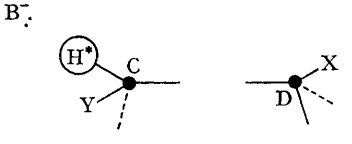
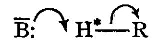
Nuclear Magnetic Resonance and Bimolecular Eliminations

By W. T. DIXON
(*Bedford College, Regent's Park, London N.W.1*)

As two molecules approach one another, their electrons tend to be redistributed so that the potential energy is kept as small as possible at any given moment. Eventually the system reaches a point where the potential energy is at a maximum (*i.e.*, at the transition state) and thereafter it loses potential energy as it disintegrates into the products of the interaction. In this Communication we shall consider the period before the transition state is reached in nucleophilic *E*2 or *E*1*cB* reactions[1].



As the base B:⁻ approaches a hydrogen atom H* in the molecule H*–R, its negative charge becomes dissipated to a more or less extent over the fragment R at the same time as the bond (covalent) B–H is formed. It is reasonable to suppose that the more easily the negative charge drifts away from B:⁻ in this situation, the easier it will be for the hydrogen atom H* to be eliminated. There may or may not be synchronous loss of Y⁻ from C or X⁻ from D. Now bonds between hydrogen atoms and nonmetals are usually relatively independent of other bonds in a molecule, and it follows from this that the distribution of charge in the R fragment in the initial stages of the reaction



is the same as that in the negative ion R⁻. In simple MO theory, the delocalisation of the charge from B:⁻ occurs mainly *via* the highest occupied MO of R⁻, which is the same as that occupied by the odd electron in the radical R·. Furthermore, it has been shown that the spin density at a proton in R· is approximately proportional to the spin–spin coupling of that proton with the H* nucleus.[2] Now the greater the degree of delocalisation of the odd electron in R·, the lower is the coupling constant between H* and a given type of vicinal proton; also, from the above arguments, the more favourable is elimination of H* under nucleophilic attack. As a test for these ideas we examine first some effects of conformation in alkene derivatives:

TABLE. *Coupling constants*[3] J (*c./sec.*) *in some halogenoethylenes*

	$CH_2:CH_2$		$CH_2:CHBr$	
Molecule	*cis*	*trans*	*cis*	*trans*
J	11·6*	19·1†	0·1	15·2
J/J_{ref}	1	1	0·61	0·80

	$CH_2:CHCl$		(*cis*) $CHCl:CHCl$		(*trans*) $CHCl:CHCl$	
Molecule	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
J	7·3	14·6	5·3	—	—	12·1
J/J_{ref}	0·63	0·76	0·46	—	—	0·63

† Reference.

From the Table we can see that maximum delocalisation, and hence preferred elimination, occurs when a proton is *trans* with respect to a halogen atom. This is to be expected from the coupling constants in ethylene, which indicate that more of the excess of negative charge tends to collect on the atom *trans* rather than *cis* with respect to H*. In a similar way we would expect *trans*-elimination to be favoured in cyclohexyl halides (J_{trans}~12, J_{gauche}~4 c./sec.)[3] but *cis*-elimination when vicinal atoms are held in eclipsing positions (*e.g.*, in cyclopropanes J_{cis}~9, J_{gauche}~5 c./sec.).[3] A special case of *cis*-elimination occurs when aryl halides (J_{ortho}~9, J_{meta}~2·5, J_{para}~1 c./sec.) react with certain nucleophiles to give benzyne intermediates. The so called Saytzeff rule can also be explained, in these terms, for from the vicinal coupling constants[3] *i.e.*, CH_3CH_3 (8), $(CH_3)_2CH_2$ (7·3), and $(CH_3)_3CH$ (6·8 c./sec.), we would expect preferred elimination from tertiary carbon [*e.g.*,: $(CH_3{}^1)_2{\cdot}CH^2{\cdot}CH^3{\cdot}Cl{\cdot}CH_2{}^4{\cdot}CH_3{}^5$ $J_{1,2}$~6·8, $J_{4,5}$~7·3 c./sec., therefore elimination of H^2 preferred.]

If we wished to compare rates of elimination from different molecules, the situation becomes more complex, since we then have to take into account the ease of loss of halogen ion *etc.*, and this is affected by solvent and the substituents on the D carbon atom.

(*Received, March* 17*th*, 1967; *Com.* 262.)

[1] K. A. Cooper, M. L. Dhar, E. D. Hughes, C. K. Ingold, B. J. MacNulty, and L. I. Woolf, *J. Chem. Soc.*, 1948, 2043, and following papers; D. V. Banthorpe, "Studies in Chemical Structure and Reactivity," ed. J. H. Ridd, Methuen, London, 1966, ch. 3; D. V. Banthorpe, "Elimination Reactions", Elsevier, New York, 1963.

[2] W. T. Dixon, *Theor. Chim. Acta*, 1966, **6**, 359; *Chem. Comm.*, 1966, 870; *Mol. Phys.*, 1966, **11**, 601.

[3] J. W. Elmsey, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance", Pergamon, Oxford, 1965, ch. 10.