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NOTE

Secondary hydrogen isotope effects and vibrational frequency shifts

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We have recently reported that trideuteration in the methyl group of toluene, or in one such group of *m*-xylene, reduces the equilibrium constant of π-complex formation with chloranil by about 7 per cent.[1] This effect is in the same direction as those found in solvolysis, where hyperconjugative electron release from a β- or *para*-CD_3 group is interpreted as being less effective than from a CH_3 group.[2,3] Streitwieser and his collaborators[4] have recently amplified and rendered quantitative the usual view that these effects arise from the crowding of vibrational levels in the electron deficient transition state (or product molecule in an analogous thermodynamic effect). In their model, since the toluene moiety of the complex is certainly electron deficient relative to toluene itself, the observed effect is in the predicted direction, its magnitude requiring a total shift to lower frequencies of some 100 cm^{-1}, shared amongst the six methyl stretching and bending modes.

We have noted that the isotope effect for one CD_3 group is the same in toluene and *m*-xylene. The standard free energy of complex formation varies in a roughly linear manner with the number of methyl groups,[5] so that each methyl group can be considered as acting independently. Furthermore, the methyl frequencies of different polymethylbenzenes are nearly identical.[6,7] It follows that the "level crowding" hypothesis can be tested by a comparison of the infra-red spectra of hexamethyl-

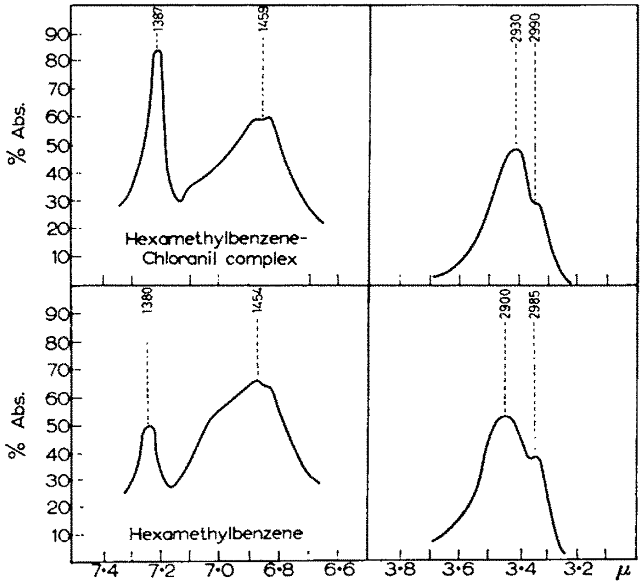

Fig. 1.

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benzene with that of its solid complex with chloranil[8] (both in KBr). In the two relevant regions chloranil is transparent and hexamethylbenzene has no other infra-red active fundamentals.[9]

It is clear from Fig. 1 that the relevant bands shift to *higher* frequencies in the complex, the total shift estimated for the six methyl modes being about 50 cm^{-1}. Evidently in this system, and perhaps in general, hyperconjugative electron release from a methyl group does not lower the appropriate force constants, and the observed isotope effect, which is almost certainly related to hyperconjugative electron release, occurs *in spite of* frequency shifts and not because of them.

Streitwieser *et al.*[4] have also interpreted the effect of deuteration on acid and base strength[10] in terms of vibrational frequency shifts. The frequencies from recent vibrational analyses of acetate ion[11] and acetic acid,[12] introduced in their equations,[4] do not account for an appreciable isotope effect in either direction.

It is clearly advisable to refrain from applying the "level crowding" hypothesis to any and all isotope effects until convincing experimental evidence in its favour is obtained. No such objection, however, applies to Streitwieser's "α-effect",[4] where a definite hybridisation change occurs.

The necessity of considering both inductive and hyperconjugative effects has been pointed out in an earlier communication.[13] On the basis of recent theoretical work[14] we believe that *both* types of effect can be ascribed to configurational differences arising from the anharmonicity of the symmetrical stretching and bending modes.[15]

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