Tetrahedron. Vol. 29, pp. 3853 to 3855. Pergamon Press 1973. Printed in Great Britain

SOME OBSERVATIONS ON THE STEREOSPECIFICITY OF WEAKLY BOUND COMPLEXES OF ORGANIC MOLECULES

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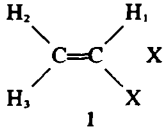
(*Received in the UK* 12 *March* 1973; *Accepted for publication* 2 *June* 1973)

Abstract—Vinyl bromide-benzene/p-xylene and acrylonitrile-benzene/p-xylene complexes have been studied by measuring the ^1H chemical shifts induced in the vinyl protons by the aromatic molecules. Evidence is presented that indicates that the complexes are 1 : 1, and values for the equilibrium quotient, K_x, and the full induced shift Δ_c, are deduced for each proton; similar values of K_x are obtained for each of the three vinyl protons. It is shown that the molecular interactions are specific. However, the complexes cannot be considered to have fixed geometry, but molecules involved take up a variety of relative orientations.

There have been few rigorous NMR investigations of transient formation of complexes between aromatic compounds and polar molecules that have several non-equivalent resonant nuclei. Those that have *may* have led to erroneous conclusions because of the problems inherent in common procedures for processing experimental data; these problems have been partially rationalized only recently.[1] Consequently, few firm conclusions have been reached about the stereospecificity of the interactions between polar molecules and aromatic molecules. In an effort to elucidate this point, which may be relevant to an understanding of the mechanisms of organic preparative reactions, we have studied the reactions between vinyl compounds (**1**) and separately benzene and p-xylene.



X = Br or CN

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As the experimental data were to be processed using the modified[1] Benesi-Hildebrand procedure, the compositions of the samples were dictated by the criteria given in reference 1. Thus for each vinyl - aromatic system about eight samples were studied. Each sample contained a constant low mole fraction of the vinyl solute and the amount of aromatic compound (x_B) was varied between samples in the approximate range 0·7–1·0 mole fraction, by the addition of cyclohexane. The multiplicity of the vinyl ABC spectra and the relative insensitivity of the spectrometer employed limited the amount of vinyl compound used to about 0·04 mole fraction.

Data Processing. The ABC spectra (ca 32) were analysed mainly using the iterative procedure LAOCOON 3, due in its original form to Castellano and Bothner-By[2], on a KDF 9 computer; the root mean square errors at convergence and the possible errors in the parameter sets were usually less than 0·05 Hz. For some samples, containing vinyl bromide with benzene, the procedure did not converge and the spectra were then analysed by the so-called trace-invariance method.[3,4]

Each reaction was assumed (with some subsequent justification) to have 1 : 1 stoichiometry. Therefore, the values of K_x, the equilibrium quotient devoid of activity coefficients, and Δ_c, the total shifts induced in the vinyl solute due to complex formation, for each reaction were deduced using Eq 1 in which Δ_{obs} is the difference between a vinyl proton shift in the presence of aromatic and that in cyclohexane alone.

$$\frac{1}{\Delta_{obs}} = \frac{1}{K_x x_B \Delta_c} + \frac{1}{\Delta_c} \qquad 1$$

The experimental data were processed on an ICL 1905 computer using a program known as BHCURVEFIT[5] which generates K_x and Δ_c from the gradient and intercept of the tangent to the curve of a plot of Δ_{obs}^{-1} vs x_B^{-1} at $x_B = 1{\cdot}0$. It should be noted that x_B was defined basically as in Ref 1. The values deduced for K_x and Δ_c for the four reactions studied are given in Table 1 (they should be considered significant only to the first decimal place).

DISCUSSION

The validity of these values given in Table 1 depends of course on the assumption that each complex is of the 1 : 1 type, and some justification for this is available.

It first has to be demonstrated that the shift of each vinyl proton is influenced by the same (one or

Table 1. Values of K_x and Δ_c for each of the solute protons in various vinyl solute-aromatic reactions

Reaction	Hydrogen	K_x	Δ_c/ppm
Acrylonitrile-p-xylene	1	0·99	1·533
	2	0·81	1·687
	3	0·97	1·305
Acrylonitrile-benzene	1	1·52	1·355
	2	1·26	1·572
	3	1·87	1·059
Vinyl bromide-p-xylene	1	0·57	1·035
	2	0·41	1·281
	3	0·63	0·608
Vinyl bromide-benzene	1	1·58	0·649
	2	1·03	0·863
	3	2·22	0·333

more) aromatic molecule, and hence by the same equilibrium. A generally applicable approach can be derived to elucidate this point, as follows. When considering the shift of any two hydrogens (i and j) in a sample of fixed composition an equation such as 2 applies; ρ is the

$$\Delta_{obs}^{i\,or\,j} = \rho\,\Delta_c^{i\,or\,j} \qquad 2$$

ratio of the number of moles of complex to the initial number of moles of vinyl solute. It follows from Eq 2 that Eq 3 should hold irrespective

$$\frac{\Delta_{obs}^{i}}{\Delta_{obs}^{j}} = \frac{\Delta_c^{i}}{\Delta_c^{j}} \qquad 3$$

of the stoichiometry of the reaction if this is solely responsible for the shifts of i and j. Thus the ratio of the observed shifts for different protons in the same solute should be independent of the composition of the samples used in studying the reaction. Table 2 gives some typical data, for the acrylonitrile-benzene reaction, relevant to Eq 3. The constancy of the ratios $\Delta_{obs}^{i}/\Delta_{obs}^{j}$ proves that the shifts induced in each of the vinyl proton resonances are caused by the same aromatic molecules and only one equilibrium is involved. Having established this, it appears that the similar values obtained for K_x (Table 1) for the three vinyl protons in a particular reaction indicate the choice of 1:1 stiochiometry to be correct. It should be noted that the *same* values for K_x cannot be expected due to the site dependence of non-bonded solvent effects[6] which will influence Δ_{obs} and hence the values of K_x and Δ_c deduced therefrom; if K_x is in error so must Δ_c be because the analysis of eqn 1 depends on the product $K_x\Delta_c$. The site effect could also account for the small variations in the values given in Table 2.

Table 2. Ratios of the Δ_{obs} values for the different proton pairs in various samples used in the study of the acrylonitrile-benzene reaction in cyclohexane at 306·6 K

x_B	$H_1:H_2$	$H_1:H_3$	$H_2:H_3$
0·6345	0·954	1·156	1·211
0·6991	0·952	1·164	1·223
0·7624	0·950	1·175	1·236
0·7988	0·945	1·175	1·244
0·8338	0·945	1·180	1·249
0·8824	0·938	1·173	1·251
0·9152	0·934	1·178	1·261
0·9624	0·940	1·183	1·259

The three values of Δ_c given in Table 1 for each reaction are sufficiently different to show that in each case the order for the three protons appears to be $H_2 > H_1 > H_3$. Even if the errors in K_x and Δ_c are recognised, the more precise data in Table 2 shows that this order is genuine. Assuming these induced shifts are due entirely to screening arising from the aromatic ring current[7] the implication of the observed order is that the site of attachment of the aromatic to the vinyl molecule is at or near to H_2. There can therefore be little doubt that there is a strong site-specific affinity of the aromatic molecule for the vinyl solute. However, the relative orientation of the two molecules remains ambiguous. A particular orientation might only be allowed or, as suggested by Engler and Laszlo[8], the aromatic molecule might be allowed a range of orientations relative to the vinyl solute.

So far as the fixed model is concerned reference to 1 suggests that the complexes could be thought of as being formed in such a manner that the dipolar axis of the vinyl compound (roughly along the C-X bond) is aligned, or nearly so, with the six-fold axis of the aromatic molecule and with the most electropositive hydrogen (H_2) closest to the ring. it is then tempting to use the data deduced by Johnson and Bovey[7] for the screening produced by the ring current of benzene, to deduce from the Δ_c values unique structures for the complexes. In the case of the vinyl bromide-benzene complex a specific geometry can be found which is consistent with the Δ_c values. In terms of aromatic ring radii (1 r.r. = 1·39 Å) the coordinates (radial, axial) of the vinyl hydrogens relative to the centre of benzene would most probably be (0·870, 2·854), (1·200, 2·194) and (1·462, 3·240) for H_1 H_2 and H_3 respectively. However, the values of Δ_c for the protons of acrylonitrile with benzene are collectively (not individually) too high to assign a specific geometry to the complex. It appears therefore that the fixed geometry model may not be correct. Moreover, the following observations suggest that the Engler and Laszlo model may explain better the experimental data.

It is noticeable for both solutes that on changing from benzene to p-xylene K_x decreases while Δ_c increases. Also in the case of either benzene or p-xylene the value of Δ_c for a particular proton is much higher for acrylonitrile than for vinyl bromide. Superfically the variations in Δ_c would appear consistent with the fixed geometry complex bound by a dipole-induced dipole energy. Because the dipole moments of acrylonitrile and vinyl bromide are ca 3·9 D and 1·4 D respectively and the polarizabilities of benzene and p-xylene are ca $0{\cdot}987 \times 10^{-29}$ and $1{\cdot}363 \times 10^{-29}\,m^3$ respectively, the expected order of interaction energies would follow the listing in Table 1. Other things being equal, an increase in interaction energy would decrease the intermolecular separation and increase Δ_c, as observed. However, the values of K_x cannot be explained on a similar basis. The implication of the variation in these is that steric features of the aromatic and possibly of the vinyl compounds are important. In view of the accessibility of H_2 it appears that the steric factors of the solvent are effective by virtue of limitations imposed on the possibilities of its approach to this site. It appears therefore that the complex observed on the NMR time scale is the average of a variety of isomeric 1 : 1 complexes, the allowed relative molecular orientations in which are governed by electrostatic and steric interactions.

CONCLUSIONS

It must be concluded that the interactions between simple vinyl and aromatic molecules are highly specific. However, it appears that the complexes do not have a unique geometry but take up a variety of preferred orientations corresponding to the formation of isomeric 1 : 1 complexes. No doubt this will not prove to be a general rule because as the interaction energy between molecules increases and steric factors become important, the allowed relative orientations of the complexing molecules will be restricted.

EXPERIMENTAL

The ^1H spectra were obtained at 60·004 MHz and 306·6 K using a Perkin-Elmer R10 spectrometer. The spectral measurements were made relative to internal cyclohexane using the conventional sideband technique. The modulation signals were derived from a Muirhead-Wigan D-890 A oscillator and their frequencies measured with a Venner 3336 counter. The frequency of each absorption in the ABC spectra was measured six times to minimize random errors and the average values used in the subsequent calculations. Each of the compounds studied was the best commercially available and was used without further purification.

Acknowledgment—One of us (R.R.Y.) thanks the Commonwealth Commission for a Scholarship.

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