The Decarboxylation of Azulene-1-carboxylic Acid.
II. Carbon-13 Isotope Effects[1]

H. H. Huang[2] and F. A. Long[3]

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. *Received December 12, 1968*

Abstract: Carbon-13 isotope effects have been determined for the decarboxylation of azulene-1-carboxylic acid in aqueous solutions at 25° under two different sets of acidities. At acidities below 0.01 $M\ C_{H^+}$, where on the basis of previous studies the rate-determining step should be almost exclusively a slow proton transfer, virtually no C^{13} isotope effect is observed. In contrast, at acidities of 0.3 $M\ C_{H^+}$ an almost "full" isotope effect is observed, k_{12}/k_{13} being 1.035 in one series of experiments and 1.043 in a second. At this acidity the postulated mechanism and the rate parameters derived from it for this case indicate that about 90% of the reaction occurs by carbon–carbon bond rupture of a 1-protonated ampholyte, $AzH^+CO_2^-$, leading to carbon dioxide and the uncharged aromatic as products. This excellent agreement of the C^{13} isotope effects, when combined with earlier evidence from kinetic behavior and deuterium solvent isotope effects, gives very strong support to the proposed mechanism.

The decarboxylation of azulene-1-carboxylic acid in aqueous media is notable in that in dilute acid solutions at 25° it shows an abrupt change from a first-order dependence of rate on acidity at low concentrations to independence of acidity at higher concentrations.[4] The change in behavior is particularly striking for solutions of constant ionic strength. It is almost as evident for solutions of perchloric acid in going from 0.001 *M* hydrogen ion concentration to 0.5 *M* but is somewhat obscured at the higher concentrations by contributions from a positive general salt effect.

The dependence on acidity can be quantitatively explained by the following mechanism which has been adapted[4] from a recently proposed slightly more general mechanism.[5,6] The species AzH^+COOH and AzH^+COO^- are protonated on the 1-carbon and both

$$\mathrm{AzCOOH + H_3O^+ \underset{k_2}{\overset{k_1}{\rightleftarrows}} AzH^+COOH + H_2O} \qquad \text{(I)}$$

$$\mathrm{AzH^+COOH + H_2O \underset{k_6}{\overset{k_5}{\rightleftarrows}} AzH^+COO^- + H_3O^+} \qquad \text{(III)}$$

$$\mathrm{AzH^+CO_2^- \xrightarrow{k_7} AzH + CO_2} \qquad \text{(IV)}$$

participate as kinetic intermediates; *i.e.*, they are present at very low concentrations. The essence of the postulated mechanism is that protonation on the 1-carbon is required but that only the ampholyte $AzH^+CO_2^-$ decomposes at a measurable rate. This then allows the proton-transfer step I to be rate determining at low acidities, but permits the carbon–carbon bond rupture of the ampholyte to become rate determining at higher acidities.

Using steady-state approximations for the intermediates and invoking the assumption that $k_5 \gg k_2$ (since proton loss from carbon is slow relative to loss from oxygen) leads to the following expression for the experimental first-order rate coefficient for decarboxylation.

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

If one treats k_1 and the ratio k_2k_6/k_5k_7 as parameters, the observed rate data for perchloric acid catalysis at constant ionic strength of 0.5 can be fitted in a very satisfactory way by the equation

$$k_{\text{obsd}} = \frac{5.80 \times 10^{-3}[\mathrm{H_3O^+}]}{1 + 26.3[\mathrm{H_3O^+}]} \qquad (2)$$

Further analysis of the parameters of eq 1 has shown that the required values of $k_1 = 5.8 \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$ and $k_2k_6/k_5k_7 = 26.3\ M^{-1}$ are reasonably consistent with the various processes involved in the postulated mechanism.[4] Thus, the observed value of k_1, which is a 1000-fold smaller than for protonation of azulene,[7] is not surprising in view of the electron-attracting nature of the carboxyl group. It is also in keeping with evidence from other experiments[8] that protonation at a substituted carbon atom is less facile than at an unsubstituted site. Similarly, consideration of the various protonation and deprotonation steps indicates that k_2k_6/k_5 is approximately 10^6 and therefore that k_7, the rate coefficient for the final C–C bond fission, is about 10^5 sec^{-1}, a plausible value, although no strictly analogous reaction is available for comparison.

Evidence that the intermediate AzH^+COOH does not itself decarboxylate comes from the fact that decarboxylation becomes very slow at $-H_0$ values above 5. At these high acidities, the principal species is the normal conjugate acid, protonated at the 3-carbon.[4] This should be in equilibrium with the species AzH^+COOH (with 1-carbon protonation), and the latter should be present at much higher concentrations than in dilute acid. However, in spite of this, decarboxylation at very high acidities does not occur.[4]

Deuterium solvent isotope effects have provided additional useful evidence for the proposed mechanism. When the protonation step I is rate determining, a value

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(2) On leave from the University of Singapore, Singapore.

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

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of k_{H_2O}/k_{D_2O} of from 2 to 3 would be expected. At higher acidities, when the C–C bond-rupture step IV is rate controlling a smaller isotope effect is predicted. The available data are in harmony with these expectations.[4]

The evidence accumulated so far provides strong, though not conclusive, support for the proposed mechanism. It is possible, however, to strengthen this evidence still further by investigating C^{13} isotope effects for this reaction since they should be quite different for the acid-catalyzed and acid-independent regions. We have now obtained such additional isotopic information.

Experimental Section

C^{13} isotope studies for two series of solutions were made, one at constant ionic strength of 0.5 and the other without added salt. Because of the complex acidity dependence of the reaction, it was considered desirable to run the decarboxylation reactions with a hydrogen ion catalyst and with water as the reaction medium in keeping with previous work. The low solubility of azulene-1-carboxylic acid in water (1.7×10^{-4} mole/l.) then made it necessary to work with large volumes of solution in order that sufficient amounts of CO_2 would be evolved for collection and measurement. Our final choice of 1 l. as the volume of working solution represents a practical compromise between ease of operation and the desirability of having the amount of CO_2 evolved as large as possible. In spite of this balancing of opposing factors, we found it difficult to avoid having to manipulate volumes of CO_2 as low as 0.2–0.3 ml (NTP) for runs corresponding to 10–15% of reaction. The general procedure adopted for a given run is as follows: 1 l. of the acidic solution of required strength was made up from distilled water which had been boiled for 2 hr. This was transferred to a "gas bubbler" fitted with a fritted disk of "fine" porosity, the whole being attached to a vacuum line with four traps placed in series immediately after the gas bubbler. The first of these traps is of the conventional cold-finger type, the second a spiral type. The third and fourth, designed for even higher collection efficiency, were constructed from 5-mm and 3-mm glass tubing coiled after the fashion of a heat radiator (five and nine turns, 10 cm high, respectively). Prior to each experiment CO_2-free helium gas from a cylinder was allowed to bubble through the magnetically stirred aqueous solution for about 2 hr; this ensured that the residual dissolved CO_2 in the solution was completely removed, as shown by mass spectrometric tests. The vacuum line was also swept with helium during the latter stages of the CO_2-degassing process to ensure that the whole system was free from CO_2. About 32 mg of the substrate in 1 ml of dimethyl sulfoxide was then introduced into the solution by means of a syringe through a septum in a small side arm of the "bubbler," taking care to prevent the entry of any extraneous CO_2 from the atmosphere. Before the initiation of the reaction, the first three traps were immersed in acetone–Dry Ice mixtures (to trap out water vapor), while the fourth trap was immersed in liquid nitrogen (to trap the CO_2 evolved from the decarboxylation reaction). The flow rate of the helium gas was adjusted to *ca.* 80 ml/min for 100% reaction, 180 ml/min for 20% reaction at 0.3 *M* acid concentration, and *ca.* 100 ml/min for 10–15% reaction at acid concentration of 0.01 and 0.006 *M*. The collection of CO_2 was stopped at the appropriate times by turning off the helium gas and closing the appropriate stopcocks. The CO_2 collected in the fourth trap was further purified by distillation under high vacuum through a fifth, conventional trap (at Dry Ice temperature) and was eventually collected in a sample bulb immersed in liquid nitrogen. This distillation was repeated two or three times, after which the mass spectrometric spectrum usually showed negligible traces of water, the only impurity expected to be present. All CO_2 analyses of the isotopic ratio C^{13}/C^{12} (45/44) were carried out with a Consolidated-Nier "Isotope-Ratio" mass spectrometer.[9] The results are given in Table I which shows isotopic ratios corrected for variations in tank CO_2 values. The isotope effects,[10] expressed as k_{12}/k_{13}, were corrected for incomplete resolution and for the presence of O^{17}.

Table I. Kinetic Carbon Isotope Effects on the Decarboxylation of Azulene-1-carboxylic Acid at 25°

No. of expts	$[HClO_4]$, *M*	Extent of reaction, %	CO_2 analyses $(45/44) \times 10^4$	k_{12}/k_{13}
		No Salt Added		
5	0.32	11	111.59 ± 0.40	1.035 ± 0.007
4	0.01	9	115.09 ± 0.60	1.000 ± 0.008
2	0.32	99.99	114.86 ± 0.10	...
2	0.01	99.90	115.03 ± 0.50	...
		Constant Ionic Strength of 0.5 *M*		
5	0.32	13	110.81 ± 0.60	1.043 ± 0.008
5	0.006	11	114.28 ± 0.45	1.008 ± 0.007
3	0.32	99.99	114.33 ± 0.36	...
2	0.006	99.90	115.10 ± 0.40	...

In the estimation of the fraction of the reaction that has occurred during time *t*, a fraction which is needed for the calculation of the isotope effect, a realistic approach appears to be to treat the production of CO_2 from the reaction and its extraction from the solution as a consecutive first-order rate process

$$A \xrightarrow{k_a} B \xrightarrow{k_b} C$$

where k_a and k_b are rate constants characteristic of the process of CO_2 production and its extraction, respectively. k_a is known from available kinetic data; k_b can be estimated reasonably well from test decarboxylation experiments with standard samples of sodium bicarbonate for various helium flow rates. Thus, for the flow rates used in the experiments with 0.3 *M* solutions (180 ml/min), the half-life is about 6 min; hence $k_b = 0.115$ min^{-1}. Similarly, the half-life of the extraction process at a flow rate of 100 ml/min is about 10 min; hence $k_b = 0.0691$ min^{-1} in this case. These estimates, based on standard treatments of consecutive first-order reactions, are used in the calculation of the isotope effects in Table I. An alternative method of estimating the fraction of the reaction is simply to assume that the CO_2 collected in the fourth trap after time *t* corresponded to the total amount of carbon dioxide produced in time *t* by the decarboxylation process. This is obviously an overestimate since it is most unlikely that all the CO_2 evolved during a given time period, short of complete reaction, can be totally extracted in that time. Fortunately, calculations show that although estimates of the fractions of reaction by this method are about 1.5 times larger than those previously mentioned, the final calculated isotope effects are fairly insensitive to these uncertainties which, therefore, do not significantly affect our conclusions.

Kinetic runs for decarboxylation at 25° without added salt were performed in the dilute acid region over the range 0.001–0.1 *M* $HClO_4$ to supplement the data already available under similar conditions. The experimental procedures and methods of calculation were essentially the same as those previously used.[4] The results are summarized in Table II.

Table II. Rate Coefficients for Decarboxylation of Azulene-1-carboxylic Acid at 25° without Added Salt

C_{HClO_4}, *M*	k_{obsd}, sec^{-1} $\times 10^4$	C_{HClO_4}, *M*	k_{obsd}, sec^{-1} $\times 10^4$
0.00098	0.0365	0.0102	0.274
0.00102	0.0353	0.0298	0.552
0.00286	0.0877	0.0998	1.080
0.00318	0.0888	0.30	1.680

Discussion

We shall consider first the C^{13} isotope data obtained at constant ionic strength. In addition to the qualitative implications of eq 2, namely that the reaction kinetics are dominated by slow proton transfer (I) at low acidities but by slow C–C bond fission (IV) at high acidities, it is possible from the rate law to make more quantitative predictions concerning the relative im-

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[9] We are grateful to Dr. L. Friedman and his colleagues at the Brookhaven National Laboratory for assistance with these measurements.

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portance of steps I and IV in determining the rate of the decarboxylation reaction. Examination of eq 2 shows that the fraction of the azulenecarboxylic acid system undergoing either of the two rate-determining steps in a given solution depends only on the acid strength: at ionic strength 0.5 M for the slow proton-transfer step, the fraction is $1/(1 + 26.3[H_3O^+])$; for the slow C–C bond-fission step, it is $26.3[H_3O^+]/(1 + 26.3[H_3O^+])$. From these expressions we have estimated the magnitudes of the C^{13} isotope effect for the high and low acid regions that may be expected if the implications of the rate expression (2) are indeed correct. These calculations are summarized in Table III. The experimental results in Table II show quite clearly that a large isotope effect is observed for the 0.3 M acid solutions, but only a very small one is found for the 0.006 M acid solutions. More precisely, if the full isotope effect is taken[13] as $k_{12}/k_{13} = 1.045$, then the values 1.043 and 1.008 correspond to *ca.* 95 and 15% of the full effect, respectively. We wish to point out, however, that a range of "full" isotope effect values ($k_{12}/k_{13} = 1.0343$–1.060) has been reported in the literature for other reactions,[10–18] thus introducing an element of uncertainty here, and that the errors of our measurements do not permit a sharper precision than *ca.* ±20% in the final result. Despite these limitations, our results for the C^{13} isotope effect are clearly quite consistent with the size of the predicted effect and afford unambiguous evidence for a rate-determining carbon–carbon bond rupture at high acidities but not at low. This is, of course, the prediction of the postulated mechanism.

Table III

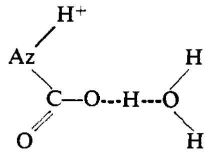
$[HClO_4]$, M	Ionic strength, M	Fraction with rate-determining proton transfer	Fraction with rate-determining C–C bond fission
0.32	0.5	0.11	0.89
0.006	0.5	0.86	0.14
0.32	0.32 (no salt added)	0.13	0.87
0.01	0.01 (no salt added)	0.82	0.18

These conclusions receive further support from a similar analysis of the data obtained without adding salt to maintain a constant ionic strength for all the solutions. The existence of a positive salt effect has the consequence that it is now neither possible nor correct to attempt to fit eq I to the kinetic data (Table II) over the entire range of acidity studied. However, over a more limited low acidity range, say up to 0.1 M perchloric acid concentration, the salt effect should be negligible, and one is justified in obtaining a best fit of eq I to the available data. The best fit then gives

$$k_{\text{obsd}} = \frac{32.8 \times 10^{-4}[H_3O^+]}{1 + 21[H_3O^+]} \qquad (3)$$

whence the fractions of the system going by the two different rate-determining steps can be worked out as before. For high acid concentrations, *e.g.*, at 0.3 M $HClO_4$, where the C^{13} isotope studies have been made, we can assume that eq I is still applicable, provided that a small salt effect correction is made. This can be done with the aid of eq 2 and 3 which, in effect, give the dependence of k_1 on the ionic strength up to 0.5 M. Assuming a linear relationship between log k_1 and electrolyte concentration, we obtain $k_1 = 43.85 \times 10^{-4}$ at 0.3 M $HClO_4$, whence k_2k_6/k_5k_7 emerges as 22.8. Hence, the fraction of the system going by the two different rate-determining steps can again be calculated. The results of these calculations are collected in Table III. Comparison of these results with the observed C^{13} isotope effects leads to the same conclusion as before, namely that the predicted and observed effects are broadly consistent within experimental errors.

Bourns[16] has emphasized that although a stepwise mechanism has been established for a large number of electrophilic aromatic substitution processes, there are some reactions, such as decarboxylation, where the kinetic intermediate species is so short-lived that unless their existence is proven, the possibility of a one-state (or concerted) reaction mechanism cannot be ruled out. The decarboxylation of azulene-1-carboxylic acid would appear to come under this category. It is conceivable that instead of the stepwise mechanism (steps I–IV), a concerted process could apply in which protonation of the acid, the formation of the ampholyte $AzH^+CO_2^-$, and the rupture of the carbon-carbon bond take place in a single step with



as the transition state. The presence of a solvent isotope effect k_{H_2O}/k_{D_2O} which is greater than unity, and the fact that proton transfer is the dominant slow step at low acidities rather than a preequilibrium step, can be accommodated by the concerted mechanism. However, two pieces of evidence would weigh against this possibility. Firstly, it has been noted that the solvent deuterium isotope effect decreases significantly, from 2.15 to 1.17, on going from low acid to high acid strength.[4] On a concerted mechanism with the transition state mentioned, a smaller change would be expected since the departing proton in the reaction coordinate would still make a sizable contribution to the isotope effect. A second and perhaps more convincing piece of evidence comes from the C^{13} isotope effect. The stepwise process (I–IV) predicts that an increase in acid strength would result in an increase in the magnitude of the C^{13} isotope effect by favoring the reverse of step III and thus causing step IV to be increasingly rate determining. By contrast, the concerted mechanism would require the magnitude of the C^{13} isotope effect to be independent of acid strength since the species H_3O^+ is not involved in any reversible

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process. The data in Table I clearly favor the stepwise mechanism.

It may be noted that for both sets of data it can be concluded that at high acidities the C^{13} isotope effect, expressed as $k_{12}/k_{13} - 1$, is in the order of from 0.038 to 0.045. This fact, that the C^{13} isotope effect is essentially "full" when the carbon–carbon bond rupture step is rate determining, is itself of considerable interest. From the earlier mentioned analysis of the rate equation, it was concluded that the rate coefficient for step 7, the carbon–carbon bond rupture, is in the order of 10^5 sec^{-1}. This implies that this reaction is very fast and indeed the resultant calculated free energy of activation for the step is only $\Delta F^* = 10.6$ kcal/mole which, in turn, implies a potential energy valley for the process of from 8 to 10 kcal. Recalling that C^{13} isotope effects of about 0.040 also characterize very much slower bond rupture processes, one can conclude that the magnitude of the isotope effect is independent of the depth of the potential energy valley for the process. This is the well-known prediction of isotope theory.

Complexation in Acetonitrile of Tetramethylguanidinium (BH^+) Sulfate with Bisulfate, $BHSO_4^-$, and BH^+ Ions[1]

I. M. Kolthoff and M. K. Chantooni, Jr.

Contribution from the School of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received November 16, 1968*

Abstract: From the data obtained from conductance, differential vapor pressure, and solubility measurements in acetonitrile as solvent, it has been concluded that the tetramethylguanidinium ion (BH^+) forms a host of complex salts and ions with sulfate. The normal sulfate is present in solution as a stable dimer, $\{(BH)_2SO_4\}_2$, which dissociates into $(BH)_3SO_4^+$ and $BHSO_4^-$ ions, the ionic dissociation constant, K^d, being about 7×10^{-5}, while its solubility product $K_{sp} = 3.5 \times 10^{-7}$. In mixtures with a molar ratio of B:H_2SO_4 of 1.5 the solutions contain $(BH)_2SO_4\cdot BHHSO_4$ which dissociates into $(BH)_3SO_4^+$ and HSO_4^-; $K^d \sim 4 \times 10^{-4}$. This compares with a K^d of $BHHSO_4$ of 5×10^{-3}. Part of the complex is present as the dimer, $\{(BH)_2SO_4\cdot BHHSO_4\}_2$, the dimerization constant being of the order of 1.5×10^1. In mixtures with a molar ratio of B:H_2SO_4 of 1.67 a large fraction of sulfate is present as the complex $\{(BH)_2SO_4\}_2BHHSO_4$ which dissociates into $(BH)_5(SO_4)_2^+ + HSO_4^-$ with $K^d \sim 10^{-3}$. This has been substantiated by solubility measurements of $\{(BH)_2SO_4\}_2$ in dilute sulfuric acid. In a mixture of tetraethylammonium bisulfate ($K^d \sim 3 \times 10^{-2}$) with excess of B the reaction $B + HSO_4^- \rightleftharpoons BHSO_4^-$ occurs. The bisulfate also forms with $\{(BH)_2SO_4\}_2$ the complexes $Et_4N(BH)_2SO_4\cdot HSO_4$ and $Et_4N(BH)_2SO_4\cdot BHSO_4$ which are fairly strong electrolytes. Two complexes are formed between $\{(BH)_2SO_4\}_2$ and BHPi (picrate):$(BH)_2SO_4$BHPi and $\{(BH)_2SO_4\}_2$BHPi, the latter yielding the $(BH)_5(SO_4)_2^+$ ion. Conductometric and potentiometric titrations of sulfuric acid and of tetraethylammonium bisulfate with tetramethylguanidine in the absence and presence of the hydrogen-bond donor *p*-bromophenol are reported and interpreted.

In previous papers it was shown that the sulfate ion in acetonitrile (AN) has a great affinity toward uncharged hydrogen-bond donors[2] and forms a homoconjugate with the hydrogen-bond donor bisulfate ion[3] which is very unstable because of repulsive Coulombic forces. In the present study of the neutralization of sulfuric acid with tetramethylguanidine (B), it was found that the reaction of the acid with two molecules of B to form the normal sulfate, denoted for simplicity as $(BH)_2SO_4$, was close to complete, although on the basis of the acid strength of the bisulfate ion ($pK^d_{HSO_4^-} = 25.9$[3]) and the basic strength of B ($pK^d_{BH^+} = 23.3$[4]) the reaction should be highly incomplete. The only interpretation of the stability of $(BH)_2SO_4$ is that it is a very weak electrolyte, the sulfate ion concentration in its solutions being extremely small. In the salt the charge of the sulfate ion is neutralized by BH^+. Therefore, it is expected that the normal sulfate salt by hydrogen bonding forms stable conjugate ions with HSO_4^-, $BHSO_4^-$, and BH^+. Also, the ion $BHSO_4^-$ formed by reaction in AN of BH^+ with SO_4^{2-} is expected to be stable.

From conductometric and potentiometric titrations in AN of sulfuric acid and of tetraethylammonium bisulfate with tetramethylguanidine (TMG) and from differential vapor pressure (DVP) measurements in sulfuric acid–TMG mixtures conclusions could be drawn regarding the identity of the various hydrogen-bonded species. In order to confirm these conclusions solubility determinations were made of $(BH)_2SO_4$ in solutions containing various concentrations of sulfuric acid. To obtain an estimate of the stability of the $(BH)_2SO_4BH^+$ ion (and also the $\{(BH)_2SO_4\}_2BH^+$ ion), solubility determinations of $(BH)_2SO_4$ were made in solutions containing BH picrate. The salts formed, $(BH)_2SO_4\cdot$BHPi and $\{(BH)_2SO_4\}_2$BHPi, are strong electrolytes in AN. Most solubility determinations involving BH picrate were made in the presence of an excess of B in order to suppress acid–base dissociation of the salt (*vide infra*).

$$\{(BH)_2SO_4\}_2 \rightleftharpoons B + (BH)_2SO_4\cdot BHHSO_4$$

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