

fore increase the rate by making the reaction medium more aqueous. However, once the addition of the salt has brought about sufficient melting to make the water concentration not limited, no further change in the rate would be expected on further increase of salt concentration. All the experimental results obtained in this study agree with these expectations. In ice at  $-10^\circ$  the spontaneous hydrolyses of acetic anhydride and  $\beta$ -propiolactone are both depressed. The addition of potassium chloride is found to increase the spontaneous rates until a rate is reached which is essentially independent of the concentration of salt. It is known, in support of this explanation, that foreign substances are not in general incorporated into ice crystals.

All the bimolecular reactions studied showed enhanced reaction rates in ice, presumably due to the concentration of the catalyst in the liquid regions. However, the addition of a salt, which would increase the size of the liquid regions and thus dilute the reactants, lowers the rate of reaction. Clearly, the lower the concentration of electrolytes (KCl, HCl), the smaller will be the liquid regions and the greater the concentration effect. The data show that as the catalyst concentration is lowered the rate enhancement as determined by the catalytic coefficient increases. However, at very low HCl concentration the rate of reaction decreases as the water concentration becomes limiting. The very great rate enhancements reported by Prusoff<sup>3</sup> and by Grant, *et al.*,<sup>4</sup> are larger than those obtained in the present study where the ionic strength was as high as 0.1 *M*. Our more detailed study did not confirm the very large values obtained by Prusoff but, in most cases studied, large rate enhancements were obtained when catalytic coefficients were determined at very low ionic strength.

The n.m.r. spectra of pure water, 0.01 *M* aqueous potassium chloride, and 0.05 *M* aqueous potassium chloride were determined at  $-5$ ,  $-10$ , and  $-25^\circ$ . The spectra seem to indicate the presence of regions of liquid water in ice crystals when an electrolyte is present. The spectrum of ice has no distinctive features but with the 0.01 *M* salt solution two sharp peaks of similar height appear at all temperatures. One of these disappears in the 0.05 *M* solution at  $-5$  and  $-10^\circ$ , and at

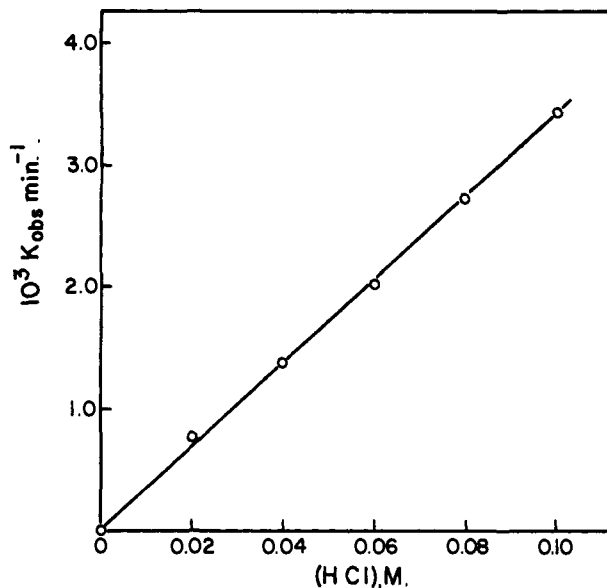


Fig. 11.—The observed pseudo-first-order rate constants for the dehydration of 5-hydro-6-hydroxydeoxyuridine at  $30^\circ$  plotted against concentration of hydrochloric acid.

$-25^\circ$  the spectrum is indistinguishable from that of pure ice. A complete explanation of these results has yet to be developed and, clearly, further study is necessary.

If the explanation of the rate enhancements and depressions found on moving from water to ice are simply concentration effects, no new mechanistic factors are introduced. The phenomenon may be of some synthetic interest and further studies in that direction are being carried out.

**Acknowledgments.**—The authors wish to express their sincere thanks to Dr. E. Wasserman of Bell Telephone Laboratories for obtaining the n.m.r. spectra. Our grateful thanks are due also to Mrs. S. J. Benkovic, whose enthusiasm and skill were of the greatest possible help. This work was supported by a grant from the National Science Foundation.

[CONTRIBUTION FROM THE NORTH AMERICAN AVIATION SCIENCE CENTER, CANOGA PARK, CALIF.]

## Solutions of Solids in Molten Reciprocal Salt Systems

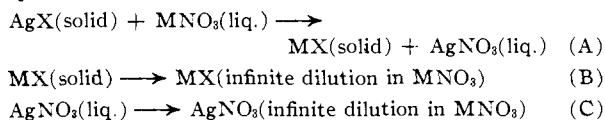
BY MILTON BLANDER AND E. B. LUCHSINGER

RECEIVED AUGUST 13, 1963

Electromotive force measurements were made to obtain standard heats of solution ( $\Delta H_{\text{soln}}$ ) and solubility products ( $K_{\text{sp}}$ ) of AgI and AgBr in molten alkali nitrates ( $\text{NaNO}_3$ ,  $\text{KNO}_3$ , or mixtures of the two). The measured values are in good agreement with values of  $\Delta H_{\text{soln}}$  and  $-RT \ln K_{\text{sp}}$  calculated from a cycle similar to one proposed by Flood, Førland, and Grjøtheim and shown in text equations A, B, and C. Our results confirm the general usefulness of the cycle in making predictions, *a priori*, in molten salt systems of this class.

### Introduction

A prediction of the standard heats of solution ( $\Delta H_{\text{soln}}$ ) and solubility products ( $K_{\text{sp}}$ ) of solids in molten reciprocal salt systems may be made by the use of a simple cycle first proposed by Flood, Førland, and Grjøtheim (FFG).<sup>1</sup> As an example, for the dissolution of solid silver halides (AgX) in molten alkali nitrates ( $\text{MNO}_3$ ) one method of writing the cycle consists of the three steps



with processes such as A generally leading to the largest contribution to the estimated values of the standard heat of solution or of the standard free energy of solution ( $-RT \ln K_{\text{sp}}$ ) of AgX.<sup>1,2</sup> Where direct measurements are not available, good estimates of the relatively small changes of the standard heat or free energy changes in the processes B and C may be made by comparison with similar mixtures.

In essence, the use of this cycle, with the aid of generally available thermodynamic data on the pure com-

(1) H. Flood, T. Førland, and K. Grjøtheim, *Z. anorg. allgem. Chem.*, **276**, 289 (1954).

(2) M. Blander, J. Braunstein, and M. D. Silverman, *J. Am. Chem. Soc.*, **85**, 895 (1963).

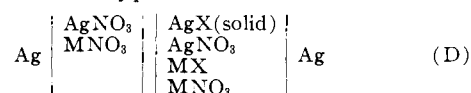
ponents for the calculation of step A, reduces the problem of the thermodynamics of dissolution in ternary reciprocal salt systems to that of dissolution in binary systems (as in processes B and C). As there are fewer binary systems<sup>3</sup> and as the standard heats and free energies of dissolution involved in them are, generally, small relative to process A, the problem is considerably simplified. This method of estimation is operationally more useful and sound than the Born cycle which has been used previously.<sup>2,4</sup>

In this study we tested the predictions of the FFG cycle by comparing the standard heats and free energies of solution calculated from the cycle with values of these quantities obtained from electromotive force measurements. The standard free energies of solution ( $-RT \ln K_{sp}$ ) of AgI in molten NaNO<sub>3</sub> and KNO<sub>3</sub> and of AgI and AgBr in an equimolar mixture of NaNO<sub>3</sub> and KNO<sub>3</sub> were obtained in an isothermal titration experiment using the method of Flengas and Rideal.<sup>4</sup> The standard heats of solution of AgI in NaNO<sub>3</sub> and in equimolar NaNO<sub>3</sub>-KNO<sub>3</sub> were obtained by e.m.f. measurements in which the temperature of a solution of known composition saturated with solid AgI was varied. The predicted heat of solution of solid AgCl in molten KNO<sub>3</sub> has been shown previously to correspond to the measured heat of solution.<sup>2</sup> Measurements such as ours in equimolar mixtures of NaNO<sub>3</sub> and KNO<sub>3</sub> have been made previously,<sup>4</sup> and the present results confirm those measurements. However, we feel that the precision of our measurements of the heats of solution is better and provides a more adequate test of the predictions from the cycle.

The thermodynamic solubility product (in mole fraction units) for saturated solutions of silver halides in molten nitrates may be calculated from the equation

$$K_{sp} = a_{Ag^+} a_{Cl^-} = a_{AgNO_3} a_{KCl} \quad (1)$$

in solutions dilute enough in the solute silver and halide ions so that the activity of the solvent is essentially unity. The standard states for the activities of the solutes are chosen so that the activity coefficients are unity at infinite dilution of all solutes and the concentration units are equivalently mole ratios or ion fractions. The activity of AgNO<sub>3</sub>,  $a_{AgNO_3}$ , may be measured directly in cells of the type<sup>5</sup>



Because of the nonideal behavior of solutions of silver and halide ions, care must be exercised in deducing values of  $a_{MX}$ . In dilute solutions of the solutes, the nonideal behavior has been related to associations of the silver and halide ions to form associated species such as AgX, Ag<sub>2</sub>X<sup>+</sup>, AgX<sub>2</sub><sup>-</sup>, etc., and the activities of the components may be written as

$$a_{MX} = R_{MX} - R'_{AgX} - R'_{Ag_2X} - 2R'_{AgX_2^-} \quad (2)$$

$$a_{AgNO_3} = R_{AgNO_3} - R'_{AgX} - 2R'_{Ag_2X} - R'_{AgX_2^-} \quad (3)$$

where  $R$  is the total stoichiometric concentration (mole ratio) of the indicated component in solution and where  $R'$  is the concentration of the indicated associated species in solution.<sup>6</sup> In the heat of solution measurements discussed here, the concentrations of MX were chosen high enough so that an insignificant fraction of

(3) For example, with 50 different cations and 50 different anions one can make 122,500 binary systems and over 1,500,000 simple reciprocal systems containing two cations and two anions.

(4) S. N. Flengas and E. Rideal, *Proc. Roy. Soc. (London)*, **A233**, 443 (1956).

(5) M. Blander, F. F. Blankenship, and R. P. Newton, *J. Phys. Chem.*, **63**, 1259 (1957).

(6) J. Braunstein, M. Blander, and R. M. Lindgren, *J. Am. Chem. Soc.*, **84**, 1529 (1962).

the X<sup>-</sup> ions in solution were associated as soluble associated species, and in the measurements of  $K_{sp}$  the concentrations were chosen so that the only significant associated species was AgX. This was confirmed by our  $K_{sp}$  measurements. This could only be done in systems in which the solubility products were low enough so that only a small concentration of Ag<sup>+</sup> ion was in solution. Consequently, if the concentration of halide ion was high enough (*i.e.*, much higher than the concentration of Ag<sup>+</sup> ion), only a relatively small fraction of the X<sup>-</sup> ions was present as associated species. Therefore, under the conditions for which the heats of solution were measured, the activity of MX could be set equal to the concentration. This choice, which simplified the calculations, was made with the aid of the measured association constants.<sup>7,8</sup> The solubility of AgI in solutions of KI in KNO<sub>3</sub> was too high at temperatures above 375° to obtain reliable values of the  $K_{sp}$ , and consequently the heat of solution was not measured in this system.

### Experimental Procedure and Results

The apparatus and technique have been described previously.<sup>2,4,5,7</sup> Two separate sets of e.m.f. measurements were made. In one set, the method of Flengas and Rideal<sup>4</sup> was used for the determination of  $K_{sp}$  and in a second set the heats of solution were determined.

In the method of Flengas and Rideal a solution of AgNO<sub>3</sub> in the right-hand electrode compartment of the cell (D) was titrated isothermally with alkali bromide or iodide to obtain the  $K_{sp}$ . The activities of AgNO<sub>3</sub> left in solution after precipitation with a given quantity of halide were calculated from the measured e.m.f. With the addition of a large enough excess of the halide, the activity of MX could be calculated from the relation

$$a_{MX} = \frac{n_{MX} - n_{AgNO_3}}{n_{MNO_3}} + a_{AgNO_3} \quad (4)$$

where  $n_i$  is the total number of moles of component  $i$  added to the solution. The use of this equation is predicated on the assumption that the X<sup>-</sup> ions which are not "free" in solution are either precipitated from solution as solid AgX or tied up as the soluble associated species AgX. From the association constants measured in these solutions<sup>7,8</sup> and from the resulting constancy of the calculated values of  $K_{sp}$  at different concentrations of titrant, this assumption was shown to be valid at the concentrations of solutes used in these measurements. Typical data are given in Table I for the titration of AgNO<sub>3</sub> with NaI in molten NaNO<sub>3</sub>.

TABLE I

TYPICAL DATA OBTAINED IN AN ISOTHERMAL TITRATION OF AgNO<sub>3</sub> BY NaI IN MOLTEN NaNO<sub>3</sub> AT 349°

$R_{NaI}$  is the total number of moles of NaI added, divided by the number of moles of solvent; the initial mole fraction (or mole ratio) of AgNO<sub>3</sub> was  $1.269 \times 10^{-3}$

$-\Delta E, v.$	$R_{NaI} \times 10^4$	$a_{AgNO_3} \times 10^3$	$a_{NaI} \times 10^4$	$K_{sp} \times 10^{11}$
0.5299	19.59	6.445	6.901	4.45
.5420	21.28	5.143	8.587	4.42
.5494	22.49	4.481	9.804	4.39
.5611	24.90	3.602	12.21	4.40
.5668	26.20	3.239	13.51	4.38
.5805	30.04	2.508	17.40	4.36
.5911	33.74	2.058	21.05	4.33

The second set of measurements was made to obtain precise heats of solution. The activities of AgNO<sub>3</sub> in solutions containing MX (about  $9 \times 10^{-3}$ ) saturated with solid AgX were measured as a function of temperature in a single run in which the temperature was slowly lowered, raised, and lowered again. Measurements were taken only after the temperature had been stabilized for a few minutes. At these relatively high concentrations of MX and low concentrations of Ag<sup>+</sup> ion,  $a_{MX}$  is essentially independent of temperature and the heat of solution could be calculated from the equation

$$d \ln K_{sp}/d(1/T) = -\Delta H_{soln}/R = d \ln a_{AgNO_3}/d(1/T) \quad (5)$$

The precision of these measurements of  $\Delta H_{soln}$  was believed to be better than that of Flengas and Rideal since some of the errors due

(7) (a) A. Alvarez-Funes, J. Braunstein, and M. Blander, *ibid.*, **84**, 1538 (1962); (b) D. L. Manning, R. C. Bansal, J. Braunstein, and M. Blander, *ibid.*, **84**, 2028 (1962).

(8) M. Blander and E. B. Luchsinger, unpublished data.

TABLE II  
MEASURED VALUES OF  $K_{sp}$ ,  $-RT \ln K_{sp}$ ,  $\Delta H_{soln}$ , AND THEIR COMPARISON WITH CALCULATED VALUES

Solute	Solvent	$K_{sp}$	$T, ^\circ\text{C.}$	$-RT \ln K_{sp}, \text{kcal./mole}$		$\Delta H, \text{kcal./mole}$	
				Measured	Calcd.	Measured	Calcd.
AgI	$\text{NaNO}_3$	$4.39 \times 10^{-11}$	349	29.5	31.5	29.5	29.8
						29.6	
AgI	$\text{KNO}_3$	$6.06 \times 10^{-10}$	359	26.7	28.2		27.0
		$5.73 \times 10^{-10}$	361	26.8			
AgBr	$\text{NaNO}_3\text{-KNO}_3$ (50-50 mole %)	$8.53 \times 10^{-10}$	250	21.7	22.1	22.4	22.9
				(22.0) <sup>a</sup>		(21.3)	
AgI	$\text{NaNO}_3\text{-KNO}_3$ (50-50 mole %)	$1.40 \times 10^{-12}$	250	28.4	29.9	27.9	28.4
				(28.2)		(29.35)	

<sup>a</sup> Values in parentheses from ref. 4.

TABLE III  
STANDARD HEAT AND FREE ENERGY CHANGES FOR PROCESSES A, B, AND C

Solute	Solvent	Standard heat changes			A + B + C	Standard free energy changes			A + B + C
		A	B	C		A	B	C	
AgBr	$\text{NaNO}_3$	17.49	5.86	0.68	24.03	19.15	2.57	0.80	22.52
AgBr	$\text{KNO}_3$	17.00	5.18	-.30	21.88	18.64	3.38	(-.30)	21.72
AgI	$\text{NaNO}_3$	24.35	4.81	.68	29.84	27.90	2.80	.80	31.50
AgI	$\text{KNO}_3$	22.43	4.85	-.30	26.98	25.99	2.56	(-.30)	28.25

to differences between separate experiments under apparently identical conditions were partially compensated in performing a single run over a range of temperatures. Measured values of  $\log a_{\text{AgNO}_3}$  in solutions saturated with AgI or AgBr in molten nitrates are plotted in Fig. 1. In Table II are given values of the  $K_{sp}$ ,  $-RT \ln K_{sp}$ , and  $\Delta H_{soln}$  obtained from our measurements for the dissolution of AgI in  $\text{NaNO}_3$  and in  $\text{KNO}_3$  and for the dissolution of AgI and AgBr in 50-50 mole %  $\text{NaNO}_3\text{-KNO}_3$  mixtures. The values of  $\Delta H_{soln}$  and  $-RT \ln K_{sp}$  in parentheses are the values given by Flengas and Rideal.

### Discussion

In this section, values of  $-RT \ln K_{sp}$  and  $\Delta H_{soln}$  will be calculated from the FFG cycle and compared with the measured values. The heat and free energy changes of the reciprocal reaction (step A) at 600°K. were calculated from available data.<sup>9,10</sup> These thermodynamic quantities varied only slightly with temperature so that the calculations at 600°K. will apply at any temperature of interest.

Kleppa and Meschel have measured the heat changes for step B for a series of alkali chlorides and bromides.<sup>11</sup> They observed that the heat of solution of the solid alkali halides differed little from the heat of fusion extrapolated to the temperature of their measurements. For the dissolution of the bromides we have used their data with a small  $\Delta C_p$  correction to 600°K. For the iodides we have made the reasonable assumption that there is little difference in the general behavior of the systems studied by Kleppa and Meschel and the iodides. Thus we have approximated the heats of solution by the measured heats of fusion ( $\Delta H_f$ )<sup>12</sup> corrected to a lower temperature, assuming that  $\Delta C_p$ , the difference between the heat capacity of the liquid and solid, is 2.5 cal./mole. This is about the average value of  $\Delta C_p$  found by Kleppa and Meschel for the alkali chlorides and bromides.

The standard free energy of solution for step B is the difference between  $G^*$ , the standard free energy of the standard state of MX chosen so that the activity coefficients are unity at infinite dilution, and  $G^\square$ , the standard free energy of the solid. If solid MX is in equilibrium with the solution then

$$G^* - G^\square = -RT \ln a_{MX}$$

(9) F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," USNBS Circ. 500 (1952).

(10) (a) K. K. Kelley, "High Temperature Heat Content, Heat Capacity and Entropy Data for the Elements and Inorganic Compounds," Bull. 584, Bureau of Mines (1960); (b) K. K. Kelley and E. G. King, "Entropies of the Elements and Inorganic Compounds," Bull. 592, Bureau of Mines (1961).

(11) O. J. Kleppa and S. V. Meschel, *J. Phys. Chem.*, **67**, 668 (1963).

The phase diagrams<sup>13,14</sup> and heats of solution<sup>11</sup> of  $\text{MX-MNO}_3$  mixtures indicate relatively small deviations from ideal solution behavior<sup>15</sup>; hence for fairly dilute

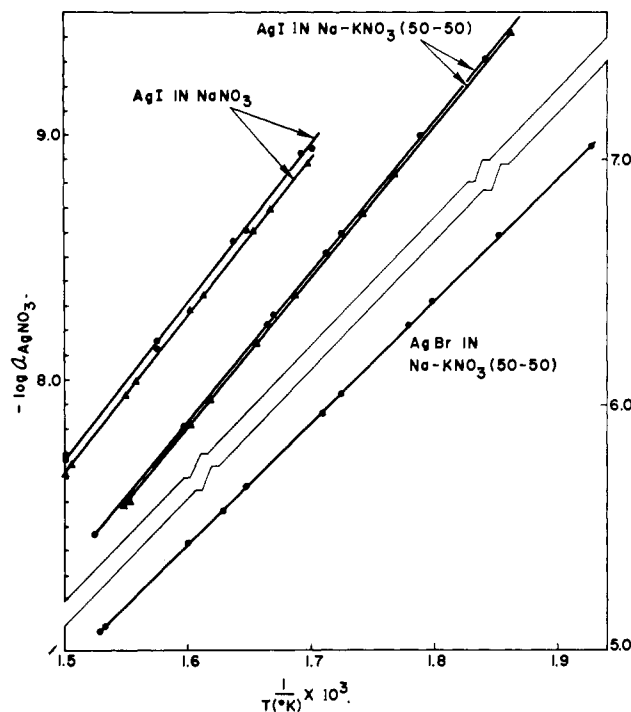


Fig. 1.—Plots of  $-\log a_{\text{AgNO}_3}$  vs.  $1/T$  used to obtain standard heats of solution.

solutions of MX only a very small error in the free energies is introduced by assuming Henry's law to hold and setting  $a_{MX} = N_{MX}$ . Here  $N_{MX}$  is the concentration of MX at which solid MX is in equilibrium with the solution at a given temperature. These data were obtained from published phase diagrams for  $\text{KNO}_3\text{-KBr}$ ,<sup>13</sup>  $\text{KNO}_3\text{-KI}$ ,<sup>14</sup>  $\text{NaNO}_3\text{-NaI}$ ,<sup>14</sup> and our own measurements on the  $\text{NaNO}_3\text{-NaBr}$  system.<sup>16</sup>

(12) A. S. Dworkin and M. A. Bredig, *ibid.*, **64**, 269 (1960).

(13) G. M. Lifshits, *Zh. Obshch. Khim.*, **26**, 20 (1956).

(14) F. I. Vasenin and A. G. Bergman, *Izv. Sektora Fiz. Khim. Analiza Akad. Nauk SSSR*, **11**, 169 (1937).

(15) This is true whether the standard state is chosen as the pure liquid or as a state chosen so that the activity coefficients are unity at infinite dilution.

(16) The solubility of NaBr in  $\text{NaNO}_3$  at 342° was measured as 13.2 mole %. A small correction of  $(G^* - G^\square)$  to 600°K. was calculated using the equation  $[d(\Delta G/T)/d(1/T)] = -\Delta H_f$ .

The heat changes for process C were obtained from the data of Kleppa, *et al.*,<sup>17</sup> and the standard free energy change for C for the dissolution of AgNO<sub>3</sub> in NaNO<sub>3</sub> from the data of Laity.<sup>18</sup> For the dissolution of AgNO<sub>3</sub> in KNO<sub>3</sub> the reasonable assumption was made that the standard free energy of solution could be well approximated by the standard heat of solution. In Table III are listed the values of the estimates for steps A, B, and C.

The sum of the standard heats or free energy changes A, B, and C are listed in Table III and are compared to the measured values of the heat of solution or of  $-RT \ln K_{sp}$  listed in Table II. The average of these quantities in pure NaNO<sub>3</sub> and in pure KNO<sub>3</sub> is listed for the Na-

(17) O. J. Kleppa, R. B. Clarke, and L. S. Hersh, *J. Chem. Phys.*, **35**, 175 (1961).

(18) R. Laity, *J. Am. Chem. Soc.*, **79**, 1849 (1957).

NO<sub>3</sub>-KNO<sub>3</sub> solutions and should be a good approximation. The errors in the calculated values are probably about 0.5 kcal./mole. The calculated values can be seen to correspond to the measurements well within the expected errors for the  $\Delta H_{soln}$  and  $-RT \ln K_{sp}$  of the bromide and for  $\Delta H_{soln}$  of the iodides. The deviations of the calculated values from the measured values of  $-RT \ln K_{sp}$  for AgI, although not very large, are greater than the estimated errors. This deviation may possibly be due to a metastable but reproducible form of AgI in our measurements (as well as those of Flengas and Rideal) or to a small error in the literature values of the thermodynamic properties of AgI. In any case, our results confirm the fact that the FFG cycle is potentially useful in the prediction of thermodynamic properties in reciprocal salt systems.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.]

## Hydrogen Exchange of Azulenes. I. Structure of the Conjugate Acids of Azulenes<sup>1,2</sup>

By JANOS SCHULZE AND F. A. LONG

RECEIVED MAY 4, 1963

Studies with fifteen azulenes, all but two substituted at the 1-position, show that all of them reversibly form a conjugate acid in strongly acidic aqueous solutions. Conductivity studies with azulene in 100% sulfuric acid indicate only monoprotonation. The ultraviolet and n.m.r. spectra of the azulenium ions measured in hydrogen and deuterium acids show that there are two principal structures for the cations. Protonation occurs on the 3- (or equivalent 1-) position for azulene and 4,6,8-trimethylazulene; it occurs on the unsubstituted 3-position for the following azulenes: 1-methyl-, 1-chloro-, 1-cyano-, 1-*p*-dimethylaminobenzyl-, 1-cyano-4,6,8-trimethyl-, and guaiazulene. Protonation occurs on the oxygen of the 1-substituent for the azulenes: 1-nitro-, 1-formyl-, 1-trifluoroacetyl-, and 1-formylguaiazulene, while it occurs on the nitrogen of 1-phenylazoazulene. 1-Nitro-4,6,8-trimethylazulene is unique in that protonation occurs on the 1- rather than the 3-position, presumably because of the resulting relief from steric interference between the nitro and the 8-methyl group. For this compound as well as for the four which protonate on the 1-substituent, the n.m.r. spectra in deuterium acids show there is facile exchange of the hydrogens at the 3-position, suggesting that minute amounts of the conjugate acid with protonation on the latter position are also formed in strong acids.

### Introduction

The kinetics and reaction mechanism of acid-catalyzed aromatic hydrogen exchange have been studied by several authors using organic compounds labeled with deuterium or tritium.<sup>3-6</sup> Colapietro and Long<sup>7</sup> showed that azulene is a suitable compound for this type of study, particularly at low acidities. They investigated the acid-catalyzed deuterium loss of azulene-*d*<sub>2</sub> (1,3) in buffer solutions using an infrared technique. Azulene in acid exchanges the two hydrogens attached to the 1- and 3-carbons.<sup>8</sup> The conclusion of this early study was that the exchange reaction exhibited general acid catalysis.

A more extensive investigation of the hydrogen exchange of azulenes seemed desirable as a variety of substituted azulenes have become available. Thus it is possible to study the influence of the substituents on the rate and mechanism. These substituted azulenes have been reviewed in detail in recent publications as has the basic theory of the azulene molecule and its conjugate acid.<sup>9,10</sup> A variety of techniques may be used

to study the reaction; for instance, n.m.r. and ultraviolet spectra give information on the position of protonation; liquid scintillation counting applied to the rate of detritiation offers increased accuracy.

This paper and those which follow give results of a broad study of the aqueous azulene system; they supplement and modify the results quoted in a preliminary publication.<sup>11</sup> In this preliminary publication it was noted that the dependence of the rate of detritiation of azulene and of 1-nitroazulene on acidity was essentially the same; in contrast, the acidity dependence of the equilibrium protonation of the two compounds differed sharply. The present study gives further information on this different behavior and summarizes information for several other azulenes.

### Experimental

**Compounds.**—Samples of four compounds, listed by name and symbol, were generously supplied by Professor K. Hafner: 4,6,8-trimethylazulene, TMAz; 1-cyano-4,6,8-trimethylazulene, CNTMAz; 1-nitro-4,6,8-trimethylazulene, NO<sub>2</sub>TMAz; 1-(*p*-dimethylaminobenzyl)-azulene, pDMABAz. Samples of 1-cyanoazulene, CNAz; 1-phenylazoazulene, PhN<sub>2</sub>Az; and 1-trifluoroacetyl-azulene, CF<sub>3</sub>COAz, were supplied by Professor A. G. Anderson; samples of 1-formylazulene, CHOAz; and 1-formylguaiazulene, CHOGuAz, by Professor D. H. Reid; samples of 1-methylazulene, MeAz, and 1-nitroazulene, NO<sub>2</sub>Az, were supplied by Professor E. Heilbronner. Commercial azulene, Az, and guaiazulene, GuAz, were purchased from the Aldrich Chemical Co., Inc., Milwaukee, Wis. 1-Chloroazulene, ClAz; 1-carboxyazulene, COOHAz; and another sample of 1-nitroazulene, NO<sub>2</sub>Az, were prepared in this laboratory by known methods.<sup>12,13</sup> The compounds were purified by recrystallization, vacuum sub-

(1) Work supported by a grant from the Atomic Energy Commission.

(2) Presented in part at the 139th National Meeting of the American Chemical Society, St. Louis, Mo., April, 1961.

(3) F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957), for a review of earlier work.

(4) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press Co., New York, N. Y., 1960.

(5) A. J. Kresge and Y. Chiang, *J. Am. Chem. Soc.*, **83**, 2877 (1961).

(6) V. Gold, R. M. Lambert, and D. P. N. Satchell, *J. Chem. Soc.*, 2461 (1960).

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

(8) A. van Tets and Hs. H. Günthard, *Helv. Chim. Acta*, **45**, 457 (1962).

(9) E. Heilbronner, in "Nonbenzenoid Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1959, Chapter 5.

(10) T. Nozoe, *Fort. Chem. Org. Naturf.*, **19**, 32 (1961).

(11) F. A. Long and J. Schulze, *J. Am. Chem. Soc.*, **83**, 3340 (1961).

(12) A. G. Anderson, Jr., J. A. Nelson, and J. I. Tazuma, *ibid.*, **75**, 4980 (1953).

(13) A. G. Anderson, Jr., R. G. Anderson, and L. L. Replogle, *Proc. Chem. Soc.*, 72 (1960).