## Energy-Level Treatment of Reaction Data

In a recent paper[1] it was shown that satisfactory explanations of certain aromatic side-chain reaction data are provided by correlation of the alterations in electron density which arise from the various electron displacements (inductive, inductomeric, mesomeric and electromeric) of the substituents with the energy-levels in the initial, transition and final states of the reaction. Such changes, relative to the energy-levels in the unsubstituted parent molecule as a reference standard, were represented by assigning arbitrary numerical values to each polar effect and thus obtaining a quasi-quantitative expression of their resultant effects on the activation energy of the reaction.

In the absence of data regarding the absolute magnitudes of the various polar effects such numerical values were, of necessity, somewhat arbitrary and in unknown units, although both in their signs and *relative* magnitudes, they satisfied the known order of electron release or attraction by the various mechanisms.

A recent paper by Audsley and Goss[2] has now provided reliable values for the primary (μ_P), induced (μ_I) and mesomeric (μ_M) dipole moments of the four monohalogenobenzenes. This data should provide at least approximately *quantitative* values for the corresponding electron displacements in the reaction previously used as an illustration[1], namely, the Menschutkin reaction

$$p - X.C_6H_4.CH_2.Br + C_5H_5N \rightarrow X.C_6H_4.CH_2.\overset{+}{N}C_5H_5\}\overset{-}{Br}.$$
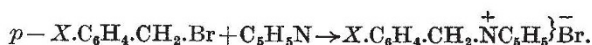
The only magnitudes which must still remain hypothetical are those (a) of the electromeric ($+ E$) effect and (b) of the reduction in the inductive ($- I$) effect, of the halogen substituent in the transition state. Changes in energy-levels due to permanent polarization effects will be proportional to some (unknown) constant multiplied by μ. Using the same values for the two unknowns as those previously employed, but substituting the values of $10^2 \mu$ (which give whole numbers of convenient magnitudes) for the various permanent polarizations, the following results are obtained :

correctness of the whole method of energy level treatment of reaction data and also suggests that the numerical values assigned to the electromeric effects probably give an approximate estimate of the *relative* magnitudes of these effects for the halogen group of substituents.

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[1] Baker, *Trans. Faraday Soc.*, **37**, 632 (1941) ; cf. Baker and Hemming, *J. Chem. Soc.*, 191 (1942).
[2] *J. Chem. Soc.*, 497 (1942).

Agricultural Research Institutes and the Future

Dr. B. A. Keen's article in Nature of September 5, p. 282, does well to invite the attention of research workers to the possible future developments in agricultural education and research in Great Britain. It may be regretted that Dr. Keen sought to restrict his remarks to arable agriculture. I venture to hope, with Sir George Stapledon, that our future agriculture will be ley farming, and that most of our farmland will cease to be classifiable into the rigid categories of 'grass' and 'arable'. This, however, is a minor point.

Dr. Keen's suggestion for co-ordinated field experimentation may be warmly welcomed, and I would stress the importance of ensuring that research localities be carefully chosen to cover the principal classes of soil. Too often in the past, expensive and well-planned field experiments have been laid down without reference to soil type. Unfortunately, the national soil survey has not been in progress long enough for even a preliminary soil map to be made ; but a considerable amount of information is available, and it would not be difficult to examine the suitability of proposed experimental areas in order to avoid the selection of non-typical sites.

Finally, although co-ordination of post-war agricultural research is inevitable, it may be hoped that the organization will not be too rigid. If a com-

RELATIVE ENERGY-LEVELS IN THE REACTION

$$p-X.C_6H_4.CH_2.Br + C_5H_5N \rightarrow X.C_6H_4.CH_2.\overset{+}{N}C_5H_5\}\overset{-}{Br}$$

| X | Reduction in energy-levels in the ground state | | | | Reduction in energy-levels in the transition-state | | | | | $E_g - E_a$ |
	μ_P	μ_I	μ_M	Total (Eg.)	μ_P	μ_I	μ_M	E	Total (Eg)	Reference standard
H	—	—	—		—	—	—			
Cl	−184	−75	+95	−164	−184	−74	+95	+2	−161	−3
Br	−172	−70	+74	−168	−172	−69	+74	+4	−163	−5
F	−176	−72	+104	−144	−176	−65	+104	∼0	−137	−7
I	−156	−64	+51	−169	−156	−63	+51	+7	−161	−8

It will be seen that the new values predict exactly the same order for the velocities of the various *p*-halogenobenzyl bromides as that previously indicated, namely, activation energies decreasing in the order H > Cl > Br > F ≈ I, in agreement with the experimental velocity sequence I ≈ F > Br > Cl > H.

This agreement, using magnitudes which have a definite physical basis, strongly supports the essential

promise is necessary between a system of complete freedom for the individual investigator and a totalitarian research system, let us err on the side of freedom even at the risk of a certain amount of overlapping.

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