

possible that, whilst one of the components obtained is due to oxidised beryllium, the other is due to the pure metal. This possibility is now being investigated.

Two other points of interest are observable in the spectrogram. First, a faint absorption line appears at the short-wave edge of beryllium  $K\alpha$ . This absorption sets in at about 111.1 Å. Secondly, there is quite a strong satellite observable on the long-wave side of  $O K\alpha$  at about 24.6 Å. More precise determinations of these wave-lengths will be published later.

Physics Laboratories,  
University College,  
London, W.C.1.

F. C. CHALKLIN.

<sup>1</sup> *Phil. Mag.*, **10**, 600; 1930. See also: Faust, *Phys. Rev.*, **36**, 161; 1930. Prins, *Z. Phys.*, **69**, 618; 1931. O'Bryan and Skinner, *Phys. Rev.*, **44**, 602; 1933.

<sup>2</sup> See Morand and Hautot, *Comptes Rendus*, **195**, 1070; 1932; **197**, 521; 1933. Prins, *Z. Phys.*, **81**, 507; 1933. F. C. and L. P. Chalklin, *Phil. Mag.* (in the press).

### Dynamics and Mechanism of Aliphatic Substitution

SLATOR<sup>1</sup> observed that alkyl halides and symmetrical ethylene di-halides react bimolecularly with sodium thiosulphate in water, but that the velocity of reaction with iodochloroethane and bromochloroethane was independent of the concentration of thiosulphate. The phenomenon under discussion is the transition in kinetic order of a reaction due to a very slight modification in the structure of one of the reactants. The problem has been discussed by E. D. Hughes and Ingold<sup>2</sup>, who reveal varied and more reliable instances of the same phenomenon. For example,  $\beta$ -phenylethyltrimethylammonium hydroxide decomposes bimolecularly, whereas halides of the corresponding *p*-nitro derivative decompose unimolecularly.

The velocity of hydrolysis of both ethyl chloride and tertiary butyl chloride depends on their concentration, but only in the former case is it influenced by the concentration of alkali. The elimination of methyl alcohol and tertiary butyl alcohol from substituted sulphonium hydroxides are processes of the second and first order respectively (E. D. Hughes and Ingold<sup>3</sup>). According to the theory of Ingold, relating to reactions of type *B*, high cationic stability of the rejectable group and low nucleophilic activity of the reagent-anion tend to favour a unimolecular mechanism, which in turn admittedly implies a relatively long life to the activated organic ion.

The question may now be raised whether the kinetic distinction observed between two similar but specific chemical reactions under ordinary conditions would persist at totally different concentrations. In principle it is possible for the order of reactions of  $B_1$  and  $B_2$  respectively to become reversed below and above a critical concentration (*c*) of the reagent anion; *c* (in gram-molecules per litre) would be related to the average life-time (*t*) of the activated organic reactant (in seconds) by the equation

$$c = \frac{A}{t} \sqrt{\frac{\mu}{T}}$$

$\mu$  is the reduced mass of the molecules concerned; and *A*, which is a function of the molecular diameters, is approximately 11. From Slator's data, *t* for iodochloroethane becomes about  $5 \times 10^{-10}$  second. The Lindemann mechanism thus leads to plausible results when applied to reactions in solution; but it is noteworthy that change in kinetic order due to variations in the concentration, although sought<sup>4</sup>,

has not yet been found. This fact, and the demarcation between mechanisms  $B_1$  and  $B_2$  may have a common origin in the limited range of dilution conventionally employed.

There is no incompatibility between the two hypotheses. On the other hand, Lindemann's theory, accepted as the explanation of a well-known effect discovered by Hinshelwood in gaseous reactions, is in a sense complementary to Ingold's theory, which derives its support from the successful prediction of the course of organic elimination reactions.

E. A. MOELWYN-HUGHES.

Physikalisch-Chemisches Institut,  
Frankfurt-am-Main,  
Germany.  
Jan. 6.

<sup>1</sup> *Trans. Chem. Soc.*, **85**, 1286; 1904.

<sup>2</sup> *NATURE*, **132**, 933, Dec. 16, 1933.

<sup>3</sup> *Trans. Chem. Soc.*, 1571; 1933.

<sup>4</sup> Stewart and Bradley, *J. Amer. Chem. Soc.*, **54**, 4183; 1932.

### Atmospheric Pressure and the Ionisation of the Kennelly-Heaviside Layer

EVIDENCE of a connexion between meteorological conditions in the troposphere, and the behaviour of radio waves reflected from the Kennelly-Heaviside layer has been noted by Colwell<sup>1</sup> in America and by Ranzì<sup>2</sup> in Italy. Again, Stagg<sup>3</sup> has discovered a relation between the diurnal variation of barometric pressure at Aberdeen and the general state of magnetic conditions over the earth. There appears little doubt that some relation exists between conditions in the troposphere and the ionosphere.

Evidence which appears to bear on the fundamental nature of the relationship has been obtained as a result of two series of experiments carried out in Melbourne and Sydney during 1931 and 1932.

In the first series, carried out at the University of Melbourne with the collaboration of Mr. R. O. Cherry, during November-December 1931, and March-April 1932, the average night intensity of the sky wave from the transmitter 3 AR (610 kc./sec.) was measured at a distance of 90 km. From the second series, carried out between Melbourne and Sydney on a frequency of 1415 kc./sec. during October 1932, it was possible to find directly the maximum ionisation density in the *E* layer from observations of the rays of known angle which penetrated that layer.

From both series a very close direct correlation is evident between the average night-time ionisation density in the *E* layer and the barometric pressure at ground-level measured at a time ranging from 12 to 36 hours after the ionisation observation. For example, if on any night the average ionisation density is greater than that on the preceding night, then the barometer invariably rises within the time interval mentioned. In most cases the time lag is near to twelve hours, the greater lag being associated with slower moving disturbances.

The results obtained in the first series of experiments are in complete accord with those of Colwell, though the explanation offered differs considerably from his. Thus, Colwell considers that the "E layer is concentrated in the regions of low pressure"<sup>4</sup>, resulting in a stronger post-sunset signal. On general theoretical grounds it is much more probable that a stronger night signal on the frequency of KDKA (980 kc./sec.), upon which station Colwell's measurements were made, would result from a decreased intensity of ionisation in the absorbing portion of the