

FORMATION AND STABILIZATION ENERGY OF VERY WEAK COLLISION COMPLEXES OF ALCOHOLS AND CARBOXYLIC ACID MONOMERS WITH NON-POLAR SOLVENTS*

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It was proved by means of infrared spectra that aliphatic alcohols and monomers of carboxylic acids formed with molecules of non-polar solvents weak collision complexes. The value of stabilization energy was estimated for the collision complexes of carboxylic acid monomers.

In previous papers of this series^{1,2} formation of very weak complexes was proved between phenol molecules and nonpolar solvent molecules. These complexes were called collision complexes^{1,2}. It was assumed that the site of phenol molecules interaction in the collision complexes was the hydroxyl group; as, however, the aromatic part of the phenol molecule could interact with other molecules as a π -electron donor (see complexes of aromatic hydrocarbons with, *e.g.*, CCl_4 , CBr_4 (refs^{4,5})), it was necessary to exclude a possible participation of the phenyl group in the formation of a collision complex. For that reason, spectra of aliphatic alcohol solutions were investigated as well as spectra of monomers of carboxylic acids in mixtures of non-polar solvents, as these solute compounds do not contain the aromatic π -system.

EXPERIMENTAL

Experimental results of this study are discussed more in detail in ref.⁶. All compounds used were of analytical purity. Procedures used in their purification, testing methods, and physical properties have been reported earlier⁶.

Infrared spectra were measured using a Unicam SP-700 spectrometer with a grating accessory for investigation in the region about 3600 cm^{-1} . The resolving power of the instrument was chosen so that no distortion of infrared band shape occurred due to the instrument function; the spectral slitwidth was in the best case about $\pm 2\text{ cm}^{-1}$. In order to measure spectra of vapours at higher temperatures, an infrared spectrometer Zeiss (Jena) UR-20 (with a LiF prisma) was employed.

* Part VI in the series Studies of Solute-Solvent Interactions; Part V: This Journal 36, 2757 (1971) see ref.³.

The scale of both spectrometers was calibrated by gaseous standards⁷, and this made it possible to read the values of wavenumbers of the collision complexes bands with a precision of about $\pm 1 \text{ cm}^{-1}$. Solutions were measured using infrasil cells 0.1 to 4 cm thick, tempered with a precision of about 0.1°C. Solution temperature was measured directly in the cell by means of a thermocouple Pt/Pt + Ir (9 : 1). Measurements of spectra of gases were carried out in a tempered steel cell with a pathlength of 10 cm under isochoric conditions at both increasing and decreasing temperature in order to check the tightness of the cell.

Solutions were prepared by making up the weighed samples to 10 ml by the solvent. The overall concentration of solutes in measuring the $\nu(\text{OH})$ band spectra of collision complexes (10^{-2} to 10^{-4} M) was chosen — with regard to the solvent transparency — so that the solute-solute interactions were negligible. Solvent mixtures were prepared in volume ratios. Preparation of the solutions and manipulation with them was carried out at 25°C.

The separation of mutually overlapping bands was carried out on a Elliott 503 computer assuming the Lorentz shape of the bands⁸.

RESULTS AND DISCUSSION

Collision Complexes of Aliphatic Alcohols

Methanol and t-butanol were chosen to study the collision complexes of aliphatic alcohols, as these alcohols occur in one conformation only, and do not exhibit the doublet structure of the $\nu(\text{OH})$ band caused by the rotational isomerism. In solutions of mixtures of two non-polar solvents they behave in a similar way as phenol. The band of their stretching OH-bond vibration exhibits a doublet structure or an asymmetry, and its exact shape depends on the composition of the solvent mixture. Infrared spectra of both alcohols were studied in solvent mixtures* $\text{C}_6\text{F}_6\text{-CS}_2$; $(\text{CFCl}_2)_2\text{-CS}_2$; $\text{C}_{11}\text{F}_{20}\text{-CCl}_4$ etc. A specific solvation of the methanol molecule in the mixture hexafluorobenzene-carbon disulphide is shown in Fig. 1. By separation obtained frequencies and $\nu(\text{OH})$ band halfwidths of the collision complexes of t-butanol with $(\text{CFCl}_2)_2$ and CS_2 in their mixtures are presented in Table I. In principle, both alcohols behave in the same way in all the systems studied; therefore, Fig. 1 and Table I may serve to demonstrate the effect. Relative intensities of the bands of both complexes in the spectra of methanol or t-butanol in solvent mixtures are proportional to the amount of the solvents in the mixture (e.g., Fig. 1); wavenumbers of the maxima of collision complex bands exhibit a bathochromic shift with the increasing refractive index of the solvent mixture as a result of a non-specific solvation of the collision complex (see values of wavenumbers in Table I).

Aliphatic alcohols also show an asymmetry of the $\nu(\text{OH})$ band in the mixture with those liquids whose molecules are capable of energetically different interactions on various interaction centers (substances like, e.g., 1-bromoheptadecane, or ethane

* C_6F_6 -hexafluorobenzene; $\text{C}_{11}\text{F}_{20}$ -perfluoromethyldecahydronaphthalene; the other fluor-containing solvents are ethane derivatives.

TABLE I

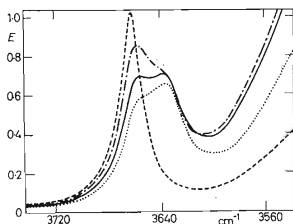
Wavenumbers $\nu(\text{OH})$ (cm^{-1}) and Halfwidths $\Delta\nu_{1/2}(\text{OH})$ (cm^{-1}) of Bands of Collision Complexes of *t*-Butanol and Acetic Acid with Components of Solvent Mixtures

Solvent composition ^a		$\nu(\text{OH})$	$\Delta\nu_{1/2}(\text{OH})$	$\nu(\text{OH})$	$\Delta\nu_{1/2}(\text{OH})$
(CFCl ₂) ₂	CS ₂	(CH ₃) ₃ COH-(CFCl ₂) ₂		(CH ₃) ₃ COH-CS ₂	
10	0	3 624.7 ± 0.1 ^b	18.8 ± 0.2 ^b	—	—
8	2	3 623.1 ± 0.2	20.2 ± 0.2	3 614.0 ± 0.6 ^b	19.2 ± 1.0 ^b
6	4	3 622.6 ± 0.2	18.8 ± 0.4	3 612.5 ± 0.3	21.4 ± 0.4
4	6	3 620.3 ± 0.3	19.6 ± 0.6	3 610.2 ± 0.2	20.6 ± 0.4
2	8	3 617.7 ± 0.5	17.2 ± 0.8	3 608.7 ± 0.2	19.8 ± 0.2
0	10	—	—	3 607.9 ± 0.03	19.6 ± 0.2
(CFCl ₂) ₂	CS ₂	CH ₃ COOH-(CFCl ₂) ₂		CH ₃ COOH-CS ₂	
10	0	3 547.5 ± 0.1 ^b	25.8 ± 0.4 ^b	—	—
8	2	3 547.3 ± 0.3	21.4 ± 1.4	3 534.4 ± 2.6	40.4 ± 3.0
6	4	3 544.3 ± 0.4	24.6 ± 1.8	3 526.7 ± 3.2	49.0 ± 8.2
4	6	3 541.7 ± 0.4	25.6 ± 2.2	3 524.0 ± 1.7	52.6 ± 2.6
2	8	3 537.5 ± 0.7	26.8 ± 3.4	3 520.3 ± 1.4	50.6 ± 2.2
0	10	—	—	3 519.4 ± 0.1	45.2 ± 0.6
C ₁₁ F ₂₀	CCl ₄	CH ₃ COOH-C ₁₁ F ₂₀		CH ₃ COOH-CCl ₄	
10	0	3 572.1 ± 0.1 ^b	16.4 ± 0.6	—	—
8	2	3 569.5 ± 0.5	16.0 ± 2.0	3 545.8 ± 1.0	26.4 ± 7.2
6	4	3 567.7 ± 0.2	21.4 ± 0.6	3 545.2 ± 0.1	32.2 ± 0.6

^a Volume ratios of both solvents in the mixture; ^b accuracy is determined from the standard deviation

FIG. 1
Bands $\nu(\text{OH})$ of Collision Complexes of Methanol in Mixtures C₆F₆-CS₂

Component ratio: — 10:0; - - - 6:4; — 5:5; ····· 2:8; *t* 25°C; *d* 0.1 cm.



derivatives $F_2BrC-CHFCl$, F_3C-CCl_3). These substances form various collision complexes with alcohol molecules depending on how both molecules are mutually oriented. Thus, *e.g.*, the $\nu(OH)$ band in *t*-butanol appears as a resolved doublet in the 1-bromoheptadecane solution (Fig. 2); the higher wavenumber component of the doublet belongs to the collision complex formed in the interaction of the alcohol molecule with the alkyl end of the solvent molecule, the other component of the doublet is due to the donor-acceptor complex of the *t*-butanol molecule with the bromine atom. At an elevated temperature the donor-acceptor complex dissociates and — as a result — the relative intensities of the corresponding bands change (Fig. 2).

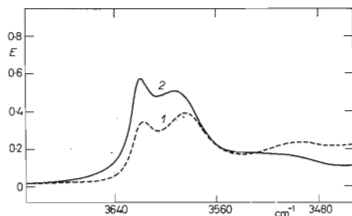


FIG. 2

Bands $\nu(OH)$ of Collision Complexes of *t*-Butanol with 1-Bromoheptadecane
Alcohol concentration 0.35M; *d* 0.1 cm; 1 at 35°C; 2 at 90°C.

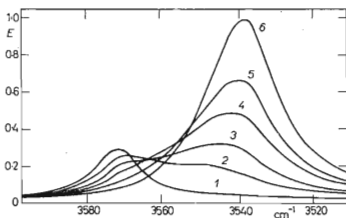


FIG. 3

Bands $\nu(OH)$ of Collision Complexes of Acetic Acid Monomer in Mixtures with $C_{11}F_{20}-CCl_4$.
The solvent ratio changes in steps 20% over the region pure $C_{11}F_{20}$ (1) and pure CCl_4 (6);
acid concentration $13.6 \cdot 10^{-3}M$; *t* 78.5°C; *d* 1 cm.

In the solutions of F_3C-CCl_3 or $F_2BrC-CHFCI$ various types of collision complexes are formed whose $\nu(OH)$ bands do not differ much in their wavenumber, and the resulting band shows only an asymmetry. In view of the appreciable similarity of the spectral manifestations of the collision complexes of alcohols and phenols it may be assumed that the center of interaction is in both cases the hydroxyl group, and that the complexes with phenols are not charge-transfer π -electron complexes with solvent molecules.

Collision Complexes of Monomers of Carboxylic Acids

Infrared spectra of very diluted solutions of carboxylic acids show both bands of dimers and bands of monomers. The band of the stretching vibration $\nu(OH)$ of the monomer occurs at 3500 cm^{-1} . Spectra of solutions of carboxylic acids in mixtures with two non-polar liquids contain doublets originating from various collision complexes, similarly as the spectra of phenols and aliphatic alcohols. Acetic acid was chosen as a model compound to study these doublets. Higher fatty acids and benzoic acid do not suit this purpose, as they are either non-uniform as far as conformation is concerned, or they contain the phenyl groups — a possible donor of aromatic π -electrons. Trifluoroacetic acid and trichloroacetic acid offer a maximum difference

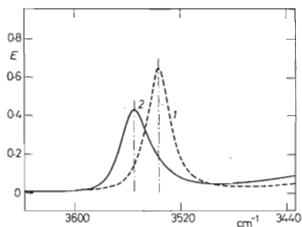


FIG. 4

Comparison of the $\nu(OH)$ Band Shapes of Collision Complexes of Acetic Acid Monomer with CCl_4 (1) and F_3C-CCl_3 (2).

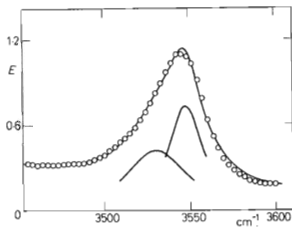


FIG. 5

Comparison of Experimental (\circ) (each third point of the digitalized spectrum plotted) and Mathematically Separated (—) Spectrum of the $\nu(OH)$ Bands of Collision Complexes of Acetic Acid Monomer with $F_2BrC-CHFCI$

Full line plot shows also the added curve of both separated bands; acid concentration $0.13M$; $t\ 40^\circ C$; $d\ 0.5\text{ cm}$.

of wavenumbers of the $\nu(\text{OH})$ band maxima in their collision complexes; however, the bands have much larger halfwidths than the corresponding bands in the acetic acid monomer and this fact would very negatively influence the precision of separation. Fig. 3 shows a typical $\nu(\text{OH})$ doublet of the spectrum of acetic acid monomer solution in the mixture perfluoro-1-methyl-decahydronaphthalene and tetrachloromethane. The values of wavenumbers and band halfwidths after separation are listed in Table I. Fig. 4 and Fig. 5 show the shape of the $\nu(\text{OH})$ absorption band of the acetic acid monomer in the solvents whose molecules contain more interaction centers. The perfect analogy in the behaviour of monomers of carboxylic acids, saturated aliphatic alcohols, and phenols is obvious.

Dimerization of Acetic Acid in the Gaseous State and in Solutions

The finding that the monomeric form of carboxylic acids forms collision complexes in non-polar solvents represents a new factor in considerations concerning dimerization of the carboxylic acids. So far this reaction was schematically written as



Our experiments show that this schematics is evidently valid only in the gaseous phase, where one may assume that molecules of the monomer and the dimer are not affected. In solutions of non-polar solvents the situation is evidently more complicated, as the monomeric form is bound in a complex with the solvent. The reaction then depends on the environment in which it occurs, on the interaction forces between the monomer and the solvent, and on the stabilization energy of the collision complex.

The formation of collision complexes of the same solute in a binary mixture of non-polar solvents is a temperature dependant equilibrium process. With increasing temperature of the solution this equilibrium shifts in the direction of the less stable collision complex. At the same time, the distribution of the solute into collision complexes between the two solvents shifts towards the statistical ratio of the collisions of the solute molecules with the molecules of both solvents. The influence of temperature on the equilibrium was investigated by following the relative intensity changes of the corresponding components of the $\nu(\text{OH})$ doublet of these collision complexes (Fig. 6).

We studied the process of dimerization of acetic acid in the gaseous phase and in solutions of perfluoro-1-methyldecahydronaphthalene; 1,1,2,2-tetrachloro-1,2-difluoroethane; tetrachloromethane and carbon disulphide. The thermodynamic quantities of dimerization indeed differ not only for the gaseous state, but also for solutions with various solvents. We interpreted the differences found in terms of the stabilization energy of the particular collision complexes. The estimation of the magnitude of the stabilization energy was based on the following energy balance. In the gaseous phase

and in diluted solutions of acetic acid an equilibrium is established between the monomer and the cyclic dimer. Contrarily to the gaseous phase, in the solution molecules of both forms of acetic acid are solvated. The monomer is solvated in a specific way — through the formation of a collision complex, and this complex is then solvated non-specifically by further molecules of the solvent in the secondary solvation sphere^{1,2}. The cyclic dimer has its primary solvation site^{1,2} occupied as a result of the hydrogen bond formation; therefore, a collision complex is not formed and the dimer is solvated only non-specifically. If we assume that the secondary solvation energy of the monomer is approximately equal to one half of the secondary solvation energy of the cyclic dimer, the stabilization energy of the collision complex of the acetic acid monomer is equal to one half of the difference between the enthalpy of dimerization in the gaseous phase and in the solvent under question.

The present results of measurements of the dimerization enthalpy of acetic acid both in the gaseous phase and in solutions fluctuate considerably according to the method used and conditions of the measurement, and even among various authors employing the same method⁹. Therefore, the measurement of the stabilization energy of the acetic acid collision complexes was based on our own experimental values.

The enthalpy of acetic dimerization is given, according to the integrated form of the van't Hoff reaction isotherm, by the temperature dependence of the equilibrium constant of this process

$$\ln K = (-\Delta H/RT) + C. \quad (1)$$

The measurement of the temperature dependence of the equilibrium constants of dimerization was carried out by determining the intensity of the $\nu(\text{OH})$ bands of

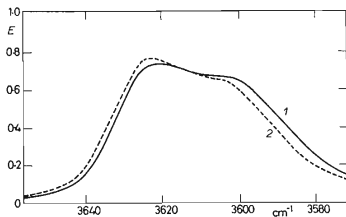


FIG. 6

Influence of Solution Temperature on the Relative Intensities of $\nu(\text{OH})$ Doublet Components of Collision Complexes of Phenol in Solvent Mixture $(\text{CFCl}_2)_2\text{-CS}_2$ (ratio 6 : 4).

1 15°C, 2 45°C.

either the acetic acid monomer (gas) or of its collision complex (solution). Assuming the validity of the Lambert-Beer law for this band, the equilibrium constant of dimerization in the gaseous phase K_p can be expressed as

$$K_p = [(E_0 - E)/2E^2 RT] \epsilon d, \quad (2)$$

where E_0 is the extinction corresponding to the total dissociation of the dimer to the monomer.

If we neglect the temperature dependence of ϵ , elimination of K_p from equations (1) and (2) leads to

$$\ln(E_0 - E)/E^2 T = (-\Delta H/RT) + C. \quad (3)$$

$-\Delta H$ was determined from the slope of the dependence $(E_0 - E)/E^2 T$ on $1/T$.

The measurement of the equilibrium dimerization constants in solutions was carried out using the modified Harris-Hobbs method¹⁰. The equilibrium dimerization constant and the molar extinction coefficient of the monomer can be calculated from the parameters of the linear dependence

$$E = (1/2K)\epsilon^2 d^2 c_0/E - (1/2K)\epsilon d. \quad (4)$$

The error in ϵ measurement (and thus in K , too) is comparable to the temperature changes of ϵ , due to a low accuracy in the determination of the parameter $(1/2K)\epsilon d$. Therefore, in the subsequent treatment of the experimental results ϵ for a given solvent was supposed to be constant. Its value was calculated as a mean of all values ϵ

TABLE II

Enthalpy of Dimerization $-\Delta H$ and Stabilization Energies of Collision Complexes $-\Delta H_s$ of Acetic Acid Monomer

State, solvent	K 25° l. mol ⁻¹	$\bar{\epsilon}$ l. mol ⁻¹ cm ⁻¹	$-\Delta H$ kcal mol ⁻¹	$-\Delta H_s$ kcal. mol ⁻¹
Gaseous phase	—	—	7.3 ± 0.2	—
C ₁₁ F ₂₀	21 900 ^a	130 ± 10.0	7.2 ± 0.6	0.1 ± 0.7
(CFCl ₂) ₂	1 040 ± 220 ^b	111.0 ± 11.7	6.4 ± 0.1	0.9 ± 0.3
CCl ₄	820 ± 370	124.7 ± 27.9	5.6 ± 0.2	1.7 ± 0.4
CS ₂	1 130 ± 570	79.6 ± 20.0	4.5 ± 0.5	2.7 ± 0.7

^a Extrapolated value over the temperature interval 80–114.5°C. ^b Extrapolated value over the temperature interval 40–90°C.

measured in the solvent under question. Using this mean value $\bar{\epsilon}$ new linear dependences were constructed from the original experimental data with the help of equation (4). When calculating the parameters of these dependences, the condition was respected that the value of the extinction coefficient calculated from them was equal to its mean value $\bar{\epsilon}$. In this way the scatter of values K as a result of the experimental error in ϵ was eliminated. The value $-\Delta H$ was calculated from the slope of the dependence

$$-\ln(a/d^2) = (-\Delta H/RT) + C', \quad (5)$$

where $a = (1/2K)\bar{\epsilon}^2 d^2$. The results are summarized in Table II.

The values show that the stabilization energy of formation of the collision complexes of acetic acid is of the order of a few kcal mol⁻¹. Its absolute value thus lies in the region of van der Waals interactions. Thus, it appears that the stabilization energy should not be disregarded in the treatment of energy balance of solutions.

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