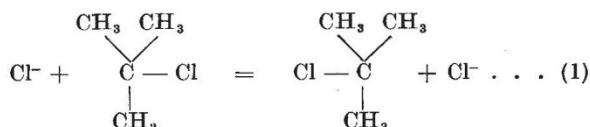


LETTERS TO THE EDITORS

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Calculation of Steric Hindrance

It seems possible to account for the steric effect of non-reacting groups on substitution rates on the lines of the following scheme, illustrated here by the example of the symmetrical substitution of *t*-butyl chloride by chlorine ions:



In the transition state, the four *t*-butyl carbons will be co-planar and the methyl groups will cause least obstruction if arranged in either of the two symmetrical positions one of which is shown in Fig. 1. This is represented in terms of a Fisher model in which the carbon atoms have the usual covalent radii of 0.77 Å. and the van der Waals' radii of 1.5 Å., while the corresponding values for the hydrogen atoms are 0.32 Å. and 1.2 Å. respectively. The valencies of the central carbon atom are co-planar, with an angle of 120° between them; the valencies of the other carbon atoms are at the tetrahedral angle. The position of the chlorine particles in the transition state will be such that the line joining their centres to that of the central carbon will be perpendicular to the plane of the carbon atoms. Further, the carbon chlorine internuclear distances will be equal. From the latest calculation of the transition state, this carbon chlorine distance has been found to be 2.3 Å., which is practically equal to the sum of the covalent radius of carbon and the ionic radius of chlorine. These chlorine particles will have a van der Waals' radius of 1.8 Å.

While a more detailed consideration, on which we will report elsewhere, shows that the presence of hydrogen atoms on the central carbon (as in the reaction $\text{Cl}^- + \text{CH}_3\text{Cl}$) does not obstruct the approach of the chlorine particles to the required distance, their replacement by methyl groups as in reaction (1) does cause an obstruction. The extent of this obstruction is indicated in Fig. 1, where the shaded sections show the areas over which penetration of the hydrogen atoms by the chlorine particle occurs. The distances between the centres of these obstructing hydrogen atoms and the centre of the chlorine particle can be calculated as 2.43 Å., which is 0.57 Å. less than the sum of the van der Waals' radii of hydrogen and chlorine.

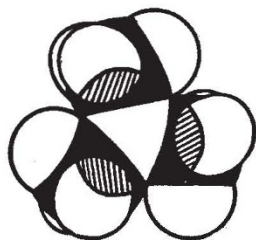


Fig. 1.

To carry out reaction (1) we have to perform six times this compression as corresponds to the penetration of the chlorine particles into the spheres of the three hydrogen atoms pointing forwards and the three hydrogen atoms pointing backwards in Fig. 1. The corresponding energy of compression has been calculated.

The difference between the covalent and van der Waals' radius of an atom is practically the same

(0.8 Å.) as that between the covalent and negative ion radius. Thus the sum of the covalent radius of carbon and the ionic radius of chlorine will be practically equal to the sum of the van der Waals' radius of carbon and the covalent radius of chlorine. Thus a fair representation of the transition state can be obtained with the Fisher models by setting to each convex side of the central carbon the flat surface of a chlorine atom. (For the central carbon with co-planar valencies a model of the benzene carbon may be used.) This is shown, in the absence of steric hindrance, in Fig. 2, where the chlorine particles

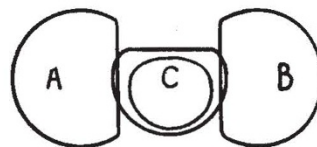


Fig. 2.

A and *B* have the covalent radius 0.99 Å. and the van der Waals' radius 1.8 Å., while the corresponding values for the carbon atom *C* are 0.77 Å. and 1.5 Å. The distance between the centres *A-C* and *B-C* is the transition state distance 2.3 Å.

By replacing *t*-butyl by *s*-propyl or ethyl, the steric effect is much reduced; partly by the lessening of the number of points of compression and partly by the possibility of avoiding compression by a bending of the carbon chlorine bonds away from the larger groups. A very considerable steric hindrance can be predicted for the reactions of the neopentyl halides.

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May 7.

¹ Baughan and Polanyi, *Trans. Faraday Soc.*, **37**, 648 (1941).

Vorticella as an Indicator Organism for Activated Sludge

It has been recognized for a number of years that the type of protozoan fauna inhabiting activated sludge in a sewage purification plant of this type affords a useful indication of the condition of the sludge. In 1936, Arden and Lockett¹ stated that they considered this test as the most useful in determining the activity of sludge and listed the common types associated with varying conditions. More recently, Barritt² has further enlarged their general findings. It has been concluded that the presence of ciliates and particularly the peritriches to the exclusion of other classes of Protozoa generally indicates a ripe active sludge. But the scope of the utility of this test has been limited by the fact that they were usually qualitative and therefore complementary only to the quantitative chemical analyses.

Preliminary observations of the activated sludge in the plant at Huddersfield indicated that the ciliates were so limited in variety as to afford a simplified case for determining quantitatively the fluctuations in their numbers and in particular of the *Vorticella* species in relation to the quality of the effluent produced. This limitation in species is probably due to the high percentage of chemical trade wastes in the sewage and is paralleled by a similar limitation of the macro-organisms in the percolating filters³.

With the exception of Saturday and Sunday, daily counts of the *Vorticella* species in the channel liquor were made by dilution and centrifuging so that one tenth of a millilitre was fully examined. Correction