

While equation (6) is expected to hold at most velocities, it probably fails at higher velocities. This is the result of the interaction of lateral diffusion in the gas phase with eddy diffusion<sup>3,4</sup>. The latter involves shuttling molecules back and forth from rapid to slow streamlines, an effect that acts essentially to increase the lateral diffusion coefficient,  $D_1$ . This additional lateral diffusion increases in proportion to flow velocity, and is thus negligible at low velocities.

Equation (6), along with necessary extensions to the present model, should be useful in suggesting ways of changing channel size, temperature, surface area, and other surface properties in a manner that is beneficial to the separability of component zones.

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<sup>1</sup> Giddings, J. C., *J. Chem. Phys.*, **31**, 1462 (1959).

<sup>2</sup> Giddings, J. C., *J. Chromatog.*, **3**, 443 (1960).

<sup>3</sup> Giddings, J. C., *J. Chromatog.*, (in the press).

<sup>4</sup> Giddings, J. C., *Nature*, **184**, 357 (1959); **187**, 1023 (1960).

### Dipole Moment Data and Hyperconjugation

It is being increasingly recognized<sup>1</sup> that the evidence for hyperconjugation from dipole moment data needs to be re-interpreted. Since the electro-negativity of an  $sp$  or  $sp^2$  carbon differs from that of an  $sp^3$  carbon, the primary moments of the  $C(sp)-C(sp^3)$  and  $C(sp^2)-C(sp^3)$  bonds are not zero, and the dipole moments of molecules such as toluene, methylacetylene, etc., may arise solely from this effect.

Recently I have published a method for the calculation of bond moments based on the principle of electronegativity equalization<sup>2</sup>, and I have now applied it to many molecules, including toluene, propylene, and butene-1. In these molecules, the atomic and homopolar dipoles cancel each other and the total moments should be given by the resultant of the vectorial sum of the primary bond moments.

From the data by Pritchard and Skinner<sup>3</sup>, the electronegativities of  $sp^3$  carbon and  $sp^2$  carbon are 2.63 and 2.88, respectively. Using the screening-constants given by Kohlrausch<sup>4</sup>, we can calculate<sup>2</sup> the value of the charge transferred in a  $C(sp^2)-C(sp^3)$  bond:  $q = 0.049$  e.u. Table 1 shows that the calculated primary moments of toluene, propylene, and butene-1, given by the product  $eqR_0$  (column 4), agree extremely well with the experimental values for the dipole moments.

Table 1

Molecule	$q$ (e.u.)	$R_0$ (Å.)	$eqR_0$ (D.)	$\mu_{exp}$ (D.)
$CH_3-C_6H_5$	0.049	1.52	0.357	$0.36 \pm 0.02$
$CH_2=CH-CH_2$	0.049	1.53	0.359	$0.35 \pm 0.01$
$CH_3-CH_2-CH=CH_2$	0.049	1.54	0.362	$0.38 - 0.30$

Bond distances from "Tables of Interatomic Distances", Special Publication No. 11, Chemical Society (London, 1958).  
Dipole moments from Marriott, A. A., and Buckley, F., "Table of Dielectric Constants and Dipole Moments of Substances in the Gaseous State", Nat. Bur. Stand. Circ. No. 537 (Washington, D.C., 1953).

These results can be valid only if the opposed  $C(sp^2)-H$  and  $C(sp^3)-H$  bond moments are equal. Now, the calculated  $C(sp^2)-H$  bond moment in ethylene is 0.40 D., and the calculated  $C(sp^3)-H$

bond moment in methane is 0.21 D., but the positive charge in the  $sp^3$  carbon of the molecules under consideration (due to charge transfer to the  $sp^2$  carbon) increases the  $C(sp^3)-H$  bond moment considerably; an iterative calculation shows that the two types of  $C-H$  bond moments cannot differ by more than 0.05 D.

It seems that the dipole moment evidence for hyperconjugation is not valid, although, since the bond moment is a ground-state property, hyperconjugation may exist in excited states and accordingly be important for the interpretation of the spectra and reactivity of molecules.

A detailed account of this work is to be submitted elsewhere.

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<sup>3</sup> Pritchard, H. O., and Skinner, H. A., *Chem. Revs.*, **55**, 745 (1955).

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### Reaction of Aromatic Compounds with a Chlorinated Coal and Aluminium Chloride

VAN KREVELEN *et al.*<sup>1</sup> have reported on the coupling of pitch molecules by chloromethylation and subsequent condensation under the influence of a Friedel-Crafts catalyst, while Iyengar, Banerjee and Banerjee<sup>2</sup> have claimed the alkylation of coals with benzyl chloride and aluminium chloride. But in these laboratories a similar type of reaction between a chlorinated low-rank coal (containing about 50 per cent of hydrolysable chlorine) and several aromatic compounds, in the presence of aluminium chloride, has given inconclusive results which suggest that alkylation may not have occurred during the reaction with benzyl chloride.

A chlorinated low-rank coal (Ellington High Main 81.0 per cent carbon, 5.1 per cent hydrogen, dry ash-free, N.C.B. Rank Code No. 802), prepared as previously described<sup>3</sup>, was treated with an aromatic compound (Table 1) under suitable conditions. The dry chlorinated coal (7 gm.) was stirred with 100 ml. carbon tetrachloride (nitrobenzene was used as a solvent in the case of aniline) and 0.5-1.0 gm. of anhydrous aluminium chloride. A blue or green colour developed at this stage, suggesting initial formation of a complex with aluminium chloride. No hydrogen chloride was evolved. The aromatic compound (aniline, toluene, chlorobenzene, dimethyl aniline or dimethylbenzylamine) was then added (2-10 gm.) and the mixture refluxed for about 7 hr. After cooling and filtering, the product was washed with carbon tetrachloride and then dried at 100°C. *in vacuo*.

The results in Tables 1-2 show that, while the changes in elementary composition correspond with the expected reaction, the results do not definitely confirm the alkylation, since there was no corresponding release of hydrogen chloride. The increase in ash content suggests the presence of aluminium compounds in the products. It is doubtful if the results quoted by Iyengar, Banerjee and Banerjee<sup>2</sup>, which do not include ash or chlorine contents,