mol. wt., 434. Found: C, 55.33; H, 8.15;[8] mol. wt. (by titration for a dibasic acid), 433.

When dried at 150° for six hours, it lost 3 molecules H_2O. Calcd. for $C_{20}H_{28}O_5S$: mol. wt., 381. Found: mol. wt. (by titration for a dibasic acid), 381, 379.5.

Dimethyl Ester of Dehydroabietic Acid Sulfonate.—Five grams of dehydroabietic acid sulfonate was neutralized to phenolphthalein with a dilute aqueous solution of sodium hydroxide and the whole was evaporated to dryness. The pale yellowish powdered residue was dried for two hours at 125° and then boiled for ten minutes with 30 g. of dimethyl sulfate. After cooling, the clear dark solution was poured into ice water and then the mixture boiled for about one hour. The separated solid was removed, washed with a hot dilute sodium bicarbonate solution and then with water; yield, about 3 g. of crude dimethyl ester. It was recrystallized from acetone and methanol, the white silky needles melting at 176.7–177.7° (corr.).

Anal. Calcd. for $C_{22}H_{32}O_5S$: C, 64.69; H, 7.86. Found: C, 64.87; H, 8.04.

Diethyl Ester of Dehydroabietic Acid Sulfonate.—This was obtained in the same manner as the dimethyl ester, from 5 g. of dehydroabietic acid sulfonate and 30 g. of diethyl sulfate. It was recrystallized from acetone and methanol, the white silky needles melting at 150.4–151.4° (corr.).

Anal. Calcd. for $C_{24}H_{36}O_5S$: C, 66.00; H, 8.32. Found: C, 66.18; H, 8.35.

Diamide of Dehydroabietic Acid Sulfonate.—Five grams of dehydroabietic acid sulfonate was mixed with about 15 g. of phosphorus pentachloride and heated for about one hour on the water-bath under reflux. After cooling, the liquid was poured drop by drop into strong aqueous ammonia cooled with ice. The precipitated solid material was removed and extracted with boiling water until free from sulfonic acid. The diamide was then crystallized from ethanol, the transparent prismatic plates melting at 254–255.5° (corr.) (with slight dec.).

Anal. Calcd. for $C_{20}H_{30}O_3N_2S$: C, 63.43; H, 7.99. Found: C, 63.22; H, 8.09.

Summary

1. A dehydroabietic acid sulfonic acid is formed on sulfonation of heat treated abietic acid. This was confirmed further by the preparation of the dimethyl ester, diethyl ester and the diamide of the sulfonic acid.

2. The fact that a dehydroabietic acid sulfonate and a lactone belonging to the tetrahydroabietic acid series are formed on sulfonation of heat treated abietic acid are additional evidence that dehydrogenation and disproportionation of abietic acid occurs on heat treatment.

SAVANNAH, GA. RECEIVED JULY 11, 1938

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[8] All analyses by Mr. S. Gottlieb, Columbia University.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, HARVARD MEDICAL SCHOOL, AND THE BIOLOGICAL LABORATORIES, HARVARD UNIVERSITY]

Alicyclic Amino Acids

BY J. P. GREENSTEIN AND J. WYMAN, JR.

I

A great amount of data is now available on the dielectric constants of solutions of various amino acids, peptides, betaines and related molecules, which exist as dipolar ions. Although an exact theory of the relation of dielectric constant to molecular properties is still lacking in the case of polar liquids, the picture which emerges from such data is fairly simple and convincing.[1] There is no question that the large positive dielectric increments of all these compounds are due to their very large moments as dipolar ions. But beyond this a correlation of these increments with the properties of the molecules, as well as other empirical considerations, has led to the conclusion that in the case of polar liquids there is an approximately linear relation between dielectric constant and volume polarization, a conclusion which has been justified to some degree by recent theoretical investigations of Onsager[2] and of Van Vleck.[3] On this basis the dielectric increments of highly polar molecules like dipolar ions should be very nearly proportional to their molar polarizations, or, in view of that part of Debye's theory relating polarization to moment, to the square of their moments. This interpretation of the dielectric increments has made it possible to assign relative values to the moments of molecules, and, in connection with further inductions from data on pure liquids, even to estimate absolute values which are not far different from those estimated on an entirely different basis. Its application in detail to the large body of data on dipolar ions containing one positive and one negative charge separated by an aliphatic chain shows that in these molecules the mean square distance between the charges is proportional to the length of the intervening chain.

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(1) J. Wyman, *Chem. Rev.*, **19**, 213 (1936).

(2) Onsager, THIS JOURNAL, **58**, 1486 (1936).

(3) Van Vleck, *J. Chem. Phys.*, **5**, 556 (1937).

This agrees with what would be expected on the basis of free rotation in the chain according to statistical considerations of Eyring[4] and Werner Kuhn,[5] and the whole picture falls together in a very consistent way.

All the aliphatic dipolar ions so far studied have been straight chain compounds as regards the structure separating the charged groups, although in many cases the molecules contain cyclic radicals of one type or another, as for example histidine or phenylglycine. In the present study we have investigated the behavior of a series of compounds in which the charged amino and carboxyl groups are attached to a six-membered aliphatic ring, namely, the 2-, 3- and 4-aminocyclohexane-carboxylic acids. In these alicyclic amino acids the situation in regard to free rotation is quite different and offers a problem of some interest in itself as well as in relation to that of rotation in the straight chain compounds.

II

The cyclohexane amino acids may be prepared by two different procedures. The first is the method of Einhorn, which consists in boiling a solution of *o*-,[6] *m*-,[7] or *p*-[8] aminobenzoic acid with sodium in amyl alcohol. In the present study, only the 2-acid was so prepared. The second method is the catalytic hydrogenation of the aminobenzoic acids, using the Adams platinum oxide catalyst. In the present investigation the hydrogenation was carried out both in aqueous suspension and in hydrochloric acid solution. The meta and para homologs were reduced smoothly to the cyclohexane forms by the catalytic procedure; the ortho acid, on the other hand, in spite of repeated crystallizations, could not be hydrogenated completely.[9] In Table I are listed the melting points of the homologous aminocyclohexane acids prepared by these methods. Details of the procedure used in the preparations are given.

4-Aminocyclohexane-carboxylic Acid.—Fourteen grams of thrice-crystallized *p*-aminobenzoic acid was dissolved in 200 cc. of warm 1 *N* hydrochloric acid. The yellowish solution was filtered into the hydrogenation vessel and shaken in the presence of hydrogen with a suspension of 4.3 g. of the Adams platinum oxide catalyst. There was very little lag in forming the black, and within three and a half hours absorption ceased when about nine liters of hydrogen gas had been consumed. At 27° and 761 mm. pressure, the amount of acid used required about eight liters of hydrogen. The difference of one liter was due to the conversion of and adsorption by the catalyst. The latter coagulated toward the end of the reaction.

TABLE I

MELTING POINTS OF THE ACIDS ACCORDING TO THE METHODS OF PREPARATION

Carboxylic acids	Melting points, °C. Na in $C_5H_{11}OH$	Pt in HCl	Pt in H_2O
2-Aminocyclohexane	273[10]	...	...
3-Aminocyclohexane	268[10]	264[a]	278[a]
4-Aminocyclohexane	303[10]	285[a]	303[10] 260[a]

[a] Results by the present authors.

The filtered, water-white solution was made up to 500 cc. and an aliquot tested for the presence of ammonia with Nessler's reagent. It was found that 0.303 g. of ammonia was present in the entire solution, indicating that about 5 g. of the starting material had become deaminated. There was a strong odor of valerianic acid in the solution, and it is probable that some di-(cyclohexyl-4-carboxy)-amine may also have been formed. No attempt was made, however, to isolate these possible by-products.

The solution was treated with a slight excess of silver sulfate, filtered and gassed with hydrogen sulfide. The filtrate from the silver sulfide, freed by aeration from hydrogen sulfide, was treated with a considerable excess of baryta, filtered and condensed *in vacuo* to remove ammonia. The residual solution was then treated carefully with dilute sulfuric acid until barium was removed quantitatively. The filtrate was then evaporated *in vacuo* until crystals appeared, transferred to a flask and treated with a large amount of absolute ethanol and dry ether. A fine white precipitate appeared. It was filtered off and washed. After drying, it weighed 6.5 g. The substance, possessing no definite crystal form, was non-hygroscopic and was crystallized three times from acetone–water mixtures.

The molecule separates with 0.5 molecule of crystal water which is removed readily on drying at 100° *in vacuo*. It is extremely soluble in water; the solution is neutral to litmus.

Anal. Calcd. for $C_7H_{13}O_2N \cdot 0.5H_2O$ (152): N, 9.2. Found: N, 9.2.

The 4-acid was again prepared by suspending 8.1 g. of *p*-aminobenzoic acid in 100 cc. of water and shaking with about 3 g. of platinum oxide catalyst in the presence of hydrogen. The uptake of gas was quite rapid. The material went into complete solution within the first hour. After three hours the reaction was at an end. The filtered solution gave a strong test for ammonia. It was evapo-

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(4) Eyring, *Phys. Rev.*, [2] **39**, 746 (1932).

(5) Kuhn, *Z. physik. Chem.*, **175A**, 1 (1935).

(6) Einhorn and Meyenberg, *Ber.*, **27**, 2466 (1894).

(7) Bauer and Einhorn, *Ann.*, **319**, 329 (1901).

(8) Einhorn and Meyenberg, *Ber.*, **27**, 2829 (1894).

(9) Heckel and Adams, THIS JOURNAL, **47**, 1712 (1925), had reduced under pressure certain of the alkyl-substituted amino phenols. In view of our inability completely to hydrogenate anthranilic acid, it is interesting to note that Heckel and Adams found it impossible to hydrogenate *o*-aminophenol; with *o*-dialkyl aminophenol only a partial reduction could be achieved.

(10) Houben and Pfau, *Ber.*, **49**, 2294 (1916). These investigators used the Willstätter catalyst in a suspension of *p*-aminobenzoic acid in water. The rate of hydrogenation was extremely slow.

rated to crystals *in vacuo*, taken up with water and the material precipitated with acetone. The amino acid was then warmed twice with 85–90% alcohol to remove the ammonia and then crystallized twice out of water–acetone as long, feathery needles. The properties of the molecule were similar to those above; yield 3.2 g.

Anal. Calcd. for $C_7H_{13}O_2N{\cdot}0.5H_2O$ (152): N, 9.2. Found: N, 9.1.

3-Aminocyclohexane-carboxylic Acid.—Fourteen grams of thrice-crystallized *m*-aminobenzoic acid was treated by the catalytic hydrogenation procedure in hydrochloric acid solution exactly as the case of the 4-compound. Complete reduction again was achieved in three and a half hours. However, ammonia determinations indicated the presence of only 150 mg. of ammonia in the solution, pointing to the deamination of about 2.5 g. of the original acid. The meta acid is, therefore, a good deal more stable toward the hydrogenation procedure than the para homolog.

The saturated 3-amino acid was isolated as in the case of the 4-acid. The yield of white, non-hygroscopic material was 8.3 g. This is extremely soluble in water and its solution is neutral to litmus. It separates with 0.5 molecule of crystal water which is removed readily on drying.

When the compound is crystallized out of concentrated aqueous solution by the addition of much acetone, it separates first as an oil. On cooling, beautiful long needles are formed, which, when dry, easily pick up a charge and are hard to handle, in this respect differing from the 1- and 4-compounds. After three such crystallizations, the substance melts at the constant value of 264°.

Anal. Calcd. for $C_7H_{13}O_2N{\cdot}0.5H_2O$ (152): N, 9.2. Found: N, 9.2.

The 3-acid also was made by hydrogenating a suspension of 11.5 g. of *m*-aminobenzoic acid in water in the presence of 3 g. of platinum oxide. Solution was complete in less than an hour and the reaction was over in five hours. The saturated amino acid was recovered in the usual manner and boiled twice with 85–90% alcohol to remove ammonia. After several crystallizations from water–acetone the material was obtained as a mass of fine needles. The properties are like those of the compound prepared from hydrochloric acid solution.

Anal. Calcd. for $C_7H_{13}O_2N{\cdot}0.5H_2O$ (152): N, 9.2. Found: N, 9.0.

2-Aminocyclohexanecarboxylic Acid.—Twenty grams of four-times crystallized anthranilic acid was dissolved in 250 cc. of 1 *N* hydrochloric acid and the hydrogenation carried out as in the previous cases. The uptake of gas began very slowly and ceased after about one-third of the theoretical amount of hydrogen had been absorbed. An ammonia determination on the solution revealed that practically all of the reduction achieved had been accompanied by deamination.

The substance, therefore, was prepared according to the method of Einhorn and Meyenberg[6] and possessed all the properties described by these authors; m. p. 273° with decomposition.

Anal. Calcd. for $C_7H_{13}O_2N$ (143): N, 9.8. Found: N, 9.6.

Throughout the remainder of the paper we designate the 3- and 4- acids with α or β according to whether they were hydrogenated in aqueous suspension or in solution in hydrochloric acid. The 2-acid, which was prepared in only one way, namely, by the amyl alcohol treatment, requires no special designation.

III

Measurements of dielectric constant were made by a resonance method previously described.[11] The results, expressed in terms of δ, the dielectric increment (the increase of dielectric constant per mole of solute per liter of solution at 25°), are given in Table II. The frequency varied between about 5.35×10^7 (λ = 5.6 m.) and 5.1×10^7 (λ = 5.9 m.). The sharpness of the settings and the accuracy of the results varied with the conductivity of the solutions as determined by very small traces of conducting impurities from which it is well-nigh impossible to free such soluble compounds by crystallization. In dealing with dilute solutions, as in the present case, errors in dielectric constant are much magnified in the values of the dielectric increments. The errors in the values of the increments given in Table II are estimated from the consistency of the dielectric constant measurements. In every case measurements were made at at least three different concentrations within the range indicated in the table. This table also contains values of the apparent molal volumes based on density measurements made with a pycnometer over a range of concentrations usually two or three times greater than that for the dielectric constant measurements. In addition to these, there are listed in the last two columns values of the two acidity constants (expressed as pK_1 and pK_2) calculated from titration data obtained on aqueous solutions with a hydrogen electrode.

Compound	δ	Concn. range, moles per liter	V	pK_1	pK_2
2	24.4 ± 0.6	0.04–0.10	108.3 ± 0.2	3.4	10.1
3α	59 ± 1	.05– .15	106.2 ± .1	4.2	10.5
3β	62 ± 4	.04– .11	103.9 ± .2	4.2	10.5
4α	62 ± 0.6	.04– .17	106.8 ± .3	4.3	10.5
4β	61 ± 2	.05– .13	103.6 ± .1	4.35	10.5

IV

It is generally accepted that cyclohexane exists in two different forms, commonly referred to as the chair and the boat, with each of which there is associated approximately the same energy, and which occur consequently with approximately the same frequency. When, as in the case of the cyclohexane amino acids, two different groups are substituted for two hydrogens attached to different carbon atoms of the ring, whether in the

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[11] Wyman, *Phys. Rev.*, **35**, 623 (1930).

1,2-, 1,3- or 1,4-positions, there are, geometrically, 24 possible ways in which the substitution can be made in the case of the chair form and 24 also in the case of the boat form, although, for reasons of symmetry, not all of these configurations are distinguishable. We will consider the latter form first. From a geometrical point of view, without regard to steric hindrance or the mutual energy of the substituted groups, this form is capable of free rotation whereby certain configurations can pass over into certain others without a deformation of valence angles. On this basis the 24 configurations fall into two classes of 12 members each, members of the same class being derivable from one another by free rotation. One class embraces what may be called the *cis* configurations, the other the *trans* configurations. For any *cis* configuration there exists a corresponding *trans* configuration obtainable from it by interchanging one and only one of the substituted groups with the hydrogen attached to the same carbon atom.

We will consider now the chair form. In this case the geometry is such that there is no possibility of free rotation. For each of the 24 possible configurations of this form there is a corresponding boat configuration, from which it arises when the ring passes through the state of strain required to convert it from the boat to the chair form. For this reason the chair configurations also fall into two classes, *cis* and *trans*, of twelve members each, members of the *cis* class having each a corresponding *cis* configuration, members of the *trans* class each a corresponding *trans* configuration, in the boat form. If, as the evidence of organic chemistry suggests, there is a constant transition back and forth between chair and boat forms then, owing to the free rotation in the boat form (neglecting steric hindrance and interaction of substituents), there also must be a constant transition between the various configurations of the chair form, and any such disubstituted cyclohexane as we are considering should exist either in a *cis* or a *trans* condition. The ring, despite its flexibility and all the free rotation associated with it, acts like a double bond to separate *cis* from *trans* configurations.

In the picture just presented no account is taken of steric hindrance, electrostatic effects, or van der Waals forces involving the substituents. Such factors certainly must influence the frequencies of occurrence of the various configurations, perhaps even so far as to rule out certain configurations entirely. Whenever energy differences between different configurations are of the order of kT (*i. e.*, 4×10^{-14} erg per molecule or 0.6 kcal. per mole at 25°), then we may expect free rotation to be greatly diminished or even completely suppressed and the molecule to be stabilized in the configuration of least energy. This seems to be the case with the 1,4-*trans*-dihalogenated cyclohexanes studied by Hassel[12,13] which have zero moments in benzene. In this case, where the moment is given by the vector sum of the two dipoles associated with the halogens, the electrostatic energy depends in a complicated way on the orientation of the dipoles with reference to the line joining them and on the cube of the distance separating them. In the case of dipolar ions like the cyclohexane amino acids, the electrostatic energy term is simply $e^2/\epsilon r$, in which e is the elementary charge, r the distance between the centers of charge of the positively and negatively ionized groups and ϵ the effective dielectric constant. For a given value of ϵ, the electrostatic energy of a dipolar ion is larger than that of a molecule containing two dipoles separated by the same distance except for very small values of r (*e. g.*, always less than 1 Å. when the moments of the dipoles do not exceed 3.3 *D*). However, in the case of solutions in water or other highly polar media, in which dipolar ions have been studied, the effective dielectric constant is probably very much greater than in the case of solutions in benzene. If we take ϵ as 80, the value for water, the electrostatic energy for $r = 3$ Å. is close to -8×10^{-14} erg, and is equal to $-KT$ at $r = 6.2$ Å. It increases with r and gives rise to an attraction between the charged groups, which tend to approach one another until the effect is overbalanced by repulsive forces due to the interference and the interaction of these groups, *e. g.*, the NH_3 and COO^- groups in the case of the alicyclic amino acids. It is impracticable to attempt to estimate quantitatively the magnitude of the potentials due to the various factors, at least for the amino acids, but it may be recalled that heats of combustion give a value of about 20×10^{-14} erg for the potential energy due to the repulsion of two methyl groups separated by 2.9 Å., in nonpolar molecules.[14] There is this difference between the amino acids and the dihalogenated

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[12] Hassel, *Z. Elektrochem.*, **37**, 540 (1931).

[13] Hassel, *Z. physik. Chem.*, **B15**, 472 (1932).

[14] H. A. Stuart, "Molekülstruktur," Verlag von Julius Springer, Berlin, 1934, p. 101.

TABLE II

		cis			trans	
Substance	d^2		Frequency	d^2		Frequency
1,2-Boat	10.45		8	18.47		4
	7.78		4	15.78		4
				10.45		4
	Av. 9.56			Av. 14.90		
Chair	10.45		12	18.47		6
				10.45		6
	Av. 10.45	Av. 10.01		Av. 14.46	Av. 14.68	
1,3-Boat	29.02		2	27.19		2
	27.23		2	26.19		2
	26.19		2	23.38		2
	15.15		2	23.17		2
	13.19		2	21.22		2
	6.70		2	23.17		2
	Av. 19.58			Av. 24.05		
Chair	29.02		6	23.38		6
	6.70		6	20.34		6
	Av. 17.86	Av. 18.72		Av. 21.86	Av. 22.96	
1,4-Boat	36.90		2	30.61		4
	36.25		4	27.57		4
	13.93		4	19.46		2
	2.34		2	14.45		2
	Av. 23.27			Av. 25.05		
Chair	25.34		6	38.97		6
	22.40		6	24.70		6
	Av. 23.87	Av. 23.57		Av. 31.84	Av. 28.44	

cyclohexanes, that in the latter the electrostatic forces between the dipoles lead to a repulsion whenever the halogens are close together.

In Table II are listed the different values of the square of the distance between the plus and minus charges which occur in the three cyclohexane amino acid dipolar ions. Certain distances occur in more than one configuration, and the number of configurations in which each distance occurs is given in the columns headed "frequency." These distances are calculated on a purely geometrical basis, without regard to interaction or interference of the NH_3^+ and COO^- groups, on the basis of the following assumptions: that all the valence angles of the carbon atoms of the ring are the same as the tetrahedral angle; that the distance between these atoms is 1.52 Å.; that the locus of positive charge of the NH_3^+ group is at the center of the nitrogen atom; that the distance between this nitrogen atom and the associated carbon atom of the ring is 1.40 Å.; that the locus of negative charge of the COO^- group is midway between the two oxygen atoms and on the line of the valence bond between the carbon atom and the associated carbon atom of the ring at a distance of 2.14 Å. from the center of the latter. It seems clear from a consideration of these figures that there is no stabilization of the dipolar ions in the configuration of least energy, as appears to be the case in the 1,4-*trans*-dihalogenated cyclohexanes. If this were so, the dielectric increment, which is a measure of the electric moment, should not be less for the 1,2-form than for the other two forms, as is actually the case, since the charged groups certainly can approach quite as close (geometrically, closer) in the case of the 1,3- and 1,4-forms as in the case of the 1,2-form, and the mutual energy of the groups must depend only on their distance.

Notwithstanding the arbitrariness and artificiality of the procedure of neglecting the interaction of the groups, it is of interest to consider the average values of the squares of the distances listed in Table II, which are also included in the table. These may be compared with mean square values for the distances between the charges in straight chain amino acids also calculated on a purely geometrical basis, making use of the same assumptions about valence angles and so on, without regard to interference, by integrating over all the possible configurations. Such values have been calculated for the α,[15] β, γ, and δ acids, and are, respectively: 8.53, 13.12, 17.71, 21.96. They increase very nearly linearly with the number of

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[15] In the case of an α acid, no averaging is required since the distance between the NH_3^+ and COO^- groups is fixed.

carbons between the amino and carboxyl groups, and the values 25.2 and 30.0 for the ϵ and ζ acids may be extrapolated with considerable assurance.(16) In Fig. 1 these values are plotted against the observed values of the dielectric increment. In the same figure are plotted the dielectric increments of the cyclohexane amino acids against the mean square distances (given in Table II) for both *cis* and *trans* forms. On the whole the two sets of data are consistent and suggest that free rotation occurs to the same degree in the cyclic compounds as in the straight chain forms. The identity of the increments of the 1,3- and 1,4-alicyclic acids suggests that the former occurs in what we have called the *trans*, the latter in what we have called the *cis*, form. It also appears that the 1,2-acid probably occurs in the *cis* form. The identity of the dielectric increments of the 1,3-α and -β preparations as well as of the 1,4-α and -β preparations suggests that these are not different. The differences of melting point between α and β preparations are probably not significant, and in any case represent a temperature range of decomposition rather than a true melting point, as in the case of amino acids generally.

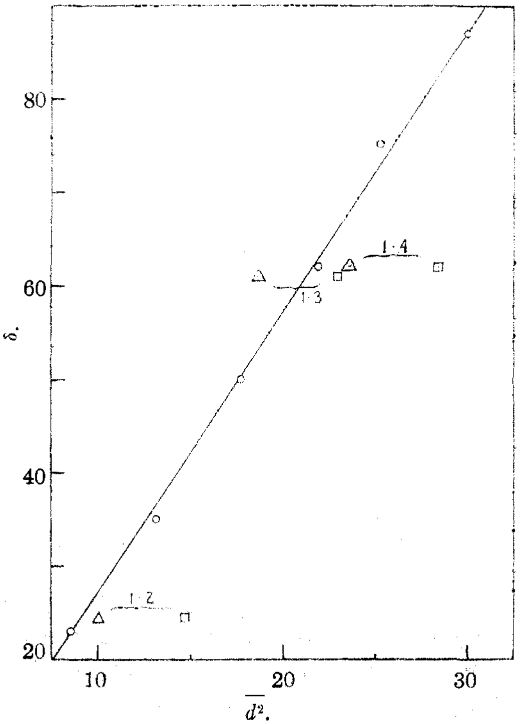

Fig. 1.—O, Aliphatic amino acids; △, *cis* alicyclic amino acids; □, *trans* alicyclic amino acids.

It should be emphasized that the procedure of correlating dielectric increments with the mean square distances calculated so arbitrarily on a geometrical basis was adopted solely as a basis for comparing the straight chain and alicyclic amino acids. The mean square values involved cannot be expected to be realized with any degree of exactness in either set of compounds. The smallest values of the distance between the NH_3^+ and COO^- groups involved in these averages are certainly too small to be physically possible, and the largest values are statistically improbable in view of the energy relations. Kuhn[5] by taking account of the coulomb forces in a statistical treatment of the case of straight chain amino acids has obtained much lower values for the mean square distances, *e. g.*, for an α-acid, 3.88; for a β-acid, 5.54; for a δ-acid 9.3; for a ζ-acid, 16.4. Nevertheless, we may expect that the effect of any interactions between the groups will be essentially the same and cause essentially the same deviations from the geometrically calculated mean square distances in both series of amino acids, and the argument for the same degree of free rotation in both types of amino acid is not seriously affected.

It is to be observed that the apparent specific volumes of the 1,3- and 1,4-acids, which have the same dielectric increments (moments) are equal and less than that of the 1,2-isomer, indicating a greater electrostriction associated with a greater moment. The relatively small differences of volume between the α- and β-preparations are probably not significant, and may well be due to slight differences of water content. It also is to be noted that the acidity constants (pK_1 and pK_2) are both very nearly the same and much like those of a δ-aliphatic amino acid (pK_1 = 4.21, pK_2 = 10.69), which has a dielectric increment of 63, about the same as that of the 1,3- and 1,4-alicyclic acids. The dissociation constants of the 1,2-acid are between those of α- and β-straight chain amino acids. This bears out the view that the effect of one charged substituent on another depends on the mean square distance between them.

Summary

A comparison of the dielectric increments of 1,2-, 1,3- and 1,4-aminocyclohexane-carboxylic acids with those of aliphatic amino acids in

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(16) An attempt to correlate the effect of one substituent on another in aliphatic acids from the values of the square of the distance between them, and based on a completely extended configuration, yielded an approximately linear relation—Greenstein, THIS JOURNAL, 58, 1314 (1936).

aqueous solution leads to the view that there is free rotation to much the same degree in both series of compounds. The correlation between dielectric increments, apparent molal volumes and acidity constants is pointed out for these alicyclic amino acids.

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CAMBRIDGE, MASS.
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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 402]

Recombination of Hydrogen Atoms. III

BY I. AMDUR

It is generally conceded that the combination of hydrogen atoms to form molecules proceeds according to a trimolecular mechanism. The presence and extent of first or second order wall reactions, as well as the efficiencies of hydrogen atoms and hydrogen molecules as third bodies, have been the subject of much controversy and speculation. Agreement among various investigators is definitely lacking. Smallwood,[1] for example, contends that it is possible to eliminate any wall reaction and that the essential recombination mechanism involves only triple collisions of hydrogen atoms, whereas Steiner[2] finally concludes that there is a small first order wall reaction, but that hydrogen molecules are the most efficient third bodies. In contradiction to this, Amdur[3] found that the assumption of a homogeneous reaction involving only triple collisions of hydrogen atoms was adequate to account for the experimental data for the relative rate of recombination of atomic hydrogen and atomic deuterium over a narrow range of composition and pressure. And yet, some time previously, Smallwood[4] and Amdur and Robinson[5] had decided that for any extended range of variables it was necessary to include a wall reaction as well as both types of triple collisions. In all the cases cited the investigators used high concentrations of atomic hydrogen (95 to 10%) produced in a discharge tube at total pressures of the order of 1 mm. Other experimenters[6] working at total pressures of the order of 10 mm. with small concentrations of atomic hydrogen (less than 1%) produced by photosensitization of mercury saturated hydrogen, report results as varied as those noted above.

In the opinion of the author, there are several reasons for these discrepancies even after one has taken into account the widely different experimental methods and range of variables. One reason is a tendency, in the treatment of experimental data, to oversimplify the formal rate equation containing the desired velocity constants. To include the proper diffusion terms in the equation involved for the recombination of hydrogen atoms in a dynamic system, for example, involves much laborious calculation and necessitates data of considerable accuracy and consistency. However, the omission of these diffusion terms, whose magnitude is small, is capable of effecting tremendous variations in the rate constants or even of yielding negative values when the constants are simultaneously solved for. The same situation results from the use of values for the fraction or partial pressure of atomic hydrogen which are of low accuracy. Finally, if the range of data is not sufficiently wide, a mechanism may be sponsored which may be quite inadequate to account for experimental results over a larger range of variables. In this connection it should be noted that several mechanisms may fit the experimental data equally well. This point has been overlooked, in some cases, possibly, due to personal prejudice regarding the correct mechanism to be assumed for the reaction.

It is the purpose of this paper to avoid, as much as possible, any arbitrary decisions by treating objectively a very large number of experimental points covering the widest possible range of composition and pressure attainable with the present experimental method. This objective treatment consists, first, of least squaring all the data to fit a family of curves for the various pumping speeds and using least square methods to calculate rate constants taking all experimental points into account; second, of rigorously deriving the rate expressions, taking into account all factors involved

(1) Smallwood, THIS JOURNAL, **56**, 1542 (1934).

(2) Steiner, *Trans. Faraday Soc.*, **31**, 623 (1935).

(3) Amdur, THIS JOURNAL, **57**, 856 (1935).

(4) Smallwood, *ibid.*, **51**, 1985 (1929).

(5) Amdur and Robinson, *ibid.*, **55**, 1395 (1933).

(6) (a) Senftleben and Riechemeier, *Ann. Physik*, **6**, 105 (1930); (b) Farkas and Sachsse, *Z. physik. Chem.*, **B27**, 111 (1934); (c) Senftleben and Hein, *Ann. Physik*, **22**, 1 (1935).