

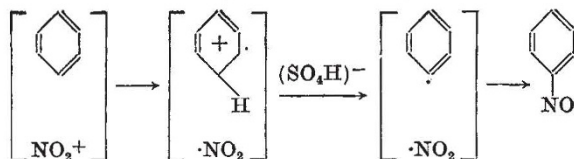
LETTERS TO THE EDITORS

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Univalent Electron Transfers in Aromatic Nitration?

WE have been studying the kinetics of aromatic nitration on the lines indicated in a prefatory publication¹, and in consequence have an opinion to offer on the question indicated by the title, which has been raised more than once recently, notably in an interesting article by Kenner².

Any process of co-ordination between an atom with an unshared electron pair and another with an open sextet can conceptually be dissected into a univalent electron transfer and a succeeding homopolar union. It has not hitherto been usual to assume such a step-wise mechanism in the absence of some evidence of dimerization or other characteristic reaction of the radicals which would be formed intermediately. However, Kenner has proposed a representation which suggests that this evidential requirement can be obviated by supposing the radicals throughout their life to remain "within the sphere of each other's action". His nitration mechanism is expressed, for the nitration of benzene in the presence of sulphuric acid, in the following approximate manner (the brackets indicate 'spheres of action'):



Whereas Kenner's ideas undoubtedly have important applications, we think that, in this particular case, the assumption which might have accounted for the general absence of radical dimerization in aromatic nitration does not in fact provide a simple and entirely satisfactory escape from this and similar difficulties. The above scheme depicts three molecular encounters, and requires the nitrating agent to exist as nitrogen dioxide from the first to the third, that is, throughout the period in which the bisulphate ion and aromatic cation are finding, and reacting with, each other. The nitrogen dioxide molecule must be assumed to remain, during this kinetic transaction, continually within the 'sphere of action' of the aromatic molecule, though presumably bound therein by van der Waals forces only. This is not an easy assumption; and since the physical theory of such forces shows that they never exclude, or greatly interfere with, each other, one is caused to wonder why the nitrogen dioxide is prevented from being also within the 'sphere of action' of the solvent sulphuric acid, to which it will also be bound by van der Waals forces, and with which introduced nitrogen dioxide reacts to give products that are not formed under normal nitration conditions.

Our kinetic work does not suggest that the attack of a nitrating agent derived from nitric acid on an aromatic ring in liquid-phase nitration is ever anything but simply co-ordinative and heterolytic, as would be illustrated by telescoping Kenner's three steps completely, or at least so extensively as to render the step-wise representation an unsatisfactory approximation. The complete mechanism of this

electrophilic substitution, including the preliminary formation of the nitronium ion, may, however, be 'unimolecular' or 'bimolecular', with appropriate kinetic differences³, according as the heterolysis of the nitric acid molecule to yield the nitronium ion NO_2^+ is rate-determining or not. The kinetics show that the unimolecular step which can become rate-determining is a reaction of the nitric acid, and not of the solvent (as we once thought) or the aromatic substance; and, since it is too slow to be explained as heterolysis of an OH-group (proton transfer), it must be interpreted as the heterolysis of an NO-bond, necessarily to form nitronium ion.

It is by no means implied that univalent electron transfers³, homopolar unions, and homolyses⁴ never play any part in nitration. We think our kinetic results show that they have a role in nitrations by, or with the catalytic help of, nitrous acid. But it is probably relevant that nitrous acid can introduce odd-electron molecules into the system, notably nitrogen dioxide. All these matters will be more fully discussed elsewhere.

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¹ *J. Chem. Soc.*, 929 (1938).

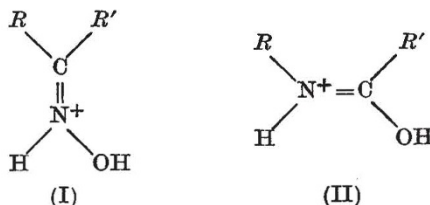
² *Nature*, 156, 369 (1945).

³ Cf. Weiss, *Nature*, 147, 512 (1941); *Trans. Faraday Soc.*, 27, 780 (1941); *J. Chem. Soc.*, 245 (1942); 468 (1943).

⁴ Hey and Waters, *Chem. Rev.*, 21, 169 (1937). Hey, *Nature*, 156, 36 (1945).

Mechanism of the Beckmann Rearrangement

HIGMAN¹ recently suggested a new mechanism for the Beckmann rearrangement which postulates that the cation (I) rearranges by rotation of the central $>C=N<$ unit through 90° to form (II). This suggestion, though ingenious, is not in accordance with the known facts.



The rearrangement of the toluenesulphonates² and picryl ethers³ of ketoximes to derivatives of amides is not prototropic and proceeds by separation of the potential anion attached to nitrogen. The evidence on the latter point is quite unambiguous. The reaction is much faster in solvents of higher dielectric constant; electron-repelling groups (R, R') accelerate the reaction, although such groups in other rearrangements (for example, pinacol-pinacolone) have a lower 'migratory aptitude'; the 2:4-dinitrophenyl ethers do not rearrange, though the picryl ethers do so readily. None of these effects would be expected on the basis of Higman's mechanism.

For the acid-catalysed Beckmann rearrangement equally definite evidence is available, and here the proton probably attacks oxygen and not nitrogen.