

STERIC EFFECTS IN PROTON AND HYDRIDE TRANSFER PROCESSES IN STRONGLY ACIDIC SOLVENTS

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Abstract—The formation of proton complexes of aromatic hydrocarbons in $\text{HSO}_3\text{F-SbF}_5$ has been investigated at low temperature. In the case of steric hindered positions as occur in biphenyl and phenanthrene another position in the molecule is protonated as in HF-BF_3 . This contradiction can be explained by the bulk of the electrophilic attacking agent. A similar result was obtained by transfer of an hydride ion to the divalent positive ion of 1,2-benzanthracene.

Our results are supported by quantum chemical calculations according to the method of Pariser, Parr and Pople.

INTRODUCTION

AN EXTENSIVE study of the behaviour of aromatic hydrocarbons in strong proton acids as well as in proton acids with Lewis acids has been made by Mackor *et al.* Their investigations mainly concerned the formation of proton complexes obtained by dissolving the aromatic hydrocarbons in HF and HF-BF_3 .¹

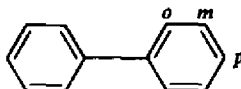
Our investigations deal with the study of the UV absorption spectra of the proton complexes derived from biphenyl, phenanthrene, tetracene and 1,2-benzanthracene in $\text{HSO}_3\text{F-SbF}_5$ at -70° . In the latter case the proton complex results from an hydride ion transfer to the related dipositive ion. The UV absorption spectra are essentially different from those obtained by Mackor *et al.* One might even doubt whether in our case proton complexes have been formed, but Birchall *et al.* have established by NMR measurements that in $\text{HSO}_3\text{F-SbF}_5$ proton complexes are present, since a methylenic group could be detected.²

UV absorption measurements revealed that in $\text{HSO}_3\text{F-SbF}_5$ solution the proton is joined to the aromatic molecule in a different position than in HF-BF_3 solution. Biphenyl for example in $\text{HSO}_3\text{F-SbF}_5$ is protonated only in the *para* position whereas in HF-BF_3 *ortho* protonation occurs. This difference may be attributed to the bulk of the attacking agent in the transition state of the proton transfer process.

The spectra were analysed with self consistent field calculations according to the method of Pariser, Parr and Pople including configuration interaction.^{3,4} The results did not differ essentially from those of Mackor *et al.* which were obtained without configuration interaction.¹

RESULTS

1. Biphenyl



In Fig. 1 the spectra of biphenyl in $\text{HSO}_3\text{F-SbF}_5$ and HF-BF_3 are shown together with the calculated absorption bands and oscillator strengths. Apparently, biphenyl in $\text{HSO}_3\text{F-SbF}_5$ is protonated in the *para* position, whereas in HF-BF_3 *ortho* protonation occurs.¹

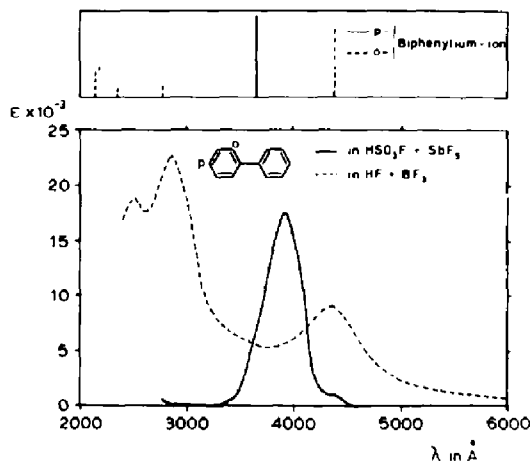


FIG. 1 Biphenyl in $\text{HSO}_3\text{F-SbF}_5$ and HF-BF_3 .

Only when biphenyl is *para* substituted with $-\text{NH}_3^+$ groups is the *ortho* position protonated. The spectrum is shown in Fig. 2.

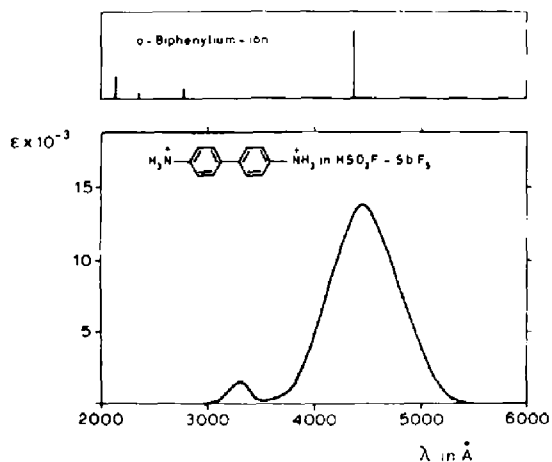
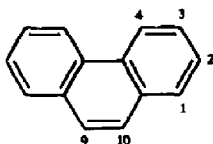


FIG. 2 *p,p'*-Diammoniumbiphenyl in $\text{HSO}_3\text{F-SbF}_5$.

2. Phenanthrene



In Fig. 3 the spectra of phenanthrene in $\text{HSO}_3\text{F}-\text{SbF}_5$ and in $\text{HF}-\text{BF}_3$ are shown. The spectrum of phenanthrene in $\text{HF}-\text{BF}_3$ at -70° given by Reid⁵ is due to a mixture of the 9- and 4-phenanthrenium ions.¹ In $\text{HSO}_3\text{F}-\text{SbF}_5$ a spectrum nearly identical with 9-methylphenanthrene in $\text{HF}-\text{BF}_3$ was obtained.¹ This shows together with the results of the calculations, that in $\text{HSO}_3\text{F}-\text{SbF}_5$ phenanthrene is protonated mainly in the 9-position and only to a very small degree in the 4-position.

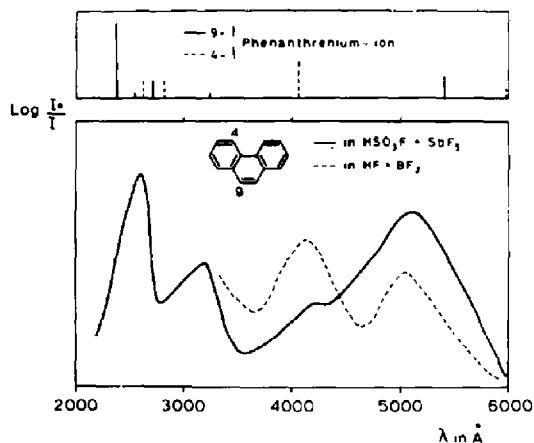
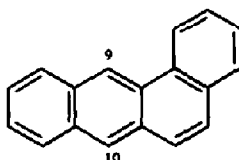


FIG. 3 Phenanthrene in $\text{HSO}_3\text{F}-\text{SbF}_5$ and $\text{HF}-\text{BF}_3$.

3. 1,2-Benzanthracene



In Fig. 4 the spectrum of 1,2-benzanthracene in HSO_3F is due to the 9- and 10-1,2-benzanthracenium ions. The proton complex corresponding to the 10-position is supposed to be more abundant. Similar observations have been made in HF -solution.⁶

When SbF_5 is added to the solution in HSO_3F , the dipositive ion is formed. From this dipositive ion the carbonium ion can be obtained by addition of an alkane,⁷ but now exclusively the 10-1,2-benzanthracenium ion is formed (see also Fig. 4). This spectrum is identical with 9-methyl-1,2-benzanthracene in HF .⁶

If the acidity of the solution of the 10-1,2-benzanthracenium ion in $\text{HSO}_3\text{F}-\text{SbF}_5$ is lowered by addition of H_2SO_4 the spectrum reveals that again the 10- as well as the 9-position is protonated.

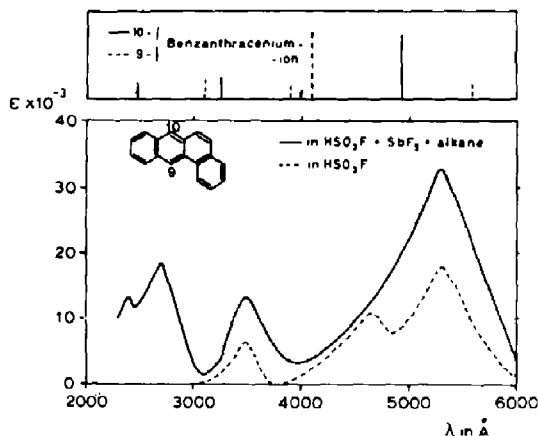


FIG. 4 1,2-Benzanthracene in HSO_3F and $\text{HSO}_3\text{F}-\text{SbF}_5$ -alkane.

The spectrum of the divalent positive ion of 1,2-benzanthracene is characterized by the following bands with the relative extinction coefficients in parentheses:

$$6700 \text{ \AA} (1) - 3900 \text{ \AA} (1) - 3300 \text{ \AA} (1.2) - 2850 \text{ \AA} (1.25).$$

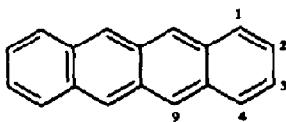
This is in good agreement with the calculated spectrum with the oscillator strengths in parentheses:

$$5900 \text{ \AA} (0.71) - 3820 \text{ \AA} (0.24) - 3480 \text{ \AA} (0.24) - 3230 (0.46).$$

The spectrum differs from the spectrum of the monovalent positive ion, which was obtained by irradiation of 1,2-benzanthracene in boric acid glass.⁹ Furthermore, no ESR absorption could be detected in $\text{HSO}_3\text{F}-\text{SbF}_5$ solution.

The probability of divalent positive ion formation in $\text{HSO}_3\text{F}-\text{SbF}_5$ is further supported by experiments with tetracene.

4. Tetracene



When tetracene is dissolved in HSO_3F , it is protonated in the 9-position. On addition of SbF_5 , the dipositive ion is formed. The spectrum is identical with the dinegative ion.⁹ Addition of an alkane changes the spectrum into the 9-tetracenium ion.

DISCUSSION

The calculated proton affinities of the *ortho* and *para* positions in biphenyl are about equal.¹⁰ However, biphenyl dissolved in $\text{HF}-\text{BF}_3$ is protonated in the *ortho* position because on protonation in this position the steric hindrance of two H atoms in the *ortho* positions decreases.^{1,10} In $\text{HSO}_3\text{F}-\text{SbF}_5$ we have only observed *para* protonation.

This disparity is attributed to differences in the transition state of the proton transfer processes. We assume that in $\text{HSO}_3\text{F}-\text{SbF}_5$ the bulk of the attacking agent—strongly solvated SO_3H^+ ions—favours the transition state for *para* protonation.

This hypothesis is supported by the experiments with phenanthrene. An illustrative picture for the transition state is given in Fig. 5.

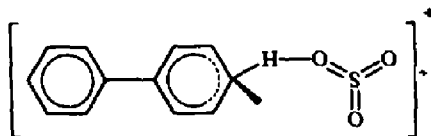


FIG. 5

In a solution of phenanthrene in $\text{HF}-\text{BF}_3$ at -70° , Reid measured an equilibrium of two carbonium ions.⁶ In our case the 4-phenanthrenium ion is present in very small amounts, probably as we were working under nonequilibrium conditions. Apparently, the high activation energy for the formation of the *ortho* biphenylenium ion and the 4-phenanthrenium ion in $\text{HSO}_3\text{F}-\text{SbF}_5$, owing to the bulk of the electrophilic agent, rules out an equilibrium of the different proton complexes.

A similar result was obtained for hydride transfer in $\text{HSO}_3\text{F}-\text{SbF}_5$. The dipositive ion of 1,2-benzanthracene, e.g. dissolved in $\text{HSO}_3\text{F}-\text{SbF}_5$ takes up a hydride ion from an alkane only in the 10-position. Evidently, the attacking hydride ion is so strongly bound with the alkyl fragment that the 9-position is also for steric reasons unfavourable. However, addition of H_2SO_4 to the solution changes the picture in such a way that the 9- and 10-1,2-benzanthracenium ions are formed. We assume that in this mixture the attacking agent is a solvated proton. Therefore, steric factors in the transition state in the process of protonation become less important. This implies that positions which are unfavourable for protonation in $\text{HSO}_3\text{F}-\text{SbF}_5$ can now accept a proton. Equilibrium can then be obtained for the different carbonium ions of the aromatic molecules.

EXPERIMENTAL

The UV absorption spectra were measured at -70° in a cell constructed by Horsman *et al.* for measurements at low temp.¹¹ The $\text{HSO}_3\text{F}-\text{SbF}_5$ mixture contained about 10% SbF_5 . After distillation of HSO_3F the solvent showed a broad absorption band at 2900 Å. This band disappeared when N_2 was passed through HSO_3F for about 30 min. The measurements were carried out at -70° since at higher temp side reactions take place.

Quantum chemical calculations. In the calculations of the spectra of the carbonium ions the differential overlap was neglected according to the scheme of Pariser, Parr and Pople.^{3,4} An IBM 360-50 computer was used for these calculations. In accordance with the FORTRAN-program, the Self Consistent Field Molecular Orbitals were first calculated. An empirical formula was used for the electronic-repulsion integrals. Using the S.C.F.M.O.'s, a configuration interaction matrix in most cases of the order 36 was constructed between singly excited states. After diagonalization of this matrix the absorption bands and oscillator strengths were calculated.

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