only iodate and borohydride, a large fraction of the borohydride undergoes hydrolysis.

It has been reasonable to assume that the mechanism of the Jensen titration is described by reaction 10 followed by reaction 11

$$IO_3^- + 8I^- + 6H^+ = 3I_3^- + 3H_2O \qquad (10)$$

$$4I_3^- + BH_4^- + 2H_2O = 12I^- + HBO_2 + 7H^+ \qquad (11)$$

Our experiments have shown that the rate of reaction of tri-iodide in acid solution is not much faster than hydrolysis. Hence, the mechanism of the Jensen titration can not be reaction 10 followed by reaction 11, since this would lead to a titration error due to hydrolysis. Intermediate oxidation states of iodine such as $+3$ or ± 1 must be formed and one or more of these must react faster than the zero valent state.

Furthermore, the rate of *generation* of tri-iodide in the Jensen procedure is not fast enough to compete with the rate of hydrolysis of borohydride. This deduction is based on the assumption that the reported rate laws for the hydrolysis of borohydride, and for the generation of tri-iodide[16] from iodate and iodide, both hold at high acidities.

Therefore, it seems likely that borohydride in the Jensen procedure reacts with an intermediate oxidation state of iodine such as IO^+ or IO^- to yield iodide. Jensen has shown that nearly a 100% excess of IO_3^- (2.67 moles iodate per mole borohydride) is required in order to get a quantitative titration. One possible explanation for this requirement is that rapid reactions involving iodate and iodide generate one mole of $+3$ iodine per mole of iodate. The $+3$ iodine, such as IO^+, then reacts with boron-containing reducing species to yield I^- at a rate which can successfully compete with the hydrolysis of borohydride. It is presumed that the other oxidation states of iodine do not react rapidly with boron-containing reducing species but rather with iodine-containing species which ultimately result in the formation of I_3^-. Such a scheme requires at least 2 moles of iodate in the Jensen titration.

Additional support for the above mechanism can be found from the suggestion[17] that one mole of IO^+ is produced per mole of iodate in acid solutions containing iodide.

Finally, in preliminary experiments we have found that hypobromite reacts faster than hypochlorite with borohydride in basic solutions. We expect that hypoiodite will react at an even faster rate. We plan to commence a detailed study of the reactions of borohydride with $+1$ halogens.

It should be pointed out that the kinetic rate law for the iodate reaction stands in contrast to the rate laws found for other oxidants with borohydride. No other system, yet investigated, has shown first order in all three species: oxidant, hydrogen ion and borohydride ion. The order with respect to oxidants has been reported to be zero for ferricyanide[7,8] and one for ketones[5,6,18] and permanganate.[9] The order with respect to hydrogen ion is zero for permanganate[9] and acetone[18] and one for water[2-5] and ferricyanide.[7,8] Like the iodate reaction, all the reactions which have been reported are first order in borohydride.

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(16) S. Dushman, *J. Phys. Chem.*, **8**, 453 (1904).

(17) K. J. Morgan, M. G. Peard, C. F. Cullis, *J. Chem. Soc.*, 1865 (1951); M. G. Peard, D. F. Cullis, *Trans. Faraday Soc.*, **47**, 616 (1951).

(18) T. Freund and N. Nuenke, *J. Am. Chem. Soc.*, **84**, 873 (1962).

[CONTRIBUTION FROM THE LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA, DEPARTMENT OF PHYSICS, UNIVERSITY OF CHICAGO, CHICAGO 37, ILLINOIS]

Basicities of the Methyl Benzenes. II. Induction in the L.C.A.O.-M.O. Framework

BY S. EHRENSON[1]

RECEIVED DECEMBER 14, 1961

The quantum chemical examination of the methylbenzene-methylbenzenium ion equilibria previously described has been extended to evaluate the importance of methyl inductive effects upon these equilibria. Employing the same semi-empirical M.O. methods as used in evaluating the methyl hyperconjugative effects, one finds that an unrealistically large inductomesomeric effect must be assigned to methyl to reproduce the relative experimental basicities, if the latter is assumed to be the sole effect. A combined model, however, where hyperconjugation accounts for two-thirds of the total effect is found to better correlate with these basicities than does either single model alone. Realistic parameter choices are used with this combination model. The theoretical results are also presented and discussed in terms comparable with the Taft $\rho\sigma$ equation where resonance and inductive effects have been separated. Some comparisons are drawn with n.m.r. results recently obtained for a number of aromatic carbonium ions.

Introduction

The conclusion was reached in an earlier paper[2] that the equilibrium basicity order of the methyl benzenes could be satisfactorily explained in terms of hyperconjugative stabilization of the product cations. The appropriate (linear combination atomic orbitals–molecular orbitals) semi-empirical self-consistent energy differences (cation minus neutral aromatic) could be quantitatively correlated with two sets of experimental data on the protonation reactions in HF media.[3,4] The results of a later, independent and more careful study of six of the thirteen aromatics[5] while qualitatively in agreement with the previous work indicated a generally greater spread between the equilibrium constants ($K_{eq.}$). Comparison of these latter results with those of the theory suggested an addi-

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(1) This work was assisted by the Office of Naval Research. Computations carried out at Wright Air Force Development, Dayton, Ohio.

(2) S. Ehrenson, *J. Am. Chem. Soc.*, **83**, 4493 (1961).

(3) D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951).

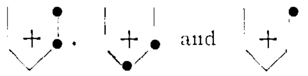
(4) M. Kilpatrick and F. E. Luborsky, *ibid.*, **75**, 577 (1953).

(5) E. L. Mackor, A. Hofstra and J. H. van der Waals, *Trans. Faraday Soc.*, **54**, 186 (1958).

tional contribution to the measured basicities above and beyond but *appearing to parallel* the hyperconjugative effects.

Further work was initiated to investigate the nature of these additional contributions. At the same time, the question of whether an alternative theoretical model might equally well or better correlate the experimental data was considered. The logical way of extending the previous studies (both with regard to superposition on, and as an alternative to the hyperconjugation model) seemed to lie in an investigation of the inductive effects exerted by the substituent methyl groups.

1. **Theory.**—Wheland's model for proton addition to an aromatic ring[6] was adopted with the inclusion of inductive electron release by methyl. The methylbenzene cations are thereby viewed as five-center conjugating systems with four π-electrons; the Coulomb integrals of these centers are taken as zero when unsubstituted or as $\delta\beta_0$ when substituted with a methyl group. For example, *ortho*-xylene is capable of giving three distinct protonated isomers, *i.e.*,



where ● signifies a position of methyl attachment. The break in the ring conjugation is at the position of protonation. The last of these isomers is produced as a result of protonation at a methyl-bearing site; here we consider this isomer equivalent to that produced by protonation in the *ortho* position of toluene.[7]

The neutral aromatics themselves are pictured as six-membered rings with the Coulomb integrals of the ring carbons changed by $\delta\beta_0$ if methyl bearing, analogous to the changes postulated for the substituted sites in the cations. Six π-electrons are considered to occupy the three lowest molecular orbitals, the construction of which will presently be discussed.

Recalling eq. 1 of ref. 2, the assumption is made that the free energy of protonation is proportional to the difference in π-electron delocalization energies between the cation and parent aromatic, *viz.*,

$$\Delta F \propto [E_\pi(\text{ArH}^+) - E_\pi(\text{Ar}) - E_{\text{H,CHR}}] = [\Delta E_\pi - E_{\text{H,CHR}}] \quad (1)$$

Here, the modification made previously (and commented upon in footnote 9[8]) which employed the resonance rather than the delocalization energies is not necessary since the number of conjugating π-electrons is always six and four respectively for the neutral aromatics and cations. $E_{\text{H,CHR}}$, which replaces E_{H^+}, may be taken as the total difference between the energy of the free proton in the acid medium and the energy of this proton bound to the ring site which it has attacked, *minus an additional term* which reflects the energetic change of this site upon protonation. We have already assumed this latter effect to be independent of whether R is hydrogen or methyl; further, it is now assumed to be independent of the particular methylated benzene in which it is operative. Therefore

$$-RT \ln K/K_S = \mu\Delta\Delta E_\pi \quad (2)$$

where the subscript s denotes the arbitrarily chosen standard protonation reaction and μ is the proportionality factor relating the π-electron delocalization and free energy differences.

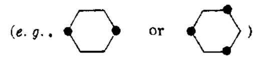
From this point the thermodynamic relations are formally the same as those developed for the hyperconjugation calculations. Thus

$$K/K_S = \frac{\sum\limits_i n_i \exp.[-\mu\Delta\Delta E_i/RT]}{\sum\limits_i (n_S)_i \exp.[-\mu\Delta(\Delta E_S)_i/RT]} \quad (3)$$

where the summation is over the individual protonated isomers, i, from the given aromatic and n_i is the number of ways isomer i may be formed in this reaction.

2. **Computations and Parameter Choices.**—The L.C.A.O.–M.O. formulation adopted was that described previously, *i.e.*, the Mulliken–Rieke overlap-included secular equation method[9] combined with a self-consistent charge redistribution procedure (the ω-technique) and bond order adjustment scheme. The mechanics of computation for the ions were also identical with those previously described.

The computations for the neutral molecules may be considerably simplified, however. It has been shown, specifically for the cases of neutral alternant hydrocarbon-like molecules with two different types of atoms

(*e. g.*, )

but apparently extendible to include cases with three or more types of atoms, that the delocalization energy is independent to a very good approximation of whether the calculation is made self-consistent or not.[10] For each of the neutral molecules of interest then, the change in delocalization energy due to methyl substitution (referred to benzene) may be expressed as $n\delta\beta_0 + \epsilon$, where n is the number of substituent methyl groups. Since ϵ is generally quite small (0.4% of the leading term for mesitylene, 0.3% for durene with $\delta = -0.1$ and ignoring the generally very small bond order corrections) it is convenient to take,

$$\Delta E_\pi \text{ } (n\text{-methylbenzene} - \text{benzene}) = n\delta\beta_0 \quad (4)$$

The ion energies were calculated employing the parameter values of ref. 2, *i.e.*, $S = 0.248$, $\beta_0 = -2.6$ ev. and $\mu = 1$. A grid of ω and δ values was examined. For the former the values 0, 1.1, 1.25 and 1.4 were employed; the δ values chosen were -0.1, -0.3 and -0.5.

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[6] G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

[7] The model used implies protonation at a ring site dearomatizes that site and effectively removes it from the conjugation system. Since the energy changes of the carbon itself are not considered, protonation of a methyl-bearing rather than hydrogen-bearing site is not distinguishable.

[8] For work described in the text as previously done and unaccompanied by a specific reference, see ref. 2. N.B., as in ref. 2, delocalization energy is the total mobile π-electron energy and therefore is not a synonym for resonance energy, as some have used it.

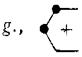
[9] R. S. Mulliken and C. A. Rieke, *J. Am. Chem. Soc.*, **63**, 1770 (1941).

[10] S. Ehrenson, *J. Phys. Chem.*, **66**, 706 (1962).

TABLE I

$\Delta\Delta E$ DEPENDENCE UPON δ,[a] $\Delta\Delta E = (-B\delta + C\delta^2)\beta_0$

Methyl[b] positions	Parent[c] hydrocarbon	B	C	Methyl[b] positions	Parent[c] hydrocarbon	B	C
..	Benzene (toluene)	−0.3548	−0.455	1,2,3	Hemimellitene (prehnetene)	0.3428	−0.263
		− .3494	− .105			.2880	.005
		− .3578	− .110			.2826	.001
		− .3666	− .089			.2678	.026
1	Toluene (*o*-xylene)	.0090	− .184	1,2,4	Pseudocumene (isodurene)	− .0646	.191
		− .1154	− .040			.1324	− .015
		− .1304	− .022			.1390	− .012
		− .1394	− .023			.1340	.008
2	Toluene (*m*-xylene)	− .3450	− .270	1,2,5	Pseudocumene (prehnetene)	.3262	− .135
		− .2266	− .066			.2382	− .016
		− .2252	− .049			.2310	− .003
		− .2254	− .039			.2230	.008
3	Toluene (*p*-xylene)	− .0026	− .242	1,3,4	Pseudocumene (durene)	.2196	.056
		− .0606	− .043			.2930	− .010
		− .0754	− .028			.2814	− .002
		− .0994	− .032			.2728	.001
1,2	*o*-Xylene (hemimellitene)	− .0510	− .021	1,3,5	Mesitylene (isodurene)	.6572	− .074
		.0058	− .013			.4052	− .025
		.0040	− .006			.3868	− .015
		.0044	− .005			.3652	− .002
1,3	*m*-Xylene (pseudocumene)	.3510	− .136	2,3,4	Hemimellitene (isodurene)	.0358	.087
		.1638	.020			.1896	− .020
		.1480	.024			.1934	− .016
		.1376	.019			.1782	.011
1,4[d]	*p*-Xylene (pseudocumene)	0	0	1,2,3,4	Prehnetene (PMB)	.3140	− .066
						.4190	− .044
						.4180	− .024
						.4072	− .009
1,5	*m*-Xylene (hemimellitene)	.3402	− .081	1,2,3,5	Isodurene (PMB)	.6560	− .273
		.1110	− .001			.5202	− .059
		.0908	.018			.5120	− .048
		.0840	.015			.4990	− .035
2,3	*o*-Xylene (pseudocumene)	− .0220	− .073	1,2,4,5	Durene (PMB)	.3170	− .186
		.0626	− .021			.3566	− .038
		.0486	.005			.3516	− .015
		.0434	.006			.3582	− .013
2,4	*m*-Xylene (mesitylene)	− .3428	− .074	1,2,3,4,5	PMB (HMB)	.6542	− .459
		− .0952	− .031			.6506	− .136
		− .0882	− .018			.6422	− .110
		− .0916	.042			.6334	− .089

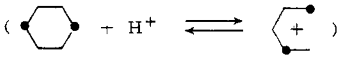
[a] Listed in column order for ω = 0, 1.1, 1.25, 1.4. [b] Positions occupied by methyl groups in the ion, *e.g.*, , are designated by 2,3. [c] Parentheses indicates protonation at methyl-bearing site. [d] Standard ion isomer.

Results and Discussion

1. Collation of Theoretical Results.—The results obtained from the grid of ω and δ values provide several insights into the important contributors to the energies. The individual ion energies, for example, when least-squares fitted for a given value of ω to the parabolic equation

$$E(\omega) = (a + b\delta + c\delta^2)\beta_0$$

referenced to their parent hydrocarbons, and then expressed relative to the values for the standard reaction



yield the parametric representations for $\Delta\Delta E$ found in Table I, *viz.*

$$\Delta\Delta E(\omega) = (A - B\delta + C\delta^2)\beta_0 \qquad (5)$$

The values of A are not presented since all are vanishingly small and apparently random (the largest is 0.0034, the average value of $|A|$ is 0.0006 ± 0.0004 and the standard deviation is 0.0007).

It is readily apparent from examination of this Table that (a) charge redistribution has a profound effect upon the values of $\Delta\Delta E$ computed; in almost every case the magnitude of this double energy difference is considerably different from the simple M.O. (ω = 0) result and usually but not always smaller. For some cases there is a rearrangement in the ordering of the $\Delta\Delta E$'s.

(b) The charge redistribution results are much more nearly linear with δ than are the corresponding values for ω = 0, as is evidenced by the appreciable sizes of the C's for the latter cases. Also, the average value of $|A|$ for ω = 0 is 0.0011 ± 0.0007, almost twice the size of this average when all values of ω are considered.

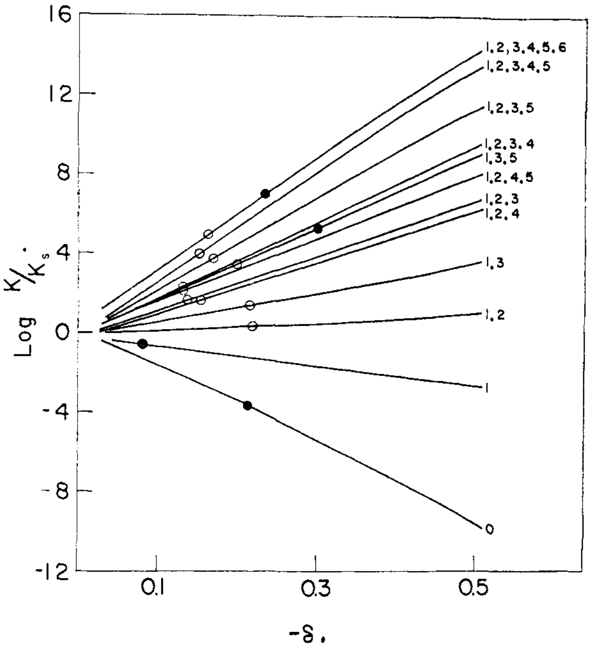


Fig. 1.—Dependence of the logarithm of the over-all equilibrium constants upon the inductive parameter of methyl, $\alpha = \alpha^0 + \delta\beta_0$. The number labels signify methyl positions in the parent aromatics. The open and closed circles indicate, respectively, the experimental values of McCaulay and Lien, and Mackor, *et al.*

(c) Surprisingly little difference exists for most cases among the $\Delta\Delta E$ values computed over the ω range 1.1 to 1.4.

Recognizing this insensitivity to ω, the value 1.25 was chosen for all comparisons to be made. This value is the same as used in the hyperconjugation calculations. Combining eqs. 2 and 5, log K/K_s values are computed and are shown in Fig. 1 as functions of δ for the range -0.1 to -0.5. The individual lines are labelled by numbers describing the methyl positions in the neutral hydrocarbons. It is of interest to note the approximate linearity of these plots bearing in mind the sum of contributions from the various isomers. This observation, in conjunction with conclusion (b), above, suggests the most important contributor to log K is the B value for the most stable isomer formed; examination of Table I confirms this point. Further, because of this approximate linearity, ω adjustments add no further flexibility to the values.

2. **Direct Comparisons with Experimental Results.**—Also shown in Fig. 1 are the experimental relative equilibrium values of Mackor, *et al.*,[5] (filled circles) and McCaulay and Lien[2] (open circles). Their results are placed upon the appropriate aromatic molecule lines from which the δ values necessary to reproduce these results may be determined, assuming the model employed is correct.[11]

It is an important fact that the experimental points from ref. 2 cluster in the δ range of -0.13 to -0.20. At the same time considerably more variation is to be found for the five points of the Mackor data. Choosing the δ value of -0.17 which represents an average for the former set, the relative K's may be back-deduced. These are to be found in the first column of Table II with the experimental results from refs. 3, 4 and 5.

The quality of agreement between the K's computed with this value of δ and each of the first two sets of data is seen to be comparable to that obtained with the hyperconjugation results. Where the latter correlation was found to quantitatively weaken for the highly substituted members of the series, however, the present comparison is seriously marred by the prehnetene–mesitylene order (and values) and the seemingly large value necessarily assigned to the methyl inductive effect to produce the tabulated correlation. The δ value of -0.17 corresponds to increases of approximately 0.5 ev. in the Coulomb integrals of the methyl-bearing ring carbons. Further, to satisfactorily fit the last column of experimental data of Table II, an even larger δ value of -0.3 (0.8 ev.) must be assumed. This choice yields K's for benzene, toluene, *m*-xylene, mesitylene and hexamethylbenzene relative to *p*-xylene of 10^{-6}, 0.01, 100, 300,000 and 10^9, respectively. Mackor found in his perturbation induction treatment that effects of essentially this size had also to be assumed.[5]

While it may not be possible to rule out inductive changes of this magnitude with complete certainty, it seems quite extreme to expect the replacement of a hydrogen atom by a methyl group to effect an almost *10% change* in the absolute magnitude of the Coulomb integral for the sp^2 carbon undergoing this substitution. Perhaps even more compelling an argument may be found in the following electronegativity comparisons. By the Mulliken method[12] which provides results essentially in agreement with the values on the Pauling electronegativity scale,[13] the methyl group is estimated to be zero to $^1/_2$ unit electropositive with respect to hydrogen. $(I + A)/2 \leq 7.0$ ev. is obtained for methyl from the values $I = 9.95$ ev.[14,15] and $A = -1.03$ ev.[15], corrected to refer to the vertical electron loss or acceptance processes from the sp^3 configuration of this radical. The given (uncorrected) affinity and potential values are for planar (or close to planar) methyl and therefore involve pπ electrons. The hybridization corrections are assumed to be the same as for the carbon *atom*, estimates of which are available from refs. 11 and 12. These are respectively 3.3 and 1.8 ev. for I and A for the planar to tetrahedral orbital geometry correction. If this electronegativity difference is to reflect an inductive effect on the order of $-0.3\beta_0$ to the substituted ring carbon, then substitution of a fluorine for a hydrogen should, by the same token, *inductively* change the Coulomb integral of such a carbon by at least 4 ev. This represents a change which is almost half the *absolute* integral value of this carbon and is on the order of $^1/_3$ the change

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[11] The data of Kilpatrick and Luborsky are not shown; they would be approximately as given by the open circles with somewhat more scatter.

[12] R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934).

[13] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 3rd Ed., 1960, p. 90.

[14] F. P. Lossing, K. U. Ingold and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 621 (1954).

[15] N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).

TABLE II

OVER-ALL EQUILIBRIUM CONSTANTS

	K_{eq} (relative to *p*-xylene)				
Hydrocarbon	Inductive model $\delta = -0.17$	McCaulay and Lien	Kilpatrick and Luborsky	Mackor, *et al.*	HCJ and inductive model
Benzene	10^{-3}	. . .	0.09	2×10^{-4}	$1\text{-}2 \times 10^{-4}$
Toluene	0.08	~0.01	0.63	0.25	0.11–0.13
o-Xylene	1.8	2	1.1	. . .	1.8
m-Xylene	10	20	26	300	90–110
p-Xylene	1	1	1	1	1
Pseudocumene	50	40	63	. . .	110–140
Hemimellitene	100	40	69	. . .	200–310
Durene	320	120	140	. . .	510–810
Prehnetene	1000	170	400	. . .	960–1700
Mesitylene	630	2800	1.3×10^4	2×10^5	$2\text{-}3.6 \times 10^4$
Isodurene	5000	5600	1.6×10^4	. . .	$0.6\text{-}1 \times 10^5$
Pentamethylbenzene	2.5×10^4	8700	2.9×10^4	. . .	$1.1\text{-}2.5 \times 10^5$
Hexamethylbenzene	1.6×10^5	8.9×10^4	9.7×10^4	1×10^7	$0.7\text{-}1.5 \times 10^6$

caused by formal ionization of an electron (the difference between the first and second ionization potentials of carbon is about 12 ev.).

Similar arguments would, as a further example, require bromine to change the Coulomb integral of iodine (in IBr compared to I_2) by at least half an ev. even though their electroaffinities, *i.e.*, $(I + A)/2$, differ by only $^3/_4$ ev.

Again, even granting the rough nature of the above estimates, these inductive effects are much too large. They would seem to be more consistent with changing atom X to atom Y rather than describing substitution of Y upon X where only an inductive effect is possible. The previous estimates of methyl inductive effects, generally much smaller than half an ev., would seem to bear out these conclusions.[16]

A more readily discernible defect of this model lies in the severe reversal by the theory of the experimental basicity order for mesitylene and prehnetine. The predicted order is opposite to those experimentally measured by composite factors of about 30 and 50 (data from refs. 2 and 3, respectively). It is indeed of interest to discover from Table I that this inversion may be directly attributed to the smaller than expected methyl substituent effects from the *ortho* and *para* positions compared to that from the *meta* position.

Viewing the protonation reactions as forming *ortho*, *meta* or *para* methyl substituted R^+ ions, the appropriate $\Delta\Delta E$ values referred to the reaction forming R^+ for $\delta = -0.2$ may be obtained to evaluate the *para–ortho* and *para–meta* $\Delta\Delta E$ ratios. The energy difference values and their ratios are illustrated for some of the possible *meta–para* comparisons in Table III. The average ratio for all possible *meta–para* pairs is 2.10 ± 0.06. Similarly, the average $\Delta\Delta E_p/\Delta\Delta E_o$ is 1.24 ± 0.02. Almost exact additivity is also found to exist within these comparisons. Twice the average ratio for the above R^+ ions substituted in both *meta* positions is 2.16 ± 0.08, in both *ortho* positions 1.26 ± 0.02. Specifically then, it is apparent how two *meta* methyl groups (in the principal ion isomer of prehnetene) are predicted to stabilize more strongly than one *ortho* group (in mesitylene) even with a statistical factor disadvantage (2 to 3).

Some attention to the possible meaning of these ratios in terms of the empirical separations of experimental substituent effects would now seem in order. The theoretical model chosen corresponds to the *I*-effect model of Taft and co-workers[17] with one important conceptual difference, *i.e.*, the direct field (electrostatic) interactions between substituents and reaction site have not been explicitly included.[18] The theoretical $\Delta\Delta E$ ratios should correspond to the *I*-ratios for given positions of substitution if these field effects were included.

TABLE III

THEORETICAL *meta versus para* METHYL INDUCTIVE EFFECTS[a]

($\delta = -0.2$)

R^+	ΔE_m	ΔE_p	$\Delta E_{ref.}$	$\Delta\Delta E_p/\Delta\Delta E_m$
0	−0.04702	−0.01601	−0.07594	2.07
1[b]	.00056	.03057	− .02698	2.09
	.00000			2.13
1,2	.02734	.05692	.00056	2.10
1,5	.04609	.07675	.01890	2.13
1,2,5	.06972	.10050	.04609	2.29

[a] All energies in units of β_0. [b] Two isomers are possible; in order 1,2 and 1,4.

That they do not precisely when the latter are excluded is of interest; I_p/I_m is unity (the only direct test). If the theoretical model correctly pictures the inductomesomeric (polarizability) effect, then either the field effect is greater from the *meta* than from the *para* position and is important enough to make I_p/I_m equal 1. or this ratio is not precisely one for the strong electrophilic reactions at ring sites. It should be recalled that the theoretical $\Delta\Delta E_p/\Delta\Delta E_m$ computed with the hyperconjugation model[2] (~12) correlated well with the R_p/R_m ratio of ~10 given by Taft for such reactions. This would seem to suggest that the resonance effect *R* is more easily realized in quantum chemical terms, probably because *I* does contain other effects not proportional to the inductomesomerism postulated.

It does not seem possible at present to explain the difference between the predictions of the theo-

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(16) *Cf.*, C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, 2052 (1953); A. Lofthus, *J. Am. Chem. Soc.*, **79**, 24 (1957).

(17) *Cf.*, R. W. Taft, Jr., and I. C. Lewis, *ibid.*, **81**, 5343 (1959).

(18) These interactions have, however, been incorporated implicitly to some unknown degree by the empirical choice of the parameters α, β and ω from experimental data on systems where direct field effects are doubtlessly operative.

retical models and the empirical results beyond the above speculations. At any rate, accepting the corrections to the relative *meta* to *para* effects suggested by the empirical treatment can only worsen our agreement with the experimental basicities cited. What the field effects from the *ortho* positions would do is yet another point which must be considered. Unfortunately, even empirical estimations are lacking here.

4. Combination of Hyperconjugative and Inductomesomeric Models.—One further model may be easily considered with the results available. We may combine the hyperconjugative and inductomesomeric models under the assumption that the major effects of methyl substitution on the basicities of interest are thereby all included. The discussion concerning our ignorance of the steric and field effects, above and in ref. 2, as well as an appreciation of the experimental difficulties in obtaining the basicities for comparison should of course be borne in mind.

The assumption has been made that this combination may be accomplished by simple addition of the effects in terms of energies of the separate models. This implies that the cross-term(s) between these π-electron effects are small relative to the terms considered, which does not seem unreasonable here.[19] If we further assume that the hyperconjugation effects are correctly calculated, the amount of inductomesomeric interaction necessary to improve the correlation between theory and experiment may be calculated.

The most convenient pair of reactions available for this calculation are the protonations of mesitylene and hexamethylbenzene (HMB), each of which forms only one ion isomer to any practical degree. Therefore, in analogy to eq. 3, with μ again unity

$$K_{\mathrm{HMB}}/K_{\mathrm{Mes.}} = \frac{6 \text{ exp. } -[(\Delta\Delta E_{\mathrm{HMB}}{}^{\mathrm{HCJ}} + \Delta\Delta E_{\mathrm{HMB}}{}^{\mathrm{I}})/RT]}{3 \text{ exp. } -[(\Delta\Delta E_{\mathrm{Mes.}}{}^{\mathrm{HCJ}} + \Delta\Delta E_{\mathrm{Mes.}}{}^{\mathrm{I}})/RT]}$$

or

$$\log\,(K_{\mathrm{HMB}}/K_{\mathrm{Mes.}})_{\mathrm{Obsd.}} = \log\,(K_{\mathrm{HMB}}/K_{\mathrm{Mes.}})_{\mathrm{HCJ}} + \log\,(K_{\mathrm{HMB}}/K_{\mathrm{Mes.}})_{\mathrm{I}} - \log 2.$$

The log inductive contributions are calculated to be 1.04 and 1.24 for the McCaulay and Lien, and Mackor results, respectively, from this equation. The δ values necessary to provide these contributions may be computed from the quadratic equations obtained from Table I; these are found to be respectively -0.06_9 and -0.07_3. The final column of Table II contains the range of relative over-all equilibrium constants calculated with these two values of δ. Note that this method of computing the methyl inductive effects does not depend upon the values of the mesitylene and HMB equilibrium constants with respect to the *p*-xylene value but only relative to each other. As a result, neither has been fixed to correspond to the experimental values. Interestingly enough the inductive contributions (δ's) from the McCaulay and Lien and Mackor data are quite similar and the results of the combined model agree as satisfactorily as we might expect with both sets of results. Certainly these theoretical results are in much better agreement with the experimental over-all equilibrium values than are the results from either model alone.

Some further comparisons are possible. Individual ion isomer equilibrium constants may be computed employing the combination model and compared to the $(n_i k_i/n_s k_s)$ values from Table II of ref. 2 and to some interesting n.m.r. results obtained by MacLean, *et al.*[20] The equilibrium constant ratio calculated for the formation of 2H$^+$- compared to 6H$^+$-pentamethylbenzenium ion using the hyperconjugation model alone is about 3:2 (statistical factor included). This prediction of protonation to be favored at a methyl-bearing rather than unsubstituted ring site disagrees with the n.m.r. spectra obtained for pentamethylbenzene (PMB) in HF. When the combined model is employed, however, this ratio is calculated to be ~1:2 (1:3 if induction is assumed as important energetically as hyperconjugation and ~1:40 if induction is the only effect with $\delta = -0.3$). The combined model produces the best agreement with the observed spectra which indicates most of the protonation to occur at the unsubstituted ring site with a lesser contribution, indicated by satellites on the methyl-hydrogen resonance peaks, from the ion isomer presumably formed by attack at the equivalent 2 and 4 positions of the hydrocarbon.

The π-electron densities are also available from the computations described and may be compared to quantities from ref. 20b where the ring proton n.m.r. shifts observed for the aromatic carbonium ions of interest were attributed to positive charges established on the ring sites. These experimentally derived positive charges are shown in Fig. 2a. Figs. 2b and 2c give the theoretical charges computed for the benzenium and 6H$^+$-pentamethylbenzenium ion respectively employing the hyperconjugation model; 2d is for the former ion assuming induction only. In all cases the parenthesized numbers are the charges normalized to the non-protonated ring sites.

Several interesting points arise from comparisons of these numbers. First, the relative *ortho*, *meta* and *para* charges predicted by the hyperconjugative and inductive models are virtually indistinguishable (Figs. 2b and d) and, second, these results are in fairly good agreement with the experimentally derived values. Somewhat less charge is theoretically predicted for the *meta* positions than is observed; it has been established however that no reasonable inductive or hyperconjugative parameters are capable of raising the positive charge on the *meta* position to 0.17. Third, the hyperconjugation model results for the benzene and PMB ions indicate that the electrons donated by the substituent methyl groups to the ring are distributed quite evenly (the total contribution from these substituents is 0.18 electrons). And fourth, the charge per hydrogen in the $=H_2$ quasi-group is predicted to change by less than 0.02 electrons be-

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(19) Perturbation theory can roughly justify this combination, recognizing the relatively small sizes and parallel directions of the methyl effects considered. In general, however, identification of the contributions of cross-terms or coöperative interactions is a difficult problem in both theoretical and empirical studies: *cf.*, R. S. Mulliken, *Tetrahedron*, **5**, 253 (1959).

(20) (a) C. MacLean, J. H. van der Waals and E. L. Mackor, *Mol. Phys.*, **1**, 247 (1958). (b) C. MacLean and E. L. Mackor, *J. Chem. Phys.*, **34**, 2208 (1961).

tween the benzenium and 6H$^+$-pentamethylbenzenium ions, Figs. 2b and c, even though a difference of ~10^6 in K_{eq} exists. Employing the combined model, this charge difference on the hydrogens is reduced to less than 0.01 electron.

At the same time, somewhat less than 0.1 of a positive charge is predicted to be established on each quasi-group hydrogen in the hyperconjugation model (~0.05 in the combined model) for both carbonium ions. Whether this agrees with the n.m.r. spectra observed for such hydrogens in some carbonium ions is rather difficult to decide, however. *E.g.*, from ref. 20b, the protons in the CHR groups of 9,10-dimethyl-1,2-benzanthracene in an aqueous fluoroacetic acid, BF_3 solvent, and of 9,10-dihydro-9,10-dimethylanthracene in CCl_4 appear at 69 and 130 cps upfield (referred to benzene). In 9,10-dimethylanthracene (in the fluoroacetic acid, BF_3 solvent) the position is 102 cps; for HMB in $HF{\cdot}BF_3$ the position is 131 cps. PMB and pyrene in $HF{\cdot}BF_3$ have their CH_2 group hydrogen peaks at 102 and 122 cps., respectively. Further examination of these systems would seem worthwhile in light of these results.

The most significant features of the combined model may be summarized as

(1) In all cases, the theoretical relative K_{eq}'s lie between those of McCaulay and Lien, and Kilpatrick and Luborsky on the one hand and those reported by Mackor, *et al.*, on the other. All sets agree qualitatively, *i.e.*, with regards to order.

(2) The deficiencies of the pure inductive and pure hyperconjugative models have been overcome by use of the combined model. For the former, the prehnetine-mesitylene order has been corrected; for the latter the predicted weak basicities of the highly methylated aromatics have been raised. The relative isomer concentrations predicted for protonated pentamethylbenzene are also found to agree better with the results of n.m.r. examination of this aromatic in $HF{\cdot}BF_3$.

(3) The inductomesomeric effect of methyl now seems more realistic. The δ values of -0.06_0 and -0.07_3 indicate that substitution of a methyl group for a hydrogen results in a Coulomb integral increase on the order of 0.15 to 0.20 ev. for the substituted ring carbon.

(4) Dividing the energy contributions of the inductomesomeric model by the total $\Delta\Delta E$ for each compound reveals this type of interaction to be responsible for between 20 and 45% ($\delta = -0.06_0$) and between 25 and 50% ($\delta = -0.07_3$) of the total energy determining the relative K_{eq}'s. The average percentages are 29 ± 6 and 33 ± 6.

Conclusions.—The inductive model which should more precisely be labelled as inductomesomeric is found to be qualitatively satisfactory in correlating the relative basicities of the methylbenzenes. However, to be solely responsible for the noted spreads in these basicities, each methyl group must change the Coulomb integral of the attached ring carbon by 0.5 to 0.8 ev. which is a quite unreasonably large effect. As well, the basicity of 1,2,3,4-tetramethylbenzene (prehnetene) is predicted to be greater than that of mesitylene, in strong disagreement with experiment. This reversal may be attributed directly to the relatively small *para* to *meta* ratio predicted for the effects from these positions. This ratio is found to be approximately two, to be compared to the *I*-effect ratio of unity found by Taft from empirical linear free energy correlations: the latter doubtlessly contain field effects which were not treated in the theoretical model. Had they been included, even greater disagreement with the experimental values for this pair, would be noted. Other correlations would likely also be weakened.

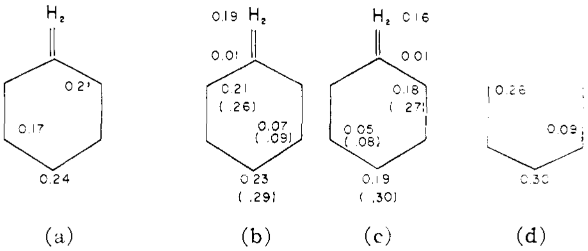

Fig. 2.—π-electron deficiencies in aromatic carbonium ions: a, benzenium ion, from n.m.r. proton shifts; b and c, benzenium and 6H$^+$-pentamethylbenzenium ions, respectively, from the hyperconjugation model; d, benzenium ion from the inductomesomeric model.

Combination of the inductomesomeric and hyperconjugative models removed the disagreements with experiment found through the use of either alone. The correct order for all 13 methyl benzenes could be reproduced and no noticeable trends in comparison with any of the experimental data could be detected through the series. Induction as pictured is found to contribute on the average about one-third of the total energy of stabilization of the cations, leaving two-thirds due to hyperconjugation. The methyl group is here found to change the neighboring (ring) carbon Coulomb integral by 0.15 to 0.20 ev.

Acknowledgments.—The several valuable discussions on this subject held with Professor R. S. Mulliken are appreciated. The computational assistance of Mr. Tracy Kinyon is also gratefully acknowledged.