

419. *Hyperconjugation. Part II.* Charge Distributions in Propylene and Some Methylbenzenes.*

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The π -electron densities in propylene and some polymethylbenzenes have been computed theoretically and correlated with their substitutional reactivity.

The effect of successive methyl substituents on the charge distribution in the benzene ring is found to be strictly additive.

Attention is drawn to the need for caution in deducing the manifestation of the hyperconjugative effect from inadequate studies of rates of reaction.

THERE are several factors which might affect the substitutional reactivity of a conjugated molecule; these include (i) stabilisation of initial and transition states due to conjugation or hyperconjugation, (ii) steric effects, (iii) the permanent charge distributions, and (iv) the polarisability of electron orbits. Indeed, when as in many hydrocarbons, the charge density is the same at each atom, this last factor appears to be most important. Nevertheless, many properties of unsaturated organic molecules may be correlated qualitatively with the distribution of electrons in the isolated molecules, for the permanent charge distribution reflects the tendency of the different positions to accept or donate electrons for incipient bond formation with nucleophilic or electrophilic reagents. The electron densities are now calculated for propylene and some methylbenzenes by the method of molecular orbitals, the parameters being the same as used previously (Part I).

When overlap is included (Chirgwin and Coulson, *Proc. Roy. Soc., A*, 1950, 201, 196) the total density of electrons at the μ th carbon atom is given by

$$q_{\mu} = \sum_{j=1}^m n_j x_{j\mu} \gamma_{j\mu}$$

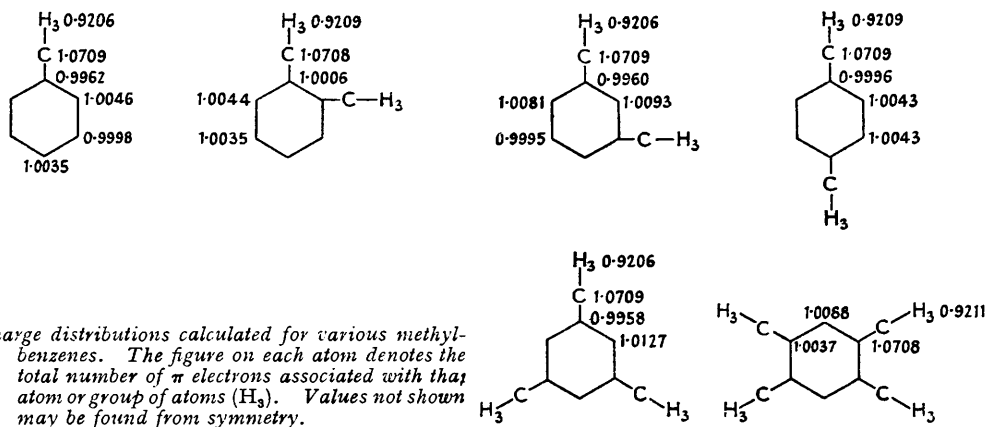
where

$$\gamma_{j\mu} = \sum_{\nu} S_{\mu\nu} x_{j\nu}$$

* Part I, preceding paper.

the summation being extended over the occupied orbitals j and the atoms ν , adjacent to μ . The calculated values of the total π -electron densities obtained in this way are shown in the following diagram.

As far as the actual numerical values are concerned, the difference between these compounds and an unsubstituted alternant hydrocarbon is not very large, and considerably smaller than what is obtained when overlap is ignored.



Comparison of the electron densities in toluene with those of polymethylbenzenes shows that the additivity which was manifested with respect to hyperconjugation energies applies equally well to the charge distributions. Thus knowing the charge distribution in toluene, that in any polymethylbenzene may at once be written. A similar result was obtained by Coulson and Jacobs (*J.*, 1949, 971) for the charge distributions in aniline and aminostilbenes. They found that the charge migrations in the 4 : 4'-compound were very little different from what would have been expected from a superposition of the migrations in the 4- and 4'-compounds, severally. The same principle was substantiated by Coulson and Longuet-Higgins (*J.*, 1949, 2805) for the charge distributions in some aza-derivatives of naphthalene and anthracene.

Recently, Condon (*J. Amer. Chem. Soc.*, 1948, 70, 1963) calculated the relative rates of chlorination for a series of polymethylbenzenes and obtained results in good agreement with the experimental values. The additivity found here provides theoretical justification for the assumption made by Condon, *viz.*, that each methyl group in a polymethylbenzene exerts the same activating influence as in toluene. Since the polar effects of methyl groups are small such a result might perhaps have been expected. When, however, two groups of opposing mesomeric character are situated *ortho* or *para* to each other, then mutual interaction is of profound importance.

The attack of electrophilic and nucleophilic reagents on conjugated systems has been discussed from two points of view. On the one hand (Wheland, *J. Amer. Chem. Soc.*, 1942, 64, 900), the π -electron energies of the transition complexes involved in substitution reactions were computed. It was found that for a given reagent R and a series of different points of attack on a given aromatic A, the reactivity is greater the lower the π -electron energy in the transition state RA. On the other hand, it has been shown (Longuet-Higgins and Coulson, *Trans. Faraday Soc.*, 1947, 43, 87) that, if two positions in a conjugated molecule differ appreciably in electron density, the centre with the higher charge, q , is more susceptible to attack by electrophilic reagents, whereas nucleophilic reagents substitute more easily at the position of lower electron density. This conclusion, it has

been shown (Coulson and Longuet-Higgins, *Rev. Sci.*, 1947, **85**, 929), is dependent on the fact that at the moment an anion or cation begins to react on part of a conjugated system the variation of the π -electron energy is directly proportional to the electron density in the region under attack and to the value in this region of the field due to the charge of the reagent. In this way, then, the close correspondence between electron density in the ground state and observed chemical behaviour is explained.

In the case of propylene, "atom 4" (cf. Figure) has the higher charge density and might be expected to be the centre most easily attacked by an electrophilic reagent. Hence a proton should add across the double bond in such a way that it becomes linked to the greater number of hydrogen atoms. In this way the "normal" Markownikoff addition is accounted for. In a similar manner the electron distribution in toluene may be correlated with its reactivity for, since the *ortho*- and *para*-positions have the greatest calculated electron densities, electrophilic reagents should attack these positions. This is in accordance with the well-known directive influence of the methyl group in the benzene nucleus.

Now the permanent charge distribution in toluene would indicate that in nitration, for example, more *ortho*-compound should be formed than *para*-compound whereas the reverse is actually the case, *i.e.*, the partial rate factor for the *para*- is greater than that for the *ortho*-position. The electronic theory of organic reactions assumes that differences in reaction rates are due only to activation-energy differences, the entropy of activation being constant. Since examination of models shows that in most *ortho*-disubstituted benzene derivatives the substituents are closer than the sum of their van der Waals radii, the proportion of *ortho*-isomer should be less than that calculated from simple considerations of electron distribution.

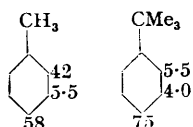
Experimental evidence for the hyperconjugative effect was early provided by studies of electrophilic substitution reactions. Thus electrophilic substitution of 4-*isopropyl*toluene occurs predominantly at the 2-position, a result which is the reverse of the accepted order of the inductive effect. On the basis of hyperconjugation, however, the position *ortho* to the methyl group should be more susceptible to electrophilic attack than the position *ortho* to the *isopropyl* group, and this was in fact Baker's explanation (*J.*, 1935, 1846). Le Fèvre (*J.*, 1933, 980) on the other hand regarded the results as demonstrating steric repulsion due to increasing size of the alkyl groups. The interpretation therefore is not entirely free from ambiguity.

A few years ago it was pointed out (Crawford, *Quart. Reviews*, 1949, **3**, 226) that relative rate data alone provided inadequate evidence for indicating the operation of the hyperconjugative effect. Recently, however, Nelson and Brown (*J. Amer. Chem. Soc.*, 1951, **73**, 5605) and Cohn, Hughes, Jones, and Peeling (*Nature*, 1952, **169**, 291) studied the nitration of toluene and *tert.*-butylbenzene. The latter workers determined the isomer distributions as well as the relative rates, thus providing results which may be interpreted

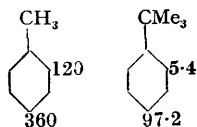
unambiguously and with some assurance. The relative rates of nitration are Me : Bu^t = 1.00 : 64 and these figures, when combined with the isomer distributions, gave the partial rate factors shown inset.

Since there are no large differences in the partial rate factors of the *para* and *meta* positions of these compounds, the large difference for the *ortho* positions is definite proof of the importance of steric requirements for *ortho*-substitution. The slightly greater partial rate factor for the *para*-position of *tert.*-butylbenzene as compared with toluene would seem to show the operation of the inductive effect; this would be expected to be enhanced in *tert.*-butylbenzene as compared with toluene. These results suggest that the hyperconjugative effect is of minor importance in nitration.

Berliner and Berliner (*J. Amer. Chem. Soc.*, 1949, **71**, 1195) found the relative rates of bromination of toluene, ethylbenzene, *isopropyl*benzene, and *tert.*-butylbenzene to be 100 : 70 : 40 : 18, these values being in good agreement with those of de la Mare and Robertson (*J.*, 1943, 279). Berliner and Berliner appreciated that increasing size of the alkyl group might account for their results and therefore considered it. Unfortunately they did not determine isomer distributions under the conditions of their experimentation but used values quoted in the literature. They calculated the partial rate factors for the *para*-



positions only and showed that this position in toluene is almost three and a half times more reactive than the corresponding position in *tert.*-butylbenzene. By combining the above relative rates with the same isomer distribution as used by Berliner the partial rate factors shown inset for the *ortho*-positions were obtained.



The very large decrease on passing from toluene to *tert.*-butylbenzene shows the operation of a marked steric effect. Furthermore comparison of this diminution (120 : 5.4) with that which occurs in nitration (42 : 5.5) shows that the steric effect is probably more pronounced in bromination than in nitration.

The greater reactivity of the *para*-position in toluene as compared with the corresponding position in *tert.*-butylbenzene would perhaps indicate that hyperconjugation is of some significance in bromination. It must be stressed, however, that this conclusion is based on an assumed isomer distribution.

The desirability of determining the *ortho* : *meta* : *para* ratios at the same time as the relative rates is emphasised. In the past, conclusions concerning the manifestation of the hyperconjugative effect have been drawn from rather inadequate rate studies. Further progress in attributing rate changes unambiguously to certain specific electronic or steric influences can only be made when rate differences are studied under conditions which isolate a single simple mechanism and are accompanied by accurate energies and entropies of activation.

Grateful acknowledgment is made to Professor C. A. Coulson, F.R.S., for suggesting the work. His great interest and helpful advice are also much appreciated.

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[Received, September 4th, 1952.]

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