162. *Secondary Hydrogen Isotope Effects. Part II.*[1] *Association Constants between Methylbenzenes and Chloranil.*

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The equilibrium constants of π-complex formation between chloranil and alkylbenzenes follow the sequence: benzene < toluene > ethylbenzene > isopropylbenzene. [α-$^2H_3$]Toluene and *m*-[α-$^2H_3$]xylene both yield association constants with chloranil that are some 7% smaller than those of the corresponding protium compounds. These results are taken as evidence for less effective hyperconjugative stabilisation by C^2H_3 than by CH_3 in this system. Secondary isotope effects and the steric and the electronic factors affecting the stability of charge-transfer complexes are discussed in the light of these results.

It was shown in Part I [1] that secondary hydrogen-isotope effects can be legitimately discussed in terms of the usual electronic substituent effects, without the necessity of direct recourse to shifts in vibrational frequencies. Evidence was presented from equilibrium measurements for an inductive isotope effect, and confirmatory kinetic evidence was cited. Kinetic isotope effects presumably related to hyperconjugation are well known (for references see Part I), principally in solvolytic reactions, but they could not be confirmed in related equilibrium studies.[2] In this paper, evidence is presented for a hyperconjugative isotope effect on the stability of charge-transfer complexes between aromatic hydrocarbons and the electron-acceptor chloranil, and some insight is afforded into the factors governing the stability of these complexes.

Charge-transfer complexes have been extensively investigated.[3] Although the donor strength of alkylbenzenes does not show a clear trend in terms of either the inductive or the hyperconjugative electron-releasing power of the alkyl substituent, there are two limiting types of behaviour: on the one hand, complexes with hydrogen chloride become stronger with increased branching of the alkyl group, indicating predominance of inductive electron-release; [4] on the other, the stabilities of the picric acid complexes of the monoalkyl-benzenes [5] and -naphthalenes [6] follow the Baker–Nathan order: [7] H < Me > Et > Pr^i > Bu^t, a reactivity order which is generally taken as *prima facie* evidence for predominant hyperconjugation. One might indeed expect hyperconjugation to be important in complexes of the latter type since they are 1 : 1 complexes with parallel rings some 3—3·5 Å apart, in which one may presume strong overlap between the respective electron-rich and electron-deficient π-orbitals of the donor and the acceptor molecules. In the examples studied, however, the increasing steric requirements of the alkyl group, superimposed on its increased facility for inductive release, would reproduce the same sequence, so that this sequence cannot be taken as evidence that hyperconjugation plays a significant role in stability of complexes.[5,6]

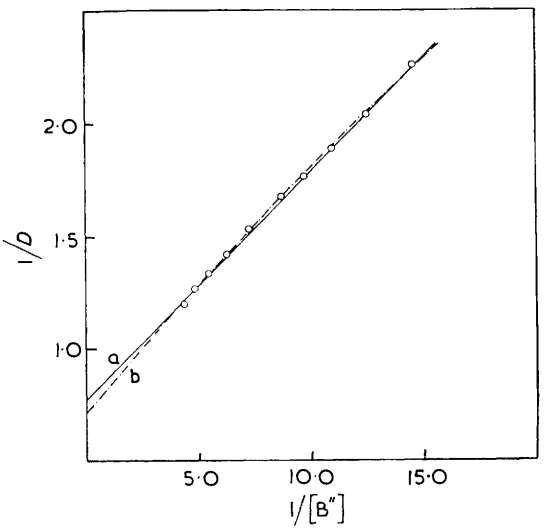
Procedure and Results.—In the present study, chloranil was chosen as the acceptor since it shows a relatively high sensitivity to substituents in the donor molecule and could be expected to behave similarly to picric acid. The competitive method, developed by Foster [8] and applied by Foster, Hammick, and their collaborators to complexes between chloranil and aromatic hydrocarbons,[9,10] was adopted, although, in order to be applicable to the measurement of isotope effects, more care had to be taken about temperature

[1] Part I, preceding paper.
[2] Lichtin, Lewis, Price, and Johnson, *J. Amer. Chem. Soc.*, 1959, **81**, 4520.
[3] See, *e.g.*, (*a*) Andrews, *Chem. Rev.*, 1954, **54**, 713; (*b*) Orgel, *Quart. Rev.*, 1954, **8**, 422.
[4] Brown and Brady, *J. Amer. Chem. Soc.*, 1952, **74**, 3570.
[5] Anderson and Hammick, *J.*, 1950, 1089.
[6] Gardner and Stump, *J. Amer. Chem. Soc.*, 1957, **79**, 2759.
[7] Baker and Nathan, *J.*, 1935, 1844.
[8] Foster, *Nature*, 1954, **173**, 222.
[9] Corkill, Foster, and Hammick, *J.*, 1955, 1202.
[10] Foster, Hammick, and Parsons, *J.*, 1956, 555.

control, preparation of solutions, and reproducibility in general. This method involves competition for a small quantity of acceptor (A) between the donor under investigation (B′) and a stronger reference donor (B″). The relevant equation is:

$$K' = \frac{D_0 - D_1}{D_1}\left(\frac{1 + K''[\mathrm{B}'']}{[\mathrm{B}']}\right), \qquad (1)$$

where D_0 is the optical density at the maximum of absorption of the AB″ complex in a solution containing a small amount of chloranil and the reference donor in stoicheiometric



Plots of $1/D$ against $1/[\mathrm{B}]$ for the *N*-methylaniline–chloroanil complex.

Full line: "least squares" linear plot: (a) $1/D = 0{\cdot}775 + 0{\cdot}1018/[\mathrm{B}'']$. $K'' = 7{\cdot}6$ l. mole^{-1}.

Broken line: "least squares" quadratic plot: (b) $1/D = 0{\cdot}716 + 0{\cdot}1166/[\mathrm{B}''] - 8{\cdot}085 \times 10^4/[\mathrm{B}'']^2$. K'' (initial) = 6·2; K'' (final) = 9·5.

Alkylbenzene–chloranil complex association constants in cyclohexane

	This research (18·0° ± 0·2°)		Ref. 10 (19° ± 1°)
Alkylbenzene	No. of sets *	K' (l. mole^{-1}) †	K' (l. mole^{-1})
Benzene	6	0·79 ± 0·01	0·56
Toluene	8	1·37 ± 0·01	1·7
m-Xylene	6	2·37 ± 0·01	2·9
Ethylbenzene	4	1·04 ± 0·01	—
Isopropylbenzene	4	0·80 ± 0·02	—
[α-$^2H_3$]Toluene	4	1·28 ± 0·01;	K_D/K_H = 0·93[4]
m-[α-$^2H_3$]-Xylene	3	2·19 ± 0·02;	K_D/K_H = 0·92[4]

* Each set consists of five points, each point at different [B′]. † Mean of all sets and standard deviation of the average value of K' for each set. All constants are referred to a value of $K'' = 7{\cdot}9$.

concentration [B″]; D_1 is the optical density of the same solution containing, in addition, a stoicheiometric concentration [B′] of the hydrocarbon; K' is the association constant being determined, and K'' is that of the reference donor, which has to be determined separately.

The product $K''[\mathrm{B}'']$ is conveniently of the order of unity, so the value obtained for K' will depend on that adopted for K'' but will not be directly proportional to it. As reference bases, the earlier workers used several mono- and di-alkylanilines, obtaining K'' from the presumably linear plot of $D/[\mathrm{B}'']$ against D.[11] In the present study, K'' was obtained from the equivalent plot of $1/D$ against $1/[\mathrm{B}'']$. In either case, K'' is sensitive to slight deviations from linearity.*

* The resulting lack of precision in K'' was tacitly acknowledged by the previous authors in that the association constant for chloranil–*NN*-diethylaniline in cyclohexane at 19° ± 1° is variously quoted without comment as 4·1 and 3·5 in refs. 9 and 10, respectively.

[11] Foster, Hammick, and Wardley, *J.*, 1953, 3817.

N-Methylaniline was taken as reference base. In determining the association constant of its chloranil complex, the concentrations were adjusted so that the optical density at $\lambda_{max.}$ (590 mμ) was well within the linear region of the spectrophotometer ($D_0 = 0{\cdot}4$—$1{\cdot}4$). Solutions were made up at the temperature of the determination and the optical cells were kept at $18{\cdot}0° \pm 0{\cdot}2°$. From six sets of measurements, of five points each, we obtained: $K'' = 8{\cdot}0 \pm 0{\cdot}7$ l. mole^{-1}; from four additional sets of ten points each, we obtained $K'' = 7{\cdot}9 \pm 0{\cdot}3$ l. mole^{-1}.

At first sight, the fact that our value for K'' is considerably larger than 5·0 l. mole^{-1}, the value obtained by Foster and Hammick, is disturbing. However, careful consideration of the " ten-point " plots, illustrated in the Figure, shows that although a straight line fits the data adequately, a quadratic equation does so somewhat better. Moreover, plotting the best straight line through any four or five adjacent points of the ten could lead to K'' values ranging from 6 to 10, and it is evident that use of points outside the " linear " range of the spectrophotometer would extend the spread in the K'' values still more. We will not here consider possible reasons for this inability to obtain reliable absolute values of K''. It suffices for present purposes to take $K'' = 7{\cdot}9$ as a reproducible figure of doubtful absolute accuracy, and to recognise that the poor agreement with Foster and Hammick's value of K'' is without much significance.

The association constants for alkylbenzene–chloranil complexes determined in this research are shown in the Table.

Discussion

The results set forth in the Table are best discussed under three heads.

(1) *The Series Benzene, Toluene,* m-*Xylene.*—There is only qualitative agreement with the association constants obtained by the previous workers, but no more can be expected in view of the considerations outlined above. The present results show that each methyl group in the donor independently increases complex stability by a factor of about 1·7. The independent effect of each methyl group is attested by Foster, Hammick, and Parsons,[10] who show that, up to and including hexamethylbenzene, each methyl group adds a roughly equal increment to the free energy of complex formation; their mean increment is consistent with a factor of 1·9, in reasonable agreement with our results. It should be noted that the additivity per methyl group, in marked contrast to the co-operative destabilising effect of the ethyl groups in hexaethylbenzene,[10] suggests strongly that the steric requirements of the methyl groups are negligible.

(2) *Branching in the Alkyl Substituent.*—Here, as in the similar systems cited above,[5,6] the substituents fall in the Baker–Nathan order. Since isopropylbenzene forms a complex no stronger than that of benzene, it follows that the steric repulsion of the isopropyl group must be large enough to counteract not only its own inductive effect, but also any hyperconjugative interaction with its lone hydrogen atom. The extent of the latter effect thus remains open.

(3) *The Isotope Effect.*—Methyl-deuteration, in both toluene and *m*-xylene, decreases the association constant by some 7%. This requires, unless one can call in a steric isotope effect, that net electron accession to the ring be reduced in the deuterated compounds. Several factors rule against the incursion of a significant steric isotope effect in this system: (*a*) The inter-ring distance is so large that the short-range non-bonding interactions with the methyl-hydrogen atoms would be very small, as suggested also by the constancy of the free energy increment per methyl group. Isotopic differences in these small repulsions would almost certainly be negligible. (*b*) It was shown in Part I that even in a case where a steric effect of the methyl group genuinely does exist—steric inhibition of resonance in *N*-methyl-2,4,6-trinitroaniline—this effect is not significantly isotope-dependent. (*c*) Where steric isotope effects have been invoked, they have been ascribed to the greater vibrational amplitudes of the protio-molecules.[12] If such an effect

[12] Bartell, *Tetrahedron Letters*, 1960, No. 6, 13; *J. Amer. Chem. Soc.*, 1961, **83**, 3567.

operated in the present system, it would tend to increase the association constants of the deuterated hydrocarbons and could hardly be called upon to explain the observed decrease.

Falling back, as evidently we must, on differential polarisation and polarisability, we believe the most reasonable explanation to be that the smaller hyperconjugative stabilisation by trideuteromethyl than by methyl is sufficient to overcome the inductive effect in the reverse direction (Part I). The present results thus constitute evidence both for a hyperconjugative isotope effect in a system at equilibrium, and for the importance of hyperconjugation as a factor affecting the stability of charge-transfer complexes.

After our preliminary reports of these results,[13] it was shown, by comparing the infrared spectra of hexamethylbenzene and of its chloranil complex, that the " methyl " frequencies do not shift in the complex in the manner required to explain the isotope effect.[13b] It is recognised, however, that our statement that the hyperconjugative isotope effect occurs " in spite of frequency shifts and not because of them " [13b] is unfortunately worded. Although the importance of entropy in secondary isotope effects in solvolysis has recently been strikingly demonstrated,[14] it is still reasonable to suppose that most secondary isotope effects, at least in a non-polar solvent, would arise substantially from zero-point energy differences. Our findings [13] merely support the contention that it is at present impossible to predict isotope effects from naïve considerations of shifts in the frequencies of localised vibrations, and preferable to discuss them simply in terms of the usual substituent effects of organic chemistry.

Independent evidence for a hyperconjugative isotope effect in systems at equilibrium has been presented by Bender and his co-workers in ketone hemiacetal equilibria,[15] and by Arnett and his co-workers in the protonation of acetophenone.[16] Here too, the fact of the effect is considerably better established than its rationalisation in terms of frequency shifts.[15b]

It should be noted finally that in the present study, a hyperconjugative isotope effect—and confirmation of hyperconjugation as a factor in determining the Baker–Nathan reactivity sequence—has been found in the relatively inert solvent cyclohexane. This speaks against the proposed universal abandonment of hyperconjugation in favour of " steric hindrance to solvation." [17]

Experimental

Preparation of Deuterated Compounds.—As in Part I, the isotopic syntheses were tested by preparing the unlabelled compounds, which were indistinguishable from authentic samples of the same materials as regards both physical properties and chemical behaviour.

(*a*) [α-$^2H_3$]Toluene was prepared by two methods: (i) [α-$^2H_2$]Benzyl chloride (0·056 mole), prepared as described in Part I, was reduced in di(2-ethoxyethyl) ether with lithium aluminium deuteride (Metal Hydrides, Inc.). After 2 hr. at 100°, the toluene was slowly distilled from the reaction mixture. The product was washed twice with 50% sulphuric acid and once with water to remove entrained solvent, dried ($CaCl_2$), and redistilled. The yield was 70%. (ii) The alternative preparation was similar to that of Renaud and Leitch,[18] except that ααα-tribromotoluene [19] was reduced with acetic [^{2}H]acid (yield 60%). The products of the two syntheses were identical in infrared spectrum, which agreed with that reported by Wilmshurst and Bernstein [20] for ααα-trideuterotoluene. n_D^{18} was 1·4956 and 1·4955 for the products of (i) and (ii), respectively. Mass-spectrographic analyses were not carried out, but the reliability of the synthetic route was further confirmed by the analytical results for deuterated *p*-toluic

[13] (*a*) Halevi and Nussim, *Bull. Res. Council Israel*, 1958, **7**, *A*, 230; (*b*) *Tetrahedron*, 1959, **5**, 352.
[14] Leffek, Robertson, and Sugamori, *Chem. and Ind.*, 1961, 259.
[15] (*a*) Bender, Feng, and Jones, *Chem. and Ind.*, 1959, 1350; (*b*) Jones and Bender, *J. Amer. Chem. Soc.*, 1961, **83**, 6322.
[16] Arnett, Cohen, Bothner-By, Bushick, and Sowinski, *Chem. and Ind.*, 1961, 473.
[17] Shubert, Craven, Minton, and Murphy, *Tetrahedron*, 1959, **5**, 194.
[18] Renaud and Leitch, *Canad. J. Chem.*, 1956, **34**, 98.
[19] Heble, Nadkarni, and Wheeler, *J.*, 1938, 1322.
[20] Wilmshurst and Bernstein, *Canad. J. Chem.*, 1957, **35**, 911.

acid (to be reported in a subsequent publication) which was prepared from *p*-bromo-ααα-trideuterotoluene synthesised as in (*a*, i). The isotopic purity is therefore taken to be 95% or better.

(*b*) [α-$^2H_3$]*m*-Xylene was prepared in an overall yield of 55% as in (*a*, i) above from α-chloro-*m*-[α-$^2H_2$]xylene which had been prepared from ethyl *m*-toluate in a manner similar to the preparation of [α-$^2H_2$]benzyl chloride as noted in (*a*, i). n_D^{18} was 1·4968. The infrared spectrum was consistent with the presence of one methyl group and one trideuteromethyl group. Isotopic purity of $\leqslant$95% was assumed on the basis of the preparative method.

Purification of Materials.—Cyclohexane (B.D.H Reagent) was passed through silica gel (30—120 mesh) which had been activated by heating it at 300° for 15 hr. n_D^{18} was 1·4278. The ultraviolet spectrum in the 200—300 mμ range was consistent with $<10^{-4}$M-concentration of aromatic material, calculated as benzene.

Chloranil (Eastman) was recrystallised twice from glacial acetic acid.

N-Methylaniline (Eastman; " aniline and dimethylaniline free "), benzene (Eastman Spectrograde), toluene (Fisher Certified Reagent), ethylbenzene (Eastman Reagent), isopropylbenzene (Eastman Reagent), and *m*-xylene (Eastman Reagent) were each distilled twice *in vacuo* shortly before preparation of solutions.

Spectrophotometric Procedure.—The optical density was determined with a Unicam S.P. 500 spectrophotometer fitted with a constant-temperature cell-holder. Silica cells, 30 mm. long, were used. A linearity check [21] showed the results to be linear within 1% in the optical density range, $D = 0{\cdot}4$—$1{\cdot}4$.

Solutions were prepared in a thermostat-bath at the temperature of the measurement and were left for an hour at this temperature before use. Five minutes were allowed for further thermal equilibration in the optical cell before readings were taken. These were all at 590 mμ, the absorption maximum of the *N*-methylaniline–chloranil complex, at which chloranil, *N*-methylaniline, and all the hydrocarbon donors are transparent.

(*a*) *Determination of K″ of the* N-*methylaniline–chloranil complex.* Six " five-point " and four " ten-point " sets were carried out. One plot of $1/D$ against $1/[B]$ is illustrated in the Figure. The concentration of chloranil was $3{\cdot}0 \times 10^{-4}$M and that of the base varied in the range 0·03—0·25M, so that the optical density remained in the " linear " range. The plot of $D/[B]$ against D has an apparent advantage in that K'' is given directly by the slope rather than by the intercept : slope ratio. It is, however, open to the statistical objection that errors in D enter, not only into the dependent variable, but also into the independent variable. In any case, the K'' values obtained by the two treatments are substantially the same.

(*b*) *Determination of K′.* Three sets of measurements are shown below. They illustrate the internal reproducibility of each set and also the chemical identity of synthetic toluene with the purified commercial product. The precision of the measurements in which *m*-xylene was the donor is similar. For these three sets: $\lambda = 590$ mμ, $[A] = 3{\cdot}0 \times 10^{-4}$M, $[B''] = 0{\cdot}1143$M, and $K'' = 7{\cdot}9$.

(i) *Toluene* *						
[B′] (M)	0	0·166	0·249	0·332	0·415	0·498	
D	0·598	0·534	0·508	0·482	0·459	0·442	
K'	—	1·374	1·354	1·380	1·389	1·349; mean = $1{\cdot}36_9$
(ii) *Toluene* †						
[B′] (M)	0	0·166	0·249	0·332	0·415	0·498	
D	0·596	0·532	0·505	0·480	0·458	0·437	
K'	—	1·379	1·377	1·385	1·382	1·390; mean = $1{\cdot}38_3$
(iii) [α-$^2H_3$]*Toluene* †						
[B′] (M)	0	0·150	0·224	0·299	0·374	0·419	
D	0·596	0·542	0·518	0·495	0·476	0·464	
K'	—	1·267	1·277	1·297	1·282	1·292; mean = $1{\cdot}28_3$

* Purified commercial product. † Synthetic product, see (*a*, i) above.

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[21] Vandenbelt, Forsyth, and Garrett, *Ind. Eng. Chem., Analyt.*, 1945, **17**, 235.