LETTERS TO THE EDITORS

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Influence of Substitution on Organic Bond Strength

ATTEMPTS to establish the strength of organic bonds by studying the rate of decomposition of gaseous compounds have been made with success by F. O. Rice¹, but no systematic information on the influence of substitution on bond strength has been obtained. The problem was approached by R. A. Ogg² by a study of the breaking of the carbon-iodine bond in various compounds, and the present results were obtained in pursuing the same line by a new method. The vapour of the iodides at low pressure (0.01 mm.) and diluted with a carrier gas (6 mm. nitrogen or hydrogen) was passed through a tube maintained at 300–500° C., and the products were condensed and analysed for iodine and hydrogen iodide.

The assumption from which we started, that the rate-determining process is the unimolecular disruption of the C-I bond, was confirmed for ethyl iodide by varying the experimental conditions; in the other cases, however, it could only be shown that the rate of bond breaking was the main factor. Nevertheless, the large variation in the rates of decomposition (10,000 fold at 430°) justifies a comparison of C-I bond strength from the relative decomposition rates. The bond energies tabulated below were calculated from the approximate relationship

$$\log k = -Q/RT + 13,$$

using the values of k for the lowest temperature at which measurement was possible, the other conditions being comparable for all the iodides.

Iodide	Suggested bond energy	
Ethyl	52.5 kcal.	
Vinyl	56.6	Partial double-bond character.
Phenyl	54.0	
Allyl	39.0	
Benzyl	44.0	Radical degeneracy
Acetonyl	45.5	
<i>t</i> -Butyl	45.1	
Benzoyl	44.5	
Acetyl	(50.7)	

Taking ethyl iodide as our zero of reference, we note the manifestation of partial double bond character in vinyl iodide and in phenyl iodide, which is to be explained by a degeneracy of the type³

On the other hand, benzyl, allyl and acetonyl iodides clearly indicate the degeneracy of the free radical resulting from conjugation of the unshared electron with the double bond or the benzene ring.

These two effects appear to affect jointly the C-I

bond in benzoyl iodide which is weakened, but to a lesser extent than in benzyl iodide. The somewhat uncertain value for acetyl iodide may be left undiscussed; but attention should be directed to the strong reduction in bond strength in *t*-butyl iodide. This points to a degeneracy of the free radical of the type

in which the representation containing the double bond is present in nine different forms, as compared with only three forms of this type resonating in the ethyl radical⁴.

The magnitude by which the bond strength appears to vary in our experiments is of the order which might be theoretically expected. For example, in the case of allyl iodide and benzyl iodide the resonance energies of the radicals were calculated at 15.4 kcal.⁵ and 15 kcal.⁶ respectively, while our experiments indicate values of 13.5 kcal. and 9 kcal. The agreement would be improved if the resonance energy of the ethyl radical which might amount to 2–3 kcal. were taken into account.

As regards our absolute values, we note that the average bond energy attributed to C-I of about 45 kcal. is based on a C-H value of about 87 kcal.⁷ On the other hand, all estimates agree that the energy required to break the first C-H bond in methane is more than 95 kcal.⁸ and that in consequence C-I in methyl iodide is at least 53 kcal. This disagrees with the value of 43 kcal. found by Ogg² for methyl iodide, as well as for ethyl and *n*-propyl iodides, and lends support to our result of 52.5 kcal. for ethyl iodide.

E. T. BUTLER.
M. POLANYI.

The University,
Manchester.

¹ Rice, F. O., *et al.*, *J. Amer. Chem. Soc.*, **54**, 3529 (1932); **55**, 4245 (1933); **56**, 214 (1934).

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³ Brockway, L. O., Beach, J. V., and Pauling, L., *J. Amer. Chem. Soc.*, **57**, 2705 (1935). Brockway, L. O., and Palmer, K. J., *J. Amer. Chem. Soc.*, **59**, 2181 (1937). Ketelaar, J. A. A., *Rec. Trav. Chim.*, **58**, 266, 302 (1939).

⁴ Evans, M. G., and Polanyi, M. discuss this type of resonance in a forthcoming paper.

⁵ Coulson, C. A., *Proc. Roy. Soc., A*, **164**, 383 (1938).

⁶ Pauling, L., and Wheland, G. W., *J. Chem. Phys.*, **1**, 367 (1933).

⁷ Pauling, L., "The Nature of the Chemical Bond", 53.

⁸ v. Hartel, H., and Polanyi, M., *Z. phys. Chem.*, **11**, 97 (1931). Trenner, N. R., Morikawa, K., and Taylor, H. S., *J. Chem. Phys.*, **5**, 203 (1937). Burton, M., *J. Chem. Phys.*, **7**, 1072 (1939).

⁹ Ogg, R. A., *J. Amer. Chem. Soc.*, **56**, 526 (1934).