus isotope effects on the ionization of formic⁹ and acetic¹⁰ acids, together with activity coefficients recommended by Bates.¹¹ All of the rate constants used in this profile refer to an ionic strength of 0.10 M, except for those at $pC_{H^+} > 0.1$, for which ionic strength = acid concentration (0.2–0.5 M).

DISCUSSION

Rate Profiles

The rate profiles for hydrolysis of phenyldiazoacetic acid shown in Figure 2 consist of linear portions situated either diagonally with unit slope or horizontally with zero slope. These linear portions are connected to one another by curved regions that may be classified as either upward bends or downward bends, depending on the direction the profile takes in going from a horizontal to the adjacent diagonal portion. The profile for hydrolysis in H₂O solution shown in Figure 2 then has, starting at the high acidity end, an upward bend followed by a downward bend followed by another upward bend, while the less extensive profile for hydrolysis in D₂O solution has an upward bend and a downward bend that are the analogs of the first two bends of the H₂O profile. Upward bends generally signify changes in reaction mechanism, i.e. changes in the species undergoing reaction, while a common cause of downward bends is changes in the state of ionization of acidic or basic groups on the substrate while it undergoes reaction by the same mechanism.¹²

These generalizations may be applied to the present case by postulating the following reaction scheme. The first diagonal portion of the rate profile of Figure 2 for hydrolysis in H₂O at high acidity represents simple reaction of H⁺ with non-ionized phenyldiazoacetic acid through protonation on its diazo carbon atom. As the acidity is lowered, this mechanism gives way to C-protonation of the substrate in its more reactive carboxylate ion form. This change in mechanism occurs at acidities where phenyldiazoacetic acid is still largely non-ionized, and reaction must therefore take place by rapid ionization of the substrate producing the carboxylate ion plus a proton followed by slower C-protonation of the ion. Since a proton is first produced and is then used up in this scheme, the overall reaction is independent of proton concentration, and that gives rise to a horizontal portion of the rate profile and an upward-bending connection between this portion and the preced-

ing diagonal part. At still lower acidities, the equilibrium between phenyldiazoacetic acid and the phenyldiazoacetate ion shifts to the side of the ion; the ion then becomes the form of the substrate in the initial state of the reaction by this mechanism, and the rate once more becomes proportional to hydrogen ion concentration. This generates another diagonal part of the rate profile and gives a downward bending connection with the previous horizontal part. Eventually, however, the hydrogen ion concentration becomes too low to maintain reaction by this mechanism at a faster rate than that for C-protonation of the ion by solvent water, and the latter new mechanism then takes over. This produces another horizontal portion of the rate profile with an upward bending connection to the previous diagonal part. The rate profile for hydrolysis in D_2O solution may be interpreted in a corresponding way, with omission of the final section involving protonation by solvent water made necessary by the more limited extent of the data.

The rate law that corresponds to this reaction scheme is shown in equation (4):

$$k_{\text{obs}} = \frac{(k_{L^+}[L^+]^2 + k'_{L^+}Q_a[L^+])}{Q_a + [L^+]} + k'_0 \quad (4)$$

where L denotes either isotope of hydrogen, i.e., H or D, and k_{L^+} is the rate constant for reaction of phenyldiazoacetic acid with the hydrogen ion, k'_{L^+} and k'_0 are the rate constants for reaction of phenyldiazoacetate ion with the hydrogen ion and with water, respectively, and Q_a is the acidity constant of phenyldiazoacetic acid (Q_a is a concentration ratio appropriate to the ionic strength, $\mu = 0.10$ M, at which it was determined). Non-linear least squares fitting of this expression to the experimental data gave the following results:

$$\begin{aligned} k_{H^+} &= (3.45 \pm 0.14) \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}, \\ k_{H^+} &= (2.26 \pm 0.06) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}, \\ (k'_0)_{H_2O} &= (1.92 \pm 0.08) \times 10^{-6} \text{ s}^{-1}, \\ (Q_a)_{H_2O} &= (2.98 \pm 0.11) \times 10^{-4} \text{ M} \quad (pQ_a = 3.53 \pm 0.02), \\ k_{H^+}/k_{D^+} &= 2.97 \pm 0.22, \quad k'_{H^+}/k'_{D^+} = 2.28 \pm 0.34 \\ (Q_a)_{H_2O}/(Q_a)_{D_2O} &= 4.26 \pm 0.78. \end{aligned}$$

The lines shown in Figure 2 were drawn using these parameters; it may be seen that they reproduce the data well.

This good fit supports the reaction scheme on which this analysis was based. Additional evidence comes from the isotope effect on the acidity constant $(Q_a)_{H_2O}/(Q_a)_{D_2O} = 4.3 \pm 0.8$; values of this magnitude are typical for the ionization of carboxylic acids.¹³

Reaction mechanism

The acid-catalyzed hydrolysis of aliphatic diazo compounds can occur either by rate-determining protonation

of the diazo carbon atom or by rapid and reversible diazo carbon protonation followed by a subsequent slow step. Hydronium ion isotope effects can distinguish between these two mechanisms: for rate-determining protonation this isotope effect is usually in the normal direction ($k_{H^+}/k_{D^+} > 1$) whereas for rapidly reversible protonation it is commonly the inverse ($k_{H^+}/k_{D^+} < 1$).¹⁴ The fairly strong normal isotope effects observed here for the hydrolysis of both undissociated phenyldiazoacetic acid and the phenyldiazoacetate ion, $k_{H^+}/k_{D^+} = 3.0$ and $k'_{H^+}/k'_{D^+} = 2.3$, respectively, argue for a rate-determining proton-transfer mechanism in both cases.

Rate-determining proton-transfer reactions should also show general acid rather than specific hydrogen ion catalysis, and the strong increase in reaction rate with increasing buffer concentration found for the hydrolysis of phenyldiazoacetic acid in all of the buffers studied here and illustrated in Figure 3 suggests that this is the case. This dependence of rate on buffer concentration, however, could also signify general base catalysis, and to distinguish this from general acid catalysis it is necessary to measure reaction rates at more than one buffer ratio. This was done for acetic acid buffers: measurements were made at $[HOAc]/[OAc^-] = 1/3, 1$ and 3 (see Table 1). In these solutions hydrolysis occurs through the carboxylate form of phenyldiazoacetic acid, with the substrate largely but not completely in this form. Operational catalytic coefficients obtained as slopes of buffer dilution plots, $\Delta k_{\text{obs}}/\Delta[\text{buffer}]$, were therefore corrected for incomplete substrate ionization by multiplying by $Q_a/(Q_a + [H^+])$, where $[H^+]$ is the hydrogen ion concentration of the buffer. Analysis of the relationship between true catalytic coefficients obtained in this way and the fraction of buffer present as acid, $f_A (= [HA]/([HA] + [A^-]))$,

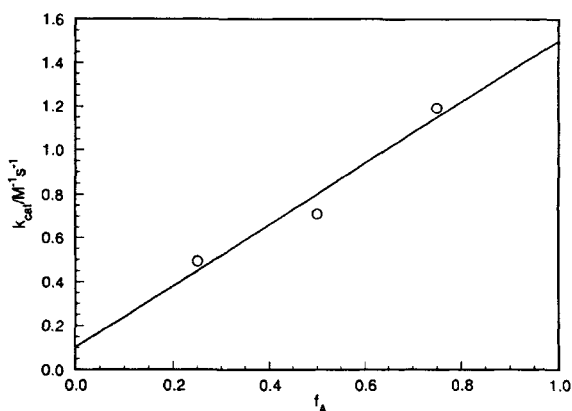


Figure 3. Relationship between fraction of buffer present in acid form and catalytic coefficients for the hydrolysis of phenyldiazoacetic acid in aqueous acetic acid buffer solution at 25 °C

illustrated in Figure 3, then showed the buffer catalysis to be wholly of the general acid type: least squares fitting of the expression shown in equation (5) to the data gave $k_{\text{HA}} = 1.50 \pm 0.17 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{B}} = 0.099 \pm 0.166 \text{ M}^{-1} \text{ s}^{-1}$.

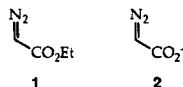
$$k_{\text{cat}} = k_{\text{B}} + (k_{\text{HA}} - k_{\text{B}})f_{\text{A}} \quad (5)$$

The different slopes of the buffer dilution plots shown in Figure 1 indicate that there is an isotope effect on the buffer catalyzed reaction. Evaluation of this isotope effect requires correction of operational catalytic coefficients for incomplete substrate ionization and conversion of the results into general acid catalytic coefficients. When this is done, the isotope effect $k'_{\text{HA}}/k_{\text{DA}} = 3.86 \pm 1.02$ is obtained for catalysis by formic acid and $k'_{\text{HA}}/k'_{\text{DA}} = 6.16 \pm 1.71$ for catalysis by acetic acid. The normal direction and appreciable magnitude of these isotope effects confirm assignment of a rate-determining proton transfer mechanism to this reaction.

The catalytic coefficients for formic and acetic acids also provide a two-point Brønsted plot whose slope is $\alpha = 0.55 \pm 0.05$. This is a reasonable value for a fairly facile reaction such as the present one.

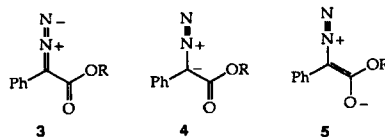
Relative reactivities

The rate constants determined here for diazo carbon protonation of phenyldiazoacetic acid and phenyldiazoacetate ion by the hydrogen ion, combined with that for the corresponding methyl ester reported before,² provide the relative rates given in Scheme 1. The results show that the reactivities of the acid and ester are similar but that of the ion is considerably greater. This appears to be the first comparison of reactivities of a diazo acid or ester with that of the corresponding carboxylate ion. The rate of hydrogen ion-catalyzed hydrolysis of ethyl diazoacetate (1)¹⁵ is known to be 10^5 times less than that of the diazoacetate ion (2)¹⁶ but the mechanisms of these two reactions are different: whereas the hydrolysis of diazoacetate ion occurs by rate-determining protonation of diazo carbon, carbon protonation of ethyl diazoacetate is rapid and reversible and a subsequent step is rate determining; the rate constants of these two reactions consequently provide no information about the relative rates of carbon protonation of the ester and the carboxylate ion.



Scheme 1

CH_3 or a negative charge. The rate of carbon protonation will be governed by the negative charge density at the diazo carbon atom, and this will rise in proportion to the contribution to the overall resonance hybrid made by structure 4, which puts electron density on this carbon, but it will be diminished by the contributions made by structures 3 and 5, which take electron density away from this carbon. Since in the case of the ion structure 5 puts a negative charge on a group that is already negatively charged, this structure will contribute less here than in the case of the acid and the ester; structure 4 will consequently contribute more, and the rate of diazo carbon protonation of the ion will be faster than that of the acid or ester.



Diazo group substituent effect

The unusual lability of the diazo group has impeded assessment of its effect as a substituent on the reactivity of other functional groups. The present determination of the acid dissociation constant of phenyldiazoacetic acid, for example, appears to be the first estimate of the acidity of an α -diazocarboxylic acid.

The acidity constant determined here is a concentration quotient expressed in terms of concentrations rather than activities, but this quantity may be converted into a thermodynamic acidity constant by applying appropriate activity coefficients. Use of values recommended by Bates,¹¹ with PhCO_2^- as a surrogate for $\text{PhCN}_2\text{CO}_2^-$, gives $\text{p}K_{\text{a}} = 3.70$. Comparison of this result with $\text{p}K_{\text{a}} = 4.32$ for phenylacetic acid,¹⁸ the unsubstituted analog of phenyldiazoacetic acid, shows the diazo group to be acid strengthening by a factor of 4.

This weak substituent effect can be understood as the combined influence of opposing resonance and polar effects. As pointed out in the section above, resonance structure 5 will make a stronger contribution to the hybrid structure of the acid than to that of the carboxylate ion, and this will stabilize the acid relative to the ion, thereby reducing its acid strength. The diazo substituent, on the other hand, is a dipolar group with the positive end of its dipole near the point of attachment; this will have an acid-strengthening effect. Evidently the polar effect is stronger than the resonance effect, for the result is a mild increase in acidity.

The markedly greater rate of carbon protonation of a diazo carboxylate ion over that of the corresponding acid or ester may be understood by considering the resonance structures 3–5, in which R can be either H,

ACKNOWLEDGEMENTS

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