

## Visible Glow Discharge at Very Low Potentials

It is a well-known phenomenon in gas-filled photo-electric cells that, if the cathode is exposed to illumination, a faint glow is visible within the cell at anode potentials well below the striking potential, that is, below the potential at which the self-maintained discharge starts. Owing to the fact that, as a rule, this glow is of low brightness as compared with the light source which is used to cause the photo-electric emission, it is difficult to establish the anode potential at which the glow begins.

This glow can, however, be observed in complete darkness if a photo-cell of the silver-oxygen-caesium type, which is sensitive to infra-red radiation, is exposed to a light source through an infra-red filter. By experiments with such a photo-cell containing argon, it was found that a glow is visible at anode potentials as low as 18 volts (the current in this case was 1  $\mu$ amp.), that is, at a potential only slightly above the ionization potential of argon. This means that a glow commences as soon as ionization by collision takes place.

When the anode potential is gradually reduced from higher values to 20 volts the discharge, which at first fills the whole cell, recedes to the immediate neighbourhood of the anode. This effect is to be expected, because at low anode potentials the photo-electrons will not have sufficient energy to cause ionization by collision until they have almost reached the anode.

I am indebted to Dr. G. B. Harrison, of Messrs. Ilford, Ltd., for directing my attention to the fact that in gas-filled photo-cells a glow is visible at low anode potentials if the cells are observed in darkness.

A. SOMMER.

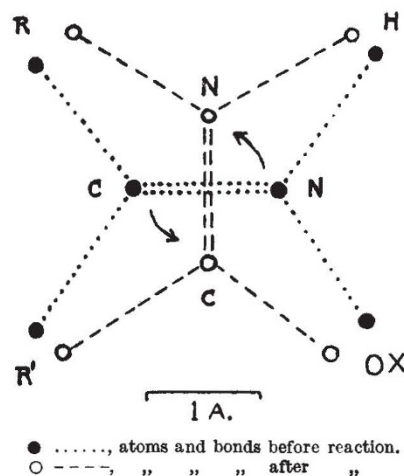
Cinema Television, Ltd.,  
London, S.E.26.  
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## Mechanism of the Beckmann Rearrangement

I HAVE recently received my copy of *Chemical Reviews* for December 1944 and find in it yet one more survey of the Beckmann rearrangement and confession of failure to 'explain the mechanism' in the classical sense.

The diagram shows scale drawings of the oxime before rearrangement (full circles and dotted lines) and the  $RN:CR'OX$  resulting from the change (open circles and dashed lines) superimposed so as to have the same centre of gravity, and minimum rotational movement of the heaviest parts. Both compounds are represented with a proton attached to the nitrogen atom: this is probably the case under most reaction conditions, but is not a necessary feature of the views advanced here. It will be seen that it is only the carbon and nitrogen atoms which move an appreciable distance. The only other movements required are of the atoms directly attached to these, and these movements can all be taken up in the first instance by a  $10^\circ$  bending of the links. The contribution of this to the activation energy can be estimated from the spectroscopic data on bending frequencies—which are mostly of the order of  $600\text{ cm.}^{-1}$ —and amounts to between 20 and 50 kcal./mole depending on the masses of the attached atoms.

The 'mechanism' of a reaction in the classical sense means the order in which valency bonds are broken and made. We are familiar with a partial abandonment of this in the recognition that in a reaction such as halogen exchange between halide ions and alkyl halides there is a simultaneous 'make' of one link and 'break' of another, and it is further recognized that whenever the activation energy of a reaction is less than the dissociation energy of the bonds which are broken, some such simultaneous make-and-break occurs. In more detail, as the nuclear configuration passes from that of the reactants to that of the products, it passes through an intermediate or transition form which may be regarded as a distortion of either. Therefore distorted forms of the initial and final bond systems are both possible approximately canonical forms for the



electronic configuration in the transition state, and the actual configuration will be a resonance hybrid of these. This results in a diminished restoring force or 'weakness' towards any thermal vibration which tends to carry the reactant over into the product.

The description of the previous paragraph applies word for word to the Beckmann change. However, (1) it is probably necessary for the slow thermal movements of the attached groups to be in a favourable phase for reaction to occur (otherwise larger bending of the links is involved) and (2) when reaction does occur the number of bonds made and broken is relatively large, so that the reaction appears complicated. But it is essentially a one-stage mechanism defying further analysis, and, moreover, the word 'migration' is an extremely misleading term. The mechanism as outlined explains all the qualitative features of the Beckmann and allied reactions—the intramolecularity, the *trans* migration, and so on, and also semi-quantitatively the effects of substituents in the groups. It may be added that a similar explanation can be drawn up for the pinacol-pinacolone group of rearrangements, including as a natural consequence the Walden inversion which occurs on the carbon atom which remains capable of optical activity.

BRYAN HIGMAN.

Pentevale, Dunstone Road,  
Plymstock,  
Plymouth.  
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