effects are reflected in the measured hydration numbers, they would be expected to be even larger in the case of the trivalent metal ions such as Al^{3+}.

A larger hydration number was obtained for $CaCl_2$ than for $MgCl_2$, and this would not have been expected unless the primary hydration number for Ca^{2+} were larger than 6.0, or unless solvent-separated ion pairing is more predominant in $MgCl_2$ solution than $CaCl_2$ solutions (assuming that if ion pairing does occur in these solutions it would affect only the secondary hydration layer). It is interesting to note that Swift and Sayre[28] using a quite different technique also obtained a larger hydration number for Ca^{2+} than for Mg^{2+}.

Despite the problems associated with this technique, we feel that it can be useful in providing further understanding not only of hydration in the alkali metal series but also of ion–ion interactions. Some of the interpretive difficulties may lie in the basic assumption that the total effective hydration number and δ_s do not change over the temperature range measured and in this sense, the technique will require more investigation before more definitive assignments are possible.

Acknowledgment. One of the authors (R. W. C.) wishes to acknowledge the financial assistance provided by the University of North Carolina Materials Research Center Contract SD-100 with the Advance Research Projects Agency. We would also like to acknowledge the National Science Foundation Grant 325-NAT-190 for the purchase of the Varian HA-100 used in these studies.

(28) T. J. Swift and W. G. Sayre, *J. Chem. Phys.*, **44**, 3567 (1966).

Radiation Chemistry of the α-Amino Acids. γ Radiolysis of Solid Cysteine[1]

by Donald B. Peterson,[2] John Holian, and Warren M. Garrison

Lawrence Radiation Laboratory, University of California, Berkeley, California 94720 *(Received November 13, 1968)*

The γ radiolysis of solid cysteine is shown to yield hydrogen, hydrogen sulfide, ammonia, and cystine as major products. Radiolysis data are also given for a series of related compounds: cystamine, N-acetyl cysteine, S-methyl cysteine, glycine, and alanine. The proposed reaction schemes provide a basis for correlating the radiation chemistry of these solid-state systems.

Introduction

Radiolysis of the simpler α-amino acids such as glycine and alanine leads to deamination as a major chemical consequence both in aqueous solution[3] and in the solid state,[4] and there is accumulating evidence that the intermediate processes of deamination in the solid state are closely analogous to those that occur in aqueous solution. For example, in aqueous solution the ionization step[5]

$$H_2O \rightsquigarrow H^+, OH, e_{aq}^- \quad (1)$$

is followed by[6]

$$e_{aq}^- + NH_3^+CH(R)COO^- \longrightarrow NH_3 + \dot{C}H(R)COO^- \quad (2)$$

$$OH + NH_3^+CH(R)COO^- \longrightarrow H_2O + NH_3^+\dot{C}(R)COO^- \quad (3)$$

where e_{aq}^- represents the hydrated electron. The experimental evidence is that e_{aq}^- adds initially to the C=O linkage of the carboxyl group and that dissociation of the reduced intermediate then ensues.[6b,c] Subsequent interactions of $\dot{C}H(R)COO^-$ and

(1) This work has been supported by the U. S. Atomic Energy Commission.

(2) Department of Chemistry, University of San Diego, San Diego, Calif.

(3) (a) W. M. Dale, J. V. Davies, and C. W. Gilbert, *Biochem. J.*, **45**, 93 (1949); (b) G. Stein and J. Weiss, *J. Chem. Soc.*, 3256 (1949); (c) C. R. Maxwell, D. C. Peterson, and N. E. Sharpless, *Radiation Res.*, **1**, 530 (1954); (d) B. M. Weeks and W. M. Garrison, *ibid.*, **9**, 291 (1958).

(4) (a) W. M. Dale, J. V. Davies, and C. W. Gilbert, ref 3a; (b) B. Rajewski and K. Dose, *Z. Naturforsch.*, **12B**, 384 (1957); (c) G. Meshitsuka, K. Shindo, A. Minegishi, H. Suguro, and Y. Shinozaki, *Bull. Chem. Soc. Jap.*, **37**, 928 (1964); (d) A. Minegishi, Y. Shinozaki, and G. Meshitsuka, *ibid.*, **40**, 1271 (1967); (e) W. C. Gottschall, Jr., and B. M. Tolbert, *J. Phys. Chem.*, **72**, 922 (1968).

(5) For a recent review of the radiation chemistry of water, see M. S. Matheson, Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1965, p 45.

(6) (a) W. M. Garrison, Lawrence Radiation Laboratory Report No. UCRL-10827, May 1963; *Radiation Res. Suppl.*, **4**, 1964; (b) B. M. Weeks, S. A. Cole, and W. M. Garrison, *J. Phys. Chem.*, **69**, 4131 (1965); (c) R. L. S. Willix and W. M. Garrison, *ibid.*, **69**, 1579 (1965); (d) R. L. S. Willix and W. M. Garrison, *Radiation Res.*, **32**, 452 (1967).

$NH_3^+\dot{C}(R)COO^-$ yield keto acid and fatty acid as the major organic products,[3c,d] *e.g.*

$$NH_3^+CH(R)COO^- + \dot{C}H(R)COO^- \longrightarrow NH_3^+\dot{C}(R)COO^- + CH_2(R)COO^- \quad (4)$$

$$2NH_3^+\dot{C}(R)COO^- \longrightarrow NH_2^+{=}C(R)COO^- + NH_3^+CH(R)COO^- \quad (5)$$

$$H_2O + NH_2^+{=}C(R)COO^- \longrightarrow NH_4^+ + RCOCOO^- \quad (6)$$

where the hydrolysis of the labile imino acid intermediate occurs essentially instantaneously.

The identification of reaction 2 prompted the suggestion[6a] that dissociative electron capture is also involved in the formation of ammonia as a major product in the radiolysis of the α-amino acids in the solid state. Ionic processes in these irradiated polar solids would then be represented by

$$NH_3^+CH(R)COO^- \rightsquigarrow NH_3^+\dot{C}(R)COO^- + H^+ + e^- \quad (7)$$

$$e^- + NH_3^+CH(R)COO^- \longrightarrow NH_3 + \dot{C}H(R)COO^- \quad (8)$$

where reactions 7 and 8 are the stoichiometric equivalents of reactions 1 to 3. Reactions 4 and 5 which may occur in part in the solid are completed on dissolution of the irradiated solid in water.

It has since been established elsewhere[7] that glyoxylic and acetic acid are indeed formed as major products in the γ radiolysis of solid glycine with $G(NH_3)$ = G(glyoxylic acid) + G(acetic acid) = 5.

The NH_3^+ group in these solid-state systems does not appear to act as a proton donor

$$e^- + NH_3^+CH(R)COO^- \longrightarrow H + NH_2CH(R)COO^- \quad (9)$$

since hydrogen yields in the γ radiolysis of both glycine and alanine (measured after dissolution) are quite low with $G(H_2) \leq 0.2$.[4c,d]

The recent results obtained with paramagnetic resonance methods provide convincing physical evidence of the importance of reaction 8 in the radiolysis of the simpler α-amino acids in the solid state:[8] on irradiation at 77°K the initially observed radical has the electron located at the carboxyl group and on warming to intermediate temperatures the initial radical dissociates to yield $\dot{C}H(R)COO^-$.

Turning now to a consideration of the effects of SH substitution on the radiation chemistry of the α-amino acids we note that in the radiolysis of cysteine, $NH_3^+CH_2(CH_2SH)COO^-$ in oxygen-free aqueous solution the processes of deamination are wholly absent; the reactions of e_{aq}^- and OH occur exclusively at the sulfur moiety[9]

$$e_{aq}^- + RSH \longrightarrow HS^- + NH_3^+CH(\dot{C}H_2)COO^- \quad (10)$$

$$OH + RSH \longrightarrow H_2O + NH_3^+CH(CH_2\dot{S})COO^- \quad (11)$$

In the present work we examine the role of the SH function as a competing locus of reaction in the γ radiolysis of cysteine in the solid state. Data on a number of related (sulfur-containing) compounds are also included. Although there have been numerous studies of the paramagnetic resonance properties of irradiated cysteine,[10] the detailed radiation chemistry of this system has not been elucidated.

Experimental Section

Sample Preparation and Irradiation. All of the organic materials were of reagent grade or of the highest purity available from Nutritional Biochemical Corp., Cyclo Chemical Corp., and Mann Research Laboratories Inc. In some instances several recrystallizations from water were required to obtain acceptable "blank" readings in the various analytical procedures described below.

Pyrex ampoules containing 1-g samples of the polycrystalline solids were degassed on the vacuum line for about 24 hr and then sealed off with the torch and irradiated in a 10-kc ^{60}Co Gamma-Cell (ambient temperature ~35°) at a dose rate of 1.3×10^{18} eV/g min [$G(Fe^{3+}) = 15.5$, ϵ_{305} 2180 at 24°].

Analyses. Gaseous products were pumped off following complete dissolution of the irradiated solid in degassed water which was introduced through a break-seal connection to the vacuum line. Gaseous products were identified and assayed by mass spectrometry (Consolidated 120) and by gas chromatography (Aerograph A90-P3). The dissolution step was made immediately after completion of the irradiation.

Ammonia was determined by a modification of the Conway diffusion method[11] in which a slurry of MgO was used to release ammonia from a solution of the irradiated sample in the outer compartment of the diffusion cell. Conventionally, a saturated K_2CO_3 solution is so employed, but we found that hydrolytic degradation of cysteine in the K_2CO_3 solution leads to excessively high blanks. Diffusion of ammonia

(7) (a) G. Meshitsuka, private discussion, Sept 1963; (b) G. Meshitsuka, Y. Shinozaki, A. Minegishi, K. Shindo, and H. Suguro, Annual Report Tokyo Metropolitan Isotope Center, Vol. 2, 1963. See also ref 4c, d.

(8) (a) H. C. Box, H. G. Freund, and J. Budzinski, *J. Amer. Chem. Soc.*, **88**, 658 (1966); (b) J. W. Sinclair and M. W. Hanna, *J. Phys. Chem.*, **71**, 84 (1967).

(9) (a) D. El Samahy, H. L. White, and C. N. Trumbore, *J. Amer. Chem. Soc.*, **86**, 3175 (1964); (b) D. A. Armstrong and V. G. Wilkening, *Can. J. Chem.*, **42**, 2631 (1964).

(10) For example, see (a) W. Gordy, W. B. Ard, and H. Shields, *Proc. Nat. Acad. Sci. U. S.*, **41**, 983 (1955); (b) T. Hendriksen, *J. Chem. Phys.*, **37**, 2189 (1962); (c) M. K. Pulatov and O. A. Azizova, *Biofizika*, **9**, 33 (1964).

(11) E. J. Conway, "Microdiffusion Analysis," Crosby Lockwood and Sons, Ltd., London, 1962.

from the MgO solution to the acid compartment (0.1 N H_2SO_4) is complete in 8 hr. Diffusates were assayed by means of Nessler reagent. Control runs showed no interference from amines.

The "NH_2-free" fraction consists of the totality of organic products that contain an SH group but no NH_2 group. This fraction was isolated by passing the dissolved sample through ion-exchange resin (AG-50W-X8, Bio-Rad Laboratories) in the acid form. Cysteine and amino derivatives are retained by the column. The "NH_2-free" fraction was collected and assayed for total SH function after the method of Ellman.[12] β-Mercaptopropionic acid was identified by filter-paper chromatography.[13]

Pyruvic acid and total carbonyl were determined after the methods of Johnson and Scholes[14] and Lappin and Clark,[15] respectively.

Hydrogen sulfide was also determined by the Conway technique.[11] Irradiated samples were dissolved in dilute air-free 0.1 M NaOH and transferred to the outer chamber of the diffusion cell. The solution was then acidified with 10% H_2SO_4 to liberate H_2S which was collected in 0.1 M NaOH in the inner compartment after a diffusion period of ~5 hr. The diffusates were assayed nephelometrically (Bi_2S_3). Mercaptans do not interfere in this procedure.

Cystine is sufficiently insoluble in water (~2.5×10^{-4} M at 25°) to permit a gravimetric determination. Irradiated samples were dissolved in air-free water and allowed to stand for several hours to allow for equilibration. Cystine was removed by filtration through a tared sintered-glass filter and dried (*in vacuo*) at 100°. A series of blank and "spiked" runs determined the solubility corrections. The specificity of all analytical methods was established in a series of blank and control runs. Reproducibility of the datum is indicated in Table I.

Results and Discussion

G values for the various products formed in the γ radiolysis of solid polycrystalline L-cysteine at 35° are summarized in Table I. Dose–yield plots for all products are linear up to doses in the range 10^{21} eV/g; typical plots are shown in Figure 1. Yields of hydrogen, hydrogen sulfide, and ammonia from a number of related sulfur-containing compounds are given in Table II.

Table I: Product Yields in the γ Radiolysis of Solid L-Cysteine

Product	G
Hydrogen	3.1 ± 0.1
Hydrogen sulfide	1.5 ± 0.1
Ammonia	1.8 ± 0.1
Cystine	5.0 ± 0.5
"NH_2-free" fraction	1.0 ± 0.1
Pyruvic acid	≤ 0.1
Total carbonyl	≤ 0.1

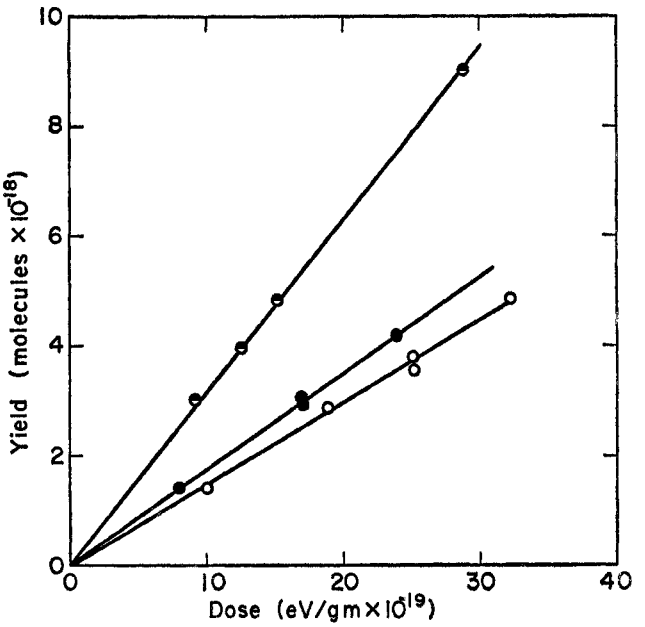

Figure 1. Production of hydrogen (◓), ammonia (●), and hydrogen sulfide (○), from solid cysteine as a function of γ-ray dosage.

The fact that carbonyl products are not liberated in any appreciable yield, $G(>CO) \sim 0.1$, on dissolution of the irradiated cysteine in water indicates that little of the observed ammonia, $G(NH_3) = 1.8$, arises through hydrolysis of labile imino derivatives of the type $NH_2^+{=}C(CH_2SH)COO^-$. Apparently reactions akin to steps 4–6 of the "glycine" mechanism do not contribute to the radiation chemistry of solid cysteine.

The low carbonyl yields also show that the overall stoichiometries

$$RSH \rightsquigarrow H_2 + NH_2^+{=}C(CH_2SH)COO^- \quad (12)[16]$$

$$RSH \rightsquigarrow H_2S + NH_3^+C(=CH_2)COO^- \quad (13)$$

are unimportant since it is clear that the organic products of reactions 12 and 13 would yield carbonyl compounds on dissolution (amino acrylic acid $NH_3^+C(=CH_2)COO^-$ is tautomeric with imino propionic acid $NH_2^+{=}C(CH_3)COO^-$).

We suggest that the radiation chemistry of solid cysteine may be interpreted in terms of the reaction scheme

$$RSH \rightsquigarrow R\dot{S} + H^+ + e^- \quad (14)$$

$$RSH \rightsquigarrow R\dot{S} + H \quad (15)$$

(12) G. L. Ellman, *Arch. Biochem. Biophys.*, **82**, 70 (1959).
(13) E. P. Kennedy and H. A. Barker, *Anal. Chem.*, **23**, 1033 (1951).
(14) G. R. A. Johnson and G. Scholes, *Analyst*, **79**, 219 (1954).
(15) G. R. Lappin and L. C. Clark, *Anal. Chem.*, **23**, 541 (1951).
(16) For purposes of simplicity we use the symbol RSH to represent the cysteine zwitterion, $NH_3^+CH(CH_2SH)COO^-$.

followed by

$$H + RSH \longrightarrow H_2 + R\dot{S} \quad (16)$$

$$\longrightarrow H_2S + NH_3{}^+CH(\dot{C}H_2)COO^- \quad (16a)^{17}$$

$$e^- + RSH \longrightarrow NH_3 + \dot{C}H(CH_2SH)COO^- \quad (17)$$

$$e^- + RSH \longrightarrow H_2 + NH_2CH(CH_2\dot{S})COO^- \quad (18)$$

$$\longrightarrow H_2S + NH_2CH(\dot{C}H_2)COO^- \quad (18a)$$

and by the radical removal steps

$$RSH + \dot{C}H(CH_2SH)COO^- \longrightarrow R\dot{S} + CH_2(CH_2SH)COO^- \quad (19)$$

$$RSH + NH_2CH(\dot{C}H_2)COO^- \longrightarrow R\dot{S} + NH_2CH(CH_3)COO^- \quad (20)$$

$$2R\dot{S} \longrightarrow RSSR \text{ (cystine)} \quad (21)$$

where reaction 21 occurs mainly on dissolution, although we cannot rule out the possibility that some dimerization occurs in spur regions[18] along the track of the Compton electron.

The ionization act, reaction 14, as formulated here, incorporates the concept that a parent positive ion in a polar medium is converted instantaneously to the corresponding radical species through reaction of the type $RH^+ + RH \rightarrow R + RH_2{}^+$.[19] Localization of the radical site at sulfur position would be expected on energetic grounds;[20] epr studies show that $R\dot{S}$ represents the long-lived radical in γ-irradiated cysteine at room temperature.[10] We assume that any contribution of excited states will arise through homolytic cleavage of the labile S–H bond as shown in reaction 15.[21]

Table II: Comparative Product Yields in the γ Radiolysis of Cysteine and Related Compounds in the Solid State

	G		
	H_2	H_2S	NH_3
Cysteine $NH_3{}^+CH(CH_2SH)COO^-$	3.1	1.5	1.8
Cystamine $(NH_3{}^+CHCH_2SH)Cl^-$	5.6	1.2	<0.1
N-Acetyl cysteine $CH_3CONHCH(CH_2SH)COOH$	0.5	0.9	<0.1
S-Methyl cysteine $NH_3{}^+CH(CH_2SCH_3)COO^-$	~0.2	...[a]	5.1
Glycine $NH_3{}^+CH_2COO^-$	~0.2		5.2
Alanine $NH_3{}^+CH(CH_3)COO^-$	~0.2		5.4

[a] H_2S was not anticipated nor was it observed as a product from S-methyl cysteine; other measurements with S-methylcysteine gave $G(CH_4) \sim 0.5$; $G(CH_3SH) \leq 0.1$. These results indicate that e^- is not captured *via* dissociative attachment at the sulfur locus; the observed H_2 and NH_3 yields suggest that the "glycine" mechanism is of major importance in the radiolysis of S-methyl cysteine.

The evidence is that ammonia liberation from cysteine occurs almost exclusively through the dissociative capture of e^- as formulated in reaction 17. This step is, of course, the analog of reaction 8 of the glycine mechanism. The formation of ammonia *via* reaction 17 liberates the $\dot{C}H(CH_2SH)COO^-$ radical which we assume abstracts H from the labile S–H bond of cysteine (step 19) to yield β-mercaptopropionic acid. A "NH_2-free" fraction of organic products is produced with $G \geq 1.2$ (Table I) and β-mercaptopropionic acid has been identified as a constituent of this fraction. The fact that the observed yield of "NH_2-free" products is somewhat less than the ammonia yield, $G(NH_3) = 1.8$, is not too surprising since one might expect that a fraction of the $\dot{C}H_2(CH_2SH)COO^-$ radicals formed in reaction 17 would undergo the rearrangement

$$\dot{C}H_2(CH_2SH)COO^- \longrightarrow CH_3(CH_2\dot{S})COO^- \quad (22)$$

in competition with the H abstraction step 19. On dissolution, the radicals $CH_3(CH_2\dot{S})COO^-$ are then removed through combination with cysteine radicals $R\dot{S}$.

That e^- adds initially to the carboxyl C=O linkage of cysteine (as in the reaction of e^- with solid glycine) is supported by the results obtained with cystamine $NH_3{}^+CH_2CH_2SH$ (Table II). We find that cystamine which does not contain the carboxyl group as a trapping center for e^- does not yield ammonia in any appreciable yield $G(NH_3) \leq 0.1$.

The SH group of cysteine represents a competing trapping center for e^-.[22] In fact, as we have noted e_{aq}^- in aqueous solutions of cysteine reacts exclusively through dissociative attachment to yield $H\bar{S}$ (H_2S). On the other hand, recent studies[23,24] of the radiation chemistry of thiophenol and ethyl mercaptan in the pure liquid state indicate that dissociative capture reactions of the type

$$RSH + e^- \longrightarrow R + H\bar{S} \quad (23)$$

$$RSH + e^- \longrightarrow R\bar{S} + H \quad (24)$$

do not occur; these liquid systems are considerably less polar than water and the evidence is that reactions 23 and 24 become exothermic only if solvation energies in a polar medium can be utilized in the overall ener-

(17) G. Navon and G. Stein, *Israel J. Chem.*, **2**, 151 (1964).

(18) A. O. Allen, *Discussions Faraday Soc.*, **12**, 79 (1952).

(19) T. F. Moran and W. H. Hamill, *J. Chem. Phys.*, **39**, 1413 (1963).

(20) (a) T. L. Cotrell, "The Strengths of Chemical Bonds," Butterworth and Co. Ltd., London, 1954; (b) D. A. Ansdell and F. M. Page, *Trans. Faraday Soc.*, **58**, 1084 (1962).

(21) Reaction 15 represents a major process in the photolysis of cysteine in the solid state as recently shown by H. C. Box, H. G. Freund, and E. E. Budzinski, *J. Chem. Phys.*, **45**, 809 (1966).

(22) The radical RSH^- has been identified in γ-irradiated cysteine at 77°K (ref 10c).

(23) G. Lunde and R. R. Hentz, *J. Phys. Chem.*, **71**, 863 (1967).

(24) J. J. J. Myron and R. H. Johnson, *ibid.*, **70**, 2951 (1966).

getics.[23,25] Whether or not such factors are involved in the reactions of e^- in a polar solid such as cysteine we cannot say.

However, simple dissociative attachment of e^- need not necessarily be involved in steps 18 and 18a. An alternate explanation is that e^- is captured by the sulfhydryl group to give RSH^- and that chemistry then ensues as a consequence of proton transfer from an adjacent NH_3^+ group.[26] Some evidence for such concerted action is to be found in the fact that $G(H_2) + G(H_2S)$ from N-acetylcysteine, $CH_3CONHCH(CH_2SH)COOH$, is markedly lower than the corresponding value for cysteine as shown in Table II. However, as formulated here, reactions 18 and 18a represent only the overall stoichiometries.

The reaction scheme given in eq 14–21 leads to the product relationship $G(H_2) + \frac{1}{2}G(H_2S) + \frac{1}{2}G(NH_3) = G(RSSR)$. We find experimentally that $G(H_2) + \frac{1}{2}G(H_2S) + \frac{1}{2}G(NH_3) = 4.8$ and that $G(RSSR) = 5$. The combined yields of the radiation-induced steps 14 and 15 is given by $G_{14} + G_{15} = G(H_2) + G(H_2S) + G(NH_3) = 6.4$. We cannot separately evaluate the contributions of ionization and excitation *via* reactions 14 and 15, respectively, since we have no knowledge of the relative yields of the branching reactions 16 and 16a, and 18 and 18a.

(25) For a discussion of the effects of solvation energy on reactions of the type $RX^- \longrightarrow R + X^-$, see J. A. Ward and W. H. Hamill, *J. Amer. Chem. Soc.*, **87**, 1853 (1965).

(26) As noted in our discussion of reaction 9, the evidence is that the NH_3^+ group itself does not react with e^- to yield hydrogen. See also ref 6b.

Solvation Enthalpies of Various Nonelectrolytes in Water, Propylene Carbonate, and Dimethyl Sulfoxide[1]

by C. V. Krishnan and Harold L. Friedman

Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11790
(Received November 18, 1968)

The heats of solution of a number of nonelectrolytes, mostly alcohols and hydrocarbons, have been measured in the solvents water, propylene carbonate, and dimethyl sulfoxide at solute concentrations low enough so that solute–solute interactions are negligible. The solvation energies for the aliphatic compounds exhibit additive group contributions in propylene carbonate and dimethyl sulfoxide and a nonadditive "structural" contribution in water. This simple analysis is less successful for the aromatic compounds. The structural effect in the enthalpy of hydration of the normal alcohols ranges from about −2.5 kcal/mol for methanol to about −8.5 kcal/mol for amyl alcohol. Its plot as a function of chain length tends to level off near amyl alcohol. The enthalpy of the hydrogen bond from a normal alcohol to the solvent is near −8.1 kcal/mol in dimethyl sulfoxide and −6.2 kcal/mol in propylene carbonate.

I. Introduction

The measurements reported here were made in the course of a study of solvation enthalpies of ionic species[2] where, in the attempt to interpret the results, a need developed for the corresponding data for uncharged species. These are reported separately because a number of unexpected features make them of interest in a wider context than the study of ion solvation alone.

The data are treated to see to what extent the enthalpies of transfer of various molecules from one medium to another can be decomposed into group contributions. In the simplest such treatment one would organize the data so that, in each case, one of the two media was the dilute gas phase; the resulting enthalpies of transfer would be solvation enthalpies. In the present work this practice has been followed only to a limited extent for two reasons. The primary one is that in the work with ionic solutes[2] the enthalpies in the gas phase are often not accessible to experiment. Indeed, they almost never are for polyatomic ions. There is evidence that one may circumvent this by employing a nonhydrogen-bonding solvent of high dielectric constant having only minimal basic and acidic tendencies as a reference medium for enthalpies of

(1) Grateful acknowledgment is made of the support of this work by the National Institutes of Health.

(2) H. L. Friedman, *J. Phys. Chem.*, **71**, 1723 (1967).