[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.]

Hydrogen Exchange of Azulenes. II. Acid–Base Equilibria in Aqueous Solutions[1,2]

BY F. A. LONG AND JANOS SCHULZE

RECEIVED MAY 4, 1963

Spectrophotometric procedures have been used to make quantitative measurements of the equilibrium protonation of the following azulenes in aqueous solutions of perchloric acid: 1-methylazulene, 1-formylazulene, 1-chloroazulene, 1-carboxylazulene, 1-cyanoazulene, 1-nitroazulene, 1-nitro-4,6,8-trimethylazulene, 1-(p-dimethylaminobenzyl)-azulene. Monoprotonated conjugate acids are formed from all of these except for the last which first protonates at low acidities on the dimethylamine group and further protonates at higher acidities on the azulene ring. Acidities for half-protonation of the azulenes range, on an H_0 scale, from −0.36 for 1-methylazulene to −4.68 for 1-nitroazulene. A stepwise procedure leads to thermodynamic pK values for five of the azulenes. For all of those azulenes protonating on the 3-carbon of the ring the values of d log I/dH_0 are large, ranging from 1.6 to 1.9. For the two azulenes protonating on the oxygen of the 1-substituent, the analogous slopes are much smaller and are very close to unity. Spectral data are given for the azulenes and their conjugate acids.

Introduction

Paper I of this series discussed the structures of the conjugate acids of fifteen azulenes and showed the existence of two principal types of azulenium cations: those protonated on the unsubstituted 3- (or 1-) carbon and those protonated on the oxygen of a substituent present at the 1-position.[3] 1-Nitro-4,6,8-trimethylazulene constituted a special case in that, presumably for steric reasons, protonation occurred at the already substituted 1-position. The present paper gives the results of a quantitative study of the acid–base equilibria in aqueous solution between the various azulenes and their conjugate acids. The correlation between the structures of the conjugate acids and the dependence of the degree of protonation on acidity is of particular interest. A related point is the determination of the basicity of the azulene as a function of type of substituent and position of protonation.

The first quantitative study on the basicity of azulene was carried out using a two-phase solvent mixture and colorimetric analysis.[4] It was concluded that in strong acid there was a reversible protonation and that azulene is a very strong base relative to other aromatic hydrocarbons.[5] This high basicity is due to the great stability of the azulenium cation, structure I, which is a substituted tropylium ion.

I　　　　II
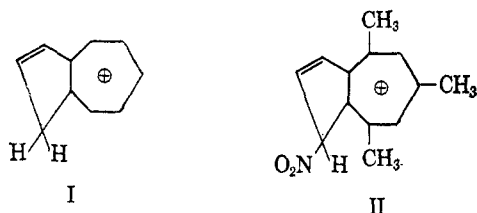
Plattner, Heilbronner, and Weber made some quantitative measurements of the two-phase equilibria and reported that the somewhat complex distribution coefficient, $[AzH^+]_{aq}/[Az]_{org}$, varied with the Hammett acidity function, h_0, to about the second power. Because of the uncertainties in variations of distribution coefficients with medium, this result cannot be compared directly with results from a one-phase aqueous system. It is suggestive, however, of an unusually large dependence of indicator ratio on acidity. These same authors determined an approximate pK for the azulenium ion in the mixed solvent, ether–formic acid. The data indicated a value very close to that of o-nitro-

aniline at room temperature, i.e., a pK value of about −0.29.[6,9]

Although the water solubility of azulene is very low, the ultraviolet absorption of both the base and acidic forms is sufficiently large to make a study of the acid–base equilibrium in a one-phase aqueous acidic system relatively straightforward. Preliminary data on this equilibrium have been published,[7] indicating that for an aqueous phase the slope of log I vs. $-H_0$, where I is the indicator ratio $[AzH^+]/[Az]$, is about 1.9 and that the H_0 value for half-protonation is −0.92. Both of these results are close to the earlier values from the more complex solvent system. This same spectrophotometric procedure is also applicable to aqueous solutions of the other azulenes, even where the water solubility is considerably less than that of azulene itself.

Experimental

Solubility Measurements.—Saturated aqueous solutions of the various azulenes were prepared at 25°, and the optical density of the filtered solution was measured, normally at the maximum of the absorption peak which occurs for all azulenes at close to 280 mμ. Extinction coefficients for the chosen wave length were determined from measurements of aqueous solutions containing 2 to 5% ethanol and made up to give an optical density of about 0.8. Solubilities were calculated from the relation $cd = c'd'$ where c and c' are the unknown and known concentrations and d and d' are the respective optical densities. Table I gives the results. The estimated accuracy of the values is ±15%.

TABLE I
SOLUBILITIES OF AZULENES IN WATER AT 25°

	10^{-5}				10^{-5}
Compound	mg./l.	mole/l.	Compound	mg./l.	mole/l.
Az	15	11	COCF$_3$Az	12	5
MeAz	21	14	pDMABAz	2	0.5
CNAz	49	32	PhN$_2$Az	0.2	.1
ClAz	12	7	GuAz	0.8	.4
NO$_2$Az	26	15	NO$_2$TMAz	2	.9
CHOAz	30	19	TMAz	4	2
COOHAz	29	17			

Absorption spectra were taken on a Cary Model 14 recording spectrophotometer using quartz window cells with optical path lengths of 0.5, 1.0, 5.0, and 10.0 cm. Tables II and III summarize the spectral features of the azulenes and azulenium ions studied.

Indicator Ratios.—The procedure for determining these was essentially that of a spectrophotometric titration of aqueous solutions of the azulenes with solutions of perchloric acid. All studies were made at room temperature, 25 ± 2°.

Table IV gives details of a typical study, in this case for 1-cyanoazulene which protonates on the 3-carbon.[3] Wave lengths used for each study were chosen so as to obtain maximum sensitivity of measurement. In one case, that of azulene, separate studies were made at three wave lengths, 280, 352, and 573 mμ. The results for the three studies were in good agreement, but the best precision came from the study at the wave length with highest extinction coefficient, 280 mμ.

(1) Work supported by a grant from the Atomic Energy Commission.

(2) Presented in part at the 139th and 140th National Meetings of the American Chemical Society, St. Louis, Mo., April, 1961, and Chicago, Ill., September, 1961.

(3) J. Schulze and F. A. Long, J. Am. Chem. Soc., **86**, 322 (1964); part I.

(4) P. A. Plattner, E. Heilbronner, and S. Weber, Helv. Chim. Acta, **32**, 574 (1949); **33**, 1663 (1950).

(5) V. Gold and P. L. Tye, J. Chem. Soc., 2172, 2181, 2184 (1952).

(6) P. A. Plattner, E. Heilbronner, and S. Weber, Helv. Chim. Acta, **35**, 1036 (1952).

(7) F. A. Long and J. Schulze, J. Am. Chem. Soc., **83**, 3340 (1961).

Table II
Absorption Maxima (λ_m in Å.) and Molar Extinction Coefficients (ϵ_{max}) for Azulenes in Water (2% Ethanol)[a]

#			1	2	3	4	5	6	7	8	9
1	Az	λ_{max}	2350	2740	2800			3250	3385		5730
		ϵ_{max}	18500	52900	47300			3300	4400		350
2	MeAz	λ_{max}	2390	2740	2785			3450	3610		6200
		ϵ_{max}	15200	42200	48300			3750	1750		600
3	CNAz	λ_{max}	2320	2800	2850	2900	2960	3370	3460	3620	5400
		ϵ_{max}	22000	32900	42700	40700	53000	4800	5200	7050	650
4	ClAz	λ_{max}	2360	2745	2795	2845	2900	3350	3440	3600	6200
		ϵ_{max}	14400	30500	38000	32000	28500	2800	3450	2100	300
5	COOHAz	λ_{max}	2320	2870	2920	2975		3655			5310
		ϵ_{max}	19800	41500	38900	44800		7150			450
6	pDMABAz[b]	λ_{max}	2410	2800				3360	3460	3610	6000
		ϵ_{max}	23500	49200				3800	4800	2650	400
7	TMAz	λ_{max}	2460	2855	2905			3330	3460		5400
		ϵ_{max}	21200	35000	32900			3200	3800		700
8	PhN$_2$Az[c]	λ_{max}	2355	2830	3370	4400					
		ϵ_{max}	21700	16700	11000	17900					
9	NO$_2$TMAz[c]	λ_{max}	2420	2900	3300	4330					
		ϵ_{max}	27900	12800	12200	10800					
10	NO$_2$Az[c]	λ_{max}	2210	2340	2730	3210	4200				
		ϵ_{max}	23600	19500	14400	14500	15000				
11	CHOAz[c]	λ_{max}	2170	2680	3115	3800	5050				
		ϵ_{max}	15600	7950	23800	9200	450				
12	CF$_3$COAz[c]	λ_{max}	2180	2710	3160	3960	4850				
		ϵ_{max}	23800	10800	24200	12100	1050				

[a] The molar extinction coefficients of the visible peaks are uncertain because of the low solubilities.   [b] Spectrum of this compound after protonation on the nitrogen, see text; spectrum taken in 25% aqueous ethanol.   [c] The spectra of these compounds show different characteristics from the other azulenes and no attempt has been made to classify their absorption bands with those of the others.

Table III
Absorption Spectra of Azulenium Cations in 70% Aqueous HClO$_4$

Az	λ_{max}	2230	2600	3520		
	ϵ_{max}	19300	29700	14000		
MeAz	λ_{max}	2260	2670	3650		
	ϵ_{max}	23800	20900	12400		
CNAz	λ_{max}	2140	2600	3375		
	ϵ_{max}	22200	26000	9250		
ClAz	λ_{max}	2290	2690	3600		
	ϵ_{max}	26300	15800	10200		
COOHAz	λ_{max}	2160	2600	3380		
	ϵ_{max}	23500	30200	10800		
pDMABAz[a]	λ_{max}	2220	2645	3620		
	ϵ_{max}	23300	21300	13200		
PhN$_2$Az	λ_{max}	2140	2430	2880	3310	5160
	ϵ_{max}	18700	16500	9800	9100	31100
TMAz	λ_{max}	2355	2680	2790	3550	
	ϵ_{max}	24000	36800	14300	13900	
NO$_2$TMAz	λ_{max}	2400	2710	3500		
	ϵ_{max}	17300	31600	7650		
NO$_2$Az	λ_{max}	2340	2965	3120	3690	4580
	ϵ_{max}	21900	9800	9200	16200	8200
CHOAz	λ_{max}	2220	2290	3300	3850	
	ϵ_{max}	17800	17800	19100	6900	
CF$_3$COAz[b]	λ_{max}	2360	2770	3050	3260	3650	4030
	ϵ_{max}	33300	7700	15600	15700	10800	8200
CHOGuAz	λ_{max}	2430	2680	3420	4050	
	ϵ_{max}	19700	11200	16000	8600	

[a] The spectrum is for the diprotonated species; see text.   [b] Solvent is oleum (15% SO$_3$).

The indicator ratios were calculated from the relationship

$$I = [BH^+]/[B] = (\epsilon - \epsilon_B)/(\epsilon_{BH^+} - \epsilon)$$

where [B] and [BH$^+$] are molar concentrations of unprotonated and protonated forms, and ϵ, ϵ_B, and ϵ_{BH^-} are molar extinction coefficients of the solution and of the unprotonated and protonated azulenes at a given wave length, respectively.

Conversions from weight per cent perchloric acid to molarity and H_0 were made using the 25° density data of Markham for aqueous perchloric acid[8] and the H_0 data of Paul and Long.[9]

(8) A. E. Markham, J. Am. Chem. Soc., **63**, 874 (1941).
(9) M. A. Paul and F. A. Long, Chem. Rev., **57**, 1 (1957).

Table IV
Spectrophotometric Titration of 1-Cyanoazulene
1-cm. quartz cells; Cary 14 spectrophotometer; wave length 296 mμ

	Concentration of HClO$_4$			
	Wt. %	Moles/l.	$-H_0$	Log I
1	40.88	5.28	2.38	-1.784
2	44.15	5.86	2.74	-1.407
3	50.88	7.14	3.72	-1.201
4	51.78	7.32	3.85	-1.029
5	53.10	7.59	4.05	-0.894
6	55.28	8.05	4.37	-.353
7	55.70	8.14	4.44	-.326
8	56.08	8.22	4.49	-.248
9	56.02	8.21	4.48	-.228
10	56.35	8.28	4.53	-.073
11	57.12	8.45	4.66	+.045
12	57.24	8.48	4.67	+.130
13	57.80	8.60	4.76	+.254
14	58.16	8.69	4.83	+.392
15	58.70	8.81	4.91	+.591
16	60.50	9.24	5.23	+1.010
17	62.15	9.62	5.51	+1.557

Reagents and Compounds.—The azulenes have been described in the first paper of this series. Reagent grade 70% perchloric acid was used for the preparation of all acid solutions.

Results and Discussion

The available data indicate that in the presence of aqueous solutions of strong acids the azulenes undergo a reversible monoprotonation. As will be noted later, the presence of selected substituents can modify this statement, but does not change the basic conclusion. The previous paper summarizes qualitative evidence on this protonation. The quantitative studies of the ultraviolet spectra are in agreement with these conclusions and also indicate that, in general, medium effects on the spectra of the azulenes and azulenium ions are comparatively small. This is indicated by the observation that with increasing acidity, the absorption spectra of azulene exhibit three satisfactory isosbestic points.
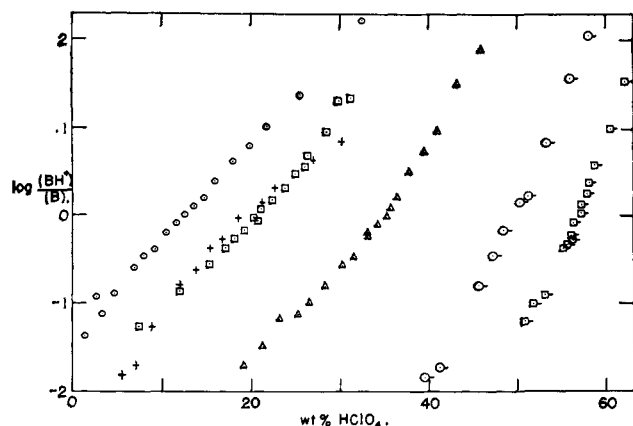
Fig. 1.—Log I vs. perchloric acid concentration for: methyl-azulene, $\odot$; 1-(p-dimethylammoniumbenzyl)-azulene, $+$; azulene, $\square$; 1-chloroazulene, $\triangle$; 1,3,5-trimethoxybenzene, $\odot$; 1-cyano-azulene, $\square$.

Similar behavior is shown by most of the azulenes studied.[10]

A second illustration that only relatively small medium effects are operative is shown by plots of the data in the form of spectrophotometric titration curves. At intermediate acidities the curves have the expected shape while at high and low acidity they asymptote to a constant value of the optical density, thereby indicating small medium effects.

Medium effects are slightly more evident for compounds protonating on the substituent, e.g., CHOAz and NO$_2$Az, as well as for the previously mentioned COOHAz. The effect on the spectrum of a gradual shift from a nonpolar to a highly polar solvent is particularly large for the 1-nitroazulene,[11] but the medium effects from changes in acidity of solutions of aqueous acids are not large even for this compound and a quite satisfactory equilibrium study can be made.

The compound 1-(p-dimethylaminobenzyl)-azulene represents a special case. At very low acidities this compound is protonated on nitrogen, leading to a substituted anilinium ion. This has only a slight effect on the ultraviolet spectrum as would be expected since the substituent is not in conjugation with the azulene structure. At considerably higher acidities there is a marked color change, due to protonation on the 3-carbon of the azulene skeleton. Hence in this case the protonation equilibrium is really of the type

$$\text{Me}\overset{+}{\text{N}}\text{HRAz} + \text{H}^+ = \text{Me}\overset{+}{\text{N}}\text{HRAzH}^+$$
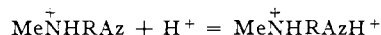
As can be seen in Fig. 1, the behavior of the protonation equilibrium for this case is very close indeed to that for the uncharged azulenes. This indicates that, for carbon protonation, the activity coefficient ratios $f_{\text{AzH}^+}/f_{\text{Az}}$ and $f_{\text{RAzH}^{+2}}/f_{\text{RAz}^+}$ are affected by solvent changes in a very similar way.

The results of the indicator ratio studies are summarized in Fig. 1 and 2 and Table V. Figure 1 includes only azulenes which protonate on carbon, although it does include for comparison the results of Kresge and Chiang for protonation of 1,3,5-trimethoxybenzene for which

Fig. 2.—Log I vs. perchloric acid concentration for: 1-formyl-azulene, $\odot$; 1-carboxylazulene, $\times$; 1-nitroazulene, $\square$.

carbon protonation is also postulated.[12] The essentially similar behavior of these compounds is evident. On an analogous plot to Fig. 1, but using an H_0 scale for the acid concentration, the log I data for azulenes which protonate on carbon lead to straight lines over extended ranges. The data occasionally depart from linearity at very large or very small values of the indicator ratios, but, in view of the experimental difficulties in precisely determining these extreme ratios, this is not surprising. We conclude that for all of the indicators of Fig. 1, log I is linear in H_0 within experimental error.

TABLE V

PROTONATION CHARACTERISTICS OF AZULENES

Compd.	Acidity where [BH$^+$]/[B] = 1		$-\dfrac{d \log I}{dH_0}$	Type of protonation[*]	
	C_{HClO_4}	$-H_0$		N.m.r.	Ultraviolet
MeAz	1.22	0.36	1.6	C	C
pDMABAz	2.16	.86	1.7	..	C
Az	2.30	.92	1.9	C	C
CHOAz	2.75	1.12	1.1	O	O
ClAz	4.17	1.80	1.8	C	C
NO$_2$TMAz	5.06	2.26	...	C	C
COOHAz	6.9	3.5	0.9	C?	C?
CNAz	8.36	4.59	1.8	C	C
NO$_2$Az	8.48	4.68	1.0	O	O

Table V summarizes the significant characteristics of these protonation equilibria. The listed acidities give the "half-protonation" value for each azulene; when given in H_0 units it can be thought of as a kind of uncorrected "pK" value. The slopes, $-$d log I/dH_0, result from plots similar to Fig. 1 but using H_0 acidities and it is noteworthy that for all of the azulenes of Fig. 1 this slope is in the range of from 1.6 to 1.9. In view of a similar high slope for protonation of trimethoxybenzene this large value of the slope appears to be characteristic of carbon protonation of aromatic molecules.[13]

Since the log I vs. $-H_0$ slopes for those azulenes which protonate on carbon differ considerably from unity, the value of H_0 at which $I = 1$ is not equal to pK for the acid. Fortunately the Hammett stepwise procedure for obtaining the pK values is still valid provided that the log I vs. acidity curves are parallel for the regions in which they overlap. This is evidently

(10) The situation with COOHAz illustrates a perturbing effect of a substituent. The spectra of this compound in a series of aqueous acid solutions leads to a reasonably satisfactory isosbestic point, but the curves for the least acidic solution and especially for a solution in pure water clearly miss the isosbestic intersection point. The reason is that in these latter solutions a significant fraction of the 1-carboxyl compound is present as a carboxylate ion and the ultraviolet spectrum of this, as confirmed by studies in solutions in dilute sodium hydroxide, is slightly different from that of the un-ionized acid.
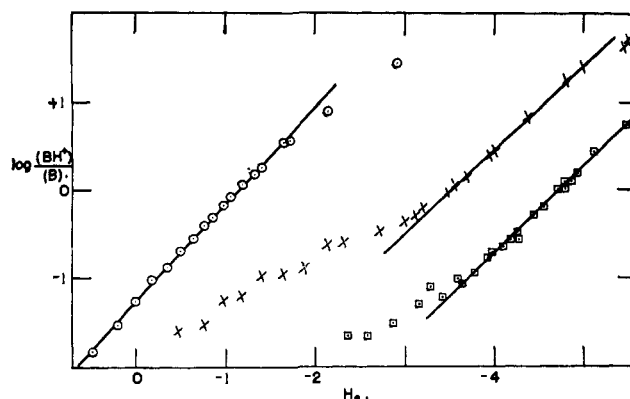
(11) J. Schulze and F. A. Long, to be published.

(12) A. J. Kresge and Y. Chiang, Proc. Chem. Soc., 81 (1961); also private communication from Dr. Kresge concerning some corrections to the data of this paper.

(13) It should be noted, however, that the reported high slope for 1,3,5-trimethoxybenzene is somewhat controversial. Schubert and Quacchia[14] have repeated the indicator ratio study and report that for solutions in 40 to 60% aqueous perchloric acid, $-$d log I/dH_0 has the value 1.26, substantially smaller than the Kresge and Chiang value of 2.0.

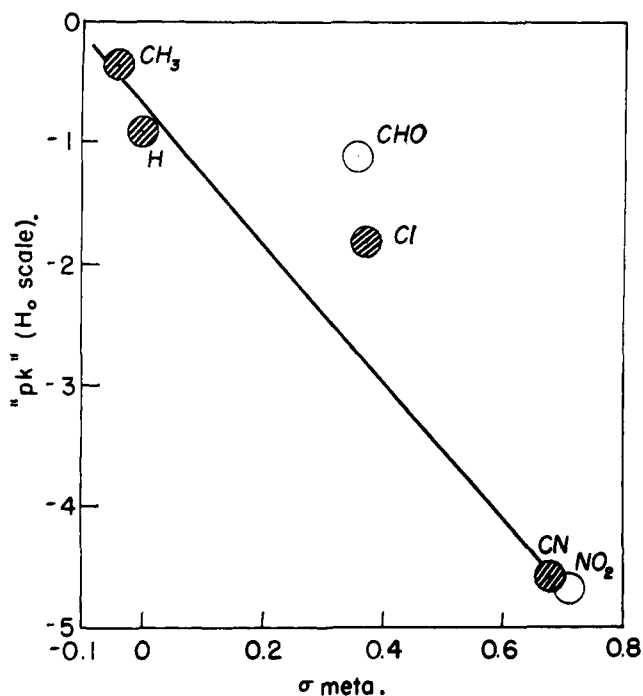(14) W. M. Schubert and R. H. Quacchia, J. Am. Chem. Soc., 84, 3778 (1962).

Fig. 3.—Apparent "pK" values of 1-substituted azulenes vs. σ_{meta} values for substituents. Filled circles are for azulenes which protonate on the 3-carbon; open circles are for protonation on oxygen of 1-substituent.

true for the species of Fig. 2. Thus, if the pK for one of the azulene cations is known, those for the others may be calculated from the relation

$$pK_2 - pK_1 = \log (I_2/I_1)_{const.\ acidity}$$

The thermodynamic pK of the methylazulene may be obtained by extrapolating the function ($\log I$ — $\log$ [H$^+$]) to infinite dilution in the manner proposed by Paul and Long.[15] This type of plot gives a satisfactorily linear extrapolation and leads to a pK for this acid of —0.83 at 25°. Use of this value and the stepwise procedure for the other species of Fig. 1 leads to the following approximate pK values: azulene, —1.7; p-dimethylaminobenzylazulene, —1.7; 1-chloroazulene, —3.4; 1,3,5-trimethoxybenzene, —5.1; 1-cyanoazulene, —6.8.

Figure 2 includes data for two azulenes which protonate on the oxygen of the 1-substituent, CHOAz and NO$_2$Az, and also data for one somewhat uncertain case, COOHAz. The important characteristic of the 1-formyl- and 1-nitroazulenes is that the slope —d log I/dH_0 is essentially unity; it is 1.1 for the first of these and 1.0 for the latter. Put another way, these species are behaving essentially as "Hammett bases" for which a slope of unity is expected. This sharp distinction between protonation of oxygen and protonation on carbon is not at all surprising, but to find the different behavior in such closely related compounds as two sets of substituted azulenes is a somewhat dramatic result.

The data of Fig. 2 for 1-carboxyazulene suggest that some additional complexity is entering for this case. At high acidities the log I data are linear in H_0 with a slope of 0.95. It is reasonable that at these higher acidities the carboxyl group is being protonated.[16] It is, however, inconsistent with the data of part I which, subject to some uncertainty, indicate protonation on carbon. Furthermore the log I data depart from linearity at I-values of about $^1/_4$ and produce an

(15) Reference 9, pp. 5–8.
(16) R. Stewart and K. Yates, J. Am. Chem. Soc., 82, 4059 (1960).

unusual lengthy "tail." For these reasons we conclude that further investigation of this compound is needed.

It is evident from Table V that there is a pronounced effect of substituents on the basicity of azulenes, both when the protonation is on carbon and when on a substituent. This is illustrated more directly in Fig. 3 which is σ–ρ plot of H_0 values for which $\log I$ = 0 (apparent "pK" values) vs. σ-values for a group of 1-substituents under the assumption that the σ-values for these are the same as the σ_{meta} values for the benzene system.[17] The straight line of the figure is drawn for only the species which protonate on carbon. The high numerical value of the slope, ρ = 6, indicates a marked dependence of acid strength on substituent.

The acid strength of 1-nitro-4,6,8-trimethylazulene is surprisingly low, i.e., a half-protonation H_0 value (Table V) of —2.26 relative to a value of —4.68 for 1-nitroazulene. As noted in part I, there is good evidence to support the belief that the trimethyl compound protonates on the substituted 1-position leading to structure II.[18] The presumed consequence of this is to relieve steric strain which otherwise exists between the nitro and the 8-methyl group, and therefore the stability of conjugate acid II should be higher, in agreement with the observed data.

The particularly interesting group of azulenes is that in which protonation occurs on an unsubstituted carbon. The point of specific interest is the acidity dependence of the protonation equilibria. The four compounds of this group which have been studied show slopes of log I vs. —H_0 of from 1.6 to 1.9 indicating that they do not behave like Hammett bases. Kresge,[12] considering his similar data for trimethoxybenzene, suggested that the appropriate acidity function to use was H_R', defined as H_R — log a_{H_2O}. This is a plausible suggestion on two counts. Firstly —H_R, and hence —H_R' which will differ only slightly from —H_R at intermediate and low acidities, increases with acid concentration at about twice the rate as —H_0. Thus the observed slopes of 1.6 to 1.9 are indicative of an approximate agreement with H_R'. Secondly, Deno, Groves, and Saines[19] noted that the protonation of diaryl olefins follows H_R' rather well, and this reaction is closely comparable to the protonation of aromatic hydrocarbons.

Detailed consideration of the problem suggests, however, that neither H_R nor H_R' should be a truly satisfactory function for hydrocarbon protonation. The protonation equilibrium from which they derive is of the type

$$ROH + H^+ = R^+ + H_2O$$
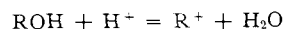
and the two functions are defined as

$$H_R = -\log C_{H^+}f_{H^+}f_{ROH}/f_{R^+}a_{H_2O}$$

$$H_R' = H_R - \log a_{H_2O} = -\log C_{H^+}f_{H^+}f_{ROH}/f_{R^+}$$

where f_{ROH} and f_{R^+} are activity coefficients for the carbinol and carbonium ion species, both referred to a standard state of infinite dilution. If the H_R' function is to be appropriate to hydrocarbon protonation, then for the acidity range of interest the ratio f_{ROH}/f_{R^+} must be a good surrogate for the ratio f_M/f_{MH^+} where M is a hydrocarbon base.

The rather obvious reason why the H_R' acidity function need not and probably will not be appropriate for hydrocarbon bases has to do with the fact that the basic species is itself a carbinol. Studies of the activity coefficients of neutral species in the presence of strong acids or other electrolytes have shown a marked specificity of behavior, one obvious reason being differences

(17) H. H. Jaffé, Chem. Rev., 53, 191 (1953).
(18) J. Schulze and F. A. Long, Proc. Chem. Soc., 532 (1962).
(19) N. C. Deno, P. T. Groves, and G. Saines, J. Am. Chem. Soc., 81, 5790 (1959).

in hydrogen bonding.[20,21] The role of hydrogen bonding in determining the activity coefficient behavior has been considered in some detail recently by Deno and co-workers as has the implication of the results to acidity functions.[22,23] They emphasize that a major term to be considered for all activity coefficients is the volume term, a point which had been given extensive treatment by McDevit and Long.[24] In addition to this term which enters for all species and which has to do only with their size, Deno, *et al.*, argue that the most important single term is one involving hydrogen bonding. Since carbinols will be heavily involved in hydrogen bonding, this implies that an acidity function which contains an activity coefficient term for carbinol will

(20) L. P. Hammett and R. Chapman, *J. Am. Chem. Soc.*, **56**, 1282 (1934).

(21) N. C. Deno and C. Perizzolo, *ibid.*, **79**, 1345 (1957).

(22) N. C. Deno, H. E. Berkheimer, and Ch. Spink, to be published.

(23) N. C. Deno and Ch. Spink, to be published.

(24) (a) W. F. McDevit and F. A. Long, *J. Am. Chem. Soc.*, **74**, 1773 (1952); (b) F. A. Long and W. F. McDevit, *Chem. Rev.*, **51**, 119 (1952).

probably be substantially different from one involving only hydrocarbon species. Arguments of this sort led Deno, *et al.*, to conclude that perhaps the simplest and most general acidity function would be one in which the basic species was simply a hydrocarbon and the conjugate acid was simply the protonated form of this.

The data of Fig. 1 involve bases and conjugate acids which fall in this category. They can, in fact, be used to generate an acidity function and the resulting function differs significantly both from H_R and H_R'. Detailed discussion of this function will, however, be postponed, partly because of uncertainties encountered with one of the indicators of Fig. 1[13] and also because of other recent illustrations of unusual indicator behavior,[25] all of which suggest the need for some further study of base systems before presenting this acidity function development.

(25) R. L. Hinman and J. Lang, *Tetrahedron Letters*, **21**, 12 (1960); Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961, p. 98Q.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.]

Hydrogen Exchange of Azulenes. III. Kinetics and Mechanism of the Acid-Catalyzed Detritiation Reaction[1,2]

BY JANOS SCHULZE AND F. A. LONG

RECEIVED MAY 4, 1963

The detritiation of azulene-H³(1) is general-acid catalyzed and in aqueous formate–formic acid buffers at 25° the first-order rate coefficient is $k_{obsd} = 0.183C_{H^+} + 1.16 \times 10^{-3}C_{HFm}$. From temperature coefficient studies, the Arrhenius parameters for the catalysis by strong acids are: $E_A = 16.0$ kcal. mole^{-1} and $\Delta S^* = -10$ cal. deg.$^{-1}$ mole^{-1}. For catalysis by both strong and weak acids the ratio of rates for deuterium exchange to tritium exchange is $k^D/k^T = 2$. The strong acid-catalyzed exchange of tritium is 1.61 times faster in the solvent D_2O than H_2O; in intermediate H_2O–D_2O mixtures the rate ratios are in accord with predictions of the Gross–Butler theory. By combining the results for kinetic hydrogen isotope and solvent hydrogen isotope effects and assuming an A-S$_E$2 mechanism *via* a conjugate acid intermediate, it is possible to calculate isotope effects for the rate coefficients for the individual steps. The numerical results are very similar to those reported recently by Kresge and Chiang for detritiation of 1,3,5-trimethoxybenzene. Detritiation rates for 1-nitro-, 1-formyl-, and 1-cyanoazulene are much slower than for azulene and in aqueous perchloric acid the rates follow the Hammett acidity function with log k *vs.* $-H_0$ slopes of from 1.05 to 1.2. The considerable differences between the acidity dependence of the kinetics of hydrogen exchange and of equilibrium protonation for these molecules is consistent with the fact that some of them protonate on oxygen and others on carbon. The kinetic and isotopic effects for the hydrogen exchange of azulenes are closely similar to those for several other aromatic proton exchange reactions and it is concluded that the A-S$_E$2 or "orthodox" mechanism applies in all the cases so far reported.

Introduction

The acid-catalyzed rate of exchange of the hydrogens of aromatic molecules has had extensive investigation in recent years for at least two reasons. One is that the reaction represents a particularly simple example of electrophilic aromatic substitution and its mechanism is therefore of considerable interest. A second reason is that the reactions normally occur at a measurable rate for concentrated aqueous solutions of strong acids so that the observed kinetics can aid in understanding the role of acidity functions both in general and as they apply to this class of reaction. The general problem of the application of acidity functions and a consideration of some of the early results for this particular reaction were considered in an early review.[3] In addition, the aromatic hydrogen exchange reaction has itself been recently reviewed *in extenso*.[4] Of the various research groups who have contributed to the understanding of this reaction, the discussions of those associated with

(1) Work supported by a grant from the Atomic Energy Commission.

(2) Presented in part at the 139th and 140th Meetings of the American Chemical Society, St. Louis, Mo., April, 1961, and Chicago, Ill., September, 1961.

(3) F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957).

(4) V. Gold, "Aromatic Hydrogen Exchange. Vol. II. Friedel–Crafts and Related Reactions," Interscience Publishers, London, 1963.

Gold,[5] Melander,[6,7] Eaborn[8], and Kresge[9] are particularly relevant to the present considerations.

A major problem from a mechanism standpoint has been that with most aromatic molecules the exchange rate does not become measurable until concentrated solutions of strong acids are utilized. This forces attention on questions of appropriate measurements of acidity. It also precludes utilization of the simplicities inherent in dilute solution studies: ideal behavior, unity value for activity coefficients, etc. The significance of this point arose early in the discussion of mechanisms. Gold and co-workers had found that for many benzene derivatives the rate of exchange of the aromatic hydrogens followed the Hammett acidity function h_0 to very nearly the first power.[6] Applying the Zucker–Hammett hypothesis they concluded that an A-1 reaction mechanism was indicated, implying that the reaction involved a pre-equilibrium proton

(5) V. Gold, R. W. Lambert, and D. P. N. Satchell, *J. Chem. Soc.*, 2461 (1960), and earlier references therein.

(6) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1959.

(7) L. Melander and S. Olsson, *Acta Chem. Scand.*, **10**, 879 (1956).

(8) C. Eaborn and R. Taylor, *J. Chem. Soc.*, 3301 (1960).

(9) (a) A. J. Kresge and Y. Chiang, *J. Am. Chem. Soc.*, **83**, 2877 (1961); **81**, 5509 (1959); (b) *Proc. Chem. Soc.*, 81 (1961); (c) *J. Am. Chem. Soc.*, **84**, 3976 (1962).