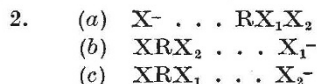


with the mutual proximity of the two Cl atoms; and we should find, in particular, that *cis* di-chloro ethylene reacts faster than the *trans* isomer. All this has been confirmed by experience⁴. Moreover, the accelerating effect of halogen substitution should increase in the series F, Cl, Br, I, which represents the sequence in which the tendency to react with sodium increases; which also has been confirmed over a wide range of observations⁴.

In the electron transfer discussed above the attachment of the electron to the halide molecule is clearly a manifestation of the *electron affinity* of the latter particle. The accelerating influence of a negative substituent on the reactivity of a molecule is thus seen to go parallel to the substituent's contribution to the electron affinity of the latter.

The observed parallelism in the influence of negative groups on the rate of sodium reaction as compared with the rate of substitution by a negative ion^{4,5} can be explained by the presence of additional resonance in the transition state, similar to that which we derived for the sodium vapour reaction. In a substitution reaction $X^- + \text{RX}_1\text{X}_2 = \text{XRX}_2 + \text{X}_1^-$ the transition state will have the *threefold* resonance:

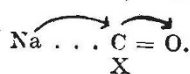


where the component state *c* is due to the presence of the negative group X_2 .

The latter type of resonance can be related to the mechanism postulated by A. Lapworth in his classical studies on the formation of the cyanhydrine anion from RCO and CN^- . In this sense we could write, for example, the accelerating effect which C = O has on the substitution of acetylhalide by halogen ions,

as being due to the tendency $\text{X}^- \dots \overset{\curvearrowright}{\text{C}} = \overset{\curvearrowleft}{\text{O}}$. We

could even extend this to represent the rapid reaction of the acetylhalides with sodium vapour in the sense



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camera described by Wilson². At room temperature photographs of the hexagonal structure were obtained. Above 230° C. the photographs were not very satisfactory owing presumably to grain growth, as the metal is too soft to be finely filed. The lines present, however, did not fit in with the face-centred cubic structure, and measurement of a photograph taken at 262° C. with copper *K*-radiation showed that the pattern was mainly that of a body-centred cubic structure with $a = 3.874 \pm 1$ Å. Some of the hexagonal structure also was present. In the accompanying table a description of the photograph is given, and the observed and calculated positions of the lines are compared. Allowing for a systematic difference due to absorption, it will be seen that the evidence for the body-centred cubic structure is quite conclusive.

| Indexes and Radiation | Intensity | sin ² θ | |
|-----------------------|-----------|--------------------|--------|
| | | Obs. | Calc. |
| 110 β | medium | 0.0645 | 0.0643 |
| 110 α | strong | 0.0791 | 0.0789 |
| 10 $\bar{1}$ 1 α | medium | 0.0847 | 0.0848 |
| 10 $\bar{1}$ 2 α | very weak | 0.1427 | 0.1412 |
| 200 α | medium | 0.1582 | 0.1578 |
| 211 β | medium | 0.1945 | 0.1929 |
| 211 α | strong | 0.2383 | 0.2366 |
| 220 α | weak | 0.3174 | 0.3155 |
| 310 β | weak | 0.3227 | 0.3216 |
| 310 α | medium | 0.3963 | 0.3944 |
| 321 β | very weak | 0.4533 | 0.4502 |
| 321 α | medium | 0.5540 | 0.5521 |
| 330 } α ₁ | weak | 0.7095 | 0.7087 |
| 411 } | | | |
| 330 } α ₂ | weak | 0.7131 | 0.7122 |
| 411 } | | | |
| 422α ₁ | very weak | 0.9452 | 0.9449 |
| 422α ₂ | very weak | 0.9500 | 0.9497 |

The values of the lattice parameters of the hexagonal structure from our photographs are: $a = 3.4496 \pm 2$ Å., $c = 5.5137 \pm 4$ Å., $c/a = 1.5984 \pm 1$, at 18° C.: these values are corrected for refractivity.

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Sept. 4.

¹ Sekito, S., *Z. Krist.*, **74**, 189 (1930).

² Wilson, A. J. C., *Proc. Phys. Soc.*, **53**, 235 (1941).

¹ Butler and Polanyi, *NATURE*, **146**, 129 (1940); Baughan and Polanyi, *NATURE*, **146**, 685 (1940); Baughan, Evans and Polanyi, *Trans. Far. Soc.*, **37** (1941).

² Evans and Polanyi, *Trans. Far. Soc.*, **34**, 11 (1938).

³ Pauling, L., "The Nature of the Chemical Bond", p. 235 (1940).

⁴ Polanyi, M., "Atomic Reactions", Williams and Norgate (1932).

⁵ Meer and Polanyi, *Z. phys. Chem.*, **B**, **19**, 164 (1932).

Structures of Thallium

THALLIUM at room temperature has a close-packed hexagonal structure, but this transforms at 230° C. into another structure which is given in the literature as face-centred cubic. This is based on the work of Sekito¹, who used specimens quenched from the melt and specimens containing other elements; his results cannot therefore be considered decisive, particularly since he does not give the purity of his materials.

We have taken photographs of Hilger thallium No. 7011 (99.995 per cent Tl) in the Debye-Scherrer

Propagation of Lightning Leader Strokes

THE interesting suggestions recently put forward by Bruce¹ with regard to the mechanism of leader strokes are largely based on data relating to glow-to-arc transition. However, laboratory experiments indicate that such transition is a cathode-dependent phenomenon, a fact specifically stated in two of the articles² cited by Bruce. The current at which the glow develops into an arc is a most variable quantity³ and is governed by the shape and material of the cathode.

Most authorities⁴ seem agreed that, in the glow discharge, electrons are liberated from the cathode by positive ion bombardment or by photo-electric effect, and also in the gas by collision processes or by