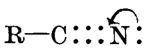
LVIII.—*The Nature of the Alternating Effect in Carbon Chains. Part XXIV. The Directive Action in Aromatic Substitution of Certain Groups containing Triple Linkings.*

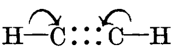
By JOHN WILLIAM BAKER, KENNETH ERNEST COOPER, and CHRISTOPHER KELK INGOLD.

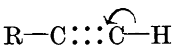
LANGMUIR has suggested that in the nitrogen molecule the two atomic nuclei and two electrons in addition to the K-electrons are enclosed within a single octet (*J. Amer. Chem. Soc.*, 1919, **41**, 903). This may be regarded as a special form, applied to certain examples (N_2,CO, and CN′), of the following more general principle :—When six valency electrons are mutually shared by two atomic nuclei, the system tends to appropriate two, or four, additional electrons in order to form a stable association of eight, or if possible, of ten, electrons. Usually the appropriation will be incomplete, and it may affect shared or unshared electrons; the limiting special case in which four unshared electrons are completely appropriated corresponds to Langmuir's hypothesis divested of its assumed octet and of its highly particularised stereo-electronic suppositions.

The appropriation of unshared electrons belonging to either or both of the combined atoms will be accompanied by a loss of basic character; the appropriation of shared electrons will confer on the molecule a tendency to ionisation, tautomerisation, etc. Owing to the lability of the unshared electrons in the tervalent nitrogen atom, the effect reaches a maximum when these can be absorbed and hence nitrogen (10*e*-group) and nitriles (8*e*-group) are non-basic, although according to customary electronic formulation they contain the unshared electrons of a tertiary amine. When the electrons required to form a stable 8*e*- or 10*e*-group are shared with hydrogen, the intrinsic tendency of the latter to pass into the cationic condition co-operates in favour of ionisation, and hence in hydrocyanic acid one hydrogen atom, in alkylacetylenes one hydrogen atom, and in acetylene two hydrogen atoms, are replaceable by elements (metals) which, having greater stability in the form of their cations, can become combined by electrovalencies to the organic anion (CN′, RC_2', C_2'') with minimal disturbance of the stable electron-groups.


$:N:::N:$

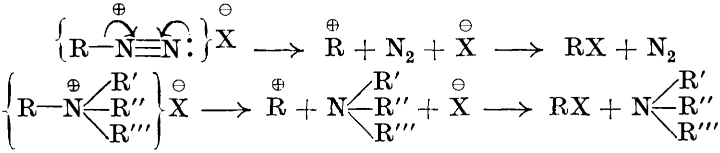

$R{-}C:::N:$


$H{-}C:::C{-}H$


$R{-}C:::C{-}H$

The same effect transmitted through a carbon atom (and augmented by other influences) is observed in nitriles possessing an α-hydrogen atom.

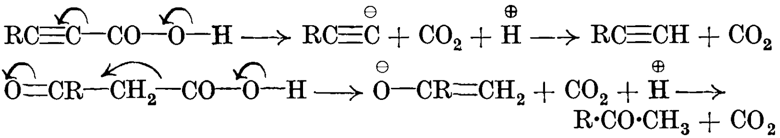
When the shared electrons bind atoms other than hydrogen, different phenomena may arise. Thus diazonium salts decompose more easily than other quaternary ammonium salts because the quaternary group in the former has an enhanced power of withdrawing electrons from the hydrocarbon radical (compare Hanhart and Ingold, J., 1927, 250) :



$$\{R-\overset{\oplus}{N}\equiv N:\}\overset{\ominus}{X} \longrightarrow \overset{\oplus}{R} + N_2 + \overset{\ominus}{X} \longrightarrow RX + N_2$$

$$\left\{R-\overset{\oplus}{N}\begin{matrix}R'\\R''\\R'''\end{matrix}\right\}\overset{\ominus}{X} \longrightarrow \overset{\oplus}{R} + N\begin{matrix}R'\\R''\\R'''\end{matrix} + \overset{\ominus}{X} \longrightarrow RX + N\begin{matrix}R'\\R''\\R'''\end{matrix}$$

To take one other example from the many available, acetylenic acids lose carbon dioxide on heating, whereas olefinic and saturated acids do not unless an electron-sink is present; in fact the decompositions of propiolic acid homologues and β-ketonic acids, etc., are closely comparable :



$$RC\equiv C-CO-O-H \longrightarrow RC\equiv\overset{\ominus}{C} + CO_2 + \overset{\oplus}{H} \longrightarrow RC\equiv CH + CO_2$$

$$O=CR-CH_2-CO-O-H \longrightarrow \overset{\ominus}{O}-CR=CH_2 + CO_2 + \overset{\oplus}{H} \longrightarrow R\cdot CO\cdot CH_3 + CO_2$$

These conclusions receive independent justification from the experiments recorded below on the orienting influence in aromatic substitution of certain groups containing the triple linking. For example, we find that phenylpropiolic acid on nitration yields as much as 8%, and ethyl phenylpropiolate 6%, of the *m*-derivative, in contrast with cinnamic acid and its ester, which yield *op*-products practically exclusively. We have no hesitation in ascribing this effect to the triple linking, rather than to any greater electron-attraction by the acetylene-bound carboxyl group as compared with the olefin-bound carboxyl group, because the difference of electron strain in the linkings binding the carboxyl groups in the two cases is in the wrong sense. This is shown, not only by the much greater tendency of acetylenic acids to lose carbon dioxide, but also by their much greater strengths as compared with the corresponding olefinic (and saturated) acids :

	$k\times10^5$.		$k\times10^5$.		$k\times10^5$.
n-Butyric acid ...	1·5	α-Crotonic acid	5·6	Tetrolic acid ...	246
β-Phenylpropionic acid ...	2·3	Cinnamic acid ...	8·6*	Phenylpropiolic acid	590

* Mean of values for ordinary and *allo*-modifications.

Hence the electron-attracting power of the acetylenic bond in phenylpropiolic acid is distributed between the two directions, and the *m*-orientation observed represents only a part of the total effect of the group.

No exact estimate of the proportion of *m*-derivative formed on nitration of benzonitrile appears to have been made previously. We find that, on nitration at 0° in nitric acid, 81% of the *m*-nitro-compound is produced. Phenylacetonitrile yields 14% of the *m*-derivative under similar conditions, showing that the *m*-orienting influence of the cyano-group is considerable even when transmitted through an interposed methylene group. The much greater *m*-orienting power of the cyano-group than of the acetylenic group is in accordance with the view (Baker and Ingold, J., 1927, 832) that the electrons mutually shared by C and N in $\cdot C\vdots N$ must be unequally shared, since they will be more under the control of the more powerful atomic nucleus (N), and that the effect of this must be to produce a *m*-orienting dipole. It may be pointed out that the recognition of these superimposed effects in the cyano-radical tends to favour our view that the additional electrons required to form the stable binuclear electron-groups considered are not *shared* (in the ordinary sense) by the two nuclei in the fully formed group. Admittedly this inference relates primarily to the 8*e*-group; but if it were applied to the 10*e*-group it would dispose of Langmuir's binuclear octet.

Finally, it should be remarked that the feeble basicity of azo- and nitroso-compounds (that their basicity is not nil is shown by their conversion into their amine oxides, azoxy- and nitro-compounds by oxidation) requires some extension of the above principles to include certain associations of two nuclei having originally four mutually shared and four unshared electrons. The facile elimination of nitrogen from dihydropyrazoles and aliphatic azo-compounds is a further indication in the same direction, and the fact that this reaction does not readily occur with aromatic azo-compounds is illuminated by reference to the analogous decomposition of diazonium salts. Here the presence of the positive charge, and the greater stability of the 10*e*-group originating in six shared electrons, render the series more labile as a whole, but the above mechanism of decomposition necessitates that the stability of an individual of the series $\{RN_2\}^{\bullet}X'$ should depend on the power of the variable radical R to hold electrons; hence, stability diminishes in the series $NO_2{\cdot}C_6H_4{-}>C_6H_5{-}>CH_3{\cdot}C_6H_4{-}>$ ------ >alphyl–. In azo-compounds RN_2R', the stability should be higher throughout, but should nevertheless be least when R = alphyl.* These consider-

* In " mixed " azo-compounds the group which most readily parts with electrons will determine the decompostion: *e.g.*, $CPh_3\overset{\curvearrowright}{-}N{=}N{\rightarrow}Ph \longrightarrow CPh_3^{\oplus} + N_2Ph^{\ominus} \longrightarrow CPh_3^{\oplus} + N_2 + Ph^{\ominus} \longrightarrow CPh_4 + N_2$ (Gomberg and Berger, *Ber.*, 1903, **36**, 1090).

ations raise the question whether the large electron affinity of the carbonyl group is not partly attributable to the cause indicated.

A consideration of the stabilities of the compounds mentioned appears to show that 2 electrons in the 10*e*-group are *less* firmly bound than the remaining 8. This is the reverse of Langmuir's idea, and presumably has implications relating to the spectroscopy of nitrogen and cyanogen (it may not apply to acetylene).

EXPERIMENTAL.

(A) *Acetylene Derivatives.*

(i) *Nitration of Phenylpropiolic Acid.*—This substance can be nitrated quantitatively, but the reaction requires very careful control and is best performed on a small scale in thin-walled test-tubes cooled in a bath of liquid ammonia. The acid (1·023 g.) was added during 15 minutes in very small portions with rapid mechanical stirring to 15 g. of freshly distilled absolute nitric acid at a temperature slightly below − 30°. After a further 15 minutes the solution was poured into ice and water, and the nitro-acids were extracted with much ether. The extract was evaporated, the evaporation being almost completed at the ordinary temperature, and the residue, which contained nitric acid, was repeatedly mixed with a little water and nearly dried over potassium hydroxide in a vacuum desiccator, and was finally dried until the weight became constant (yield 1·35 g. = theoretical) (Found: C, 56·4; H, 2·9. Calc.: C, 56·5; H, 2·6%). On oxidation with boiling permanganate at low concentration, nitrobenzoic acids were obtained in 85% yield; *p*- and *m*-nitrophenylpropiolic acids under the same conditions yielded the corresponding nitrobenzoic acids in 85% and 88% yield respectively. The mixed nitrobenzoic acids contained *para* 65·0%, *meta* 8·0% (benzoic acid, nil). Hence the proportion of *m*-nitrophenylpropiolic acid formed on nitration is 7·7% (rounded to 8% in the introduction). *Ortho*, by difference, 27%.

(ii) *Nitration of Ethyl Phenylpropiolate.*—This experiment was carried out like the preceding one, excepting that the mixture formed on pouring the nitric acid solution into ice-water was made alkaline with sodium carbonate before being extracted with ether. The apparent yield of nitrophenylpropiolic esters was 90%, but this contained 3% of un-nitrated material (below). The aqueous solution was acidified and treated in accordance with the description given above for the isolation of nitrophenylpropiolic acids, 10% of which was obtained, accounting for the rest of the material. The bulk of the ethyl *p*-nitrophenylpropiolate (51·8%) was readily separated in a pure condition by crystallisation from methyl alcohol, and the remaining mixture was oxidised (yield 96%) to nitrobenzoic acids by means of very dilute permanganate. The mixed acids contained benzoic acid (estimated by sublimation at 100°) equivalent to 3·0% of un-nitrated ethyl phenylpropiolate. After separating the nitrobenzoic acids and applying the usual corrections, including one for the material which had escaped nitration, we obtained *para* 57·9%, *meta* 6·1%, *ortho* (by difference) 36·0%, and it does not affect the rounded proportion of *meta-* (6%) whether the 10% of hydrolysis occurred before or after nitration.

We had hoped to include in this communication an account of the nitration of phenylacetylene and tolane, but in spite of many attempts we have not yet succeeded in establishing suitable conditions for the quantitative nitration of these substances.

(B) *Nitriles.*

(i) *Nitration of Benzonitrile.*—The benzonitrile was run very slowly from a weight-pipette into 15 parts of well-stirred absolute nitric acid at 0°, and the mixture was kept at this temperature for a further 2·5 hours. It is essential that no rise of temperature should occur, since otherwise the hydrolysis becomes perceptible. After admixture with ice-water and sufficient potassium carbonate the nitro-nitriles were extracted with ether (yield quantitative). There was no acid product. In the first of the three experiments, the results of which are recorded below, 23·8% of pure *m*-nitrobenzonitrile was separated by crystallisation from ligroin, and the remaining mixture was hydrolysed by boiling for 16 hours with 50% (by weight) sulphuric acid, a process which was quantitative both in this instance and in preliminary experiments on the separate isomerides. In the second and third experiments the whole product was quantitatively hydrolysed without preliminary separation. As in the cases of benzamide, benzoic acid and benzoyl chloride (Cooper and Ingold, J., 1927, 836) the proportion of *p*-isomeride is of the order of the correction for the solubility of *p*-nitrobenzoic acid in chloroform and we cannot assign a definite figure to it; the chief by-product is *o*-nitrobenzonitrile. For the *m*-isomeride we obtained (i) 80·0%, (ii) 80·0%, (iii) 81·6%. Mean, 80·53% (given as 81% in the introduction).

Nitration of Phenylacetonitrile.—Salkowski has shown (*Ber.*, 1884, **17**, 507) that the meta-isomeride is formed in the nitration of this substance, but his method did not enable us to estimate the proportion. We used the method of hydrolysis and subsequent oxidation to nitrobenzoic acids, supplemented by comparative experiments with the separate isomerides. For this purpose *o*-nitrophenylacetonitrile was prepared by Bamberger's method

(*Ber.*, 1886, **19**, 2635). The *m*-isomeride was obtained by Heller's method (*Annalen*, 1908, **358**, 357), but in the purification of the product it was found advisable to distil the crude oil obtained by extraction with benzene; the unchanged *m*-nitrobenzyl chloride distilled first at 155—160°/3 mm., and the cyanide at about 180°/3 mm. It was still impure (m. p. 50—55°) and was therefore crystallised from dry ether, in which the cyanide is sparingly soluble and the chloride easily soluble (m. p. 61°). The *p*-isomeride was obtained by nitrating phenylacetonitrile and crystallising the product from alcohol.

Phenylacetonitrile was slowly added to 15 parts of nitric acid (*d* 1·49) at − 10° to − 15°, and the product was mixed with ice, nearly neutralised with dilute sodium hydroxide solution, and made alkaline with sodium hydrogen carbonate. The crystalline product was collected, washed, and dried (yield 86·8%), and the filtrate was extracted with ether (yield 11·2%); total yield 98% (Found: C, 59·1; H, 3·8. Calc.: C, 59·3; H, 3·7%). The main fraction on crystallisation from alcohol yielded 62·6% of pure *p*-nitrophenylacetonitrile; the residues and the extracted fraction were oxidised separately, and the nitrobenzoic acids separated as usual. In another experiment (yield 98·5%) the whole product was hydrolysed and the nitrophenylacetic acids were oxidised to nitrobenzoic acids (yield 89%), which were separated. Comparative experiments with *o*-, *m*- and *p*-nitrophenylacetonitriles gave the appropriate nitrobenzoic acids in 85%, 80% and 86% yields respectively, from which we conclude that the alteration in the proportion of isomerides which takes place when a mixture of nitrophenylacetonitriles is hydrolysed and oxidised under the conditions employed is inconsiderable. The results of the two experiments were as follows: *ortho*, 16·5, 17% (by difference); *meta*, 14·5, 14%; *para*, 69, 69%.

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