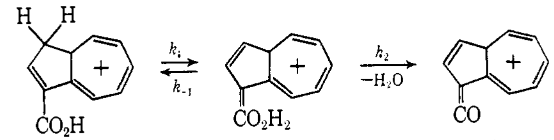
protonated intermediate present in low concentrations in solution, *i.e.*



AzH$^+$ I P

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 3.7×10^{-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.

The Decarboxylation of Azulene-1-carboxylic Acid in Acidic Aqueous Solution[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 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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(1) Work supported by a grant from the Atomic Energy Commission.

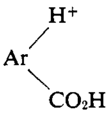
(2) To whom requests for reprints should be made.

(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.

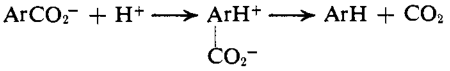
(4) F. H. Verhoek, *J. Am. Chem. Soc.*, **61**, 186 (1939); D. Trivich and F. H. Verhoek, *ibid.*, **65**, 1919 (1943).

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

The observed behavior of aromatic carboxylic acids with electron-repelling substituents is quite different. The work of Schubert[7] and Willi[8] demonstrates a dependence of rate on acidity and suggests that the mechanism is A-SE2, *i.e.*, a rate-determining attack of an acid on the carboxylated carbon of the aromatic ring leading, in Schubert's proposed mechanism, to a transition state or reaction intermediate of the type

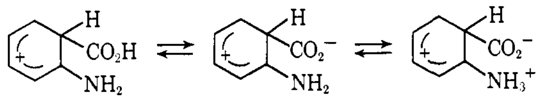


Contrasting with this, for substituted salicylic acids, Willi[8] found that the data were consistent with a kinetic mechanism directly involving the anion rather than the acid.



$$ArCO_2^- + H^+ \longrightarrow \underset{CO_2^-}{ArH^+} \longrightarrow ArH + CO_2$$

Dunn[9] also proposed a mechanism involving the protonated anion as the intermediate species for the decarboxylation of 4-methyl- and 4-methoxyanthranilic acids. The most interesting feature of this particular study was that at pH <1 increasing acidity appeared to inhibit the decarboxylation process. Unfortunately, these systems are quite complex and the presence of zwitterions makes interpretation of data difficult. The authors were, however, able to propose a mechanism consistent with their observations in terms of three possible intermediates.



i ii iii

They concluded that the decarboxylation path probably went exclusively through the intermediate ii, but because of the complex nature of the system decarboxylation *via* species i and iii could not be completely excluded.[10]

More recently Los, *et al.*,[11] reported data for a large number of 4-aminobenzoic acids with differing substituents at the 2 and 6 positions. For the case of the 2-OH compound, an inhibition of decarboxylation was again reported. In order to rationalize their observations the authors proposed the general reaction mechanism of eq 1–4.

$$RCO_2H + H_3O^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} RH^+CO_2H + H_2O \tag{1}$$

$$RCO_2^- + H_3O^+ \underset{k_4}{\overset{k_3}{\rightleftharpoons}} RH^+CO_2^- + H_2O \tag{2}$$

$$RH^+CO_2H + H_2O \underset{k_6}{\overset{k_5}{\rightleftharpoons}} RH^+CO_2^- + H_3O^+ \tag{3}$$

$$RH^+CO_2^- \xrightarrow{k_7} RH + CO_2 \tag{4}$$

The species RH^+CO_2H and $RH^+CO_2^-$ involve protonation at the 1-carbon of the ring and are both assumed to be reaction intermediates present at small concentrations. The k_1 step accounts for the normal acid catalysis. A shift at higher acidities to reaction 4 as rate determining permits an explanation for the moderate fall-off from first-order acid catalysis which was observed in a few instances. As support for this proposal, the authors turned to the Schubert decarboxylation studies in concentrated sulfuric acid and to data on ^{13}C and deuterium solvent isotope effects.[12]

Some indirect support for the proposal that the reaction goes *via* an intermediate of the type $RH^+CO_2^-$ can be obtained from data for a slightly different but analogous reaction, namely the bromodecarboxylation of aromatic acids reported by Grovenstein.[13] The systems again show acid inhibition of a decarboxylation process, and the kinetics are consistent with a mechanism proceeding *via* an intermediate formed by electrophilic attack on the anion of the acid.

In order to obtain some more direct and simple evidence on these mechanisms, it is very desirable to have data for reaction of simple carboxylic acids in dilute aqueous media, where electrolyte and other medium effects are best understood. From this standpoint most of the earlier systems have had disadvantages. The amino-substituted aromatic carboxylic acids often decarboxylate at low acidities, but interpretation is complicated by the possible participation of numerous acidic and basic species. Other substituted benzoic acids, *e.g.*, mesitoic acid, decarboxylate at measurable rates only in concentrated media where quantitative measurement of acidity is difficult and where other medium effects must usually be reckoned with.

From these standpoints, azulenecarboxylic acid is distinctly advantageous. The compound is free from substituent group problems and decarboxylates at a convenient rate in dilute acid solutions at room temperature. In addition, previous protonation studies[14,15] have yielded a good deal of information on the properties of the carbon-protonated intermediates involved.

Experimental Procedures

Details of the preparation of azulenecarboxylic acid and the conductivity apparatus are given in a previous paper.[15] The spectra of $AzCO_2H$ in water and in aqueous 72% perchloric acid are invariant with time. However, in more dilute acid solutions the compound

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(6) E. R. Glick, *Chem. Ind.* (London), 716 (1955).

(7) (a) W. M. Schubert, *J. Am. Chem. Soc.*, **71**, 2639 (1949); (b) W. M. Schubert, J. Donohue, and J. D. Gardner, *ibid.*, **76**, 9 (1954); (c) W. M. Schubert, R. E. Zahler, and J. Robins, *ibid.*, **77**, 2293 (1955).

(8) A. V. Willi and J. F. Stocker, *Helv. Chim. Acta*, **37**, 1113 (1954); A. V. Willi, *ibid.*, **40**, 1053 (1957); **43**, 644 (1960); *Trans. Faraday Soc.*, **55**, 433 (1959); *Z. Naturforsch.*, **13a**, 997 (1958); A. V. Willi, C. M. Won, and P. Vilk, to be published (further studies on decarboxylation of aromatic amino acids).

(9) G. E. Dunn, P. Leggate, and I. E. Scheffler, *Can. J. Chem.*, **43**, 3080 (1965); see also G. E. Dunn and J. Buccini, submitted for publication.

(10) A. V. Willi, C. M. Won, and P. Vilk (private communication) have very recently studied the decarboxylation of unsubstituted anthranilic acid at 70 and 85° in solutions of hydrochloric acid of up to 4 *M*. Analysis of the kinetic data lead them to conclude that at low acidities the rate is governed by slow proton transfer but that at high acidities a carbon–carbon bond cleavage is rate controlling.

(11) J. M. Los, R. F. Rekker, and C. H. T. Tonsbeek, *Rec. Trav. Chim.*, **86**, 622 (1967).

(12) For a review of the isotope effects see ref 3.

(13) E. Grovenstein, Jr., and U. V. Henderson, Jr., *J. Am. Chem. Soc.*, 78, 569 (1956); E. Grovenstein, Jr., and G. A. Ropp, *ibid.*, 78, 2560 (1956).

(14) (a) B. C. Challis and F. A. Long, *ibid.*, 87, 1196 (1965); (b) L. C. Gruen and F. A. Long, *ibid.*, 89, 1287 (1967); (c) J. L. Longridge and F. A. Long, *ibid.*, 89, 1292 (1967).

(15) J. L. Longridge and F. A. Long, *ibid.*, **90**, 3088 (1968).

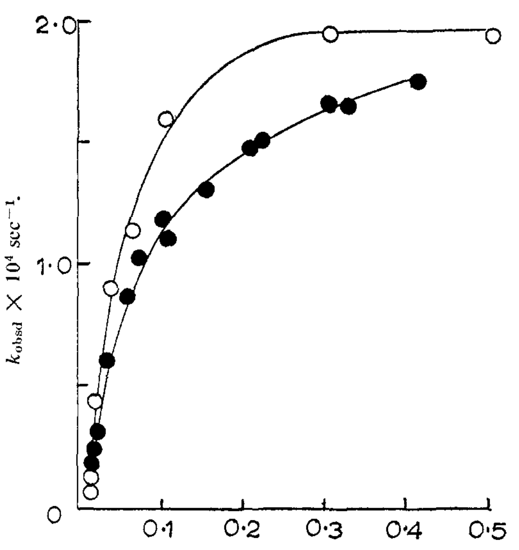

Figure 1. Kinetics of decarboxylation of $AzCO_2H$ in dilute aqueous perchloric acid solutions at 25°: ○, constant ionic strength, I = 0.5 M($NaClO_4$ + $HClO_4$); ●, no added salt.

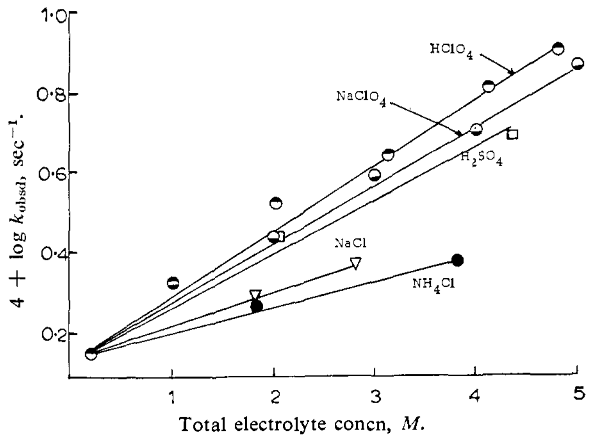

Figure 2. Salt effects on the "high acid" kinetics of decarboxylation of $AzCO_2H$. All solutions but those of H_2SO_4 contain 0.2 M $HClO_4$.

is unstable. Spectroscopic studies showed that the spectral change had good isosbestic points and the spectrum of the compound formed was readily identified as that of azulene. In other words, a decarboxylation process occurs in dilute acid solutions. The kinetic investigation of this process shows that the reaction follows a first-order rate law to greater than 90% completion. For any given acidity an identical rate coefficient could be obtained using either the rate of disappearance of the 300-mμ peak for $AzCO_2H$ or the rate of increase of the 274-mμ peak of the azulene produced. However, in the case of the azulene peak, the data were poorer, the reaction exhibiting good first-order behavior over a much smaller fraction of reaction. This is due to the instability of aqueous solutions to azulene to uv light. As a result, the 300-mμ peak was used throughout the study. All measurements were made at 25 ± 0.1°.

Results and Discussion

The significant facts about the decarboxylation of azulenecarboxylic acid in aqueous solutions are these.

(a) In water at low acidities, *e.g.*, pH values of from 5 to 8, the compound is stable indefinitely.

(b) In solutions of strong acids at concentrations ranging from C_{H^+} of 0.001 to 0.03 M, decarboxylation occurs at a rate which depends on the first power of the hydrogen ion concentration.

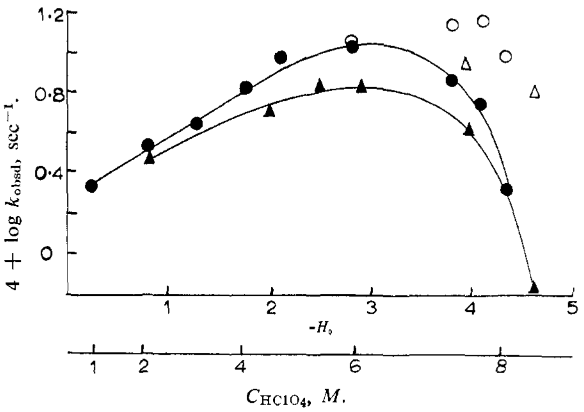

Figure 3. Kinetics of decarboxylation of $AzCO_2H$ in aqueous perchloric and sulfuric acids: ●, $HClO_4$; ○, $HClO_4$ corrected for protonation; ▲, H_2SO_4; △, H_2SO_4 corrected for protonation.

(c) At higher acidities, *i.e.*, from C_{H^-} of 0.3 to 6 M perchloric acid, decarboxylation continues but the rate, except for a general salt effect, is independent of acidity.

(d) At still higher acidities the rate of decarboxylation decreases; this decrease coincides with a protonation of the molecule on the 3-carbon implying that the conjugate acid of the molecule is stable.

(e) At very high acidities, *e.g.*, 72% perchloric acid, where protonation at the 3-carbon is complete, solutions of the acid are stable indefinitely.

The data to support these statements are given in Figures 1-3 and Table I. The lower curve of Figure 1 gives data for decarboxylation rates in aqueous solutions of perchloric acid of increasing strength. The observed first-order rate coefficient initially increases linearly with acidity and then shows an abrupt change to a lower dependence on acidity. This latter behavior which, as Figure 2 shows, extends to still higher acidities, exhibits an acidity dependence of d log k_{obsd}/d($-H_0$) ≅ 0.3, a low value which suggests that what is really involved is an acid-independent process with a sizeable positive salt effect. Two types of experiments confirm this. The upper curve of Figure 1 shows the dependence of rate on acidity for solutions with a constant total electrolyte concentration of 0.5 M. Here it is evident that an acid-dependent decarboxylation is replaced at an acidity of C_{H^+} ≅ 0.1 M by an acid-independent process.

Figure 2 gives additional studies of salt effects and confirms this conclusion. The values of k_{obsd} are for solutions which are 0.2 M in perchloric acid, *i.e.*, in the "high acid" region, to which increasing concentrations of various electrolytes are added. The ordering of the effects of the several salts is quite typical of a general salt effect.[16] Of particular note is the very similar effects of the two electrolytes $HClO_4$ and $NaClO_4$.

The decarboxylation behavior at still higher acidities is shown in Figure 3. For solutions of either perchloric acid or sulfuric acid, an abrupt decline in rate sets in at an H_0 value of about −3. This rapid decline in rate at high acidities occurs in the acidity range where previous studies[15,17] have shown that carbon protonation

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[16] See A. A. Frost and R. G. Pearson, "Kinetics and Mechanism, A Study of Homogenous Chemical Reactions," John Wiley and Sons, Inc., New York, N. Y., 1961, Figure 2, p 152; W. F. McDevit and F. A. Long, *Chem. Rev.*, **51**, 119 (1952).

[17] (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).

at position 3 begins to be appreciable. Nmr studies[15] show that the species protonated at position 3 is the sole species present in 72% perchloric, and in this solvent the compound is completely stable over a 24-hr period. Thus the observed reduction in rate is due to a decrease in the concentration of the neutral molecule which is the species capable of decarboxylation. This conclusion is borne out quantitatively. Using the indicator ratio data of Longridge and Long,[15] the ratio of the stable protonated form BH^+ to the neutral species B can be calculated. Then for the higher acidities where formation of the C-3 protonated species is appreciable, the observed rates can be corrected by a factor to take into account loss of reactant due to protonation. The data in Figure 3 (open points) show that when this correction is made, within experimental error, the rate continues to increase with $-H_0$.

Thus the behavior of the kinetics in concentrated acid solutions, which initially appeared complex, is to be explained as due to a positive salt effect followed by an inhibition due to C-3 protonation.

From a mechanistic standpoint the acidity region of particular interest is that where the hydrogen ion ranges from 0.001 to 0.5 *M*, *i.e.*, where the rate changes from acid dependent to acid independent. The p*K* of the azulenecarboxylic acid is 5.5.[15] Hence the undissociated form is already the dominant species at $C_{H^+} = 0.001$ *M*, and the change in acidity dependence at still higher acidities cannot be explained by a conversion of anion to undissociated acid. The most obvious sort of mechanism to invoke is carbon protonation along the lines of the earlier proposed mechanisms. But before considering the quantitative implications of these, it is useful to explore the suitability of other different mechanisms.

A conceivable way to explain the abrupt change in acid dependence which occurs at $C_{H^+} \simeq 0.2$ *M* is to invoke a preequilibrium protonation of some sort and to assume that beyond the transitional acidity the dominant species is a protonated form which either does not itself decarboxylate or which decarboxylates slowly in an acid-independent step. An illustrative mechanism would be

$$\mathrm{AzCO_2H + H_3O^+ = AzCO_2H_2^+} \quad \text{equilibrium}$$

$$\mathrm{AzCO_2 + H_2O^+ \longrightarrow AzH + CO_2 + H_2O} \quad \text{slow}$$

Formally one can in fact propose a general equilibrium of the type $A + H^+ = AH^+$, treat the equilibrium constant *K* for it as an adjustable parameter, and see whether there is a value of *K* which will fit the observed changes of rate in the transitional region. We have tried this and find that a *K* value of 0.035 will permit a good fit of the data over the acidity range $C_{H^+} = 0.001$ to 0.5 *M*. The important question, however, is whether there is a plausible equilibrium protonation available. Our answer is that we see none.

The reaction cannot be protonation on the aromatic ring since this has been studied and is known to occur only at much higher acidities.[14,15,18–20] A conceivable protonation is on an oxygen of the carboxylic acid group to give $AzCO_2H_2^+$. Since the azulene ring is decidedly basic, its carboxylic group might protonate at much lower acidities than ordinary aromatic carboxylic acids. Evidence for a sizeable enhancement for side-chain protonation is in fact given in the figures in Table I. However, this enhancement necessarily involves conjugation with the electronic system of the azulene ring and a consequent large change in uv spectrum when the conjugate acid is formed. In fact, however, the spectrum of the azulenecarboxylic acid is observed to be essentially the same in 0.5 *M* perchloric acid as in very low acidities which appears to rule out extensive side-chain protonation.

Table I. p*K* Values for Side-Chain Protonation

Aromatic	pK_{BH^+}	Azulene derivative	pK_{BH^+}
Aldehydes	$(-4.6 \text{ to } -5.1)^a$	1-Formylazulene	-1.1^c
Nitrobenzene	-11.4^b	1-Nitroazulene	-4.7^c

[a] W. M. Schubert and R. E. Zahler, *J. Am. Chem. Soc.*, **76**, 1 (1954). [b] M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957), Table I. [c] Reference 17a.

Further evidence against the occurrence of an equilibrium protonation reaction which is complete at low acidities comes from conductivity studies using the procedure developed by Weber and Heilbronner to study protonation of azulenes.[21] Following the methods used by these authors, solutions of azulenecarboxylic acid were prepared in anhydrous formic acid and their conductivities compared with similar solutions of compounds, *e.g.*, aniline, known to form conjugate acids in acidic solvents. Even though the solvent formic acid is sufficiently acidic to react completely with the substrate, if in fact the *K* for the aqueous reaction were 0.035, no conductivity enhancement was observed.

There are other conceivable possibilities such as ion-pair or dimer formation, but no evidence for these was found and these species seem most improbable for aqueous solutions with substrate concentrations of roughly 10^{-5} *M*. We return, therefore, to the more usual sort of mechanism where species with protonation on carbon appear as reaction intermediates.

The mechanism we propose as consistent with all of our data is that of eq 1, 3, and 4. Here RH^+CO_2H and $RH^+CO_2^-$ are reaction intermediates which involve protonation on the 1-carbon of the ring and which are present in only small concentrations in dilute solution. This is the Los, *et al.*, mechanism[11] with omission of their step of carbon protonation of the carboxylate anion, a step which is not relevant at the acidities involved here.

Using the steady-state approximation one obtains

$$\text{rate} = \frac{k_1k_5k_7[\mathrm{RCO_2H}][\mathrm{H_3O^+}]}{k_7(k_2 + k_5) + k_2k_6[\mathrm{H_3O^+}]}$$

Previous studies[14] have shown that the process k_2 for proton loss from carbon proceeds relatively slowly compared with k_5 for loss of a proton from oxygen. Therefore, it can be assumed that $k_2 \ll k_5$ and the

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(18) W. M. Schubert, J. Donohue, and J. D. Gardner, *J. Am. Chem. Soc.*, **76**, 9 (1954).

(19) N. C. Deno, C. U. Pittman, Jr., and M. J. Wisotsky, *ibid.*, **86**, 4370 (1964).

(20) S. Hoshino, H. Hosoya, and S. Nagakura, *Can. J. Chem.*, **44**, 1961 (1966).

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

equation simplifies to

$$\text{rate} = \frac{k_1[\mathrm{RCO_2H}][\mathrm{H_3O^+}]}{1 + (k_2k_6/k_5k_7)[\mathrm{H_3O^+}]} \qquad (5)$$

or

$$k_{\mathrm{obsd}} = \frac{k_1[\mathrm{H_3O^+}]}{1 + (k_2k_6/k_5k_7)[\mathrm{H_3O^+}]} \qquad (6)$$

Equation 5 is clearly of the correct form to give the required transition from acidity dependence at low acidities to acid independence as the acidity increases. It is quantitatively satisfactory also. By rearranging eq 6 into a linear equation, and using a graphical method to apply it to the dilute acid solution data, it was possible to fit the experimental results extremely well by the expression

$$k_{\mathrm{obsd}} = \frac{5.80 \times 10^{-3}[\mathrm{H_3O^+}]}{1 + 26.3[\mathrm{H_3O^+}]} \qquad (7)$$

as shown in Table II. The "observed" data of this table are for solutions which contain perchloric acid at the stated $C_{\mathrm{H^+}}$ concentrations and enough added sodium perchlorate to give a total electrolyte concentration of 0.5 *M*.

Table II. Comparison of Observed Rate Coefficients with Those Calculated from Eq 7

$C_{\mathrm{H^+}}$, *M*	k_{obsd}, $\mathrm{sec^{-1}} \times 10^5$	k_{calcd}, $\mathrm{sec^{-1}} \times 10^5$
0.00102	0.575	0.575
0.00296	1.57	1.59
0.01	4.33	4.58
0.03	9.11	9.71
0.06	13.12	13.48
0.10	16.05	15.96
0.30	19.83	19.50
0.50	19.76	20.50

The fact that a good fit of the data is obtained does not in itself prove that the proposed mechanism is correct. There are, however, a number of other factors which independently give support to this interpretation. One important criterion to test the mechanism is that the parameters of eq 7 must be consistent with our knowledge of the species and processes involved and with observed rate and equilibrium constants for related reactions. For azulenecarboxylic acid it is fortunate that reactions of similar type to those involved in the suggested mechanism have been previously studied[14,15] and data on their rates and equilibria are available.

Comparison of eq 6 and 7 reveals that the proposed mechanism requires

$$\begin{aligned} k_1 &= 5.8 \times 10^{-3}\ M^{-1}\,\mathrm{sec^{-1}} \\ k_2k_6/k_5k_7 &= 26.3\ M^{-1} \end{aligned} \qquad (8)$$

The requirement of a k_1 value of 5.8×10^{-3} M^{-1} $\mathrm{sec^{-1}}$ for proton transfer to a carbon of an aromatic ring is qualitatively consistent with numerous studies of similar slow proton transfers.[14,22] For quantitative comparison, the data of Challis, corrected to 25° and for reaction at a single site, give for protonation of azulene a k_1 value of 3 M^{-1} $\mathrm{sec^{-1}}$. It is reasonable that k_1 for protonating the present substrate at the 1-position should be a 1000-fold smaller. In the first place, a $\mathrm{CO_2H}$ group should be relatively electron attracting and hence lead to a slower rate. Furthermore, it is well established that, except where relief of steric strain is involved, protonation on substituted carbon is more difficult than on an unsubstituted site, implying a slower rate.

The more complex analysis is that of eq 8. As a preliminary, we label some equilibrium constants as follows.

$\dfrac{k_2}{k_1} = K^{\mathrm{C}}_{\mathrm{RH^+CO_2H}}$ the dissociation constant for loss of a proton from the *carbon* of $\mathrm{AzH^+CO_2H}$

$\dfrac{k_5}{k_6} = K^{\mathrm{O}}_{\mathrm{RH^+CO_2H}}$ the dissociation constant for loss of a proton from the *oxygen* of $\mathrm{AzH^+CO_2H}$

Let us first consider a value for k_2. For azulenes the reaction of $\mathrm{XAzH_2^+}$ with the base water to give XAzH has a rate coefficient of about 10 $\mathrm{sec^{-1}}$. In the present case, knowing that protonation at nonsubstituted sites is strongly favored, a reasonable estimate for k_2 is 10^3 $\mathrm{sec^{-1}}$. Hence

$$\frac{k_2}{k_1} = K^{\mathrm{C}}_{\mathrm{RH^+CO_2H}} = \frac{10^3}{6 \times 10^{-3}} \simeq 10^5$$

This value is consistent with our knowledge of p*K*'s of carbon-protonated azulenes.

The other acid dissociation constant $K^{\mathrm{O}}_{\mathrm{RH^+CO_2H}}$ can be estimated more straightforwardly by assuming that the adjacent positive charge will affect the p*K* of the carboxylic group to the same extent as does the ammonium ion in protonated glycine where the charged species shows a lower p*K* by about 2.0 units.[23] Since the p*K* of the $\mathrm{AzCO_2H} = 5.5$,[15] $K^{\mathrm{O}}_{\mathrm{RH^+CO_2H}}$ is estimated to be $\simeq 10^{-3}$.

We assume that the reverse of step 3 is diffusion controlled with, therefore, a value of k_6 of about 10^{10} M^{-1} $\mathrm{sec^{-1}}$, which leads to $k_5 \simeq 10^7$ $\mathrm{sec^{-1}}$. This value of k_5 when compared to the estimated value of $k_2 = 10^3$ $\mathrm{sec^{-1}}$ is consistent with the inequality $k_5 \gg k_2$ as was assumed in our simplification of the kinetic calculations.

There remains the question of the value of k_7. The process is one where a large but not diffusion-controlled reaction rate would be predicted. Equation 8 along with the estimated values for k_2, k_6, and k_5 indicates that to fit the observations a value of $k_7 \simeq 10^5$ $\mathrm{sec^{-1}}$ would be required.

It is difficult to obtain an independent estimate for k_7. A number of related rate studies have been made, but none seems to be for a reaction which is strictly analogous. The rate of dehydration of $\mathrm{H_2CO_3}$ is not a very satisfactory model as it does not involve a species with a pronounced charge separation. The value of $k = 15$ $\mathrm{sec^{-1}}$ for this process is clearly not of the right magnitude.[24] Data for enzyme-catalyzed decarboxyla-

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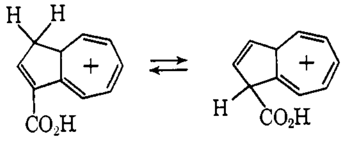
[22] See also A. J. Kresge and Y. Chiang, *J. Am. Chem. Soc.*, 81, 5509 (1959); 83, 2877 (1961); 84, 3976 (1962); *Proc. Chem. Soc.*, 81 (1961).

[23] E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids, and Peptides Monograph," Reinhold Publishing Corp., New York, N. Y., 1943, p 96.

[24] M. Eigen and L. de Maeyer, "Rates and Mechanisms of Reactions," Vol. VIII, Part 2, S. L. Friess, E. S. Lewis, and A. Weissberger,

tions[25] show that much higher decarboxylation rates are possible. Another possible model reaction, for which data are available, is the decomposition of metal chelate complexes. This process, which involves charged species and requires the separation of relatively large molecules, has been observed to proceed rapidly, and rate constants of 10^5 sec^{-1} are not unusual.[26] Tentatively we conclude that a value of $k_7 \simeq 10^5$ is reasonable. Thus within the approximations made, the proposed reaction mechanism, taken in conjunction with the observed data, is consistent with our prior knowledge of the processes involved.

The mechanism requires that the species RH^+CO_2H does not decarboxylate except *via* ionization to the anion and there is evidence to support this restriction. In 72% perchloric acid two species are present in solution,[15] and presumably in equilibrium, namely



iv v

Although, as evidenced by the observed carbon protonation, the equilibrium heavily favors species iv, the concentration of species v (the possible decarboxylation intermediate) must be considerably higher in 72% perchloric than it is in dilute aqueous acid solution. However, in spite of the increased concentration of this species, no decarboxylation occurs, illustrating the stability of the proposed intermediate.

Deuterium isotope studies, which have been useful in similar mechanistic considerations,[3,11] are also useful here. Under the conditions where protonation of the carboxylic acid is rate determining, a reasonably large deuterium isotope effect would be expected, *i.e.*, $k_{H_2O}/k_{D_2O} \simeq 2$-$3$. When the reaction becomes acid independent, the k_7 process, step 4, dominates the kinetics. Under these conditions the isotope effect would be due largely to the influence of the solvent on the isomerization equilibrium combined with a small secondary effect on the k_7 process. Using data for azulene[14b] and deuterioacetic acid[27] to estimate the effect of D_2O on the combined equilibria 1 and 3, it is possible to estimate the over-all effect. These calculations predict a lower isotope effect for the acid-independent reaction, $k_{H_2O}/k_{D_2O} \simeq 1.5$.

The experimental data presented in Table III show that the observed isotope effects are of the expected relative size, even though the observed values for the acid-independent reaction ($C_{H^+} = 0.4$ and 0.5 *M*) are of somewhat lower magnitude than predicted. This is additional support for the proposed mechanism.

The relative simplicity and high basicity of azulenecarboxylic acid make it especially suitable for an analysis of the mechanism of aromatic decarboxylation. The data of the present study strongly support the conclusion that decarboxylation proceeds in this case only *via* the ampholyte $RH^+CO_2^-$. Equally significant is that for this system no other plausible mechanism can be advanced which is capable of explaining the remarkable change from acid-catalyzed to acid-independent behavior in a dilute acid medium.

Table III[a]

H^+, *M* ($HClO_4$)	k_{obsd}, sec^{-1} × 10^5 D_2O	H_2O	k_{H_2O}/k_{D_2O}
0.01	2.02	4.33	2.15
0.02	3.65	7.08	1.94
0.4	15.70	19.83	1.26
0.5	16.93	19.83	1.17

[a] $I = 0.5$ *M* ($NaClO_4$).

It has been suggested by Los[10] that this mechanism, involving reaction *via* the ampholyte, may be generally applicable to a large number of aromatic decarboxylation reactions. Considering only solutions which do not have complicating amino groups, there is certainly good evidence for decarboxylation proceeding *via* ampholyte intermediates. For the case of 2,4,6-trihydroxybenzoic acid, Schubert and Gardner[28] showed that the reaction proceeds exclusively *via* protonation of the anion over a wide range of acidity 0.014–5.0 *M*. In addition, the ^{13}C isotope studies of Bourns[3,29] show that the rate-determining step apparently changes, being initially the protonation rate of the anion and at higher acidities becoming due to the rate of decomposition of the ampholyte formed. Similar behavior is also reported for dihydroxybenzoic acid.[29,30]

Applicability of the mechanism to other systems is less certain. The decarboxylation of mesitoic acid is particularly interesting in this respect. Although ^{13}C isotope effects in concentrated acid[31,32] clearly show that the breaking of a C–C bond occurs in the rate-determining process, the measurements cannot distinguish whether RH^+CO_2H or $RH^+CO_2^-$ is the intermediate involved.

In addition, the dependence of the decarboxylation rate on acidity is closely similar to that for the decarbonylation reaction for closely related systems such as mesitaldehyde and 2,4,6-triethylbenzaldehyde,[7c,33] where the mechanism cannot invoke ionization of the intermediate RH^+CHO *via* the loss of a proton from the formyl group. Thus ionization of RH^+CO_2H for mesitoic acid may not be necessary for decarboxylation to proceed.

In attempting to apply his general mechanism to this system, Los[11] utilizes the reduction of kinetic rate in solutions of higher acidities than 83% H_2SO_4 as evidence that the species $RH^+CO_2^-$ is involved. However, this reduction in rate is far from dramatic and can also be readily rationalized in terms of the large medium changes to be expected as the solvent changes from 80 to 100% sulfuric acid. In addition, the ex-

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Ed., Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1963, Table IV, 2(b).

(25) M. F. Utter, "The Enzymes," Vol. 5, Academic Press Inc., New York, N. Y., 1961, Chapter 19, p 319.

(26) See ref 24, Table V.

(27) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Table 22, p 188.

(28) W. M. Schubert and J. D. Gardner, *J. Am. Chem. Soc.*, **75**, 1401 (1953).

(29) A. N. Bourns to A. V. Willi, private communication.

(30) K. R. Lynn and A. N. Bourns, *Chem. Ind.* (London), 782 (1963).

(31) A. A. Bothner-By and J. Bigeleisen, *J. Chem. Phys.*, **19**, 755 (1951).

(32) W. H. Stevens, J. M. Pepper, and M. Lounsbury, *ibid.*, **20**, 192 (1952).

(33) W. M. Schubert and R. E. Zahler, *J. Am. Chem. Soc.*, **76**, 1 (1954).

istence of a species with a strongly basic site such as $RH^+CO_2^-$ seems unlikely where the solvent is of sufficiently high acidity to cause appreciable protonation of the carboxylic acid itself.[18] We therefore conclude that, while the mechanism for decarboxylation of azulenecarboxylic acid proceeds only *via* the ampholyte $RH^+CO_2^-$ and evidence suggests that this type of species is frequently involved for other systems, it is questionable whether it is an essential intermediate for all aromatic decarboxylations.

Thermal Diffusion in Nuclear Reactor Fuels

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Received November 29, 1967

Abstract: Experiments of Beisswenger, Bober, and Schumacher on the thermal diffusion of mixtures of CeO_2–UO_2 and PuO_2–UO_2 are discussed in the light of the authors' kinetic model of thermal diffusion. The heats of transfer Q^+ are derived from these experiments: for CeO_2–UO_2 at 2050°K, $Q^+ = 25$ kcal/mol; for PuO–$_2UO_2$ at 2673°K, $Q^+ = 58$ kcal/mol. In both cases the result of the kinetic model that the heat of transfer should be lower than the heat of activation for the rate-determining step is confirmed. A few remarks on future work are added.

Recently Beisswenger, Bober, and Schumacher obtained first results from a systematic experimental study of thermal diffusion in mixtures of CeO_2–UO_2 and PuO_2–UO_2.[1] One reason their data are of special interest is that they were able for the first time to reach a common interpretation of their own and other experimental work and to draw important conclusions of a general nature concerning the segregation of uranium and plutonium mixtures in oxide fuel of nuclear reactors. I would like to make a few remarks concerning the interpretation of these results, and I am very happy to contribute thereby to this memorial issue to Peter Debye. It was in Debye's laboratory about 30 years ago that we did our first experimental and theoretical work on thermal diffusion in condensed phases, work that gained much by the interest and stimulating advice of Debye.[2] The present work of Beisswenger, *et al.*, is directly linked with these studies. At that early date no one was able to foresee that today in nuclear reactors, inside mixed oxide fuel pins, temperature gradients of hitherto unknown size appear that could make segregation of uranium and plutonium by thermal diffusion a primary technical and safety problem.

If segregation in a temperature gradient reaches equilibrium, the molar fractions λ and $1 - \lambda$ of the two components are connected with the Soret constant

$$S = \frac{1}{\lambda(1 - \lambda)} \frac{d\lambda}{dT} \qquad (1)$$

In this case diffusion and thermal diffusion are in equilibrium

$$-D \text{ grad } \lambda - D'\lambda(1 - \lambda) \text{ grad } T = 0 \qquad (2)$$

with D = diffusion constant and D' = thermal diffusion constant. One gets

$$S = -D'/D \qquad (3)$$

It is well known from the work of Eastman and Wagner[3] that the heat of transfer Q^+ that characterizes the equilibrium is connected with S by

$$S = Q^+/RT^2 \qquad (4)$$

In our above-mentioned earlier work, a kinetic interpretation of eq 4 has been developed for the case that the diffusion process involves activated steps of migration or of exchange of places in which case the temperature dependence of the diffusion constant is as follows

$$D = D_0 \exp(-q/RT) \qquad (5)$$

where D_0 does not depend strongly on temperature and q = energy of activation.

From the kinetic interpretation it follows that in general q consists of different parts that refer to different positions of the migration step; namely, q_H = energy necessary at the primary position of the migrating particle; q_R = energy necessary to open the lattice to let the migrating particle pass, q_L = energy necessary to open a hole at the new position. From this kinetic model a relation between Q^+ and the difference $q_H - q_L$ follows.

$$Q^+ = q_H - q_L \qquad (6)$$

More generally we expect a relation of the type

$$Q^+ \leq q \qquad (7)$$

In case there is not just one atom migrating through a lattice, but the elementary step consists of the exchange of places of particles, the model has to be adapted correspondingly, but the conclusions that yield eq 6 and 7 are in principle the same. With respect to

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(1) (a) A. A. Bauer, H. Beisswenger, *et al.*, Argonne Conference on Safety, Fuels and Core Design of Fast Reactors, Oct 1965, ANL-7120, Argonne National Laboratory, Argonne, Ill., p 400; (b) H. Beisswenger, M. Bober, and G. Schumacher, *J. Nucl. Mater.*, **21**, 38 (1967); (c) H. Beisswenger, M. Bober, and G. Schumacher, Proceedings of the IAEA Symposium on Plutonium as a Reactor Fuel, Vienna, 1967, p 273.

(2) P. Debye, *Ann. Physik*, **36**, 284 (1939); H. Korching and K. Wirtz, *Naturwiss.*, **27**, 110 (1939); K. Wirtz, *Physik. Z.*, **44**, 221 (1943); *Z. Physik*, **124**, 482 (1948).

(3) E. D. Eastman, *J. Am. Chem. Soc.*, **48**, 1482 (1926); **50**, 283, 292 (1938); C. Wagner, *Ann. Physik*, **3**, 629 (1929); **6**, 370 (1930).