

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

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

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

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

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

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

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

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

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

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## Hydrogen Exchange of Azulenes. III. Kinetics and Mechanism of the Acid-Catalyzed Detritiation Reaction<sup>1,2</sup>

BY JANOS SCHULZE AND F. A. LONG

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The detritiation of azulene-H<sup>3</sup>(1) is general-acid catalyzed and in aqueous formate-formic acid buffers at 25° the first-order rate coefficient is  $k_{\text{obsd}} = 0.183C_{\text{H}^+} + 1.16 \times 10^{-3}C_{\text{HFm}}$ . From temperature coefficient studies, the Arrhenius parameters for the catalysis by strong acids are:  $E_A = 16.0$  kcal. mole<sup>-1</sup> and  $\Delta S^* = -10$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>. For catalysis by both strong and weak acids the ratio of rates for deuterium exchange to tritium exchange is  $k^{\text{D}}/k^{\text{T}} = 2$ . The strong acid-catalyzed exchange of tritium is 1.61 times faster in the solvent D<sub>2</sub>O than H<sub>2</sub>O; in intermediate H<sub>2</sub>O-D<sub>2</sub>O mixtures the rate ratios are in accord with predictions of the Gross-Butler theory. By combining the results for kinetic hydrogen isotope and solvent hydrogen isotope effects and assuming an A-SE2 mechanism *via* a conjugate acid intermediate, it is possible to calculate isotope effects for the rate coefficients for the individual steps. The numerical results are very similar to those reported recently by Kresge and Chiang for detritiation of 1,3,5-trimethoxybenzene. Detritiation rates for 1-nitro-, 1-formyl-, and 1-cyanoazulene are much slower than for azulene and in aqueous perchloric acid the rates follow the Hammett acidity function with  $\log k$  vs.  $-H_0$  slopes of from 1.05 to 1.2. The considerable differences between the acidity dependence of the kinetics of hydrogen exchange and of equilibrium protonation for these molecules is consistent with the fact that some of them protonate on oxygen and others on carbon. The kinetic and isotopic effects for the hydrogen exchange of azulenes are closely similar to those for several other aromatic proton exchange reactions and it is concluded that the A-SE2 or "orthodox" mechanism applies in all the cases so far reported.

### Introduction

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

Gold,<sup>5</sup> Melander,<sup>6,7</sup> Eaborn<sup>8</sup>, and Kresge<sup>9</sup> are particularly relevant to the present considerations.

A major problem from a mechanism standpoint has been that with most aromatic molecules the exchange rate does not become measurable until concentrated solutions of strong acids are utilized. This forces attention on questions of appropriate measurements of acidity. It also precludes utilization of the simplicities inherent in dilute solution studies: ideal behavior, unity value for activity coefficients, etc. The significance of this point arose early in the discussion of mechanisms. Gold and co-workers had found that for many benzene derivatives the rate of exchange of the aromatic hydrogens followed the Hammett acidity function  $h_0$  to very nearly the first power.<sup>5</sup> Applying the Zucker-Hammett hypothesis they concluded that an A-1 reaction mechanism was indicated, implying that the reaction involved a pre-equilibrium proton

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

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

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

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

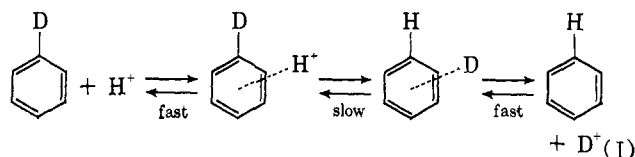
(1) Work supported by a grant from the Atomic Energy Commission.  
(2) Presented in part at the 139th and 140th Meetings of the American Chemical Society, St. Louis, Mo., April, 1961, and Chicago, Ill., September, 1961.

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

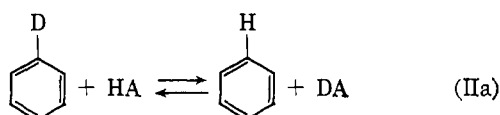
(4) V. Gold, "Aromatic Hydrogen Exchange. Vol. II. Friedel-Crafts and Related Reactions," Interscience Publishers, London, 1963.

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

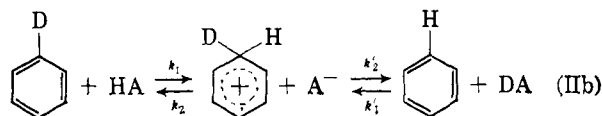
transfer to an intermediate species.<sup>10</sup> Since the overall isotope exchange reaction must be symmetrical, except for isotope effects, this is schematically



The postulated slow step is an intramolecular exchange from one form of the intermediate to the other. It was, however, soon pointed out<sup>3</sup> that the available evidence did not rule out a direct one-step slow proton transfer reaction, *i.e.*, a reaction following the A-SE2 mechanism. For the symmetric isotope exchange situation this mechanism in its simplest form is schematically



However, as Melander<sup>6,7</sup> has emphasized, it is entirely plausible that the reaction occurs through a comparatively stable intermediate conjugate acid



The significant point is that in contrast to the A-1 mechanism, this A-SE2 mechanism predicts general acid catalysis.

To establish general catalysis it is necessary to study a reaction in aqueous solutions which are sufficiently dilute that the limiting law approximations for activity coefficients and the ionic strength principle are valid. This implies either measuring exceedingly slow rates or working with aromatic species whose basicities are considerably greater than those of benzene and its simpler derivatives. This was one reason why azulene was initially selected for the present studies. Specifically, the early work of Plattner and co-workers had shown that the apparent  $pK$  of the conjugate acid of azulene was only about  $-0.7$ .<sup>11</sup> But another almost equally important reason for selecting azulene was that it was an unsubstituted hydrocarbon, *i.e.*, that it had no other base sites than the carbons of the ring. For the azulene ring, both theory and experiment had indicated that the basicity of the carbons at the 1- and equivalent 3-positions was uniquely high.<sup>12,13</sup> Initial studies with azulene- $H^2(1,3)$  showed that the deuterium exchange was acid catalyzed as expected. Of more significance, the exchange was found to be subject to general acid catalysis by such acids as formic and acetic.<sup>14</sup> Since a very similar result had been found by Kresge and Chiang for aromatic hydrogen exchange of 1,3,5-trimethoxybenzene,<sup>9a</sup> this was taken as strong indication that the A-SE2 mechanism might constitute the general explanation for this proton exchange reaction.

Further work with the acid-base equilibria of 1-substituted azulenes and with the structures of the azulonium ions has shown that although protonation com-

monly occurs on the unsubstituted 3-carbon, this is not invariably true in that protonation occasionally occurs on the substituent and in one case on the substituted 1-carbon.<sup>12,15,16</sup>

The present paper gives details of a study of the aromatic hydrogen exchange of azulenes with emphasis on a comparison of the behavior of different types of azulenes and on the problem of the reaction mechanism.

### Experimental

**Tritiated Azulenes.**—A similar procedure was used for the preparation of all the tritiated compounds and is illustrated here for the preparation of azulene- $H^3(1)$ . To a solution of 100 mg. of azulene in 1.5 ml. of ether, 1 ml. of tritiated water and 1 ml. of 70% aqueous perchloric acid were added, resulting in a homogeneous solution. After 3 min. the solution was poured into 750 ml. of water; the mixture was extracted with ether which was washed, dried, and purified by repeated chromatography on alumina.

In view of the known high basicity of the 3- (or 1-) position of azulene it was expected that tritiation would only occur at this site. Strong support for this view comes from the n.m.r. spectra of azulenes in strong acids. Independent of whether protonation is on the 3-carbon, or on the oxygen or nitrogen of a substituent, the n.m.r. spectra of the conjugated acids invariably show a peak due to a proton (or to two protons) on the 3-carbon, and this peak disappears when the n.m.r. of the conjugate acid is studied in a deuterated medium, indicating facile proton exchange at the 3-position.

**Kinetic experiments** were made by conventional procedures. Aqueous solutions of acids and of the azulenes were separately brought to temperature and then mixed to initiate the reaction. Final volume was normally 100 ml.; 10-ml. aliquots were removed and at definite times were put into separatory funnels which contained a quenching solution along with just 15 ml. of xylene. After extraction and separation, the xylene solution was briefly dried. Then 10 ml. of the dry xylene solution was pipetted into a scintillation counting vial along with 5 ml. of phosphor solution. Samples were then counted in a TRI-CARB scintillation counter. Rate coefficients were determined from plots of  $\log(C - C_\infty)$  vs. time where  $C$  and  $C_\infty$  are observed and background counts, respectively. In all cases the reactions were uncomplicated and accurately first order. Temperatures were controlled to  $\pm 0.02^\circ$ .

For the studies of general acid catalysis, a series of formic acid-sodium formate buffer solutions was prepared with use of sodium chloride to give solutions such that, after final dilution, the ionic strength was 0.1 and the hydrogen ion concentration was constant. Under the assumption that the influence of ionic strength on the dissociation constant of formic acid is the same as on acetic acid,<sup>17</sup> the calculated ionization constant was  $K_{0.1} = 2.884 \times 10^{-4}$  for 25° at an ionic strength of 0.1. The resulting acidity of the set of buffered solutions was  $C_{H^+} = 5.77 \times 10^{-4}$  mole/l.

### Results

The influence of aqueous acids on the rate of the tritium loss of azulene- $H^3(1)$  at 25° is summarized in Table I and Fig. 1. Table I shows that the reaction is acid catalyzed and that in solutions of strong acids the reaction is accurately first order in concentration of hydrogen ion. The listed average second-order rate coefficient of  $k_{H^+} = 0.183$  l. mole<sup>-1</sup> sec.<sup>-1</sup> was obtained by averaging the data for only the two higher acid concentrations but inclusion of the data at the lowest acidity only decreases the average to 0.180. Figure 1 gives the results for studies with formic acid-formate ion buffer mixtures, all at a constant hydrogen ion concentration of  $5.77 \times 10^{-4}$  M and at a constant ionic strength of 0.1. The straight line through the points is deliberately drawn through the value calculated for zero formic acid concentration from the rate coefficient as determined with strong acids. The equation for the resulting line is

$$k_{\text{obsd}}^T = k_{H^+}C_{H^+} + k_{FH}C_{FHm} \\ = 0.183C_{H^+} + 1.16 \times 10^{-3}C_{FHm}$$

It is clear from the figure that the formic acid data extrapolate essentially to the point calculated from the

(15) J. Schulze and F. A. Long, *Proc. Chem. Soc.*, 364 (1962).

(10) V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 3609 (1955).

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

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

(13) E. Heilbronner in D. Ginsburg, "Nonbenzenoid Aromatic Hydrocarbons," Interscience Publishers, Inc., New York, N. Y., 1959, p. 171.

(14) J. Colapietro and F. A. Long, *Chem. Ind. (London)*, 1056 (1960).

(16) F. A. Long and J. Schulze, *J. Am. Chem. Soc.*, **86**, 327 (1964); part II of this series.

(17) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1958, p. 676.

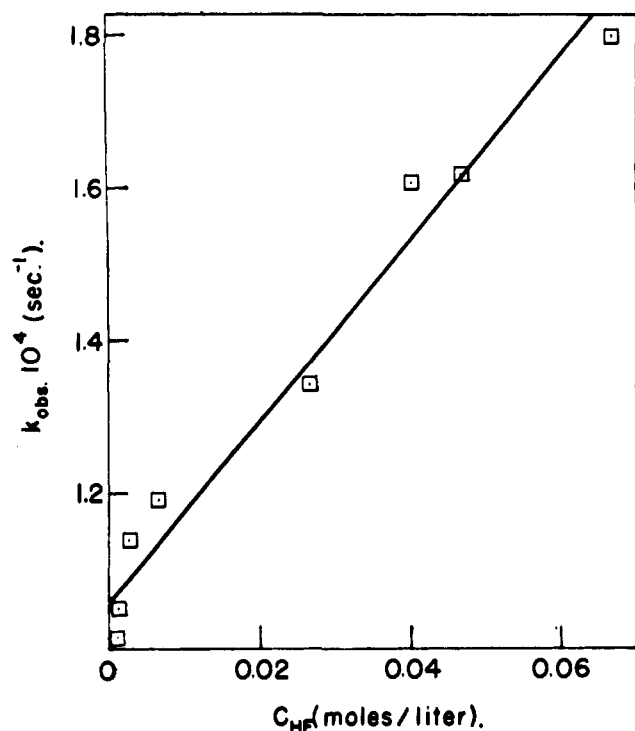


Fig. 1.—Acid-catalyzed tritium loss of azulene-H<sup>3</sup>(1) in formic acid-formate buffers at 25°.

data for strong acids and that in this sense the data of Table I and Fig. 1 are consistent.

For the acid-catalyzed dedeuterium of azulene-H<sup>3</sup> (1,3) Colapietro and Long<sup>14</sup> have as the analogous equation to the above

$$k^{\text{D}}_{\text{obsd}} = 0.36C_{\text{H}^+} + 2.7 \times 10^{-3}C_{\text{H}_2\text{Fm}}$$

Comparison of the two equations reveals that the kinetic isotope effect,  $k^{\text{D}}/k^{\text{T}}$ , for the azulene exchange is approximately 2 for catalysis by either a strong or a weak acid. This is a comparatively large isotope effect since it corresponds to a several-fold larger number for the more commonly measured ratio,  $k^{\text{D}}/k^{\text{T}}$ . The observed  $k^{\text{D}}/k^{\text{T}}$  value compares well with the ratio of 2 to 3 reported by Gold, Lambert, and Satchell<sup>5</sup> for the similar reactions of *p*-cresol and also with the value of 2.1 recently reported for the proton exchange reaction of 1,3,5-trimethoxybenzene.<sup>9c</sup> Apparently a large kinetic isotope effect is a consistent feature of the aromatic proton exchange reaction.

TABLE I  
DETRITIATION OF AZULENE AT 25° IN HCl-KCl SOLUTIONS,  
IONIC STRENGTH, 0.1

[H <sup>+</sup> ], mole/l <sup>1</sup>	$k_{\text{obsd}}$ , sec. <sup>-1</sup>	$k_{\text{H}^+}$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>
0.001	$1.70 \times 10^{-4}$	0.170
.001	$1.82 \times 10^{-4}$	.182
.001	$1.74 \times 10^{-4}$	.174
.005	$9.40 \times 10^{-4}$	.188
.005	$9.21 \times 10^{-4}$	.184
.005	$9.45 \times 10^{-4}$	.189
.010	$1.79 \times 10^{-3}$	.179
.010	$1.75 \times 10^{-3}$	.175

Studies have also been made of the solvent isotope effect, specifically of the detritiation of azulene-H<sup>3</sup>(1) in mixtures of H<sub>2</sub>O-D<sub>2</sub>O at 25° (Fig. 2). The observed value of  $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}}$  of 1.61 is virtually identical with the analogous values observed for detritiation of *p*-cresol,<sup>5</sup> 1.62, and of 1,3,5-trimethoxybenzene,<sup>9a</sup> 1.69. Assuming the validity of mechanism IIb, it is straightforward to derive from these ratios the isotope effects for the

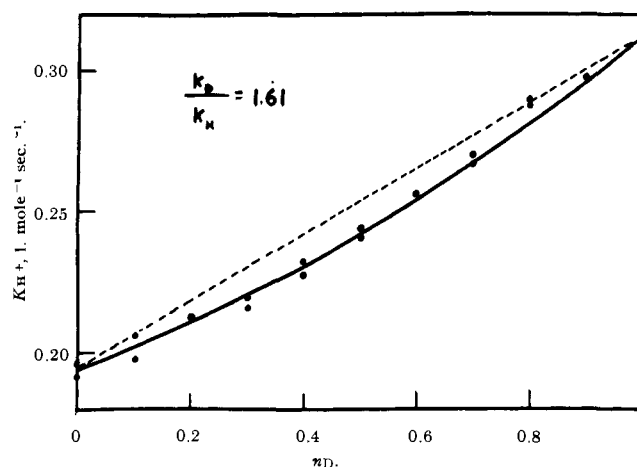


Fig. 2.—Detritiation of azulene-H<sup>3</sup>(1) in mixed H<sub>2</sub>O-D<sub>2</sub>O solvent at 25°; C<sub>H</sub><sup>+</sup> = 0.005 M.

individual rate coefficients  $k_1$  and  $k_2$ . This analysis was recently made by Kresge and Chiang for trimethoxybenzene.<sup>9c</sup> As is suggested by the similarity of the above experimental ratios, the results of a similar analysis with azulene are virtually identical. Specifically, we obtain  $k_1^{\text{H}_2\text{O}}/k_1^{\text{D}_2\text{O}} = 2.4$  and  $k_2^{\text{H}}/k_2^{\text{D}} = 5.6$ . The latter value, although slightly smaller than that reported by Kresge and Chiang, is still close to the maximum expected for a C-H break in a methylene group.

The dependence of the azulene detritiation rate on the atom fraction of deuterium in the H<sub>2</sub>O-D<sub>2</sub>O solvent is very similar to that observed by Gold, *et al.*,<sup>5</sup> for *p*-cresol. Specifically the data in both cases closely obey the "cubic" Goss-Butler equation rather than the alternative "linear" equation.<sup>18</sup>

The azulene detritiation in 0.005 M perchloric acid has been studied at five temperatures ranging from 0 to 42°. The data are very well fitted by the Arrhenius equation and lead at 25° to the following activation parameters using rate coefficients expressed in l. mole<sup>-1</sup> sec.<sup>-1</sup>:  $E_A = 16.0$  kcal. mole<sup>-1</sup>;  $\Delta S^* = -10.1$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>;  $\Delta F^* = \Delta H^* - T\Delta S^* = 19.0$  kcal. mole<sup>-1</sup>. These values are in accord with expectation. Specifically the entropy of activation is essentially the normal value for a second-order reaction; it is also close to the value obtained for such related aqueous reactions as the protodeboronation of *p*-methylbenzeneboronic acid<sup>19</sup> for which  $\Delta S^* = -15.5$  in 55% sulfuric acid and the ketonization of ordinary enols for which a  $\Delta S^*$  value of about -10 has been calculated.<sup>20</sup> Both of these reactions presumably involve slow proton transfers. No directly comparable data for the aromatic proton exchange reaction appear to be available.

Table II gives data on the exchange rates of three other tritiated azulenes, all of them considerably less basic than azulene itself. The exchange rates are sufficiently slower for all three to permit useful comparison of the rates with the  $H_0$  acidity function. Plots of  $\log k_{\text{obsd}}$  vs.  $-H_0$  are linear in all cases<sup>21</sup> and the resulting slopes vary from 1.05 to 1.2. A comparison of the rate and equilibrium data for these azulenes is given in Table III. As noted previously, there is a striking difference with the various azulenes in the

(18) For a discussion and comparison of these theories, see E. A. Halevi, F. A. Long, and M. A. Paul, *J. Am. Chem. Soc.*, **83**, 305 (1961).

(19) H. G. Kuivila and K. V. Nahabedian, *ibid.*, **83**, 2159, 2164, 2167 (1961).

(20) R. Bakule and F. A. Long, *ibid.*, **85**, 2313 (1963).

(21) For none of the studies of Table II is the acidity high enough to protonate a significant fraction of the azulene being studied. Hence, it is appropriate to plot  $\log k_{\text{obsd}}$  directly against  $-H_0$ .

TABLE II  
 EXCHANGE RATE COEFFICIENTS AT 25°

Tritiated compound <sup>a</sup>	CHClO <sub>4</sub> , moles/l.	H <sub>0</sub>	k <sub>obsd</sub> × 10 <sup>4</sup> , sec. <sup>-1</sup>
NO <sub>2</sub> Az	1.09	-0.27	0.090
	1.56	- .56	.170
	1.93	- .75	.249
	2.80	-1.14	.927
	3.39	-1.42	1.71
	3.98	-1.71	2.68
	4.46	-1.95	7.68
	4.88	-2.16	11.7
	5.36	-2.43	20.6
	CNAz	0.35	+0.35
0.58		+ .10	0.489
1.13		- .30	1.51
1.56		- .56	2.82
1.98		- .78	5.47
2.42		- .93	10.0
2.74		-1.12	14.6
3.12		-1.29	25.2
3.68		-1.56	45.4
CHOAz		0.24	+0.54
	0.56	+ .12	0.831
	1.12	- .30	2.13
	1.55	- .56	3.72
	1.96	- .76	7.06

<sup>a</sup> Symbols are explained in paper I.

value of  $d \log I/dH_0$ , where  $I$  is the indicator ratio, depending on whether protonation occurs on a ring carbon or on a substituent oxygen. This difference is *not* reflected in the kinetics since all the azulenes show  $H_0$  slopes close to unity. Since it can be assumed that the transition state for exchange in every case involves attack of an acid on the 3-carbon, this closely similar kinetic acidity dependence is the expected result and the fact that there is a difference in the equilibrium protonation of those molecules which carry an oxygenated substituent is largely irrelevant to the kinetic analysis. Similarly, when conjugate acids of different structure are formed, the relative ease of equilibrium protonation need not reflect the relative speeds of exchange of the proton on the 3-carbon and a comparison of the fourth and sixth columns of Table III is a good illustration of this point. In fact, the comparative rates indicated by the sixth column of Table III probably constitute the best available comparison of the relative carbon basicities of these four azulenes.

 TABLE III  
 COMPARISON OF EQUILIBRIUM AND KINETIC EXCHANGE PROPERTIES

Compound	Site	Equil. protonation		Exchange rates	
		$d \log I/dH_0$	$-H_0$ for $I = 1$	$-d \log k_{obsd}/dH_0$	$-H_0$ for $\log k_{obsd} = 4$
Az	C	1.9	0.92	1.00 <sup>a</sup>	-3.2
CHOAz	O	1.1	1.12	1.05	0.0
CNAz	C	1.8	4.59	1.20	+0.1
NO <sub>2</sub> Az	O	1.0	4.76	1.08	+1.2

<sup>a</sup> Not a significant value since the kinetics were studied at acidities so low that  $\log C_{H^+}$  and  $-H_0$  are identical.

In connection with these data it should be noted that a correlation of exchange rates for hydrogens at the 3-carbon with  $\sigma_m$  values for the 1-substituent is only moderately successful. The values of  $\sigma_m$  for the substituents and the value of  $\log k$  at a standard acidity of  $H_0 = 0$  are: for H, as the 1-substituent,  $\sigma_m = 0$  and  $\log k = -0.75$ ; for CHO,  $\sigma_m = 0.382$  and

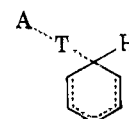
$\log k = -3.92$ , for CN,  $\sigma_m = 0.68$  and  $\log k = -4.12$ ; for NO<sub>2</sub>,  $\sigma_m = 0.71$  and  $\log k = 5.3$ . These data do not give a very satisfactory linear plot. However, they do suggest an approximate  $\rho$ -value of  $-6$ , indicating a pronounced substituent effect in the expected direction.

## Discussion

The kinetics of the acid-catalyzed aromatic hydrogen exchange have now been studied for a wide range of species and conditions. There have been changes in the character of the aromatic ring system and in the type and number of substituents. Basicities have ranged from as high as that of azulene to as low as that of benzene. In spite of these variations, the evidence is strong that the same essential mechanism applies in all cases. Since, in the past, this has occasionally been questioned, it is useful to summarize the evidence: A. The reaction follows the acidity function  $H_0$  with a slope ranging from 1 to 1.5 in virtually all cases.<sup>22</sup> B. General acid catalysis has been observed for two molecules of different type and different basicity, azulene and trimethoxybenzene. C. The relative rates in the solvents D<sub>2</sub>O and H<sub>2</sub>O are very similar in all cases studied, as are the rates in mixed H<sub>2</sub>O-D<sub>2</sub>O solvents. D. The kinetic hydrogen isotope effect is closely similar in the cases studied, the  $k^D/k^T$  ratio being approximately 2.

The mechanism which is indicated by the observation of general acid catalysis and which Eaborn and Taylor<sup>8</sup> label "orthodox" in view of its similarity to the usually accepted mechanism for electrophilic substitution is the one we have earlier given as IIb. Clearly the acid-catalyzed results are not consistent with the "outer complex" mechanism proposed by Gold and Satchell.<sup>23</sup> And since it appears that the same essential mechanism holds for the various aromatic substrates, we conclude, in agreement with most workers in the field, that there does not appear to be a need for the "outer complex" mechanism in the interpretation of any of the available exchange data.

The essential feature of the A-SE2 or "orthodox" mechanism is contained in the statement that the structure of the transition state is schematically



The points of importance are: (1) participation of a general acid; (2) some stretching of the other C-H bond; (3) some trend toward a  $\sigma$ -bond at the carbon where exchange occurs with a concomitant perturbation in the resonance character of the ring system. All of these effects should vary in some degree as the basicity of the substrate changes.

A point of considerable interest is whether this exchange reaction goes by way of a true  $\sigma$ -complex

(22) This point needs some qualification in view of the Eaborn and Taylor results with benzene and toluene. These authors report that with both toluene-H<sup>+</sup>(3) and benzene-H<sup>+</sup> the rates of exchange in aqueous sulfuric acid give curved  $\log k$  vs.  $-H_0$  plots with slopes ranging from perhaps 1.5 to 2. We have no quarrel with either these values or the authors' conclusion that there is no linear relation between the rate of exchange and the  $H_0$  function. The purpose of the present discussion is to argue that the acidity dependence of the exchange reaction is much the same for the various substrates. Actually, the data for the benzenes, and indeed the data for the azulenes also, do suggest that there is a trend toward larger values of the slope for the less basic substrates but, as we will show later, this is a result which argues only for some slight expected changes in transition state properties rather than any basic change in mechanism.

(23) V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 3609, 3619, 3622 (1955); 2743 (1956).

intermediate, *i.e.*, by way of the symmetric  $\sigma$ -bonded conjugate acid. This is virtually equivalent to asking whether the mechanism is actually IIb or is something nearer to IIa? When, as for the azulenes, the conjugate acid can itself be easily formed and studied, it is most plausible to assume its participation. Furthermore, as Melander<sup>6,7</sup> has noted, similar stable intermediates are plausible participants in most electrophilic substitutions. The implication of reaction *via* the conjugate acid is illustrated semiquantitatively for azulene itself in Fig. 3. The position of the minimum for the intermediate can be determined since the  $pK$  of azulene is known to be  $-1.7$ .<sup>16</sup> This leads to  $\Delta F^\circ$  for the equilibrium protonation of roughly 2.5 kcal./mole. Since  $\Delta F^*$  for the exchange reaction is 19 kcal./mole, the general shape of Fig. 3 is established.

An important implication of Fig. 3 is that the kinetics of formation of the conjugate acid species or of its decomposition should be predictable from data on the exchange reaction. For the particular case of azulene the predicted rates, under experimentally attainable conditions, are slow enough to be measurable. This suggests the possibility of directly verifying

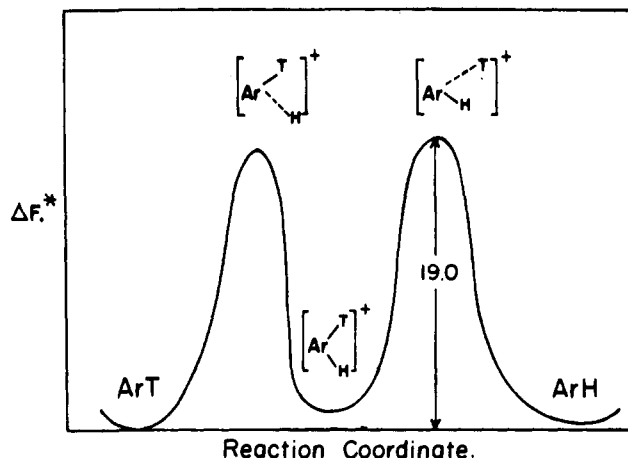


Fig. 3.—Free energy pattern of the acid-catalyzed detritiation reaction of azulene- $H^+(1)$ .

that the exchange reaction does proceed *via* the conjugate acid intermediate and experiments along this line are now in progress.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON, WIS., AND THE DIAMOND ALKALI CO., PAINESVILLE, OHIO.]

## Strain Energies in Hydrocarbons from Heats of Combustion. II. Concerning the Possibility of a Transannular Interaction in 1,8-Cyclotetradecadiyne<sup>1</sup>

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Heats of combustion of solid  $C_{14}H_{28}$  and  $C_{14}H_{20}$  and heats of sublimation from Knudsen effusion studies have been used to show that there is no appreciable transannular interaction in 1,8-cyclotetradecadiyne.

Some preliminary combustion calorimetric data led Wotiz and co-workers<sup>3</sup> to suggest that an appreciable transannular interaction between the triple bonds was present in 1,8-cyclotetradecadiyne. These data actually yielded a negative heat of formation while one would predict about +70 kcal./mole for the heat of formation of the gas from normal bond energies. A more detailed study was undertaken to see if there was unequivocal evidence for strong transannular bonding in this molecule.

### Experimental Results

Carefully purified samples of both the 1,8-cyclotetradecadiyne ( $C_{14}H_{20}$ ) and its saturated analog cyclotetradecane ( $C_{14}H_{28}$ ) were used in these high-precision measurements. Heats of oxidation were measured in the oxygen bomb calorimeter described by Frisch.<sup>4</sup>

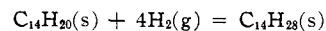
In Tables I and II are presented the heat of oxidation data for the solids  $C_{14}H_{28}$  and  $C_{14}H_{20}$ . From four combustions of  $C_{14}H_{28}$ , a heat of formation of  $-88.94 \pm 0.98$  kcal./mole was obtained, in good agreement ( $\pm 0.03\%$ ) with data on  $C_{14}H_{28}$  reported by Coops, *et al.*<sup>5</sup> For the alkyne, a heat of formation of  $+35.31 \pm 0.56$  kcal./mole was obtained from five runs (Table II). Carbon was produced in several of the runs and cor-

rected for at the rate of 7.84 cal./mg. These data were derived using a density<sup>6</sup> of 0.942 g./cc. for  $C_{14}H_{28}$  and 1.040 g./cc. for  $C_{14}H_{20}$  and the molecular weights of 196.379 and 188.316, respectively.

Vapor pressure measurements were made by the Knudsen technique on both  $C_{14}H_{28}$  and  $C_{14}H_{20}$  with the vacuum microbalance.<sup>7</sup> A dewar flask thermostat was used for temperature control with a light bulb serving as a heater. The results are summarized in Tables III and IV. The two experiments for  $C_{14}H_{28}$  were averaged, weighted by the reciprocal of their uncertainties, to yield  $\Delta H_s = 32.21 \pm 0.35$  kcal./mole, from which the heat of formation for the gas was derived as  $-56.73 \pm 0.76$  kcal./mole. The single set of data on  $C_{14}H_{20}$  gave  $\Delta H_s = 39.68 \pm 0.76$  kcal./mole and the resulting heat of formation of the gas is  $+74.99 \pm 0.95$  kcal./mole.

### Discussion

The oxidation data yield the heats of formation of the solids; one derives, for the reaction



a heat of  $-124.25 \pm 0.91$  kcal./mole. With the heats of sublimation one finds the heat of hydrogenation in the vapor phase to be  $-131.72 \pm 0.95$  kcal./mole. Conn, Kistiakowsky, and Smith<sup>8</sup> have determined the heat of hydrogenation of dimethylacetylene in the

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(1) Presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962.

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