PROTON-ACCEPTOR POWER OF 1,1,3,3-TETRAMETHYLGUANIDINE: HYDROGEN BONDING AND PROTONATION IN INERT SOLVENTS

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According to potentiometric measurements the basicities of alkyl-substituted guanidines are very high with pK_a values of 13.4-13.9 [1], i.e., they are more basic than aliphatic amines. The same result is obtained from pK_a measurements on guanidines and amines in alcoholic solutions [2, 3] and in DMSO [4, 5]. In a series of investigations [6, 7] and in work referred to by the authors of [6, 7] 1,1,3,3-tetramethylguanidine was used for the investigation of the kinetics of the transfer of a proton from CH acids in organic solvents. Regarding the proton-acceptor powers of guanidines in interaction with proton donors (weak acids) little is known; equilibrium constants of the formation of hydrogen-bonded complexes of p-fluorophenol and 5-fluoroindole with 1,1,3,3-tetramethylguanidine and the ^{19}F NMR spectra of these complexes in inert solvents have been measured [8-10]. According to these data, 1,1,-3,3-tetramethylguanidine has high proton-acceptor power, close to that of hexamethylphosphoric triamide and of triphenylphosphine oxide and lower than that of tertiary aliphatic amines. In the present work with the object of determining the role of the hydrogen bond in the protonation of organic bases we have studied the interaction of 1,1,3,3-tetramethylguanidine with OH-containing proton donors of various strengths in solution in aprotic solvents CCl_4 and $CHCl_3$.

In the interaction of 1,1,3,3-tetramethylguanidine with alcohols, phenol, and p-chlorophenol (I)-(VI) (Table 1) in CCl_4 and $CHCl_3$ a hydrogen bond is formed with the imino nitrogen atom (OH···N). The IR spectrum then contains a broad ν(OH) band of the complex, shifted toward lower frequencies; with rise in the proton-donor power of ROH the shift increases, the width of the band increases, and the latter shows definite structure (absorption of CH groups is superimposed on it). The low-frequency part of this band shows up most clearly for phenols (Fig. 1, curve 2). In the spectrum of 1,1,3,3-tetramethylguanidine the band most sensi-

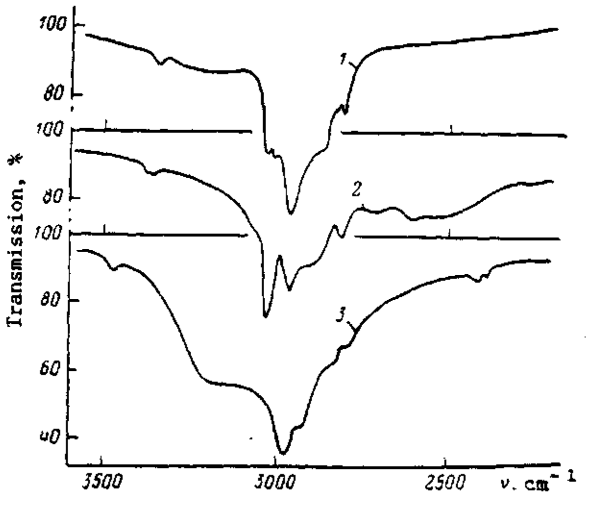

Fig. 1. IR spectra of chloroform solutions of equimolecular mixtures of 1,1,3,3-tetramethylguanidine with methanol (1), phenol (2), and pentachlorophenol (3). Concentration of components 0.2 M.

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TABLE 1. Thermodynamic Characteristics of Complexes of 1,1,3,3-Tetramethylguanidine with Alcohols and Phenols in Solution in CCl_4 and in $CHCl_3$

Donor No.	Proton donor	CCl_4		$CHCl_3$	
		$K_{25\,°C}$, liter/mole	ΔH, kJ/mole	$K_{25\,°C}$, liter/mole	ΔH, kJ/mole
I	Isobutyl alcohol	16	26	—	—
II	Methanol	25	32	—	—
III	Trichloroethanol	250	33	40	26
IV	Trifluoroethanol	520	38	75	29
V	Phenol	790	40	140	32
VI	p-Chlorophenol	2900	41	350	33
VII	o-Chlorophenol	140	33	100	46
VIII	2,4-Dichlorophenol	400	41	460	48
IX	2,6-Dichlorophenol	3000	71	3200	65
X	Pentachlorophenol	10^6	~80	10^6	~75

tive to the hydrogen bond is ν(C=N) at 1593 cm^{-1}, which with interaction with proton donors is converted into a broad doublet at 1575 and 1600 cm^{-1}, the integral intensity of which rises appreciably. The bands at 1092, 1392, and 1503 cm^{-1} are weakened and shifted to higher frequencies. The weak ν(NH) band of 1,1,3,3-tetramethylguanidine at 3348 cm^{-1} (3345 cm^{-1} in $CHCl_3$, ε_{max} 33 liter·$mole^{-1}cm^{-1}$, A ~ 660 liter·$mole^{-1}cm^{-2}$) is shifted on interaction with phenol OH···N by about 10 cm^{-1} toward higher frequencies and is broadened, but is scarcely changed in integral intensity.

The value of the equilibrium constant of the reaction of the formation of the molecular complex measured on the basis of the intensity of the ν(OH) band of the free proton-donor molecules does not depend on the concentration; the values of K found at 25°C and the enthalpies of the complexes ΔH are given in Table 1. It can be seen that 1,1,3,3-tetramethylguanidine is an extremely active proton acceptor in the hydrogen bond, comparable in proton-acceptor power with the strongest bases among neutral molecules. For complexes of aliphatic alcohols with amines, amine oxides, and phosphine oxides equilibrium constants of 1-10 liter·$mole^{-1}$ and enthalpies of 8-20 kJ/mole are characteristic [11, 12], i.e., 1,1,3,3-tetramethylguanidine is stronger than these acceptors and is close in enthalpy of complex formation to chloride and bromide ions in tetralkyl-ammonium and -phosphonium salts [13, 14]. It should be noted that the nitrogen of the imino group in diphenylketenimine is a very much weaker proton acceptor, and the energy of the hydrogen bond formed by it with propyl alcohol is close to 15 kJ/mole [15]. Halogen-substituted alcohols with DMSO, tetramethylurea, and hexamethylphosphoric triamide form complexes with ΔH ~ 23-31 kJ/mole, the strength of the hydrogen bond between trifluoroethanol and triethylamine is 37 kJ/mole [16, 17], and the enthalpy of the interaction of phenol (often used as a standard proton donor [18, 19]) with amines and ethers is 27-40 kJ/mole [11], so that, in these systems also, 1,1,3,3-tetramethylguanidine is the strongest proton acceptor. The same follows from data in [20] on the energetics of complexes of p-chlorophenol.

From Table 1 it can be seen that for solutions in chloroform the values of K and ΔH are lower than in CCl_4; this is in keeping with known data on the influence of the solvent on the thermodynamic parameters of the hydrogen bond [21] and is mainly to be explained by the stronger interaction of free proton-acceptor and proton-donor molecules with $CHCl_3$ molecules than with CCl_4.

Independent spectroscopic parameters characterizing the ability of organic compounds to form a hydrogen bond are provided by values of the low-frequency shift Δν and the increase in the integral absorption coefficient ΔA of the ν(XH) band of the standard proton donor. In the complex of 1,1,3,3-tetramethylguanidine with phenol values of Δν [change in the position of the center of gravity of the ν(OH) band] and ΔA were found to be 810 cm^{-1} and $17 \cdot 10^4$ liter·$mole^{-1}cm^{-2}$, respectively, which are appreciably greater than the shift and change in the absorption coefficient of the ν(OH) band in the complexes of phenol with aliphatic amines and amine oxides and sulfides [18, 19]. In the complex with methanol the shift in the ν(OH) band is 395 cm^{-1}, whereas this quantity for pyridine, triphenylarsine, and dimethyl sulfide oxides lies in the range 300-350 cm^{-1} [11]. It is interesting that the assessment of the basicity of 1,1,3,3-tetramethylguanidine from the correlation between pK_a and Δν(OD) of

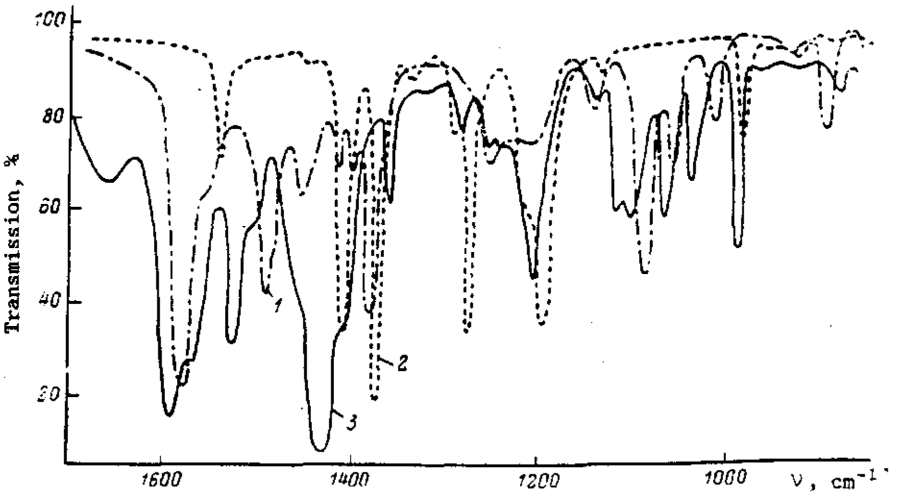

Fig. 2. IR spectra of chloroform solutions of 1,1,3,3-tetramethylguanidine (1), pentachlorophenol (2), and their equimolecular mixture (3). Concentration 0.2 M.

methanol-d [22], namely $pK_a \sim 12$, does not contradict the value of 13.4 found in [1] [the measured shift $\Delta\nu(OD)$ is 260 cm^{-1}].

A different spectral situation is found in the interaction of 1,1,3,3-tetramethylguanidine with stronger proton donors: 2,4- and 2,6-dichlorophenols (VIII) and (IX) and pentachlorophenol (X). In the spectra of $CHCl_3$ solutions of equimolecular amounts of 1,1,3,3-tetramethylguanidine and the proton donor the bands of 1,1,3,3-tetramethylguanidine at 1092, 1392, and 1503 cm^{-1} and some bands of the phenols disappear, and a number of new bands appear; among the latter bands of anions can readily be identified. For example, in the case of the compounds (VIII), (IX), and (X) these are the bands at 1465, 1450, and 1432 cm^{-1}, respectively. This evidences the transfer of the proton of OH of the phenol to the nitrogen atom of the imino group of 1,1,3,3-tetramethylguanidine with the formation of an ion pair; the broad intense $\nu(N^{+}H)$ band of the ion pair is situated at substantially higher frequencies than the $\nu(OH)$ band of the molecular complex. The band arising at 1660 cm^{-1} probably belongs to the $\delta(N^{+}H_2)$ vibrations of the 1,1,3,3-tetramethylguanidine cation (its intensity falls on partial deuteration). Other bands that can be regarded as characteristic for this cation lie at 1410, 1068, and 1037 cm^{-1} (Fig. 2). In CCl_4 solution it was not possible to carry out such experiments because the salt formed was precipitated.

The measurement of the thermodynamic characteristics of the reaction of ion-pair formation was also based on the $\nu(OH)$ band of free proton-donor molecules. In $CHCl_3$ solution the value of the equilibrium constant K does not depend on the phenol concentration in the range $\sim 5 \cdot 10^{-2}$-$5 \cdot 10^{-4}$ M. The measured values of K and the temperature dependence of the enthalpy ΔH calculated from them are given in Table 1.

An attempt to obtain analogous data in CCl_4 solution met with difficulties: It was found that for strong proton donors the equilibrium constant determined by the procedure described fell appreciably with the dilution of the solution (Fig. 3). This effect was most marked for highly acidic phenols, and also at lower temperatures. It may be thought that the cause of this relation lies in the association of the complexes, which is particularly clearly manifested in the cases of complexes of the ionic type [23]. Values of the equilibrium constant were determined at each temperature by extrapolation to infinite dilution. These values were used for the calculation of the enthalpy of formation of the complex. From Table 1 it follows that the enthalpy obtained for 2,6-dichlorophenol (though the extrapolation in this case is the least reliable) is typical for complexes of the ionic type, whereas for the phenols (VII) and (VIII) the values obtained are more typical for molecular complexes. The lower values of K and ΔH for complexes of 1,1,3,3-tetramethylguanidine with the phenol (VII), as compared with the compound (VI), arise from the presence of an intramolecular hydrogen bond in o-chlorophenol. Since the equilibrium constants for the phenols (VII) and (VIII) at maximum dilution are only weakly dependent on concentration, we gain the impression that in the association of molecular complexes the transfer of a proton is initiated, and dipole–dipole interaction stabilizes the ion pairs formed. As can be seen from Table 1, the en-

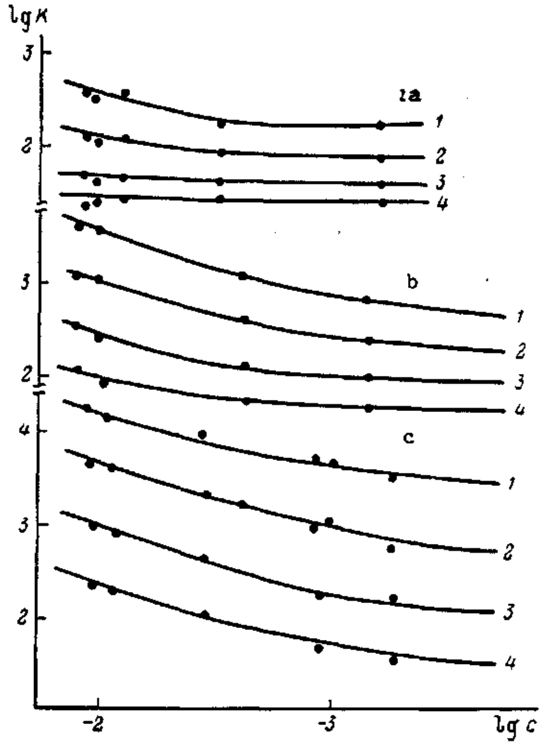

Fig. 3. Relations of the equilibrium constants of the formation of complexes of 1,1,3,3-tetramethylguanidine with phenols in CCl_4 solution to the concentrations of solutions of o-chlorophenol (a), 2,4-dichlorophenol (b), and 2,6-dichlorophenol (c). Temperature, °C: 1) 25, 2) 40, 3) 57, 4) 75.

thalpy of formation of complexes of 1,1,3,3-tetramethylguanidine with phenols (VII) and (VIII) in $CHCl_3$ solution is higher than in CCl_4, which, probably, arises from the stabilization of the ionic complex in the more polar medium (chloroform). It is not ruled out that these phenols with 1,1,3,3-tetramethylguanidine form complexes of both molecular and ionic types, which are present in equilibrium. The values given in Table 1 for K and ΔH for pentachlorophenol are extremely tentative, for they were obtained for a highly dilute solution at high temperatures (55-100°C, higher than the boiling point of the solvent); the value of $K_{25°C}$ was obtained by the extrapolation of the linear relation of $\ln K$ to $1/T$.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer. We used thermostated cells of constant width (0.005-5 cm) with windows made from KBr and CaF_2 crystals and provided with electric heaters. The temperature was measured with a copper—constantan thermocouple accurately within ±0.5°C. Alcohols, phenols, and solvents were purified by generally accepted methods; purities were checked by means of the IR spectra. 1,1,3,3-Tetramethylguanidine, supplied by the firm of Fluka, was used without further purification.

The equilibrium constants of the formation of molecular and ionic complexes of 1,1,3,3-tetramethylguanidine with proton donors were determined from the equation $K = c_{ab}/c_a c_b$, in which c_a, c_b, and c_{ab} were the concentrations of the free donor molecules, 1,1,3,3-tetramethylguanidine molecules, and molecules of the complex, respectively. The value of c_a was found from the ν(OH) band of the donor with the use of the absorption coefficient in the maximum of this band; in the working range of the free molecules of the alcohols and phenols the optical density of the ν(OH) band rises linearly with the concentration, and their self-association is practically absent. The absorption coefficient of the ν(OH) band diminishes with rise in temperature, and this dependence was taken into account in the determination of c_a. The values of c_{ab} and c_b required for the calculation of K were found from the material-balance equations: $c_{ab} = c_a^0 - c_a$, $c_b = c_b^0 - c_{ab}$ (c_a^0 and c_b^0 are the initial concentrations of the components). In the calculation of the equilibrium constants corrections were made for the dependence of c_a^0 and c_b^0 on temperature resulting from change in the density of the solvent. The value of K was found from the results of several experiments at various concentrations of the components; we always observed the condition $c_a^0 < c_b^0$, ensuring the minimum error in the determination of K. The probable error in the determination of K for the various systems lies in the range 10-30%. Measurements of K were made at 25, 36, 50, and 65°C for solutions in $CHCl_3$ and at 25, 40, 57, and 75°C for solutions in CCl_4. From the data obtained with the use of the Van't Hoff equation we found the enthalpies ΔH of the formation of the complexes; the error in ΔH does not exceed 10%, but in the case of the complexes of 1,1,3,3-tetramethylguanidine with pentachlorophenol the error in ΔH attains 20%.

CONCLUSIONS

In the reactions of 1,1,3,3-tetramethylguanidine in CCl_4 and $CHCl_3$ media with alcohols and phenols there are formed, depending on the proton-donor powers of the latter, either molecular complexes with a hydrogen bond or ion pairs formed as a result of the transfer of a proton through the hydrogen bond. 1,1,3,3-Tetramethylguanidine is a strong proton acceptor, comparable in strength with aliphatic amines.

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