in Fig. 4, we note that the Poisson-Boltzmann equation furnishes reasonably useful estimates of the ion concentration in the overall cell volume in the case of monovalent ions. The agreement in fair, but not quantitative for all concentrations. As can be seen in Fig. 4, f appreciably deviates from unity only as the simple electrolyte concentration is lowered and the polyion concentration is increased.



The f factor as a function of polyion concentration for monovalent counterions Na⁺, Li⁺, NH₄⁺ and divalent counterions (Ca⁺⁺, Mg⁺⁺)

This fact may reflect the nonideal behaviour of the solution at higher polyion concentration and probably a different influence of the counterion condensation around the polyion, i.e. the ionic concentration deviates from the expected values as the cell boundary is approached.

The discrepancy from the Poisson-Boltzmann predictions is larger for divalent counterions at the same molar concentrations even if the same trend appears.

It is noteworthy that qualitatively similar results have been obtained using the Poisson-Boltzmann equation for a system with spherical geometry in comparison with osmotic pressure determined from Monte Carlo simulations.

As pointed out by Wennerstrom [14], the Poisson-Boltzmann equation overestimates the osmotic pressure by 10 to 40 per cent for monovalent counterions while with divalent counterions the discrepancy is larger, up to one order of magnitude.

It must be noted, moreover, that for Ca^{++} ions, other counterion binding mechanisms, in addition to electrostatic one may occur. For example, it is known that calcium chloride lowers the viscosity [15] of CMC solutions and makes the electrical conductivity [5] independent of the molecular weight.

Since Ca^{++} and probably Mg^{++} ions may exert coulombic attraction between carboxylgroups on different molecules simultaneously, the validity of the cylindrical cell model fails as the polyion concentration is increased.

These considerations make the behaviour of f for the divalent counterions investigated qualitatively justified, allowing for the approximate nature of the theory.

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(Eingegangen am 25. März 1987) E 6470

The Formation of Carbenium Ions and Naked Anions by the Protonation of Phthalophenone with a Super Acid

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Chemical Kinetics / Solutions / Spectroscopy, Nuclear Magnetic Resonance / Spectroscopy, Visible / Thermodynamics

Two molecules of a strong acid such as CF_3SO_3H are necessary to cleave the lactone ring of phthalophenone. NMR and conductivity measurements reveal that the carboxylate group has to be protonated for this purpose followed by its solvation with an additional molecule of acid. But $CF_3SO_3^-$ which is simultaneously formed behaves as a naked anion in the solvent dichloromethane. CNDO-Calculations indicate a strong interaction between the charged central carbon atom and the -COOH group in $o-HOOH(C_6H_4)C^+(C_6H_5)_2$ which is accompanied by an unusually large twisting of the phenyl rings.

Ber. Bunsenges. Phys. Chem. 91, 740-745 (1987) – © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1987. 0005-9021/87/0707-0740 \$ 02.50/0

Introduction

Triphenylmethyl cations are one of the most stable carbenium ions [1,2], well known since the beginning of the century by the pioneering work of Walden [3]. The formation of these trityl ions can be favoured by acid media [4] which show a low nucleophilicity. Additionally, π -donor substituents at the phenyl rings lead to an increased stability of the ionic species [4]. In this way the characteristic absorption maximum of these carbenium ions can be shifted from 430 nm up to 650 nm. This feature is used in technical applications. For example the intensive blue colour of trityl ions with dimethylamino substituents in para position of the phenyl rings is widely used in heat and pressure sensitive copy paper [5]. For this purpose two components are incorporated via separate micro capsules in the paper. The capsules can be destroyed by the influence of heat or pressure and the contents is released. Thus an acid component, in the most cases bisphenole-A, can react with the precursor of the dye and a coloured trityl ion is formed. Cyclic tritan derivatives such as crystal violet lacton (I) are very often the carbenium ion source.



The decisive step for the formation of the highly coloured carbenium ion from compound (I) is the cleavage of the lactone ring. This reaction can be preferably studied with the model compound phthalophenone (II). The addition of acid yields only a protonation of the carboxylate group without the complication by an analogous reaction with the amine groups. As solvent system mixtures of dichloromethane and CF_3SO_3H were chosen. Dichloromethane has only minor donor properties and CF_3SO_3H [6] is a powerful super acid and generates even less stable carbenium ions. These thermodynamic and kinetic studies can be most easily performed with NMR-spectroscopy. The formation of coloured and charged species can also be directly followed by UV/VIS spectroscopy or conductivity measurements, respectively.

Experimental

NMR-spectra were recorded with a JNM-PS-100 and a JNM-GX-270. The data were transferred to a desk computer (IBM-AT) for line shape analysis. Conductivity measurements were performed with variable frequencies by a self made conductivity bridge.

Chemicals: Phthalophenone was prepared from phthalic acid anhydride and benzene followed by a Grignard reaction with C_6H_5MgBr [7]. Trifluoromethane sulfonic acid was used as purchased (Merck).

Results

Conductivity Measurements

Phthalophenone forms a nearly colourless solution in dichloromethane with a very low specific conductivity \varkappa (298 K, 0.8 M: $\varkappa = 4 \cdot 10^{-6} \Omega^{-1}$ cm⁻¹). The addition of trifluoromethane sulfonic acid, however, yields a pale yellow solution with an appreciable specific conductivity (Fig. 1). It can be seen that a characteristic end point in the titration curves is formed, for high concentrations of phthalophenone. The same effect is realized by lowering the temperature (Fig. 2).



Specific conductivity × of variable overall concentrations of phthalophenone in mixtures of CH₂Cl₂ with CF₃SO₃H at 298 K



Specific conductivity × of 0.65 M phthalophenone in mixtures of CH₂Cl₂ with CF₃SO₃H at 273 K and 298 K

NMR Studies

At room temperature the ¹H-NMR spectra of phthalophenone in CF₃SO₃H/CD₂Cl₂ show in addition to the pattern of the aromatic protons only one sharp signal which is caused by an acid proton. With decreasing temperature kinetic line broadening is observed and this singulet separates in a high field and low field part below 220 K. Further cooling reveals a splitting of the signal at $\delta = 14$ ppm below 200 K (Fig. 3). The low field signal C (T = 195 K: $\delta = 17-18$ ppm) is due to the proton in CF₃SO₃H as follows by variation of the mole ratio acid to phthalophenone. Thus the high field part at $\delta = 14$ ppm of the spectrum in Fig. 3 (signals A, B) has to be associated with a protonated species of phthalophenone. The results of spectra integration are given in Figs. 4 and 5, re-

spectively. In Fig. 4 the mole fraction x_h for the high field part (signals A, B) is plotted versus the ratio of the overall concentrations of acid to ionogen. A similar plot in Fig. 5 shows separately the mole fractions of both high field signals A and B.





100 MHz ¹H-NMR spectra in the low field range of 0.68 M phthalophenone in CH₂Cl₂ at 195 K under the addition of increasing amounts of CF₃SO₃H from top to bottom. Signals A and B proton in the -COOH group of compound (V) respectively compound (III), signal C due to the proton in CF₃SO₃H





Mole fraction x_h (high field part: sum of signals A and B) from integrating the signals in the spectra of Fig. 3 as function of the concentration ratio CF₃SO₃H to phthalophenone (concentration of phthalophenone: $\times -0.28$ M, $\triangle -0.68$ M, $\odot -0.92$ M, $\Box - 1.50$ M)



Mole fraction x for integrating both signals A and B (spectra such as those in Fig. 3) against each other as function of acid to phthalophenone (0.64 M phthalophenone, 193 K) according to 270 MHz 1 H-NMR data



Averaged chemical shifts δ in ppm (¹H-NMR at 100 MHz) of the signals in Fig. 3 relative to the low field ¹³C side band of CH₂Cl₂ for 0.82 M phthalophenone with variable amounts of CF₃SO₃H in solution (\bullet - 242 K, \times - 198 K)

Further data about the species in solution can be obtained by titration curves via chemical shifts. The resonance frequencies of signals A, B in Fig. 3 are nearly independent of the addition of acid up to an equimolar ratio whereas signal C yields a shift of 0.8 ppm to high field under this condition. Higher amounts of acid in solution lead to kinetically averaged signals. Additionally, chemical shift measurements were performed at temperatures where kinetical averaging occurs, in order to obtain data for acid in solution exceeding the equimolar ratio. These results are given in Fig. 6. Small amounts of acid yield a shift to low field whereas a high field shift is observed for a further addition of acid. The maximum point is strongly dependent on temperature.

As can be seen from Fig. 3 the high field part of the spectrum consists of two separate signals even for a very low content of acid in solution at the temperature chosen. This splitting first disappears by kinetic averaging if the temperature is increased. A further temperature increase leads to strong line broadening of these both remaining signals. A simulation of the complete three spin system with kinetic broadening was performed. In this temperature range the natural line width, however, is partially larger than the kinetic broadening and the complete line shape analysis does not give unambiguous results. Therefore the whole system was analysed according to an exchange between two sites. The life times $\tau_{\rm l}$ and $\tau_{\rm h}$ for the protons in these both environments (low (1) and high (h) field part in Fig. 3 – C \leftrightarrow A, B) are related to the corresponding mole fractions as follows:

$$\tau_l/\tau_h = x_l/x_h . \tag{1}$$

These reciprocal life times τ_1 and τ_h are plotted in Figs. 7 and 8 respectively versus the ratio of the overall concentrations of



Reciprocal life times $1/\tau_1$ (low field signal C in Fig. 3) for protons in the solvating acid as function of the concentration ratio CF₃SO₃H to phthalophenone (\times - 0.28 M, \triangle - 0.68 M, \bigcirc - 0.92 M, \square - 1.5 M) in CH₂Cl₂ at 195 K



Fig. 8

Reciprocal life times $1/\tau_{\rm h}$ (high field signals A and B in Fig. 3, Eq. (1) for protons in the -COOH groups of compounds (III) and (V) as function of the concentration ratio CF₃SO₃H to phthalophenone under the same conditions as in Fig. 7

CF₃SO₃H to phthalophenone. All data for different phthalophenone concentrations can be approximately combined in one curve.

UV/VIS Spectra

The addition of small amounts of CF₃SO₃H yields an optical absorption band at 354 nm which is due to the formation of a carbenium ion. An increasing concentration of acid shifts the 354 nm band to 334 nm and two new small bands at 460 nm and 540 nm appear.

Discussion

Thermodynamics - Conductivity

The strong increase in the specific conductivity \varkappa caused by the addition of the acid CF₃SO₃H to the solution of phthalophenone in dichloromethane, as shown in Figs. 1 and 2, indicates the formation of carbenium ions and anions. This effect is due to a strong interaction or a chemical reaction between the acid and phthalophenone since CF₃SO₃H is not soluble in pure dichloromethane. The conductometric titration curves yield a characteristic end point and the beginning of a plateau at a molar ratio of two for acid to ionogen. The sharpness of this point increases with the concentration (Fig. 1) of the reactands caused by a shift of the equilibrium. The same effect is observed by lowering temperature (Fig. 2) and therefore the underlying reaction is exothermic. These measurements show that the lactone ring is not merely opened under the formation of the -COOH group, but a second acid molecule is necessary for the solvation of either the $CF_3SO_3^-$ anions or the other reaction product, the o-carboxyl-trityl cation (III).



Thermodynamics - NMR

The integration of the NMR-spectra can be performed up to a mole ratio of 110% acid to phthalophenone in solution since a high field and low fiel part (Fig. 3: signals A, B-C) can be observed. The plot in Fig. 4 shows that the high field part which can be identified with the -COOH proton in compound (III) only represents 20-30% of the whole acid protons under the condition of equimolar acid in solution. From the conductivity studies, however, it would be expected that 1:1 ratios are observed for high concentrations and low temperatures since one solvation equilibrium was proposed under this conditions. But from NMR spectra integration it can be inferred that an additional solvation of unattacked phthalophenone plays an important role and species (IV) has to be included in the discussion. All acid protons outside of the -COOH group in compound (III) which are involved in solvation equilibria yield one kinetically averaged signal. In Fig. 4 an astonishingly steep slope up to the mole fraction of 0.3 is observed whereas further

addition of acid leads to no change. This behaviour can be explained in the following way. Minor traces of acid yield only the cleavage of the lactone ring under the formation of the -COOH group since this reaction ought to show the largest equilibrium constant of all considered interactions with acid. If a larger quantity of the anions $CF_3SO_3^-$ or the cations (III) are formed these products can be additionally solvated. For a molar amount of acid exceeding 30% of phthalophenone the mole fraction x_h decreases considerably below 0.5 since the solvation of the unattacked ionogen (II) becomes more important and (IV) is formed.



The NMR shift titrations in Fig. 6 also indicate that the carbenium ion (III) is preferably formed at the beginning of the addition of acid. Further amounts of acid yield a population of the low field signal C in Fig. 3 and therefore the averaged chemical shift in Fig. 6 increases. This effect comes to an end since the mole fraction x_h is independent of the ratio of acid to phthalophenone larger than 0.3 as shown in Fig. 4 (T = 195 K). The high field shift of the averaged signal can be explained by the high field shift of the low field signal C (Fig. 3) in parallel with increasing acid in solution whereas the high field part in the spectrum (Fig. 3: signals A, B) is nearly independent of acid concentration. The maximum is the averaged chemical shift (Fig. 6) is strongly dependent on temperature and is shifted to higher acid concentrations with increasing temperature. Therefore it can be concluded that the bend in the curve of Fig. 4 ($x_h \simeq 0.3$) is also shifted to more acid content with increasing temperature. This means that all solvation equilibria are more exothermic than the formation of the carbenium ion.

The question whether of $CF_3SO_3^-$ anions of the -COOH group of compound (III) is solvated by acid can be decided via the separate signals A, B in Fig. 3 which appear below 198 K. By slowing down this exchange process between A and B the integration ratio of the high to the low field part (signals: A, B-C) does not change. Therefore signals A, Bmust be always associated with the proton of a -COOHgroup and signal C with the solvating acid. The observed splitting (A, B) can be explained as the one proton signal of the -COOH group in two environments, i.e. the free -COOH and that solvated by acid (V). This interpretation is also supported by integration data since signal C never shows a smaller area than signal A. At amounts of acid less than 10% these signals A and B have nearly the same area. For these peaks an extreme broadening is observed below 173 K whereas the -COOH signal B (III) remains relatively sharp. Therefore the solvated species (V) seems to form a rigid lattice at very low temperatures whereas the unsolvated compound (III) can still freely rotate under this conditions. In principle signal C in Fig. 3 should also show a splitting in parallel with that in the high field part. A relatively high natural line width and a low chemical shift difference, however, make it impossible to observe this effect. This result is quite reasonable because the solvating acid always coordinates at a carbonyl group. It interacts either with -COof phthalophenone or -CO- of the -COOH group and therefore a nearly identical shift results for the acid in these both environments. But the protons in the solvated and unsolvated -COOH group are quite different which leads to an appreciable shift difference.

In triphenylmethyl cations as compound (III) another type of kinetics should also be considered in the NMR time scale, namely the rotation of the phenyl rings [8] which should be hindered by the -COOH group. The two possible conformations of the, always staggered, phenyl rings can be classified, however, as enantiomers. Therefore no distinction between these both isomers can be achieved via the ¹H-NMR signal of the -COOH proton.

Summarizing all results concerning the interactions of the acid CF_3SO_3H with phthalophenone (II) the following equilibria can be given:

 $(II) + HO_3SCF_3 \leftrightarrow (III) + -O_3SCF_3$ (2)

$$(III) + HO_3SCF_3 \leftrightarrow (V) \tag{3}$$

$$(II) + HO_3SCF_3 \leftrightarrow (IV). \tag{4}$$

The equilibria (2) and (3) are shifted more distinctly to the right side than equilibrium (4).



Total bond energy E_r of compound (III) according to CNDO calculations as function of the -COOH group rotation (angle φ), for different phenyl ring twistings (20°, 30°, 35°, 50° from top to bottom). The minima in the curves near $\varphi = 120^\circ$ and 300° represent the most favourable interactions of the COH and C=O oxygen atoms with the central carbon atom

Structures - UV/VIS Spectra

More detailed data about the structure of the carbenium ion (III) can be obtained by CNDO quantum mechanical calculations. In Fig. 9 the total bond energy E_r for all possible orientations of the – COOH group is given. The energy E_r yields minima for the conformation of the – COOH group in which the oxygen atoms give strong interactions with the positive central carbon atom of the carbenium ion (III). The applied CNDO program also allows calculations concerning the position of the optical main band of the carbenium ion (III). A satisfactory accordance between the experimental finding (354 nm) and the theory (375 nm) can only be achieved if the twisting of the phenyl rings in the propeller arrangement is increased to 50° . This angle is nearly twice of that which is usually assumed for the unsubstituted trityl ion [9]. An enlarged twisting angle for the phenyl rings reduces the extent of charge delocalisation. In the case of the carbenium ion (III), however, this unfavourable arrangement is stabilized by the interaction of the localized positive charge with the -COOH group. Solvato-chromic effects should be larger for the carbenium ion (III) than in the case of the highly delocalized trityl ion and therefore small discrepancies between experimental and calculated band positions are quite reasonable.

Kinetics - NMR

A strong line broadening for both the high field and the low field part of the spectrum (Fig. 3: A, B-C) occurs in parallel with the addition of CF₃SO₃H to phthalophenone, in dichloromethane. Therefore the life times $\tau_{\rm h}$ (Fig. 8) and $\tau_{\rm I}$ (Fig. 7) of the acid protons within and outside of the -COOH group are strongly diminished with an increasing amount of acid in solution. This phenomenon can only be explained by the solvation equilibria (3) and (4). The life times τ approximately depend only on the ratio of overall concentration of acid to phthalophenone and therefore it can be concluded that these equilibria are strongly shifted towards the association with acid. A detailed analysis, however, shows that small variations with the overall concentration of phthalophenone can be observed analogously to the data in Fig. 4. But these effects are too small for an exact interpretation.

The cleavage of the lactone ring of phthalophenone according to equilibrium (2) is catalysed by the formation of the adduct (IV). In this way the nucleophilicity of the carboxyl group of phthalophenone is reduced and the rupture of the carbon-oxygen bond is favoured by the solvation of the carbonyl group. The same is true for the formation of phthalophenone from the carbenium ion (III). The acidity of the carboxyl group of the species (III) is increased by the formation of the solvated ion (V) and therefore the life time of the proton in the -COOH group is reduced. This kinetic process seems to be the rate determining step in the closure of the lactone ring as follows from an analogous intermolecular recombination reaction. The formation of trityl esters from trityl ions and anions such as CI^- or CF_3COO^- are nearly diffusion controlled [10, 11] in chlorinated hydrocarbons. Therefore the splitting of the proton from the -COOH groups in compounds (III) or (V) is the decisive step in the formation of phthalophenone from the carbenium ions (III, V) by ring closure.

We sincerely thank Prof. Dr. H. J. Freund, Erlangen, for the CNDO program and helpful discussions. Financial support by the "Fonds der Chemischen Industrie" is gratefully acknowledged.

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(Eingegangen am 5. Februar 1987)

E 6440

Test of a Symmetry Reduced Extended RISM (XRISM) Equation Against Diffraction Experiments on Liquid Benzene and Hexafluorobenzene and Evaluation of Optimized Potentials

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Liquids / Potentials / Statistical Mechanics

Symmetry reduced extended RISM (XRISM) calculations have been performed on the polar molecular liquids benzene and hexafluorobenzene. By comparing XRISM results and Monte Carlo simulation data for benzene, good agreement between both methods could be shown applying different closures. — Testing XRISM theory against X-ray and neutron diffraction experiments, it could be demonstrated that the method is suited to extract optimized Lennard-Jones (12,6) potentials. Although a good overall agreement with experimental data could be achieved, the remaining differences suggest that it is necessary to use more complicated potentials in order to obtain a full description of the structural details provided by the experiments. — A variation of the partial charges can be tentatively interpreted in terms of electrostatic interactions playing a decisive role in the determination of the short-range structure in the studied polar molecular liquids.