

# Hydrogen Exchange of Azulenes. V. The Kinetics of Proton Transfer in Acidic Aqueous Media<sup>1,2</sup>

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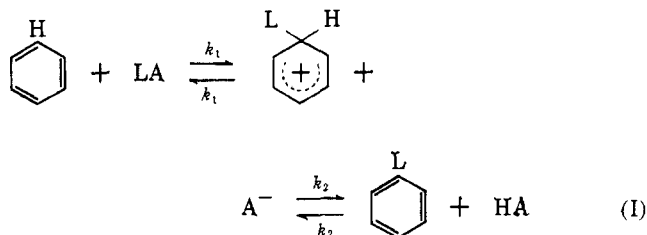
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The rates of proton transfer to and from azulene in aqueous solution have been studied as a function of temperature and acidity using a continuous fast-flow apparatus of the Hartridge-Roughton type. Parallel determination of the equilibrium protonation permits calculation of the separate values of  $k_f$  and  $k_r$ , the first-order rate coefficients for protonation and deprotonation. At 7.3° and for the acidity range from 1.5 to 4.0 M perchloric acid,  $k_f = 1.52h_0^{1.26}$  and  $k_r = 110h_0^{-0.68}$ , where  $h_0$  is the Hammett acidity function. In 1.93 M perchloric acid the Arrhenius parameters are: for protonation (sec.<sup>-1</sup> units),  $\Delta F^* = 16.0$  kcal.,  $\Delta H^* = 15.0$  kcal.,  $\Delta S^* = -3.2$  e.u.; for deprotonation (sec.<sup>-1</sup> units),  $\Delta F^* = 15.6$  kcal.,  $\Delta H^* = 12.4$  kcal.,  $\Delta S^* = -11.0$  e.u. The protonation rate, extrapolated to a 0.1 M aqueous electrolyte solution, agrees closely with a protonation rate for the same medium derived from isotopic hydrogen exchange data for low acidities. This and the Arrhenius data for the protonation provide direct, semiquantitative support for a two-stage A-SE2 mechanism for the detritiation of azulene-1-*t* and thus confirm earlier proposals.

## Introduction

The acid-catalyzed exchange of hydrogen attached to the aromatic nucleus has been subject to intensive study in recent years. The reaction is of interest because it represents the simplest kind of electrophilic aromatic substitution and also because a detailed analysis of the reaction should generate a firmer understanding of both acidity function correlations and hydrogen isotope effects for acid-catalyzed reactions in general. The wealth of data presently available has been obtained exclusively from studies utilizing the exchange of deuterium and of tritium with hydrogen itself,<sup>3-5</sup> and these have presented evidence to support a two-step A-SE2 exchange mechanism; the situation has been reviewed recently in detail by several authors.<sup>3-8</sup>

The two-stage A-SE2 mechanism for hydrogen exchange can be represented diagrammatically in the following manner, using L for the general lyon H, D, or T



The neutral molecule reacts initially with the lyon donor, either a general acid in the Brønsted sense or the lyonium ion itself, to form its conjugate acid intermediate, which then reacts with a base present in the system to produce either the initial material or the product in which substitution of hydrogen has occurred. The first step of the reaction is therefore reversible; in principle, the second step is also reversible, but, with isotopic substitution in the substrate at tracer level, the second step can be regarded as unidirectional. The expected free-energy profile for the A-SE2 mechanism is illustrated by Figure 1. The two free-energy maxima correspond to the two transition states and should be of closely similar magnitude; the free energy minimum corresponds to the relatively stable conjugate acid.

A direct study of the rate of protonation of an aromatic substrate should provide information about the first step of the A-SE2 reaction path and about the first maxima of the free-energy profile. Thus, a comparison of the rate and energetics of protonation with those for isotopic hydrogen exchange becomes a critical test for the formation of the conjugate acid as an intermediate in the exchange process, a criterion of the A-SE2 mechanism of exchange. More important, however, protonation studies permit a direct comparison of the acidity dependence of transition state and conjugate acid formation since both investigations are performed under similar solvent conditions.

Azulene is a relatively strong base and is about 50% protonated in 2.2 M perchloric acid.<sup>9</sup> Protonation is known to occur exclusively at the 1 or equivalent 3 position.<sup>10</sup> The degree of protonation increases much more rapidly with acidity than that observed for Hammett type indicators; thus, a plot of  $\log [\text{AzH}_2^+]/[\text{AzH}]$  against  $-H_0$  has a slope<sup>9</sup> of 1.84 at 25°. The rate of detritiation of azulene-1-*t* in dilute acids (0.01 M) is such that,<sup>5</sup> allowing for an isotope effect, protonation should occur with a half-life of a few milliseconds in media sufficiently acidic for the azulene to be largely protonated at equilibrium.

## Experimental

**Materials.** Baker and Adamson 70% perchloric acid to American Chemical Society specifications was used without further purification. Azulene supplied by

- (1) Work supported by a grant from the Atomic Energy Commission.
- (2) Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1963.
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- (7) (a) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1959; (b) L. Melander and S. Olson, *Acta Chem. Scand.*, **10**, 879 (1956).
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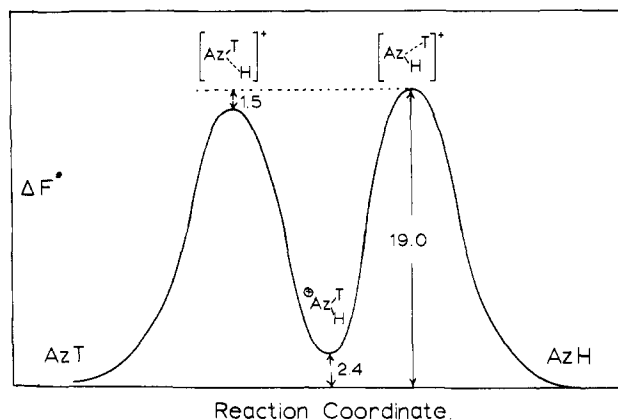


Figure 1. Free-energy profile for two-stage A-Se2 mechanism.

Aldrich was purified by first passing a solution in heptane through a neutral alumina column (Woelm No. 1) and then eluting with diethyl ether. After evaporating the ethereal solution to dryness, the solid azulene was vacuum sublimed at 50°.

**Kinetic Technique.** The reactions were studied in a continuous-flow apparatus of the Hartridge-Roughton type developed to handle concentrated solutions of strong acids and capable of mixing these solutions in less than 1 msec. Two solutions were prepared initially: one was invariably a nearly saturated solution of azulene (about  $10^{-5}$  M) in approximately 1 M perchloric acid; the other was an aqueous perchloric acid solution whose acidity was adjusted so that, when mixed with an equal volume of the acidified azulene solution, the total acidity of the combined solutions was that desired for the particular kinetic experiment. The two solutions were separately fed by a mechanical syringe pump, *via* a mixing chamber, to a quartz observation tube. The extent of reaction was measured by determining the change in light absorption at 3500 Å., the extinction coefficients of azulene and its conjugate acid at 3500 Å. are 180 and 13,200, respectively.<sup>9</sup> Generally, the observation point was kept constant, and the extent of reaction varied by altering the rate of fluid flow through the tube. A sample of the reaction solution was collected and analyzed for perchloric acid by titration against standard alkali. Apart from monitoring the light absorption, the temperature of the flowing solution was also determined by means of an iron-constantan thermocouple; indicated temperature control was to  $\pm 0.4^\circ$ .

A limited number of experiments was performed, in which either the rate of approach to equilibrium was studied from the opposite, conjugate-acid side, or the position of observation along the tube was varied. The results from these experiments agree within experimental error with those obtained from the other studies.

**Calculation of Rate Coefficients.** The recorded signal for each particular point of a kinetic experiment is illustrated diagrammatically by Figure 2. Line A and line B refer to the initial perchloric acid and unreacted azulene solutions, respectively; line C refers to the combined solutions under flow, and line D refers to the combined solutions after flow has ceased and equilibrium has been attained. The experimental results provide information on the observed first-order

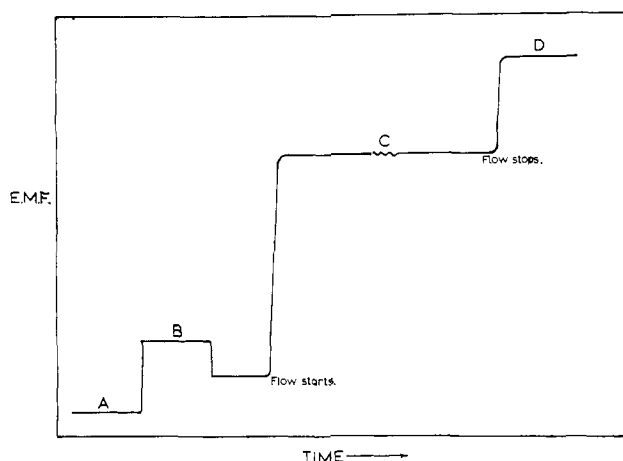


Figure 2. Schematic diagram of the recorded signal for a single kinetic point.

rate coefficient for the approach to equilibrium ( $v = k_{EX}[AzH]$ ) given by

$$k_{EX} = \frac{2.303}{t} \log \frac{[AzH_2^+]_e - [AzH_2^+]_0}{[AzH_2^+]_e - [AzH_2^+]_t} \quad (1)$$

where  $[AzH_2^+]$  refers to concentration of conjugate acid, and the subscripts e, 0, and t refer to equilibrium and to times zero and t, respectively. Thus, in terms of the recorded signal (see Figure 2) and, provided the change in absorption is quite small

$$k_{EX} = \frac{2.303}{t} \log \left[ \frac{D - \frac{1}{2}(A + B)}{D - C} \right]^t \quad (2)$$

The time of reaction (t) was calculated from the rate of fluid flow through the observation tube. Usually, the value of  $k_{EX}$  was determined from the experimental results by plotting  $\log \left[ \frac{D - \frac{1}{2}(A + B)}{D - C} \right]^t$  against t, the slope of the best straight line being equated to  $2.303/k_{EX}$ . For some experiments, especially those at the lowest acidity, in which the difference in absorption of the unreacted azulene and perchloric acid solutions was large, it proved more convenient to regard the recorded signal for the fastest flow rate as that of a hypothetical time zero, and the equations used to derive  $k_{EX}$  were adjusted accordingly. For the present work, the reaction half-lives varied from about 4 to 14 msec., and the first observation was invariably recorded after an elapsed time of about 2 msec. The reaction was accurately first order to better than 85% of the reaction, as is illustrated by the typical experiment cited in Table I.

Rate coefficients for the forward and reverse reactions,  $k_f$  and  $k_r$ , respectively, were determined from the rate of approach to equilibrium in the usual manner

$$k_f = \frac{k_{EX}}{1 + [AzH]_e/[AzH_2^+]_e} \quad (3)$$

and  $k_r = k_{EX} - k_f$ .

**Equilibrium Studies.** Solutions of predetermined acidity and known total azulene concentration were prepared by volume dilution at the experimental temperature. The acidity was checked by titration against standard alkali. The spectra were measured on a

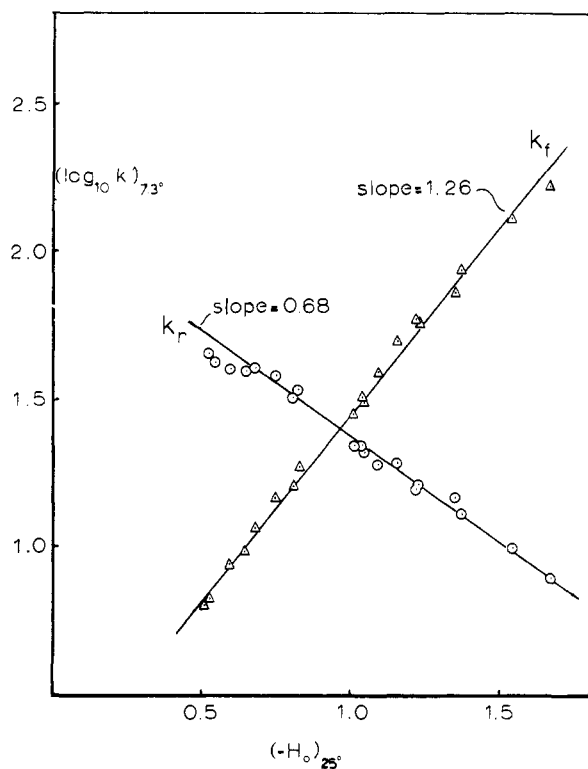


Figure 3. Plot of  $\log k_r$  and  $\log k_f$  against  $-H_0$  at  $7.3^\circ$ .

Carey Model 14 spectrophotometer so modified that the quartz cells could be maintained at a predetermined temperature to  $\pm 0.1^\circ$ . The spectra of the various solutions were recorded from 2200 to 3600 Å. against a water reference. The ratio of  $[\text{AzH}_2^+]/[\text{AzH}]$  was

Table I. Typical Kinetic Experiment (No. 16) at  $7.3^\circ$  for  $[\text{HClO}_4] = 3.275 M$

$t \times 10^3$ , sec.	% reaction	$k_{\text{EX}}$ , sec. <sup>-1</sup>
4.38	30.2	82.6
5.06	30.3	87.7
5.27	35.8	84.3
6.58	43.3	87.5
6.62	43.8	85.9
7.65	47.7	84.6
8.97	52.7	83.4
9.06	52.9	83.1
11.0	60.5	84.4
14.3	68.2	79.7
18.0	78.4	85.0
22.1	84.6	84.6
25.0	87.3	82.4
31.0	91.7	80.3
31.7	90.6	74.4
Av. $k_{\text{EX}} = 83.9 \text{ sec.}^{-1}$		

determined at several wave lengths from the relationship

$$\frac{[\text{AzH}_2^+]}{[\text{AzH}]} = \frac{\epsilon^\lambda_{\text{AzH}} - \epsilon^\lambda}{\epsilon^\lambda - \epsilon^\lambda_{\text{AzH}_2^+}} \quad (4)$$

where  $\epsilon^\lambda_{\text{AzH}_2^+}$  = extinction coefficient of the conjugate acid at wave length  $\lambda$ ;  $\epsilon^\lambda_{\text{AzH}}$  = extinction coefficient of the neutral azulene at wave length  $\lambda$ ;  $\epsilon^\lambda$  = extinction coefficient of the test solution at wave length  $\lambda$ . A

mean value was deduced. Slight decomposition of the azulene was observed in the more concentrated acidic solutions at the higher temperatures. Where necessary, the spectra were extrapolated to zero time to correct for this.

## Results

**Kinetic Studies.** The variation of the observed first-order rate coefficient ( $k_{\text{EX}}$ ) as a function of perchloric acid concentration is given in Table II. Values of the forward and reverse first-order rate coefficients ( $k_f$  and  $k_r$ , respectively) calculated from eq. 3 are also tabulated. The second and third columns of Table II list the corresponding values of  $-H_0$  and  $[\text{AzH}_2^+]/[\text{AzH}]$ . A plot of  $\log k_f$  and  $\log k_r$  against the Hammett acidity function ( $H_0$ ) is shown in Figure 3. For the protonation reaction, the equation of the best straight line by the method of least squares is  $\log k_f = 0.18 + 1.26(-H_0)$ . Thus, the acidity dependence compares well with that reported by Schulze and Long<sup>5</sup> for the detritiation of substituted azulenes in concentrated perchloric acid and also with that for isotopic hydrogen exchange of trimethoxybenzene-*t* in similar media.<sup>3</sup> The coefficient for the reverse reaction, from a simple stoichiometric standpoint, should be independent of acidity. The observed decrease in rate with acidity,  $k_r \propto h_0^{-0.68}$ , indicates a strong medium effect.

Table II. Variation of  $k_{\text{EX}}$ ,  $k_f$ , and  $k_r$  with Acidity at  $7.3 \pm 0.4^\circ$

$[\text{HClO}_4]$ , M	$-H_0$	$[\text{AzH}_2^+]/$ $[\text{AzH}]^a$	$k_{\text{EX}}$ , sec. <sup>-1</sup>	$k_f$ , sec. <sup>-1</sup>	$k_r$ , sec. <sup>-1</sup>
1.46	0.510	0.139	51.3	6.3	44.9
1.48	0.527	0.148	51.4	6.6	44.6
1.49	0.532	0.150	48.3	6.3	42.0
1.61	0.592	0.195	48.3	8.7	39.6
1.71	0.644	0.245	48.8	9.6	39.2
1.78	0.680	0.284	52.0	11.5	40.5
1.92	0.750	0.385	52.4	14.6	34.8
2.05	0.805	0.504	47.8	16.0	32.0
2.09	0.825	0.543	52.2	18.6	34.2
2.50	1.01	1.28	50.0	28.1	21.9
2.57	1.04	1.46	53.9	32.0	21.9
2.58	1.045	1.49	51.1	30.6	20.5
2.69	1.09	1.86	59.8	38.9	18.9
2.85	1.16	2.60	68.9	49.8	19.1
2.99	1.22	3.51	74.6	58.1	15.5
3.00	1.23	3.57	73.7	57.6	16.1
3.28	1.34	6.21	83.9	72.3	11.6
3.31	1.35	6.43	98.3	85.6	12.4
3.65	1.54	13.2	139	129	9.8
3.91	1.67	21.6	174	166	7.7

<sup>a</sup> From equilibrium studies at  $5.7^\circ$ .

The temperature dependence of  $k_{\text{EX}}$ ,  $k_f$ , and  $k_r$  is given in Table III for reaction in 1.93 M perchloric acid over the limited temperature range from  $7.3$  to  $19.9^\circ$ .

Table III. Variation of  $k_{\text{EX}}$ ,  $k_f$ , and  $k_r$  as Functions of Temperature for  $\text{HClO}_4 = 1.93 M$

Temp., °C.	$[\text{AzH}_2^+]/$ $[\text{AzH}]$	$k_{\text{EX}}$ , sec. <sup>-1</sup>	$k_f$ , sec. <sup>-1</sup>	$k_r$ , sec. <sup>-1</sup>
$7.3 \pm 0.4$	0.398	52.4	14.9	37.5
$12.7 \pm 0.4$	0.427	79.0	23.6	55.4
$16.7 \pm 0.2$	0.450	108	33.5	74.5
$19.9 \pm 0.2$	0.470	138	44.1	93.9

There is an appreciable increase in all three rate coefficients with rising temperature. Discussion of the results and the calculation of Arrhenius activation parameters is deferred until later.

**Equilibrium Studies.** The variation of the indicator ratio  $[AzH_2^+]/[AzH]$  with perchloric acid concentration is listed for four different temperatures in Table IV. The tabulated values are the mean of at least two independent experiments at the same temperature.

**Table IV.** Variation of  $[AzH_2^+]/[AzH]$  with Acidity as a Function of Temperature

$[HClO_4]$ , $M$	$[AzH_2^+]/[AzH]$			
	5.7°	15.5°	25°	38.6°
1.0	0.046	0.062	0.071	0.107
1.5	0.154	0.187	0.217	0.305
2.0	0.453	0.502	0.579	0.782
2.5	1.25	1.41	1.47	1.88
3.0	3.52	3.86	4.00	5.15
3.5	9.64	10.3	11.1	13.5

Thermodynamic dissociation constants ( $K_{AzH_2^+}$ ) have been determined from the data by plotting  $\log [AzH_2^+]/[AzH][H^+]$  against perchloric acid concentration and extrapolating to zero acid concentration.<sup>11</sup> The results are summarized in Table V. The value of  $K_{AzH_2^+} = 56$  at 25° agrees well with that obtained by the "overlap method" with 1-methylazulene; 1-methylazulene is

**Table V.** Thermodynamic Dissociation Constant  $K_{AzH_2^+}$  as a Function of Temperature

Temp., °C.	$K_{AzH_2^+}$ , mole l. <sup>-1</sup>
5.7	106 ± 6
15.5	69 ± 6
25.0	56 ± 6
38.6	36 ± 6

more basic than azulene, and reliable values for the indicator ratio can be measured at perchloric acid concentrations as low as 0.4  $M$ . From the variation of  $K_{AzH_2^+}$  with temperature, values of  $\Delta F^\circ = -2.4$  kcal.,  $\Delta S^\circ = -11$  e.u., and  $\Delta H^\circ = -5.8$  kcal. are obtained for the equilibrium ionization of the conjugate acid at 25°. Thus, the stability of the conjugate acid is comparable to that of azulene itself. The entropy of ionization is particularly interesting. The neutral azulene molecule itself has a very small Setchenow parameter,<sup>12</sup> and we conclude that it behaves much like benzene in aqueous solutions and is largely unsolvated. Assuming that the hydronium ion is solvated by four water molecules and that the entropy increases by  $-5$  e.u. for each water molecule "frozen" in the ionization process,<sup>13</sup> it is apparent that the azulenium ion itself must be solvated by just two molecules of water. Although Danyluk and Schneider<sup>14</sup> conclude much of the positive charge is localized in the

seven-membered ring, the n.m.r. spectrum of the azulenium cation indicates the methylene hydrogens are strongly acidic, and presumably each is solvated by one molecule of water.

## Discussion

We have chosen to correlate the kinetic data with the Hammett acidity function mainly because this is the most firmly established of several functions measured with different types of indicators. We recognize that, in the light of recent measurements,<sup>15-20</sup>  $H_0$  is not a measure of hydrogen ion activity and that, for azulene,  $H_0$  does not correlate simply with conjugate acid formation. Nonetheless, the large variation of the rate of both protonation and deprotonation on  $H_0$  clearly indicates that both reactions are particularly sensitive to the composition of the medium.

One of the reasons for undertaking the present work was to establish that conjugate acid formation was indeed a step in aromatic isotopic hydrogen exchange. The measurements of Schulze and Long<sup>5</sup> for the detritiation of azulene-1- $t$  refer exclusively to experiments performed in dilute (0.01  $M$ ) perchloric acid maintained at an ionic strength of 0.1 by the addition of neutral salts. Thus comparisons of their data with those for protonation are insignificant unless some compensation is made for the difference in media, for example, by referring all the data to a common standard state. The procedure used here involves the development of appropriate linear extrapolations to permit the calculation of rate coefficients for the infinitely dilute aqueous solution. The same functions also permit interpolation of the data to an electrolyte concentration of 0.1  $M$ , the standard medium used in the studies by Schulze and Long.<sup>5</sup>

For the equilibrium protonation data, extrapolation to the infinitely dilute standard state was accomplished by extrapolating the plot of  $\log [AzH_2^+]/[AzH][H^+]$  vs. acid molarity to zero perchloric acid concentration,<sup>11</sup> i.e., by defining the thermodynamic equilibrium constant as

$$-\log K_{AzH_2^+} = \lim_{[H^+] \rightarrow 0} \left[ \log \frac{[AzH_2^+]}{[AzH]} - \log [H^+] \right] \quad (5)$$

The kinetic data may be treated similarly. The rate law for protonation can be expressed readily in terms of activities

$$-\frac{d(AzH)}{dt} = k_f[AzH] = k_{bi}[AzH][H^+] \quad (6)$$

$$= k_{bi}^0[AzH][H^+] \frac{f_{AzH}f_{H^+}}{f^*} \quad (7)$$

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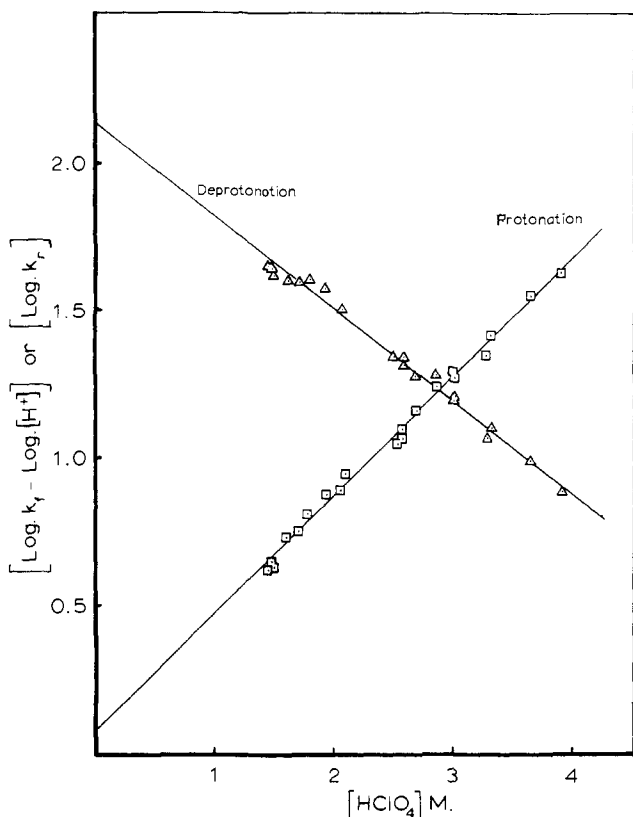


Figure 4. Linear extrapolation for protonation and deprotonation reactions at 7.3°.

Equating the right-hand sides of eq. 6 and 7 and taking logarithms produces

$$\log k_{bi}^0 = \log k_f - \log [H^+] - \log \frac{f_{AzH} f_{H^+}}{f^*} \quad (8)$$

If, by definition, the activity coefficients are referred to a value of unity at infinite dilution, then

$$\log k_{bi}^0 = \lim_{[H^+] \rightarrow 0} [\log k_f - \log [H^+]] \quad (9)$$

and a linear extrapolation should be valid, just as for the ionization equilibrium. A similar treatment of the deprotonation data leads to the relationship

$$\log k_r^0 = \lim_{[H^-] \rightarrow 0} [\log k_r] \quad (10)$$

Equations 9 and 10 are the kinetic counterparts of (5) for equilibrium protonation, and the same considerations and strictures apply to all three equations. In each case, the utilization of a linear extrapolation depends on an assumed linear dependence of a logarithm of an activity coefficient ratio on electrolyte concentration. For the kinds of ratios involved here, such behavior is consistent both with theory and with empirical evidence.

The plots for the kinetic data are shown in Figure 4; both are linear within the limits of experimental accuracy. Least-squares treatments of the data lead to values of  $k_{bi}^0 = 1.17$  l. mole<sup>-1</sup> sec.<sup>-1</sup> and  $k_r^0 = 135$  sec.<sup>-1</sup> at infinite dilution. A precise test of both extrapolations is to compare the value of the ratio  $k_r^0/k_{bi}^0$  (= 115) with the previously determined value of  $K_{AzH_2^-}$  (= 100) at the experimental temperature of

7.3°. The agreement is reasonable considering the long extrapolations.

The lower linear plot of Figure 4 leads to a value of  $k_{bi} = 1.28$  l. mole<sup>-1</sup> sec.<sup>-1</sup> at 7.3° and an electrolyte concentration of 0.1 M. Since the 1 and 3 positions of azulene are equivalent,<sup>21</sup>  $k_{bi}$  has to be divided by a statistical factor of 2 in order to obtain an equivalent coefficient for protonation at only the 1 position; thus,  $k_{bi}/2 = 0.64$  l. mole<sup>-1</sup> sec.<sup>-1</sup>. For comparison, an equivalent rate coefficient ( $k_1^H$ ) can be computed from the data of Schulze and Long for the detritiation of azulene-1-*t*. Assuming the A-SE2 mechanism, the observed rate coefficient ( $k_{EX}^T$ ) of detritiation can be expressed in terms of the rate coefficients for the component steps of Scheme I<sup>22</sup> as in eq. 11

$$k_{EX}^T = \frac{-d(AzT)/dt}{[AzT][H^+]} = \frac{k_1^T k_2^T}{k_{-1}^T + k_2^T} \quad (11)$$

$$= \frac{k_1^T e^{900/RT}}{e^{2400/RT} + e^{900/RT}} \quad (12)$$

The derivation of eq. 12 from eq. 11 is accomplished by expressing  $k_{-1}^T$  and  $k_2^T$  in terms of  $k_1^T$ , the tritium-hydrogen isotope effect, and the free energy of equilibrium protonation ( $-\Delta F_0$ ); this transposition is discussed in the Appendix.  $k_1^T$  refers to the rate of protonation of azulene-1-*t* at the 1 position and, apart from secondary isotope effects, is equivalent to  $k_1^H$ . There is good evidence, both experimental<sup>23</sup> and theoretical,<sup>23,24</sup> that these secondary isotope effects are relatively small. Thus, to a good approximation,  $k_1^T = k_1^H$ .

Interpolation of the data of Schulze and Long to the temperature of 7.3° produces a value of  $k_{EX}^T = 0.032$  l. mole<sup>-1</sup> sec.<sup>-1</sup>. Then application of eq. 12 leads to  $k_1^T = k_1^H = 0.51$  l. mole<sup>-1</sup> sec.<sup>-1</sup> for the rate of protonation of azulene at the 1 position. This indirect value agrees to within 20% with  $k_{bi}/2$  from the direct measurement of the protonation rate, an agreement lying well within the limits of the assumptions necessary to obtain  $k_1^H$ . We therefore conclude that the A-SE2 mechanism is valid for the isotopic hydrogen exchange of azulene and that the formation of the conjugate acid is a step in the reaction.

It is not possible to compute reliable values of  $k_f^0$  and  $k_r^0$  at temperatures other than 7.3° because experimental data for extrapolation are available for only a single perchloric acid concentration (1.93 M), and there is strong evidence that the slopes of plots of  $\log k_f - \log [H^+]$  and  $\log k_r$  against acid molarity are temperature dependent. Thus, the slopes of analogous plots for equilibrium protonation change from 0.69 to 0.56, in going from 5.7 to 38.6°, and the discrepancies between  $k_r^0/k_f^0$  and  $k_{AzH_2^-}$  increase with temperature if no allowance is made for these changes. In order to compare the kinetic and equilibrium data, however, operational values (*i.e.*, independent of acidity) of the various activation parameters have been computed in the usual manner. For equilibrium ionization of the azulonium ion in 1.93 M perchloric acid, the following values are obtained at 20°:  $\Delta F_E = -0.4$  kcal.,

(21) E. Heilbronner and M. Simonetta, *Helv. Chim. Acta*, 35, 1049 (1952).

(22) See ref. 5, p. 118.

(23) (a) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.*, 80, 2326 (1958); (b) see ref. 5, p. 107 ff.

(24) S. Olsson, *Arkiv Kemi*, 16, 489 (1960).

$\Delta H_E = -2.8$  kcal., and  $\Delta S_E = -8.1$  e.u. The relatively large difference between  $\Delta F_E$  and  $\Delta F^\circ$  reflects the difference in standard states. The corresponding activation parameters for both protonation and deprotonation kinetics at the same acidity and temperature are as follows: for protonation (sec.<sup>-1</sup> units),  $\Delta F_t^* = 16.0$  kcal.,  $\Delta H_t^* = 15.1$  kcal.,  $\Delta S_t^* = -3.2$  e.u.; for deprotonation (sec.<sup>-1</sup> units),  $\Delta F_r^* = 15.6$  kcal.,  $\Delta H_r^* = 12.4$  kcal.,  $\Delta S_r^* = -11.0$  e.u.

The entropies of activation are particularly interesting as they lead to a fairly firm assessment of the transition state. Since the neutral azulene molecule has a very low Setchenow parameter and must be largely unsolvated in aqueous solution, the low entropy term associated with protonation implies that the solvation of the transition state is closely similar to that of the hydronium ion itself and, therefore, probably contains four solvating water molecules. We have already concluded from the equilibrium studies that each methylene hydrogen of the azulonium ion is solvated by a single water molecule, and, thus, the observed entropy of activation for deprotonation is that expected for a net increase of two water molecules in forming the transition state. (Speculatively, it is noted that the configuration most consistent with all these observations is one in which a single water molecule from the incoming hydronium ion has been transferred to the aromatic hydrogen.)

The implications of this conclusion lend considerable support to those of Schubert and Quacchia<sup>25</sup> and of Kresge and his co-workers,<sup>18</sup> that the magnitude of acidity function correlations, either  $H_0$  or  $H_R$ , depends principally on the number of water molecules solvating the acidic species (the transition state can be regarded as an acidic moiety) and that this dependence decreases as the degree of solvation increases.

With due consideration to the reservations expressed at the beginning of the Discussion, a comparison of the acidity function dependencies of both equilibrium and kinetic protonation is particularly interesting. The respective slopes of the plots of  $\log [AzH_2^+]/[AzH]$  and  $\log k_t$  against  $-H_0$  are 1.94 and 1.26. These imply, of course, that, for equilibrium protonation,  $f_{AzH}a_{H^+}/f_{AzH_2^+}$  is proportional to  $h_0^{1.94}$  and that, for the kinetics of protonation,  $f_{AzH}a_{H^+}/f^*$  is proportional to  $h_0^{1.26}$ . These differences further illustrate recent observations made by several workers that specific structure is as important as the charge in determining the precise magnitude of an ion activity coefficient, its dependence on acidity, the consequential limitations to all acidity functions, and their use as mechanistic criteria of acid catalysis. The  $H_0$  dependence of the deprotonation reaction,  $k_r \propto h_0^{-0.68}$  serves to illustrate this point more succinctly. The observed dependence is a pure medium effect equivalent to a large dependence of  $f_{AzH_2^+}/f^*$  on acidity. Schubert, Burkett, and Schy<sup>26</sup> have recently reported a similar  $H_0$  dependence for the same kind of activity coefficient ratio in the A-1 hydrolysis of the alkyl acetals of heterocyclic aldehydes. They find the magnitude of the  $H_0$  dependence depends upon the relative solvation of the ground state (in their case the nitrogen conjugate acid) and the transition state of the

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

(26) W. M. Schubert, H. Burkett, and A. L. Schy, *ibid.*, **86**, 2520 (1964).

reaction. The same explanation can be forwarded for the deprotonation of the azulonium ion, but attempts to account for the dependence in quantitative terms are significantly unsuccessful. We have concluded from various entropy measurements that there is probably a net change of two solvating water molecules in going from the azulonium ion to the transition state, and we have shown that this conclusion accords with the number of acidic hydrogens available for solvation. On this basis, the observed acid anticatalysis for deprotonation should correlate with  $(a_{H_2O})^2$ . In reality, this is far from true; the experimental relationship is close to  $k_r$  being proportional to  $(a_{H_2O})^8$ . There is no simple account of this discrepancy, but it emphasizes that neither correlation with water activity nor entropy data alone serve little more than to rationalize the experimental results in a qualitative manner.

## Appendix

Analysis by Schulze and Long<sup>5</sup> of the detritiation of azulene-1-*t* as a function of temperature, for reaction in 0.005 *M* perchloric acid and with rate coefficients in l. mole<sup>-1</sup> sec.<sup>-1</sup> units, led to the following activation parameters:  $\Delta F_{EX}^{*T} = 19.0$  kcal. mole<sup>-1</sup>,  $\Delta S_{EX}^{*T} = -10.1$  e.u. mole<sup>-1</sup>, and  $\Delta H_{EX}^{*T} = 16.0$  kcal. mole<sup>-1</sup>. The hydrogen isotope effects associated with various steps of the postulated A-SE2 mechanism were also evaluated by combining the data for the rate of detritiation in light and heavy aqueous media with the data of Colapietro and Long<sup>4</sup> for the analogous dedeuteration of azulene-1,3-*d*<sub>2</sub> in ordinary light water. The following rate coefficient ratios were deduced:  $k_1^{H_2O}/k_1^{D_2O} = 2.4$ , and  $k_2^H/k_2^D = 5.6$ .

A detailed analysis of the data, when combined with  $\Delta F^\circ$  for the equilibrium ionization of the azulonium ion, permits the calculation of the free energy of activation for both transition states implied by the two-step A-SE2 exchange mechanism.

Assuming an A-SE2 mechanism with rate coefficients as in Scheme I, the observed rate coefficient ( $k_{EX}^T$ ) for the exchange process can be represented as a function of the rate coefficients of the component steps.<sup>22</sup>

$$k_{EX}^T = \frac{k_1 k_2}{k_{-1} + k_2} \quad (13)$$

All the coefficients of eq. 13 can be expressed in terms of their free energy of activation. Equation 13 then becomes

$$e^{-\Delta F_{EX}^T/RT} = \frac{e^{-\Delta F_1^*/RT} e^{-\Delta F_2^*/RT}}{e^{-\Delta F_{-1}^*/RT} + e^{-\Delta F_2^*/RT}} \quad (14)$$

The free-energy profile for the two-step A-SE2 reaction is illustrated by Figure 1. Both  $\Delta F_{-1}^*$  and  $\Delta F_2^*$  can be expressed in terms of  $\Delta F_1^*$  provided both the free energy for equilibrium protonation of the azulonium ion ( $-\Delta F^\circ$ )<sup>27</sup> and the difference in activation free energy for the loss of tritium compared to hydrogen from the conjugate acid  $AzHT^+$  ( $\Delta F^{H/T}$ ) are known, then

$$\Delta F_{-1}^* = \Delta F_1^* - (-\Delta F^\circ) \quad (15)$$

and

$$\Delta F_2^* = \Delta F_1^* - (-\Delta F^\circ) + \Delta F^{H/T} \quad (16)$$

(27)  $-\Delta F^\circ$  for protonation of azulene-1-*t* is actually required; the present treatment assumes this is equal to that for the protonation of azulene itself.

A value of  $-\Delta F^\circ$  ( $= 2400$  cal. at  $25^\circ$ ) has already been calculated in the text from measurements of the dissociation constant at various temperatures. The magnitude of  $\Delta F^{H/T}$  can be computed from the rate coefficient ratio  $k_2^H/k_2^D$  by the utilization of eq. 12 linking the tritium and deuterium isotope effects

$$k_2^H/k_2^T = (k_2^H/k_2^D)^{1.442}$$

The data for azulene give a value of  $k_2^H/k_2^T = 12$ , which corresponds to a  $\Delta F^{H/T}$  of 1500 cal. Thus,  $\Delta F_2^* = \Delta F_1^* - 900$  cal. and  $\Delta F_{-1}^* = \Delta F_1^* - 2400$  cal. These values when substituted in eq. 14 lead to eq. 12.

Equations 15 and 16 can be used to compute the free energies for the component steps of the detritiation reaction. Substituting in eq. 14 with values of  $\Delta F_2^* = \Delta F_1^* - 900$  cal. and  $\Delta F_{-1}^* = \Delta F_1^* - 2400$  cal. and evaluating the numerical exponential terms, it is found that

$$\Delta F_1^* = \Delta F_{EX}^*T - 2.65RT \quad (17)$$

The numerical values of  $\Delta F_{-1}^*$ ,  $\Delta F_2^*$ , and  $\Delta F_1^*$  evaluated from the observed free energy of activation via eq. 15–17, respectively, are as follows:  $\Delta F_1^* = 17.5$ ,  $\Delta F_{-1}^* = 15.1$ , and  $\Delta F_2^* = 16.6$  kcal. mole $^{-1}$ .

## Hydrogen, Rhodium, and Iridium Electrode Potentials in Lithium Chloride–Potassium Chloride Eutectic

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*A hydrogen electrode suitable for use in anhydrous molten LiCl–KCl at 450° was prepared by bubbling mixtures of purified hydrogen and hydrogen chloride over a platinized platinum flag immersed in the melt. The potential of this electrode with respect to platinum foils in contact with platinum(II) was measured. Values of free energy, enthalpy, and entropy for the reaction  $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$  calculated from the potentials of the hydrogen and chlorine electrodes were in agreement with N.B.S. and JANAF values. Standard potentials were also determined for rhodium(III)–rhodium and iridium(III)–iridium.*

Several publications<sup>3–6</sup> have established an electromotive force series in anhydrous, molten LiCl–KCl eutectic at 450°. Standard potentials were determined for metal ion–metal, metal ion–metal ion, and halogen–halide ion couples with reference to the electrode Pt(II) (1.0 M)–Pt. In this paper the preparation of a hydrogen electrode of the type HCl(g)–H<sub>2</sub>(g), Pt suitable for use in this melt is discussed, and its standard potential with respect to Pt(II) (1.0 M)–Pt is determined. Standard potentials for Rh(III)–Rh and Ir(III)–Ir were also determined.

Delimarskii and Markov<sup>7</sup> have included the hydrogen electrode in their extensive review of reference electrodes for fused-salt media. Their discussion, however, is

concerned with electrodes of the type H<sub>3</sub>O<sup>+</sup>–H<sub>2</sub>(g), Pt. Several French workers have recently studied<sup>8–12</sup> current–potential curves obtained in molten LiCl–KCl eutectic contaminated with OH<sup>–</sup> or O<sup>2–</sup> using a hydrogen gas electrode and have interpreted them on the basis of reactions involving O<sup>2–</sup>, OH<sup>–</sup>, H<sub>2</sub>O, and H<sub>3</sub>O<sup>+</sup>; additions of O<sup>2–</sup> and OH<sup>–</sup> were made, and their effects were studied. Pizzini and co-workers<sup>13,14</sup> have made studies of hydrogen evolution from molten, moist potassium difluoride, and Shams el Din<sup>15</sup> has studied hydrogen evolution in molten KHSO<sub>4</sub>. The experimental data for a hydrogen electrode of the type HCl(g)–H<sub>2</sub>(g), Pt, obtained in a study of aqueous contamination of equimolar NaCl–KCl at 700° by Littlewood and Argent,<sup>16</sup> in a melt presumably containing little or no O<sup>2–</sup> or OH<sup>–</sup>, were interpreted by these authors as indicating that equilibrium was not achieved. In this study, reversible behavior has been observed for a hydrogen electrode of the latter type under scrupulously anhydrous conditions.

Standard potentials of rhodium(III) have been determined in molten alkali sulfates by Liu<sup>17</sup> and by Johnson and Laitinen.<sup>18</sup> Iridium has not previously been studied in fused salts. Additional references on electrode potentials in fused-salt media can be found in a recent review.<sup>19</sup>

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