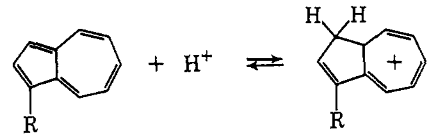
# The Protonation Equilibria of Azulene-1-carboxylic Acid[1]

**J. L. Longridge and F. A. Long[2]**

*Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. Received November 29, 1967*

**Abstract:** Azulene-1-carboxylic acid is stable in aqueous solutions of high pH. Its p*K* at 25° is 5.5, as determined by both titration and spectroscopic procedures. In dilute aqueous acid solutions, *e.g.*, $C_{H^+}$ of from 0.01 to 5 *M*, it decarboxylates slowly. At higher acidities there is a further protonation to give a stable conjugate acid. The nmr spectra for this species confirm that this protonation occurs on the carbon at the 3 position, *i.e.*, on the ring and not on the side chain. Half-protonation occurs at an $H_0$ value of −3.85, and the slope of the indicator ratio $d[C_{AzCO_2H_2^+}/C_{AzCO_2H}]/d(-H_0)$ is 1.1, *i.e.*, close to that found for a typical Hammett base. Very similar results are found for protonation of the ethyl ester. These protonation slopes are well below the values of from 1.6 to 1.9 normally observed for aromatic carbon bases. Analysis in terms of the activity coefficients of the species involved suggests that the probable explanation is extensive solvation, due to hydrogen bonding, of the species $AzCO_2H_2^+$ as compared to such simpler cations as $AzH^+$ formed from unsubstituted azulene. At still higher acidities the acid undergoes a slow reversible dehydration to form the species $AzCO^+$, and a mechanism is advanced to explain the slowness of the process. In concentrated sulfuric acid there is a still slower irreversible reaction which is most probably a sulfonation of the azulene ring.

The protonation of azulenes has been extensively studied by a number of techniques,[3,4] and the characteristics of the process



are well established. On the basis of their measurements on a large series of substituted azulenes, Schulze and Long[4] were able to characterize the compounds into those which protonated on the carbon ring and those which protonated on the side-chain substituents. Among the compounds studied was azulene-1-carboxylic acid ($AzCO_2H$), but for this compound the results were inconclusive. Nmr studies, although not completely unambiguous,[5] indicated ring-carbon protonation. This conclusion was supported by the general character of the uv spectral change, where a large characteristic peak was observed at 260 mμ on protonation.[6]

Evidence which is, however, more consistent with side-chain oxygen protonation came from spectrophotometric measurement of the variation of the protonation ratio $BH^+/B$ as a function of acidity. Azulenes shown to protonate on carbon have log $[BH^+/B]$ *vs.* $-H_0$ gradients of from 1.6 to 1.9. Azulene-1-carboxylic acid exhibited a much lower slope of 0.9, a value which is close to that found for azulenes which protonate on the side chain.[7] In addition to exhibiting an anomalously low slope, the graph for protonation of this compound was far from linear, deviating badly at lower acid concentrations. In view of the inconsistent behavior of this compound, a reinvestigation and extension of these studies was undertaken.

## Preparation of Materials and Experimental Procedure

All chemicals were reagent grade and unless specified were used without further purification.

**Azulene-1-carboxylic Acid ($AzCO_2H$).** The initial sample was generously supplied by Dr. D. H. Reid. Further samples were prepared and purified by the method of Anderson[8] using quantities of reagent similar to those employed by Leermakers and Bowman.[9] The compound melted at 181–182° in agreement with the value of Anderson. Spectral checks proved identical with data reported in the literature.

**Ethyl 1-azulate ($AzCO_2Et$)** was prepared from the acid using the same quantities and procedures as those of Leermakers and Bowman.[9] Spectral checks were again identical with the literature.

Conductivity measurements were made using three cells with approximately 5-ml capacities with varying cell constants determined using potassium chloride. The apparatus consisted of a 1-kc oscillator, a Campbell-Shackleton ratio bridge, a Leeds and Northrup precision resistance box, and a Tektronics oscilloscope as a detector. Samples for measurements were prepared and the cells filled in a glove box to prevent contamination by moisture.

The proton magnetic resonance spectra were measured using a Varian A-60 spectrometer operating at 60 Mc/sec.

Two techniques were used to determine the p*K*. These were modifications of standard procedures, required because of the relatively low solubility of $AzCO_2H$ ($1.7 \times 10^{-4}$ mole/l.). The first used a direct titration method: 1 l. of saturated aqueous $AzCO_2H$ solution in $10^{-3}$ *M* perchloric acid was titrated with 0.1 *N* standard NaOH using a microsyringe and a pH meter. A blank titration was also made with no carboxylic acid present. From the difference in the volume of the base added at a given pH, the relative concentration of the anion and acid forms of the carboxylic acid could be determined, enabling the p*K* to be calculated. In the second technique, the ratio of acid and anion concentrations was measured spectrophotometrically. A large reservoir of aqueous solution of $AzCO_2H$ was connected to a "flow through" spectrophotometer cell. The pH of the solution, varied by direct addition of concentrated acid and base to the reservoir, was continuously followed using a pH meter. As a 1-l. reservoir of solution was used, the change in total volume of the system due to the addition of acid or base could be neglected. Thus the spectrophotometric changes in the solution could be followed as a function of pH. The p*K* was assumed to be the pH at which $OD_{soln} = \frac{1}{2}(OD_{HA} + OD_A)$. Good agreement was found for data obtained by the two methods.

A Radiometer PHM4c pH meter was used throughout the study.

All spectrophotometric measurements were made on a thermostated Cary 14 instrument at 25 ± 0.1°.

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[1] Work supported by a grant from the Atomic Energy Commission.

[2] To whom requests for reprints should be made.

[3] See E. Heilbronner, "Non-benzenoid Aromatic Hydrocarbons," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, Chapter 5.

[4] (a) J. Schulze and F. A. Long, *J. Am. Chem. Soc.*, **86**, 322 (1964); (b) F. A. Long and J. Schulze, *ibid.*, **86**, 327 (1964).

[5] See ref 4a, Figure 2.

[6] See ref 4b, Table III.

[7] See ref 4b, Figure 2 and Table V.

[8] A. G. Anderson, *Proc. Chem. Soc.*, 72 (1960).

[9] P. A. Leermakers and W. A. Bowman, *J. Org. Chem.*, 29, 3708 (1964).

## Results and Discussion

The equilibrium properties of azulenecarboxylic acid can be conveniently discussed in terms of three regions depending on acidity: aqueous solutions of low acidity; concentrated acid solution (1–12 *M*) where protonation is observed; and concentrated sulfuric acid where dehydration occurs.

In aqueous solutions of low acidity the compound has the properties of a normal aromatic carboxylic acid. The p*K*, determined by direct titration of dilute aqueous solution, was found to be 5.5 ± 0.1. Spectrophotometric measurement was also possible as there are small spectral changes associated with the ionization process. Peaks at 287 and 292 m$\mu$ are formed and the 300-m$\mu$ peak is increased and displaced to 297.5 m$\mu$. Thus by measuring the absorption change at 287 m$\mu$ as a function of pH, the p*K* could be determined. The value from this procedure was found to agree exactly with the titration value, *i.e.*, $pK = 5.5 \pm 0.1$.

A measurement of the p*K* in a mixed solvent had previously been made by Leermakers and Bowman.[9] In 50% ethanol they found that the p*K*'s of azulenecarboxylic acid and benzoic acid were 6.67 and 5.46, respectively. Using the p*K* value for benzoic acid in water, 4.20,[10] and assuming that $\Delta pK$ is independent of change in solvent, this would predict a value of $pK_{AzCO_2H}$ in water of 5.4 which is in good agreement with the observed value.

The second equilibrium region of importance for azulenecarboxylic acid is that of relatively high acidity where both uv and nmr spectral properties suggest that further protonation occurs. In the previous studies, the data were interpreted as due to protonation on the 3-carbon of the azulene ring, although the earlier nmr investigation[5] contained two features which caused some uncertainty. The reported spectra in 9:1 $CF_3CO_2H$–$H_2SO_4$ showed a peak in the 4-ppm region characteristic of a methylene group, but this was strictly a doublet. In addition, a large unidentified peak was observed in the same 4-ppm region for the nonprotonated compound in acetone-$d_6$. These spectra have now been remeasured. The general character of the spectra were closely similar to the original Schulze and Long data. However, the spectra observed in the present study did reveal two important features not previously noted. In 9:1 $CF_3CO_2H$–$H_2SO_4$ the nmr investigation shows a single methylene peak in the 4-ppm region of the spectrum not a doublet.[5] In addition the spectrum in this region is found to change slowly with time, indicating that decomposition or reaction is occurring. After 4 hr the peak initially present at 4 ppm had disappeared completely. Thus the nmr spectrum reported by Schulze and Long would be expected to be a function of the time delay between mixing and measurement. The spectrum was also determined in 72% perchloric acid and the characteristic methylene singlet at 4 ppm was again observed. This was found to be completely stable over a 24-hr period. The second feature of importance concerns the nature of the confusing 4-ppm peak previously reported for the neutral molecule in solutions of acetone-$d_6$. A peak at 3 ppm was found to be characteristic of the solvent. This peak was displaced to 4 ppm by the addition of the $AzCO_2H$. Addition of water or $D_2SO_4$ to the solvent produced no new peaks in this region, only a similar displacement. Thus this peak is not in any way characteristic of the compound in solution and is probably due to the presence of moisture in these solvent. These nmr studies thus confirm that protonation in concentrated acid solutions occurs on the carbon ring at position 3 (the most basic unsubstituted site available).

There remains the apparent difficulty, with the previously observed spectrophotometric data,[7] that the gradient of the log $[BH^+/B]$ *vs.* $-H_0$ graph for azulene-1-carboxylic acid is very similar to 1-formylazulene and 1-nitroazulene compounds whose protonation has been established as being on oxygen. The previous equilibrium protonation measurements were therefore repeated with particular attention to the stability of the solutions being measured. The spectra of $AzCO_2H$ in water and 72% $HClO_4$ were in close agreement with previous data, and the compounds appeared to be completely stable in both solvents. However, in more dilute acid solutions the compound was found to be unstable. Spectroscopic studies of the reaction in dilute acid showed that the spectral change had good isosbestic points, and the spectrum of the compound formed could be firmly identified as that of azulene. In other words, a decarboxylation process occurs in dilute acid solutions. This is not unexpected as aromatic elimination reactions frequently occur when there is a bulky substituent in a position *ortho* to that being eliminated,[11] as is the case of $AzCO_2H$.

In view of this instability, the equilibrium protonation was remeasured using a technique which involved the extrapolation of the optical density data back to zero time. Three wavelengths were used, 300, 340, and 355 m$\mu$, and these gave identical results within experimental error. Data obtained at 300 m$\mu$ are presented in Figure 1 together with the original Long and Schulze measurements. From the figure it is evident that the "tail" previously observed in dilute solution has been eliminated. However, the slope remains essentially unchanged at a value of 1.1. The $-H_0$ value for half-protonation ($C_{BH^+}/C_B = 1$) was found to be 3.85, in good agreement with earlier results.

These studies were repeated for the ethyl ester of the acid. Half-protonation occurred at virtually the same value of $H_0 = -3.85$, and the slope of plots of log $[C_{BH^+}/C_B]$ *vs.* $-H_0$ was again 1.1, as Figure 1 shows. We conclude that for both cases carbon protonation occurs and that the slope indeed has a value of approximately unity.

The question remaining to be answered is whether this observed slope is really inconsistent with the previous measurements for protonation of azulenes.[4b] Leaving out of consideration the $AzCO_2H$ results, Schulze and Long were able to characterize the azulenes which they studied into two groups: those with $-d \log(BH^+/B)/dH_0$ slopes in the region 1.6–1.9 and a second group of two compounds, 1-formyl- and 1-nitroazulene, with slopes of virtually unity. As the latter two compounds were found to protonate on the side chain, the suggestion was that the protonation slope might provide a distinction as to the site of protonation of the molecule. This interpretation implicitly assumes that an activity coefficient term of the type $f_{BH^+}/f_B$ differs quite markedly depend-

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[10] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth & Co., Ltd., London, 1955, p 496.

[11] W. M. Schubert, *J. Am. Chem. Soc.*, 71, 2639 (1949).

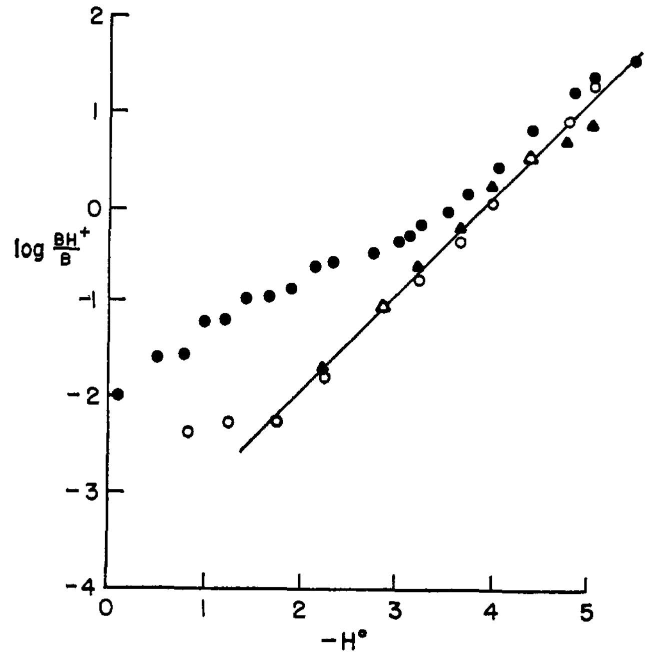

Figure 1. Equilibrium protonation of $AzCO_2H$ and $AzCO_2Et$ in perchloric acid: ○, $AzCO_2H$; ▲, $AzCO_2Et$; ●, data for $AzCO_2H$ (Long and Schulze[4b]).

ing on whether ring or side-chain protonation is occurring. More detailed analysis of the problem suggests that this is a doubtful assumption.

To discuss the situation more specifically, consider a general acid ionization of the type $RH^+ = R + H^+$, and let the species B and R refer to a Hammett indicator base and a typical carbon base, respectively. The indicator ratio $I$ is defined generally as $I = [RH^+]/[R]$; then, using the definition of $H_0$, one can write

$$\frac{d(\log I)}{d(-H_0)} = 1 + \frac{d[\log (f_R f_{BH^+}/f_{RH^+} f_B)]}{d(-H_0)} \qquad (1)$$

In other words, the departure from unity of the slope of a log $I$ *vs.* $-H_0$ plot depends directly on the behavior of the activity coefficient ratio $f_{RH^+}/f_R$ relative to the similar ratio for a Hammett indicator.

Several previous studies[12-14] have established that these activity ratios are markedly a function of the type of molecules involved. In discussing the contributions which the individual activity coefficients make to the over-all effects, it is convenient to consider separately the relative contributions of $f_{BH^+}/f_{RH^+}$ for the conjugate acids and $f_R/f_B$ for the neutral bases.

In the general case, the value of the activity coefficient of an ion or molecule in solution is influenced by a number of factors which can formally be represented by the equation[15,16]

$$\log f_S = \log f_V + \log f_E + \log f_H$$

where $f_S$ = activity coefficient of the species, $f_V$ = molecular volume contribution, $f_E$ = ion–dipole contribution, and $f_H$ = solvation contribution. For nonpolar molecules, the correlation between the variation of $f_S$ and the molecular volume has been quite successful.[17] For polar molecules an additional contribution from ion–dipole interactions, $f_E$, is present. Theoretical calculations have been made by Debye and Kirkwood to take this into consideration.[15] These studies combined with some more recent experimental data enable certain predictions to be made regarding the variation of activity coefficients of neutral molecules with particular reference to substituted azulenes. The measurements of Deno and Perizzolo[18] and McDevit and Long[15] illustrate that changes in $f_S$ with acidity are small. For example, d log $f_S$/d(% $H_2SO_4$) ≈ 0.02 for benzene, and similarly small variations were reported for benzoic acid[15] and aromatic amines.[19] Since these latter species are relatively polar, the contribution to $f_S$ due to ion–dipole forces, $f_E$, and to hydration of functional groups, $f_H$, must be almost negligible. Comparing these data with measurements for azulene,[20] d log $f_S$/d(% $H_2SO_4$) ≈ 0.013, it is evident that effects due to ion–dipole interactions must be of a minor importance in this case also. Thus, provided that the bases considered are neutral and of similar molecular size, the variations of $f_R$ and $f_B$ with acidity would be expected to be small and closely similar. The ratio $f_R/f_B$ would, therefore, be expected to have only a small influence on the over-all term, $(f_R/f_B)(f_{BH^+}/f_{RH^+})$.

For the conjugate acids, the presence of a positive charge suggests that in addition to the contributions to $f_S$ and $f_V$ and $f_E$ terms, there will be a larger $f_H$ term due to stronger solvation *via* hydrogen bonding. Thus variations of $f_{RH^+}$ as a function of acidity depend to a much greater extent on the presence of functional groups which are able to form hydrogen bonds with the solvent. This point is well illustrated by the measurements of Boyd[19] which show that for Hammett indicators, which should be strongly hydrogen bonded to the solvent *via* the $-NH_3^+$ group, large positive deviations of log $f_{BH^+}$ as a function of increasing acidity occur. Poorly solvated cations, *e.g.*, $(p\text{-}MeOC_6H_5)_3C^+$, on the other hand, show little variation in $f_{RH^+}$ as the acidity changes.

Applying these general considerations to the case in question enables a rationalization of the observations to be made. Application of eq 1 to the experimental data for azulenecarboxylic acid and azulene[4b] gives

$$\frac{d}{d(-H_0)} \log \left[\frac{f_{AzCO_2H}}{f_{AzCO_2H_2^+}} \frac{f_{BH^+}}{f_B}\right] = 0.1 \qquad (2)$$

$$\frac{d}{d(-H_0)} \log \left[\frac{f_{Az}}{f_{AzH^+}} \frac{f_{BH^+}}{f_B}\right] = 0.7 \qquad (3)$$

Thus for direct comparison

$$\frac{d}{d(-H_0)} \log \left[\frac{f_{Az}}{f_{AzH^+}} \frac{f_{AzCO_2H_2^+}}{f_{AzCO_2H}}\right] = 0.6 \qquad (4)$$

As $AzCO_2H$ and Az are closely similar in molecular volume, using the previously mentioned concepts for uncharged bases, $f_{Az}/f_{AzCO_2H}$ can to a first approxi-

(12) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, 77, 3044 (1955).

(13) See ref 4b, Figure 1, and M. T. Reagan and F. A. Long, unpublished data.

(14) R. H. Boyd, *J. Am. Chem. Soc.*, **53**, 4288 (1961); *J. Phys. Chem.*, 67, 737 (1963).

(15) W. F. McDevit and F. A. Long, *Chem. Rev.*, **51**, 119 (1952).

(16) N. C. Deno, private communication.

(17) W. F. McDevit and F. A. Long, *J. Am. Chem. Soc.*, **74**, 1773 (1952).

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

(19) R. H. Boyd, *ibid.*, **85**, 1555 (1963).

(20) R. J. Thomas and F. A. Long, unpublished results.

mation be neglected; thus

$$\frac{d}{d(-H_0)} \log \left[\frac{f_{AzCO_2H_2^+}}{f_{AzH^+}}\right] \approx 0.6 \qquad (5)$$

A value of this magnitude would only be expected if $AzCO_2H_2^+$ was salted out to a much greater extent than $AzH^+$. This observation is consistent with our generalization on hydration. The species $AzH^+$ should be poorly solvated; hence $f_{AzH^+}$ would show little variation with change in acidity. In the case of $AzCO_2H_2^+$, solvation can occur *via* the $CO_2H$ group; hence a large salting-out effect would be expected. Equation 2 shows that the salting out of $AzCO_2H_2^+$ does not in fact differ markedly from that for the Hammett indicator $BH^+$.

Following these arguments, a most significant feature of the protonated forms of nitro- and formylazulene is that the respective side chains $NO_2H$ and CHOH are capable of interacting with the solvent in a manner similar to $CO_2H$. Thus if solvation *via* functional groups, rather than molecular arrangement, is the dominant property which determines protonation characteristics, then the d log $I/d(-H_0)$ slope for $AzCO_2H$ would be expected to be similar to data for these two compounds rather than a nonsolvated azulene. This has been observed experimentally to be the case.

Utilizing data from other studies, some semiquantitative predictions can be made with regard to hydrogen-bond formation. In this respect, the data for protonation of phloroglucinol and its ethers[21,22] are useful from two standpoints. The data show first of all, that the carbon protonation d log $I/d(-H_0)$ slope of 1.1 for azulenecarboxylic acid is not unique. Secondly, as the authors in this case also explain the observed variation of the slopes in terms of hydration of the cation, an analogy can be made between this example and that of azulenes. The phloroglucinol system has one special feature, namely that the number of sites available for hydrogen bonding of the cation can be varied in the series by ether formation. Thus d log $I/d(-H_0)$ data for the non-, mono-, di-, and trihydroxy compounds gives an indication of the effect of increasing hydration of the cation on the characteristics of the protonation slope. Unfortunately the agreement between the various studies on these systems is not very satisfactory. The trimethoxybenzene data are especially poor, a d log $I/d(-H_0)$ slope of 1.26 being obtained by Schubert compared with a value of 1.6 calculated from the Kresge data by converting for $H_R'$ to $H_0$. Recent measurements in sulfuric acid[23] gave a slope of 1.5, indicating that the Schubert value may be low. Although uncertainties of this magnitude severely limit quantitative predictions, the data are still able to give an indication of the direction and approximate size of the hydration effect. From previous considerations, it would be expected that the most dramatic change in protonation slope would occur between compounds having a nonsolvated cation and those having a cation with one functional group available for hydrogen bonding with the solvent, as shown by the Kresge d log $I/d(-H_0)$ data (triethoxybenzene, $\backsim$1.7; diethoxyphenol, $\backsim$1.3; phloroglucinol, $\backsim$0.85). Using these data to calculate the effect of an increase of one solvation site on the cation, one obtains

$$\frac{d}{d(-H_0)}\left[\frac{f_{R^+(OH)}}{f_{R^+}}\right] \approx 0.4$$

This result can be compared with the value of eq 5 for the azulenecarboxylic acid–azulene case where a value of $\sim$0.6 was obtained. The agreement between these values, which is quite reasonable in view of the assumptions and uncertainties involved, substantiates our interpretation of the carboxylic acid data.

One important conclusion to come out of this study is that protonation on carbon with characteristics close to a Hammett base is not unreasonable when appreciable solvation of the cation occurs. Thus the distinction between side chain and ring protonation on the basis of d log $I/d(-H_0)$ slopes cannot be made, solvation playing a more important role than molecular arrangement in determining the variation of $f_{RH^+}$.

The final equilibrium of interest is that established in concentrated sulfuric acid. Conductivity measurements in 100% $H_2SO_4$ show much larger changes on addition of $AzCO_2H$ than would be anticipated by simple protonation,[24] suggesting 3- or 4-proton addition, which does not seem reasonable. This has been interpreted in terms of a dehydration reaction

$$AzCO_2H + H_2SO_4 \rightleftarrows AzCO_2H_2^+ + HSO_4^-$$

$$AzCO_2H_2^+ \rightleftarrows Az^+CO + H_2O$$

$$H_2O + H_2SO_4 \rightleftarrows H_3O^+ + HSO_4^-$$

This type of behavior has been reported for a number of carboxylic acids.[25] For most such compounds, the formation of $R^+CO$ only occurs in oleum solutions of varying strengths. However, for substituted benzoic acids the reaction can occur at lower acidities. This has been observed both cryoscopically[26,27] and spectrophotometrically[11] for mesitoic acid.

An interesting feature of the reaction in the present case is that in contrast to most of the other systems studied this equilibrium is not rapidly established. A

$$AzCO_2H_2^+ \rightleftarrows Az^+CO + H_2O$$

gradual spectral change is observed over a period of approximately 2 hr. This has good isosbestic characteristics, peaks at 212, 255, and 355 mμ being replaced by peaks at 230, 270, 300, and 335 mμ; the largest new maximum develops at 300 mμ (*cf.* 280 mμ for mesitoic acid). This process is completely reversible, dilution of the solution in $H_2SO_4$ with water regenerating the spectrum of $AzCO_2H$ in dilute acid solutions. In 95% $H_2SO_4$ at 25° the observed rate constant measured spectrophotometrically using the 300-mμ peak was found to be $3.5 \times 10^{-2}$ min$^{-1}$. The initial uv–visible spectra in sulfuric acid and perchloric acid are identical, suggesting that the same protonated species is present in both solutions. We believe that the dehydration equilibrium is established slowly because of the predominance of the carbon protonated form of the cation in $H_2SO_4$ solution. In order for dehydration to occur, the reaction must proceed *via* an oxygen-

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[21] A. J. Kresge, G. W. Barry, K. R. Charles, and Y. Chiang, *J. Am. Chem. Soc.*, **84**, 4343 (1962).

[22] W. M. Schubert and R. H. Quacchia, *ibid.*, **84**, 3778 (1962).

[23] M. T. Reagan and F. A. Long, unpublished data.

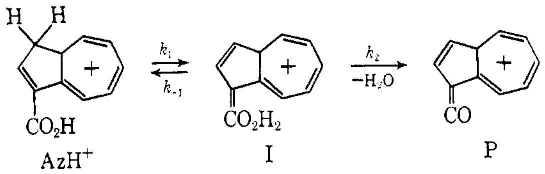
[24] See ref 4a, Figure 1.

[25] N. C. Deno, C. U. Pittman, Jr., and M. J. Wisotsky, *J. Am. Chem. Soc.*, **86**, 4370 (1964).

[26] H. P. Treffers and L. P. Hammett, *ibid.*, **59**, 1708 (1937).

[27] M. S. Newman, *ibid.*, **63**, 2431 (1941).

protonated intermediate present in low concentrations in solution, *i.e.*



Using the steady-state approximation

$$\frac{d[I]}{dt} = 0 = k_1[AzH^+] - (k_{-1} + k_2)[I]$$

therefore

$$[I] = \frac{k_1[AzH^+]}{k_{-1} + k_2}$$

$$\frac{d[P]}{dt} = k_2[I] = \frac{k_1k_2[AzH^+]}{k_{-1} + k_2}$$

As $k_{-1} \gg k_2$

$$\frac{d[P]}{dt} = \frac{k_1k_2[AzH^+]}{k_{-1}} = Kk_2[AzH^+]$$

Thus provided $K$ is very small, as spectral studies indicate, the dehydration would proceed slowly.

In addition to dehydration, a still slower process has also been observed in concentrated solutions of sulfuric acid. This process is nonreversible and proceeds with a rate constant of $3.7 \times 10^{-3}$ min$^{-1}$, the large difference in the rates enabling this reaction and the dehydration to be separated. The product for the reaction has not been identified, but its high solubility in water suggests a sulfonate. In addition, the spectra in water and $H_2SO_4$ closely resemble data for the 1,3-disulfonate of azulene[28] (Table I). It seems very probable that this final slower, irreversible process represents a sulfonation reaction.

**Table I.** Sulfonation Product Spectra[a]

| | Wavelength of peaks, mμ | | | | | |
|---|---|---|---|---|---|---|
| $H_2O$ | 275 (l) | 280 (l) | 285 (l) | 290 (l) | 340 (s) | 355 (s) |
| $H_2SO_4$ | 230 (vl) | 268 (l) | 282 (s) | 300 (s) | 320 (m) | 355 (s) |

[a] The symbols in parentheses give a rough intensity indication, ranging from very large (vl) to small (s).

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(28) K. Zimmerman, Ph.D. Thesis, No. 2199 Eidgenoissischen Technischen Hochschule, Zurich, 1953.

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# The Decarboxylation of Azulene-1-carboxylic Acid in Acidic Aqueous Solution[1]

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*Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850.* *Received November 29, 1967*

**Abstract:** Azulene-1-carboxylic acid decarboxylates at a measurable rate at 25° in aqueous solution over a wide range of acidity. In dilute solutions of a strong acid (0.001–0.03 *M*) the reaction is acid catalyzed, but at slightly higher acidities (0.06–0.3 *M*) the reaction becomes independent of acid concentration. At still higher acid concentrations (0.5–6.0 *M* $HClO_4$ or $H_2SO_4$), a gradual increase in rate is observed for which $d \log k/d(-H_0) = 0.3$, but this increase is the consequence of a positive salt effect superimposed on the pH-independent reaction. An increase in acidity beyond 6 *M* causes a rapid decrease in rate of decarboxylation due to the equilibrium formation of a stable cation by protonation of the ring at the 3-carbon. The rate data at low acidities are quantitatively consistent with a mechanism in which there is a slow protonation to give a 1-carbon protonated intermediate; the carboxyl group of this then ionizes to give a second intermediate, $RH^+CO_2^-$, which ultimately decarboxylates. Deuterium solvent isotope effects support the proposed mechanism as does an analysis of the individual rate coefficients involved. Several other conceivable mechanisms can be ruled out as inconsistent with either the rate data or other properties of the system.

Numerous quantitative studies on aromatic decarboxylation have been reported.[3] The observed characteristics, *e.g.*, the dependence of rate on acidity, the effect of substituents on rates, and the $^{13}C$ and deuterium solvent isotope effects, make it clear that more than one mechanism is involved. The work of Verhoek[4] using trinitrobenzoic acid has established that for aromatic acids with electron-attracting substituents, the loss of $CO_2$ occurs *via* a unimolecular reaction of the anion, *i.e.*, an SE1 mechanism.

$$RCO_2^- \longrightarrow R^- + CO_2 \quad \text{slow}$$

$$R^- + H_2O \longrightarrow RH + OH^- \quad \text{fast}$$

In accord with this mechanism, the reaction rate is greatest at high pH and diminishes as acid is added. Support for the proposed slow step is afforded by the observation of a full $^{13}C$ isotope effect[5] and the absence of any $D_2O$ solvent isotope effect.[6]

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(2) To whom requests for reprints should be made.

(3) For a review of earlier work, see A. V. Willi, "Saurekatalytische Reaktionen der organischen Chemie, Kinetik und Mechanismen," Monograph F, Vieweg und Sohn, Braumschweig, 1965.

(4) F. H. Verhoek, *J. Am. Chem. Soc.*, **61**, 186 (1939); D. Trivich and F. H. Verhoek, *ibid.*, **65**, 1919 (1943).

(5) P. Riesz and J. Bigeleisen, *ibid.*, **81**, 6187 (1959).