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ISOTOPE EFFECTS IN ELECTRON-DONOR-ACCEPTOR COMPLEXES INVOLVING AROMATIC HYDROCARBONS AND FLUORANIL FROM NMR SHIFT MEASUREMENTS

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Abstract—Equilibrium constants and NMR shift parameters have been determined for complexes of benzene, toluene and *p*-xylene and their perdeutero-analogues with fluoranil in cyclohexane solution from NMR shift measurements. Isotope effects are observed in the 1:1 equilibrium constants for the complexes of *p*-xylene ($K_1(D)/K_1(H) = 1.1_0$) and toluene ($K_1(D)/K_1(H) = 1.0_9$). A much smaller effect was observed for the benzene complex which could not be quantified. These results may be interpreted through either the larger electronegativity of H over D, or the greater steric requirements of H over D.

Some years ago the equilibrium constants (K) for the association of tetracyanoethylene with benzene and benzene-d_6 in cyclohexane were estimated from spectrophotometric measurements of the intensities of the intermolecular charge-transfer absorption bands characteristic of such interaction.[1] It was assumed that the ratio of donor (D) to acceptor (A) in the complex was 1:1. The results indicated an isotope effect, the ratio of the K values for the C_6D_6 to the C_6H_6 complex being 1.3 at 33°. The estimated equilibrium constants themselves were relatively small, for example $K = 1.2\,l\,mol^{-1}$ for C_6D_6–TCNE at 33°. Such small donor–acceptor equilibrium constants are notoriously difficult to determine with accuracy, principally because the absorption coefficient (ϵ_{DA}) cannot be separately determined, but has to be derived from the same data as yield the value for K. Indeed, the product term $K\epsilon_{DA}$ can be readily estimated for a 1:1 association, whereas the separate quantities K and ϵ_{DA} are difficult to evaluate.[2] In this particular experiment we had, in fact, noted that the product term $K\epsilon_{DA}$ at a given temperature was the same for the C_6D_6–TCNE and C_6H_6–TCNE systems. It seemed possible therefore that the reported differences in K values could be an artefact of the method of estimation. In the same paper, the determination from NMR shift measurements of equilibrium constants for the association of 1,3,5-trinitrobenzene with benzene and benzene-d_6 was described. No isotope effect was observed in this case.

Since that work was reported there have been some developments in the technique of data collection and of computation of equilibrium constants for this type of interaction.[3] There is now good evidence that in many π-donor π-acceptor interactions where $[D_0] \gg [A]_0$ (subscript zeros indicate the total free and complexed species), not only bi-molecular DA species, but also termolecular D_2A species can be present at significant concentrations. We have chosen to use the NMR shift method rather than use spectrophotometric methods to make a careful study of the degree of complexation of benzene, toluene and *p*-xylene and their perdeutero-analogues with *p*-fluoranil in cyclohexane solution. The results show clearly that the stoichiometry in these cases is not simply 1:1. Furthermore, the isotope effect is in the opposite sense to that which had been concluded from the original experiment.

EXPERIMENTAL

The NMR method has been described by Bailey *et al.*[3] It is a development of a method previously described by Foster and Fyfe,[4] although the basic formulation on the optical equivalent was first described by Scatchard.[5]

For the interactions:

$$D + A \rightleftharpoons DA \quad \text{let } K_1 = [DA]/[D][A] \qquad (1)$$

$$DA + D \rightleftharpoons D_2A \quad \text{let } K_2 = [D_2A]/[DA][D]. \qquad (2)$$

If, for a series of solutions in which $[D]_0 \gg [A]_0$, the chemical shift (Δ) of an NMR absorption in the acceptor is measured relative to the absorption of the same nucleus when $[D]_0 = 0$, then from the variation $\Delta/[D]_0$ with Δ, K_1 and K_2 may be evaluated along with $\Delta_0(1)$ and $\Delta_0(2)$, the chemical shifts of the measured nuclei in the acceptor in the free DA and D_2A complexes respectively relative to the shift of the same nuclei in the unassociated acceptor. If the plot of $\Delta/[D]_0$ is nonlinear, this is generally taken to mean that termolecular complex formation (eqn 2) is significant. It is important that measurements are taken over a sufficiently wide range of $[D]_0$. This determines the range of the fraction of the acceptor complexed, often referred to as the saturation fraction[6] (s). Such an amount of experimental data is necessary in order to provide for the detection of possible curvature of the plot of $\Delta/[D]$ vs Δ and for the evaluation of the parameters.

A corresponding optical technique has been described[7] in which for a series of solutions in which $[D]_0 \gg [A]_0$, $A/[D]_0[A]_0$ is plotted against $A/[A]_0$, where A is the absorbance due to the complex. Here the parameters K_1, K_2, ϵ_{DA} and ϵ_{D_2A} may, in principle, be evaluated. (The ϵ's being the absorption coefficients of the appropriate species at the wavelength of measurement).

In the NMR experiments, ^{19}F shifts were measured using a Bruker HX90 cw spectrometer operating at 84.67 MHz, all signals being referenced to the ^1H signal of the solvent. All measurements were made at 288 K. Plots of $\Delta/[D]_0$ vs Δ are shown in Fig. 1. The donor concentration for the benzene solutions range from 0.05 to 1.0 mol kg^{-1}[a] corresponding to an s-range of 0.1–0.5; for the toluene solutions the donor range was 0.015–0.9 mol kg^{-1}, corresponding to an s-range of 0.04–0.8; and for the *p*-xylene solutions donor concentration range was 0.015–0.9 mol kg^{-1} corresponding to an s-range of 0.08–0.9. In all cases the concentration of acceptor was $\sim 2 \times 10^{-3}$ mol kg^{-1}. The parameters were computed by MINDS programme[8] adapted to give also the error limits at a 99.5% confidence level.

Benzene-d_6 was purchased from Fluorochem Ltd., toluene-d_8 and *p*-xylene-d_{10} were obtained from Aldrich Ltd., and were of at least 99.5% purity. These compounds were used without

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[a] All concentrations measured in mol per kg of solution.

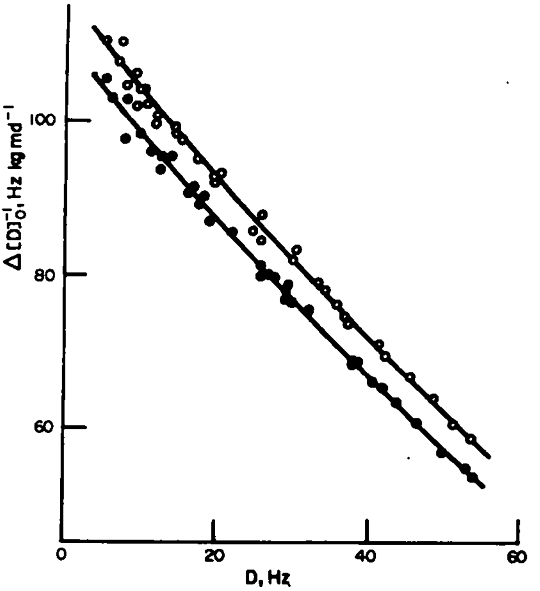

Fig. 1. Plot of $\Delta/[D]_0$ vs Δ for complexes of fluoranil with: (a) benzene ●; (b) benzene-d_6 ○ in cyclohexane at 288 K.

further purification. Other aromatic hydrocarbons were purified by standard techniques and checked by GLC. Fluoranil was purified by vacuum sublimation. Tetracyanoethylene was purified as the benzene complex followed by vacuum sublimation. Cyclohexane was BDH spectroscopic grade.

RESULTS AND DISCUSSION

In all the NMR determinations the plot of $\Delta/[D]_0$ vs Δ were curved. The computed parameters are summarised in Table 1. The values for benzene–fluoranil are not distinguishable from those for benzene-d_6–fluoranil, although the relevant plots (Fig. 1) do not coincide precisely. We therefore presume that if there is an isotope effect for the benzene-fluoranil complexes, it is only marginal. However, for the corresponding toluene and *p*-xylene complexes with fluoranil, the position is clear; in both cases K_1 for the deuterated donor is larger than K_1 for the undeuterated donor. The K_2 values are indistinguishable within experimental error. This might have been expected because of the smallness of these values. The shift values of $\Delta_0(1)$ and $\Delta_0(2)$ show no isotope effect.

Mindful of our previous investigation we have separately treated the present data on the assumption that no termolecular complexes exist—although the curvature of the plots of $\Delta/[D]$ vs Δ indicate the contrary. The parameters we obtained, namely $K_{(\mathrm{app})}$ and $\Delta_0(\mathrm{app})$ are listed in Table 1, along with the product term $K_{(\mathrm{app})}\Delta_0(\mathrm{app})$. For the benzene complexes, within the experimental error, there is no isotope effect. For both the toluene and the *p*-xylene systems the isotope effect of K_{app} is similar to that for the K_1 values. And whilst $\Delta_0(\mathrm{app})$ is independent of the particular isotopic donor, the product term, $K_{(\mathrm{app})}\Delta_0$ (app), does show a distinct isotope effect. This observation suggests that the differences for the toluene and *p*-xylene systems are real.

Since no bonds are being formed or broken in this type of complex formation, the isotope effect is secondary and consequently small. The direction of the observed effect is consistent with that usually expected in comparison between deuterium and hydrogen. Thus, an isotope effect is sometimes described in terms of the higher electronegativity of hydrogen than deuterium or because hydrogen has larger steric requirements than deuterium. For example, the ratio of the dissociation constant of HCOOH to that of DCOOH at 25° in water is 1.06–1.12.[9] This isotope effect indicates that the force constants at the isotopic position are smaller in the ion than in the undissociated acid. This leads to the argument that H is more electronegative than D. The greater electronegativity of the undeuterated donors should make them weaker donors than their deuterated counterparts, and if electron donation has any significance in the ground state of these complexes we would expect the deuterated donors to form the more stable complexes as is the case. However, from Mulliken's original work in this area,[10] it has been emphasised that there are other more major contributions to this ground state from so-called "no-bond structures". Unless these contributions are constant from the deuterated to the undeuterated donor, it is likely that their effect will overwhelm any contribution from a charge-transfer stabilization of the ground state. In that case the larger steric requirements of hydrogen over deuterium could be used to account for the isotopic difference seen in the equilibrium constants.

Table 1. Association constants K_1 and K_2 for the formation of DA and D_2A complexes respectively from various electron donors (D) with the electron acceptor fluoranil (A) in cyclohexane at 15°

	K_1/kg mol^{-1}	K_2/kg mol^{-1}	$\Delta_0(1)$/Hz	$\Delta_0(2)$/Hz	$K^a_{(\mathrm{app})}$/kg mol^{-1}	$\Delta_0(\mathrm{app})$/Hz	Int^b/kg mol^{-1} Hz
p-Xylene	5.55 ± 0.2	1.20 ± 0.05	96 ± 6	188 ± 12	2.86 ± 0.06	182 ± 2.5	520 ± 5
p-Xylene-d_{10}	6.1 ± 0.4	1.14 ± 0.08	95 ± 3	204 ± 7	3.16 ± 0.16	179 ± 5	567 ± 12
Toluene	2.85 ± 0.15	0.65 ± 0.06	76 ± 3	149 ± 10	1.47 ± 0.07	144 ± 5.5	212 ± 3
Toluene-d_8	3.1 ± 0.15	0.64 ± 0.06	74 ± 2	159 ± 10	1.58 ± 0.06	143 ± 4	226 ± 2
Benzene	2.05 ± 0.1	0.47 ± 0.04	53 ± 2	110 ± 6	1.05 ± 0.03	104 ± 2	109 ± 1
Benzene-d_6	2.05 ± 0.1	0.46 ± 0.05	55 ± 2	118 ± 8	1.05 ± 0.3	107 ± 25	112 ± 8

[a] Values of *K* and Δ_0 obtained by treating the variation of $\Delta/[D]_0$ with Δ as linear

[b] Intercept with the *x*-axis of the linear function referred to in footnote (*a*) of this table.

The value corresponds to the product term $K_{(\mathrm{app})}\ \Delta_0(\mathrm{app})$.

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