Intermediates in the Chlorine-sensitized Photo-oxidation of Methane

BOTH methyl radicals and hydrogen atoms have been proposed as chain-carriers in the photo-chlorination of methane[1-3]; and, although the former are generally favoured, in neither case has direct evidence been produced[4]. However, the theoretical heat content change of the corresponding partial reaction would be approximately zero, if methyl radicals were involved, but endothermic by 21 kcal./mole, on the basis of hydrogen atom formation.

From a recent study of the reaction, certain facts, taken in conjunction with earlier results on the photochlorination of hydrogen[5], point in each case to the same conclusion. The enhanced effect of oxygen as inhibitor suggests the removal of some other intermediate than hydrogen atoms, as does also the absence of inhibition by gaseous hydrogen chloride. Yet more convincing is evidence from the examination of end-products. Instead of hydrogen peroxide[6], the formation of formaldehyde has now been clearly demonstrated. Titanic acid was used in the former case, and the detection and estimation of formaldehyde was effected by chromotropic acid[7], the action of which was not vitiated by the presence of chlorine, although a reaction between chlorine and formaldehyde interferes with the quantitative aspect[8].

W. I. H. WINNING

Chemistry Department,
University of Edinburgh.
Nov. 18.

[1] Coehn and Cordes, Z. phys. Chem., B, 9, 1 (1930).
[2] Tamura, Rev. Phys. Chem. Japan, 15, 86 (1941).
[3] Steiner and Watson, Farad. Soc. Discussion, 2, 89 (1947).
[4] Noyes and Leighton, "The Photochemistry of Gases," 288 (Reinhold Publishing Corporation, 1941).
[5] Ritchie and Norrish, Proc. Roy. Soc., A, 140, 112, 713 (1933).
[6] Norrish, Trans. Farad. Soc., 27, 471 (1931).
[7] Bricker and Johnson, Indust. and Eng. Chem., Anal. Edit., 17, 400 (1945).
[8] Krauskopf and Rollefson, J. Amer. Chem. Soc., 56, 2542 (1934).

Halogen Replacement in Covalent Halides

PREPARATIVE experiments involving halogen substitution in mixed halides of silicon[1] have emphasized the need for obtaining some comparative measure of the ease of replacement of halogen atoms in these covalent halides. Since no such study appears to have received deliberate attention, we suggest a simple theoretical basis upon which suitable experiments for this purpose may be designed. Simplifying assumptions must necessarily be introduced into such a discussion, and we suggest that it will suffice to relate ease of replacement to bond strengths and electron affinities, and to steric factors amenable to simple geometrical treatment. Our discussion refers particularly to a displacement reaction of the type

$$Y^- + R_3SiX \rightarrow R_3SiY + X^-,$$

considered to proceed bimolecularly according to a Heitler–London mechanism.

Following Dewar[2], we assume initially that the contribution to the total activation energy due to charge displacement will be $\varepsilon(A_Y - A_X)$, where ε is the fractional displacement of charge at the transition state, and A_Y and A_X the electron affinities of Y and X respectively. If the bond Si—X has at this stage been reduced to a fraction α of its original strength and the bond Si—Y has developed to a

fraction β of its final strength, then the bond energy of the transition state will be given by $\alpha E_{Si-X} + \beta E_{Si-Y}$, and the contribution to the activation energy due to formation and breaking of bonds will be

$$(1 - \alpha)E_{Si-X} - \beta E_{Si-Y}.$$
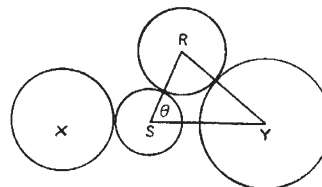
The total activation energy may therefore be written

$$\{\varepsilon A_Y - \beta E_{Si-Y}\} - \{\varepsilon A_X - (1 - \alpha)\ E_{Si-X}\} - E^*,$$

where the additional term $-E^*$ allows for other possible bond interactions excluding steric effects.

For two rather similar substituents X' and X'' in molecules R_3SiX' and R_3SiX'' competing for a particular attacking reagent Y^-, the respective values of E^* will not differ greatly, and the α values may be taken as approximately equal to $(1 - \varepsilon)$. Hence, for two such substituents the relevant $(A_X - E_{Si-X})$ values should, apart from steric considerations, afford an approximate measure of the ease of replacement, the reaction involving replacement of the substituent having the greater $(A_X - E_{Si-X})$ value possessing the lower activation energy.

In certain cases, as in the trimethylhalosilanes, steric effects may be expected to be sufficiently small to enable a direct test of the applicability of this expression ; indeed, results of experiments in which pairs of different halides of type Me$_3$SiX (where X is F, Cl or Br) are allowed to compete for methyl magnesium bromide are in accord with the expected influence of the $(A_X - E_{Si-X})$ values.

In other series of compounds in which steric effects cannot be reduced sufficiently, it would be necessary to keep these effects constant so far as possible, and we suggest that the following considerations may serve as a guide. We now consider a general case where R is sufficiently large in comparison with the central atom (designated S in the diagram) for the size of the R groups to determine closeness of packing as the attacking group (Y^-) approaches the molecule, for example, R_3SiX.

Then on geometrical grounds only, the steric factor will be smaller, the closer Y^- can approach S ; that is, the internuclear distance SY within an arrangement of closest packing will provide a measure of the ease (or difficulty) of replacement. This internuclear distance $SY = SR\cos\theta + \sqrt{YR^2 - SR^2\sin^2\theta}$, and in terms of covalent radii is $(r_S + r_R)\cos\theta + \sqrt{(r_Y + r_R)^2 - (r_S + r_R)^2\sin^2\theta}$.

Now the replacement reaction may be considered as involving competition between Y^- and X^- for attachment to the central atom, provided that X^- remains in the solution. Hence (sterically) the ease of replacement should be a function of SX/SY, possibly analogous to the inverse square law ; and since a power law will probably be involved in the major terms expressing the forces between S and Y, and S and X, it follows that to keep the steric effect approximately constant the value of SX/SY at the transition stage must be kept constant. The required condition is that the substituent groups be chosen so that :