[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

# On the Mechanism of the Nitration Process

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Haitinger,[1] by treating isobutylene, isoamylene and tertiary butyl and amyl alcohols with absolute nitric acid, obtained $(CH_3)_2C{=}CHNO_2$ and $(CH_3)_2C{=}C(NO_2)CH_3$ in small yields, mainly, however, products of oxidation; with ethylene only oxidation products were formed. However, by using a mixture of nitric and fuming sulfuric acids, Wieland and Sakellarios[2] succeeded in isolating $CH_2(ONO_2)CH_2NO_2$ from the reaction products with ethylene, but with much oxidation product. The investigation was extended by Wieland and Rahn[3] to isoamylene, which with absolute nitric acid alone gave only resinous products, but when diluted with carbon tetrachloride, gave some of Haitinger's nitroamylene along with $(CH_3)_2C(ONO_2)CH(NO_2)CH_3$. Similarly, $(C_6H_5)_2C(OH)CH_2NO_2$ was obtained from $\alpha,\alpha$-diphenylethylene and from phenanthrene the ether of 8-hydroxy-9-nitrophenanthrene.

Upon these results Wieland based an interpretation of the nitration mechanism; accordingly, nitric acid does not function as an electrolyte in addition to ethylene groups, but as $HO + NO_2$[4] forming primarily the corresponding saturated nitrohydrines. With aliphatic derivatives, the nitrohydrines either decompose into nitroalkylenes and water, undergo esterification with nitric acid to corresponding nitric esters, or these processes occur simultaneously. In support, it was shown[2,5] that ethylene nitrohydrine yields the corresponding nitric ester with nitric acid and nitroethylene with a strong dehydrating agent. To explain aromatic nitration, Wieland assumed addition of $HO + NO_2$ at conjoined, nuclear carbons, with spontaneous decomposition into a nitro derivative and water.[6]

Although Wieland's speculations on nitration have been practically universally accepted, not one of his arguments was theoretically sound and not a single conclusion was proved experimentally. In the ethylene experiment, a mixture of nitric and fuming sulfuric acids was used and the effective nitration agent in this mixture is

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(1) Haitinger, *Ann.*, **193**, 366 (1878); *Monatsh.*, **2**, 286 (1881). Kekulé, *Ber.*, **2**, 329 (1869), previously investigated ethylene. Simon, *Ann.*, **31**, 269 (1839). styrol oil; and Friedländer. *Ann.*, **229**, 203 (1885), cinnamic esters.

(2) Wieland and Sakellarios, *Ber.*, **53**. 201 (1920).

(3) Wieland and Rahn, *Ber.*, **54**, 1770 (1921).

(4) Wieland also assumed that a mixture of sulfuric acid and anhydride similarly functions as $HO + SO_2OH$. The pure acid up to 100% forms with ethylene acid ethyl sulfuric ester [Plant and Sidgwick, *J. Soc. Chem. Ind.*, **40**, 14T (1921)]; an intramolecularly better neutralized compound than ethionic acid. The mixture contains pyrosulfuric acid, which, like other mixed anhydrides of inorganic acids, must add facilely to ethylene, forming the acid sulfuric ester of ethionic acid. No experimental fact is known supporting Wieland's scheme of sulfuric acid addition. An experimental investigation on this subject is under way in this Laboratory. Since Carius obtained chlorohydrines from ethylene derivatives and hypochlorous acid, it is supposed to add as $Cl + OH$; recently, Hückel ["Theoretische Grundl. der org. Chemie," p. 298, 1931] cited this reaction in support of Wieland's views. The investigation of Noyes and Wilson [THIS JOURNAL, **44**, 1630 (1922)] has made it probable that the acid in dilute aqueous solution acts as an amphoteric substance, with $HO + Cl$ ions in relatively small proportion. Addition to an ethylene group should occur through these ions, with re-formation as they are used up, since the intramolecular neutralization of chlorohydrines is enormously greater than that of the otherwise formed, explosive, isomeric hypochlorous esters. Further hypochlorous acid could not add as $H + OCl$; it is a very weak acid ($K$, $6.7 \times 10^{-10}$) and such acids do not unite with ethylene groups. This view satisfactorily accounts for the formation of chlorohydrines, but not for the different course of addition to alkylenes and to $\alpha,\beta,\Delta$-acids; the latter additions not concurring with the positive-negative addition rule [Michael, *J. prakt. Chem.*, **60**, 465 (1899)]. Experiments in this Laboratory make it probable that the polymolecules of hypochlorous acid and ethylene derivatives break up with oxidation at the $\Delta$-carbons to form oxido compounds, which unite at once with the liberated hydrogen chloride, forming the corresponding chlorohydrines. All observations on this subject conform with this interpretation.

K. H. Meyer [*Ann.*, **398**, 66 (1913)] has concluded that nitrous acid and phenyldiazonium hydroxide function with $HO + NO$ and $C_6H_5N_2 + HO$ as addenda. Seven pairs of compounds, $RCH{=}CHR'$ and $RC(OH){=}CHR'$, were examined toward the enol bromine test and only the compounds with the latter group responded; hence, it was concluded they contain a very "active," additive $\Delta$-group. However, only one pair of the seven groups, *i. e.*, maleic and fumaric acids with enol oxalacetic acid, is known with certainty to be stereomerically comparable. No conclusion was warranted for the remaining six pairs, since a developed difference in additive capacity may appear between maleinoid and fumaroid stereomers. Upon this meager experimental basis, Meyer made the far-fetched conclusion that phenol, in contrast to benzene, contains the very "active" hydroxy enolic group, to which nitrous acid adds as $HO + NO$, in the 1,2- and 1,4-positions. The replacement of a single hydrogen in methane, or the tertiary hydrogen of isobutane, by hydroxyl, greatly increases the reactivity of a methyl hydrogen, notwithstanding the absence of an enolic group, and the *o*- and *p*-hydrogens of phenol should show a much greater facility of substitution over these atoms in benzene. A consistent interpretation of the reactions has been long known [Michael. *Ber.*, **29**, 1795 (1896); *Ann.*, **363**, 20 (1908); THIS JOURNAL, **32**, 990 (1910)]. The nitroso and diazonium groups are among the most energetic known in chemistry and are extremely additive toward atoms with a decided affinity for N and O, respectively, for diazonium nitrogens. The addition products decompose according to known rules and this simple, chemically acceptable hypothesis satisfactorily explains all the experimental facts.

Meyer assumed that diazonium hydroxide adds as $C_6H_5N_2 + OH$ to the "active" enol group of phenol, which is almost equivalent to the impossible contention that ammonium hydroxide and hydroxylamine, could add as $NH_4 + OH$ and $NH_2 + OH$.—(A. M.)

(5) Wieland and Sakellarios, *Ber.*, **52**, 898 (1919).

(6) Wieland associated himself in this hypothesis with Thiele [*Ann.*, **306**, 128 (1899)] and Holleman ["Die direkte Einführung, u. s. w.," 1912, p. 476]. Wieland's conception of benzene nitration was suggested first by Reddelien [*J. prakt. Chem.*, **91**, 220 (1915)].

not nitric acid. Markownikow[7] advanced credible reasons for accepting the more reactive, mixed anhydride $HOSO_2ONO_2$ as the actual nitration reagent in that mixture and its formation with fuming sulfuric and nitric acids cannot be doubted. Analogous mixed anhydrides, *e. g.*, nitrogen tri- and tetroxides, show a highly developed additive capacity to ethylene derivatives, forming nitro and nitroso derivatives instantaneously. Correspondingly, sulfuric–nitric anhydride should form nitro–sulfuric ester addition products; the sulfuric ester group should be displaced by the stronger nitric ester radical, forming, with ethylene, Wieland's ethylene nitro-nitric ester and pyrosulfuric acid. Further, as soon as oxidation began nitrogen tri- and tetroxides were formed and were then momentarily present during the rest of the experiments, uniting immediately with ethylene and forming, directly or indirectly by oxidation, Wieland's nitro–nitric ester. It should also be emphasized that, if nitric acid adds to isoamylene as $HO + NO_2$, according to the positive–negative addition rule, the main product should be $(CH_3)_2C(NO_2)$-$CH(OH)CH_3$, and, according to the principle of partition, a little $(CH_3)_2C(OH)CH(NO_2)CH_3$. The first nitrohydrine should be converted into the corresponding nitric ester and could not yield the $\alpha$-nitroisoamylene obtained by Wieland, but the compound would be isomeric with the ester he isolated. However, if the reaction proceeded through nitrogen tetroxide, the tertiary nitro group in the addition product would facilely undergo hydroxyl pseudosubstitution,[8] *i. e.*, through elimination of nitrous acid, followed by addition of water, and this 2-nitro-3-hydroxyisopentane should give the products obtained by Wieland. The behavior of $\alpha,\alpha$-diphenylethylene toward moist nitrogen trioxide[9] and tetroxide is relevant. With the trioxide, it first forms a blue oil, which decomposes at 0° into the nitrohydrine and nitroethylene derivatives; with dry tetroxide, Wieland[3] obtained the dinitro addition product, but the presence of even a trace of water caused formation of the $\alpha,\beta$-nitrohydrine. Since even dilute mineral acids eliminate water catalytically from tertiary carbinols[8] and water with nitrous gases is formed in the oxidation process, it is obvious that the appearance of nitroalkylenes, nitrohydrines and their nitric esters, in addition to ethylene derivatives, is entirely without theoretical significance for the interpretation of the mechanism of nitration.

The chemical behavior of ethylene derivatives toward nitric acid is dependent upon the chemical structure of the compound. With alkylenes the capacity and velocity of addition of a strong mineral acid, functioning as electrolyte, increase, generally speaking, with the strength of the acid. The velocity of formation of primary, secondary and tertiary addition products[10] increases in the order given, attaining with alkylenes the maximum value with isobutylene and slightly less with isoamylene. Quantitative data on the relation between structures of alkylenes and ease of oxidation are not available, but there can be no doubt that it increases with the relative positive polarity of the unsaturated carbons;[11] triisobutylene oxidizes in air,[12] and in isomers from a primary to a secondary carbinol group, to decrease decidedly in the tertiary derivative. On the other hand, polymerization increases with the polar differences between the unsaturated carbons.[13]

To secure comparatively normal results in the action of nitric acid upon alkylenes, it is evidently essential to restrict oxidation as much as possible, thus avoiding the secondary reactions, due to the formation of nitrous reagents, investigated by Wieland and other chemists. We found this result best realized by operating at low temperatures, with vigorous mechanical stirring, using freshly prepared, colorless nitric acid (98.6%) and diluting the acid or hydrocarbon with carbon tetrachloride, chloroform or methylene chloride. The latter solvent is stable toward the acid under the conditions used and its lower boiling point enabled a better separation of the reaction products from the solvent in several experiments.

Ethylene is the least additive alkylene toward concentrated strong acids and the formation of ethyl nitrate, under the above conditions, was very improbable. When ethylene was bubbled into 98.6% nitric acid at −30°, nitrous fumes were given off almost immediately and the acid solution added to ice water evolved gaseous products copiously. Ethylene reacted very slowly with nitric acid in methylene chloride solution at −25°, but at 0° the escaping gas contained

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[7] Markownikow, *Ber.*, **32**, 1444 (1899).

[8] Michael and Zeidler, *Ann.*, **385**, 227 (1911).

[9] Lipp, *ibid.*, **449**, 15 (1926).

[10] Michael and Brunel, *Am. Chem. J.*, **41**, 118 (1909).

[11] Michael, *J. prakt. Chem.*, **60**, 354 (1899).

[12] Butlerow, *Ber.*, **12**, 1482 (1879).

[13] Michael, *J. prakt. Chem.*, **60**, 437 (1899).

oxides of nitrogen and the reaction products decomposed with almost explosive violence when treated with ice water. Adding the reagents in inverse order led to similar results. A current of ethylene was passed into methylene chloride at −28° and nitric acid added slowly from a capillary dropping funnel to the mechanically stirred solution, yet the escaping gas contained nitrous fumes almost immediately and the oily product formed decomposed when warmed gently.

Butylene-1 shows a decidedly greater additive capacity for hydrogen bromide and water[14] than ethylene and it seemed possible that it would unite with nitric acid; on the other hand, addition would lead to a secondary nitric ester, which would be more sensitive to oxidation than the primary isomer. We made a number of experiments with this alkylene and 98.6% nitric acid, but only oxidation products were obtained. Methyl ethyl ketone was isolated as the semicarbazone from the reaction product and the ketone may have been formed by oxidation of secondary butyl nitric ester. A number of attempts were made to prepare that ester from the corresponding alcohol for a study of its properties, but, although the conditions were varied, oxidation was so rapid that the ester could not be isolated.

More satisfactory results could be expected from isoamylene and isobutylene, these alkylenes being the most additive known for acids, and tertiary esters being much more stable toward oxidation than the corresponding secondary derivatives. Trimethylethylene was added at −20° to an excess of "absolute nitric acid" in carbon tetrachloride; in striking contrast to the results of Wieland and Rahn[3] tertiary amyl nitric ester was obtained as main product, with a small quantity of higher boiling material. The tertiary ester was formed, exclusively, when 98.6% acid was added to carbon tetrachloride or chloroform solutions of isoamylene at −20° and, in subsequent experiments, the 98.6% acid was used. The tertiary ester is photosensitive and completely decomposed after three to four days at room temperature to high boiling products. The freshly prepared ester with dimethylaniline yielded dimethylaniline nitrate and isoamylene, and alcoholic sodium methylate gave a practically quantitative yield of sodium nitrate. Cold aqueous alkali did not hydrolyze the ester completely during twenty-four hours, but when warmed the mixture gave isoamylene and tertiary amyl alcohol. Isobutylene, in methylene chloride solution, reacted with 98.6% acid at −20° to yield tertiary butyl nitric ester. The constitution of the compound was established by the methods used with the tertiary amyl ester. It was shown by titration that only about 10% of acid remained unchanged in the experiments with isobutylene and isoamylene and acid in equivalent amounts. The relatively low yield obtained of the tertiary esters is largely due to the difficulty of separating the esters at reduced pressures from the solvents. By fractionating the distillates in several experiments at ordinary pressures, it was found that at low pressures about 25–30% of the ester had distilled with the solvent.

Bouveault and Wahl[15] obtained almost quantitative yields of nitric esters by the action of 98% nitric acid at 0–5° upon primary alcohols. Seconday carbinols yielded products of oxidation and, whilst Haitinger[1] obtained small yields of nitro alkylenes with the tertiary derivatives, these chemists observed only the formation of complex nitrogen compounds. Under our conditions, tertiary butyl and amyl alcohols were esterified nearly completely in a few minutes when treated with two equivalents of 98.6% nitric acid at −20 to −17°. Oxidation was not observed and the esters were shown to be identical with those obtained from the isoalkylenes. The experimental results with the isoalkylenes and tertiary alcohols are summarized in Table A.

The influence of phenyl, when introduced into an ethylene group, shows itself in strikingly increasing tendency to polymerize, *e. g.*, compare acrylic with cinnamic acid, or ethylene with $\alpha,\alpha$-diphenylethylene.[16] It was concluded above that the nitro derivatives obtained by Wieland[3,17] from diphenylethylene were due to the action of nitrous compounds, formed in the deoxidation of nitric acid. This conclusion is confirmed by the results of our experiments, for, in carbon tetrachloride or chloroform solution, the hydrocarbon did not react at 0° with nitric acid to

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(14) Michael, *J. prakt. Chem.*, **60**, 372 (1899); Michael and Brunel, *Am. Chem. J.*, **41**, 131 (1909).

(15) Bouveault and Wahl, *Bull. soc. chim.*, **29**, 956 (1903).

(16) For the literature on this hydrocarbon see Bergmann and Weiz, *Ann.*, **480**, 49 (1930); Schoepfle and Ryan, THIS JOURNAL, **52**, 4023 (1930).

(17) Previously prepared by Anschütz and Romig [*Ann.*, **233**, 327 (1886)] with other nitro products, but considered as nitric ester derivatives. Later, Anschütz [*Ber.*, **54**, 1854 (1921)] confirmed Wieland's interpretation for the first substance and assigned the structure $(C_6H_5)_2C{=}CHNO_2$ to a second product.

TABLE A

| Expt, | XV | XVI | XVII | XVIII | XIX | XX | XXI | XXII | XXIII |
|---|---|---|---|---|---|---|---|---|---|
| Isobutylene, g. | 19.7 | 18.1 | | | | | | | |
| Trimethylethylene, g. | | | | | 25 | 25 | 25 | | |
| Tertiary alcohol butyl, g. | | | 25 | 25 | | | | | |
| Tertiary alcohol amyl, g. | | | | | | | | 25 | 25 |
| Methylene chloride, cc. | 75 | 75 | 70 | 65 | | | 70 | | |
| Chloroform, cc. | | | | | | | | 50 | 50 |
| Cl₄, cc. | | | | | 75 | 75 | | | |
| Acid used, g. | 17 | 17 | 42.6 | 42.6 | 19 cc. | 19 cc. | 20 | 37 | 37 |
| Acid unchanged, g. | | | 25.7 | 21.4 | | | 1.7 | | |
| Temp., °C. | −20 to −5 | −20 to −10 | −20 to −14 | −17 to −13 | −20 to −15 | −20 to −10 | −15 to −11 | −17 to −10 | −21 to −10 |
| Time of addn., min. | 25 | 25 | 17 | 22 | 20 | 18 | 22 | 15 | 7 |
| Yield of alkyl nitrate calcd., g. | 32.0 | 32.0 | 40.2 | 40.2 | 47.5 | 47.5 | 42.2 | 37.8 | 37.8 |
| Yield of alkyl nitrate isolated, g. | 15.3 | 24.5 | 24.2 | 22.7 | 28.0 | 21.9 | 28.5 | 29.2 | 24.8 |
| Properties b. p. | | 23–24° at 4–5 mm. | 24–25° at 4–5 mm. | 21–22° at 4–5 mm. | 52–54° at 27 mm. | 26–27° at 5 mm. | 26–27° at 4 mm. | 23–24° at 4–5 mm. | 28–29° at 5 mm. |
| Properties $n^{20}_D$ | | | | | | 1.4096 | | 1.4086 | 1.4095 |
| Properties $d^{20}_4$ | | 1.014 | 1.016 | 1.015 | | 1.010 | 1.006 | 1.004 | 1.002 |
| Alkyl nitrate, g. | 5.0 | 5.0 | 5.0 | 5.0 | | | 5.0 | 10.0 | |
| Yield NaNO₃ calcd., g. | 3.6 | 3.6 | 3.6 | 3.6 | | | 3.2 | 6.4 | |
| Yield NaNO₃ found, g. | 3.5 | 3.3 | 3.4 | 3.4 | | | 3.2 | 6.4 | |
| Alkyl nitrate, g. | | | | 5.0 | | | 5.0 | | |
| Yield of dimethyl aniline nitrate calcd., g. | | | | 7.7 | | | 6.9 | | |
| Yield of dimethyl aniline nitrate found, g. | | | | 7.6 | | | 6.8 | | |
| Hydrocarbon calcd., g. | | | | 2.4 | | | 2.7 | | |
| Hydrocarbon found, g. | | | | 2.0 | | | 2.3 | | |
| Hydrolysis | | | | | | | | | (a) (b) |
| Alkyl nitrate, g. | | 5.0 | | | | 10.0 | | | 10.0 10.0 |
| Yield hydrocarbon, g. | | 1.4 | | | | 3.3 | | | 3.1 4.7 |
| Yield alcohol, g. | | | | | | 0.8 | | | 0.9 0.6 |

yield a nitrogen compound, but was changed partially into a polymer. The same polymer was obtained when diphenylmethylcarbinol was treated in chloroform solution with two equivalents of nitric acid. In glacial acetic acid solution the polymer did not react with nitric acid at room temperature, but when warmed nitrous fumes were evolved and α,α-diphenyl-β-nitroethyl alcohol was isolated without difficulty from the solution. The formation of the latter compound in the experiments of Wieland is, therefore, no proof that nitric acid adds directly and as postulated.

The Reddelien–Wieland scheme of benzene nitration is theoretically very improbable. Under usual conditions benzene is only slightly additive toward halogen, but, due to intramolecular energy changes, addition at a single pair of conjoined carbon atoms causes the two remaining pairs of carbons to acquire marked additive properties. Hence, it is possible to add six, but not two or four, halogen atoms to benzene. Nitric acid functioning as HO + $NO_2$ should behave like halogen and the above scheme should lead to tri-, not mono-nitrobenzene. Indeed, to explain the formation of trinitrobenzene, along with picric acid, on warming benzene with nitrogen tetroxide, Wieland[18] made the improbable assumption that this vigorous, deep-seated decomposition reaction, involving besides the tetroxide undoubtedly nascent oxygen, nitrous oxide and nitrous and nitric acids, proceeded by elimination of three moles of nitric acid from a primarily formed hexanitrohexahydrobenzene. Further, modified intramolecular energy relations in one of the nuclei of several higher aromatic hydrocarbons, *e. g.*, naphthalene, permit addition to a single pair of linked carbons, and, as was emphasized with reference to the nitration problem long ago,[19] such mono-addition products are comparatively stable compounds. Wieland explained the formation of the ether of 8-hydroxy-9-nitrophenanthrene from phenanthrene and absolute nitric acid, by spontaneous condensation of water from two moles of the 8-hydroxy-9-nitro derivative, first formed by addition of HO and $NO_2$ at the 8,9-carbons. At these carbons phenanthrene shows almost the additivity of alkylene carbons and the addition of nitric acid should take place. From Wieland's standpoint, therefore, it is unintelligible that an acid of 1.45 sp. gr. in acetic acid solution, should yield the 3-nitro compound,[20] as it would involve the additively, relatively inert 2,3- or 3,4-carbons. The above ether was first prepared[21] by the action of nitrous

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[18] Wieland, *Ber.*, **54**, 1776 (1921).

[19] Michael, *J. prakt. Chem.*, **68**, 506 (1903).

[20] Schmidt and Heinle, *Ber.*, **44**, 1494 (1911).

[21] Schmidt, *ibid.*, **33**, 3251 (1900). This chemist gave 154–155° and Wieland 167° as the melting point.

fumes upon phenanthrene, which indicates unmistakably that its appearance in Wieland's experiments was due to that reagent, not directly to nitric acid. By treating phenanthrene in chloroform solution at −20° with 98.6% nitric acid, we obtained a 25% yield of a compound containing the elements of nitric acid more than the original hydrocarbon. The constitution of the material was not definitely proved because of lack of material. However, when treated with sodium methylate the compound gave a small yield of sodium nitrate. The main product of the reaction appeared to be a mixture of nitrophenanthrenes which could not be separated.

Although cyclohexene adds halogen readily, the reaction with nitric acid was not simple addition. In chloroform solution at −20° the reaction was slow; after three hours 65% of acid was unchanged. At 0°, 56% acid was recovered after one hour. Only about one-half of the nitrogen product distilled even at reduced pressure; the residue was very high boiling and decomposed when heated. The distilled oil reacted with sodium methylate to give a gummy sodium derivative.

The above results prove that the observed nitration of ethylene derivatives is indirect, through nitrous gases generated in oxidative side reactions, and that unchanged nitric acid when it acts like other strong acids, functions normally, and according to the positive–negative addition rule with addition of H + $ONO_2$ to the ethenic carbons. Two interpretations, besides the untenable Reddelien–Wieland, are possible for aromatic nitration: (1) the historic substitution conception, implying direct replacement of H by $NO_2$, and (2) indirect or pseudo-substitution. The latter view is based upon the obvious fact that a Δ-oxygen of nitric acid must have a considerably higher content in free chemical energy than the partially hydrogenized O of the OH,[22] as well as a greater chemical affinity for H and, therefore, can perform more easily the work necessary to separate the H that migrates from C. The dominating motive forces in nitric acid are the chemical potential of a Δ-O for H and that of the N for aryl. From this chemical energy and affinity point of view, the nitration of benzene was represented by $C_6H_6 + HONO_2 \longrightarrow C_6H_5NO(OH)_2 \longrightarrow C_6H_5NO_2 + H_2O$.[23]

According to Giersbach and Kessler[24] two molecules of nitric acid enter into the nitration of benzene and Tronov, who accepts the viewpoint that aromatic nitration proceeds through aldolization, attaches the second acid molecule at the same carbon by a dotted line. When the simplest possible polymolecule has not the free chemical energy necessary to overcome the chemical hindrance to a reaction, it may do so by assimilating a second molecule of the reagent, but this does not imply two kinds of linkage and Tronov's assumption is supererogatory.

The course of nitration through aldolization is coördinated with one of the largest classes of organic reactions. The conception was extended later[25] to other groups of two unsaturated atoms and is associated with the fundamental organic principle that substitution reactions involving a Δ-group always proceed through addition at the Δ-atoms followed by elimination,[26] *i. e.*, they are pseudo-substitutions.

Konowalov[27] first showed that alkanes may be nitrated by heating with more or less dilute nitric acid. Wieland's scheme is obviously inapplicable here and the formation of water, by direct union of an alkane with the HO of nitric acid, with a sp. gr. as low as 1.07, is scarcely conceivable. Water in comparison with nitric acid is a decidedly basic substance; by solution in more or less water the acid loses a proportionate amount of its negative chemical energy. This partial neutralization favors pseudo-substitution over oxidation, and protects, in a measure, the formed nitro derivative.

## Experimental

**Preparation of Materials.**—Chloroform and carbon tetrachloride were dried with phosphoric anhydride; methylene chloride with calcium chloride.

Colorless nitric acid (98.6%) was prepared only as required by distilling nitric acid (1.42 sp. gr.) from concentrated sulfuric acid (1.84 sp. gr.) at reduced pressure. The absolute nitric acid (100.4%) used in experiments VI and XX

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[22] Michael, *Ber.*, **34**, 4030 (1901).

[23] Michael, *ibid.*, **29**, 1795 (1896). This interpretation was confirmed by the synthesis, in a fair yield, of nitrobenzene by the action of aluminum chloride upon a mixture of nitric ethyl ester and benzene. Nef [*Ann.*, **298**, 224 (1897)] obtained only a low yield of nitrobenzene and attributed the formation of the latter to the action of nitrous gases formed in the action of the chloride upon the nitric ester. It was intended to repeat the experiments and publish the details, but Bödtker [*Bull. soc. chim.*, [4] **3**, 727 (1908)] without knowledge of the previous work, obtained up to 32% yields of aromatic nitro compounds by the same method. Recently, Tronov and Sibgatullin [*Chem. Abs.*, **25**, 3973 (1931)] found that maximum yields (50% with benzene) are obtained by using only 0.5 mole of chloride.

[24] Giersbach and Kessler, *Z. physik. Chem.*, **2**, 676 (1888).

[25] Michael, *Ber.*, **29**, 1795 (1896).

[26] Michael, *J. prakt. Chem.*, **60**, 300, 318 (1899).

[27] Konowalov, *Compt. rend.*, **114**, 26 (1892), and later papers in the *Russian Physical-Chemical Journal*.

was prepared by adding nitric anhydride to 98.6% nitric acid. Phosphoric anhydride was added to cold 98.6% nitric acid and the mixture of nitrogen oxides distilled into a receiver maintained at 0°. The nitrogen pentoxide solidified and was filtered off in an atmosphere of nitrogen.

Trimethylethylene was prepared by warming a mixture of tertiary amyl alcohol (80 g., b. p. 100–100.5°) and 300 cc. of hydrochloric acid (1.009 *N*) on a steam-bath.[8] The hydrocarbon was dried with calcium chloride, fractionated and the final traces of alcohol removed by treatment with metallic sodium (yield, 25–30 g.; b. p. 38.5–39°).

Isobutylene[28] was obtained by adding tertiary butyl alcohol (distilled from sodium, b. p. 82.5–83°) from a dropping funnel to hydrochloric acid (1.009 *N*) heated on a steam-bath. The isobutylene passed successively through a reflux condenser, a trap maintained at 0°, a 50% sodium hydroxide solution, calcium chloride tubes cooled to 0°, two U-form tubes filled with potassium hydroxide pellets and was finally condensed in a receiver (cooled to −30°) containing a pellet of potash.

Cyclohexene was refluxed for several hours over sodium, fractionated and the portion boiling at 84.5–85.4° used in the experiments. Methyldiphenylcarbinol was prepared according to the method of Tiffeneau[29] except that ammonium chloride was used to decompose the magnesium compound. The carbinol was dehydrated by repeated distillation at ordinary pressure and the diphenylethylene finally fractionated *in vacuo*.

**I. Experiments with Ethylene.**—In I–V the gas was passed through a sintered glass inverted filter into nitric acid, contained in a cooled 30 × 200 mm. test-tube with a side-arm. The side-arm was attached to a calcium chloride tube and then to a tube containing barium hydroxide solution, excepting in II, when the escaping gas went through U-tubes cooled to −25°. Carbon dioxide was not observed in any experiment, nor was any material condensed from the escaping gas in II.

The green, clear reaction mixtures in I and II were added to ice water (gas was evolved in I) and the precipitated oils extracted with ether, the solution dried and the solvent removed at reduced pressure. One-half of the residual oil of I distilled at 4 mm. (bath temperature 100°); the remainder at 140–150°. The oily product in II completely decomposed when heated in a water-bath at 100°.

The colored reaction mixtures in III to VI separated into layers. The water-soluble, lower layer of III contained 4.6 g. of acid and the aqueous extract obtained on washing the methylene chloride solution, 6.6 g. of acid. When the methylene chloride solution in IV was added to ice water the reaction product completely decomposed. The experiment was repeated (V), using less concentrated acid solution, but the product could not be identified. In VI the ethylene was bubbled into methylene chloride so as to maintain a saturated solution, while 100.4% nitric acid was added from a capillary dropping funnel to the mechanically stirred solution. The excess ethylene swept out a small amount of nitrous fumes. The turbid reaction mixture was washed with ice water, 5% sodium bicarbonate solution, dried and the solvent removed. The residual oil (1 g.) boiled unchanged at 35 mm. when immersed in water at 50°. Portions of the aqueous extracts in I and V were evaporated *in vacuo* and left small amounts of oxalic acid. The experimental conditions and results of these experiments are tabulated.

| Expt. | I | II | III | IV | V | VI |
|---|---|---|---|---|---|---|
| Acid | 25 cc. | 5 cc. | 15 g. | 15 g. | 5 cc. | 5 cc. |
| Methylene chloride, cc. | None | None | 30 | 30 | 25 | 35 |
| Time of reaction, hrs. | 3 | 2.5 | 3 | 3 | 2 | 1.5 |
| Temp., °C. | −25 | 0 | −25 | 0 | 0 | −28 |
| Residual oil, g. | 1.5 | 1.5 | 0.2 | None | 0.5 | 1.0 |

**II. General Procedure. Adding Nitric Acid to Alkylenes and Alcohols.**—The mixing apparatus consisted of a 500-cc. three-necked flask provided with a mechanical stirrer, dropping funnel and a calcium chloride tube. The dropping funnel was replaced by a drying train of U-tubes filled with potassium hydroxide pellets, when gaseous hydrocarbons were used. The ampoule containing the butene was weighed, cooled to −30°, attached to the drying train, opened, and the hydrocarbon slowly distilled into the reaction flask. The nitric acid was added to solutions of the alkylenes or alcohols, except in XIX and XX in which trimethylethylene was added to mixtures of the acid and carbon tetrachloride. The reaction mixture was stirred for one-half to one and one-half hours after all the reagents had been mixed, then washed with ice water, a cold 5% sodium bicarbonate solution, again with ice water, dried over calcium chloride, and the solvent removed at reduced pressure. In XV–XVIII and XXI, the solvent was distilled at reduced pressure through a jacketed column of glass pearls maintained at 0° by an outside flow of ice water. The distillate, when redistilled at ordinary pressure, invariably contained part of the product (5–10 g.). The residual oil, after removing the solvent at reduced pressure, was distilled at 4–5 mm., except in XIX when the pressure was 27 mm., into a cooled receiver (−30 to −25°). The unused acid was determined in several experiments by titrating aliquot parts of the wash water used. To identify the alkyl nitrates portions were added to cold solutions containing an equivalent, or a slight excess, of sodium dissolved in 20 cc. of methyl alcohol. The solutions were warmed and most of the alcohol distilled off. The sodium nitrate was filtered, washed with a little alcohol and analyzed.

Five grams of the alkyl nitrate in XVIII and XXI was added to dimethylaniline (8 g. and 7 g., respectively) and the solutions warmed in an apparatus arranged to condense the liberated amylene at low temperature, or with isobutylene XVIII, to dissolve the evolved gas in 25 cc. of cold chloroform (−20°). The amylene was weighed and the chloroform solution of the isobutylene titrated with bromine (5.7 g.) at −20°.

The dimethylaniline nitrate was filtered and washed with dry ether. In XVIII the nitrate melted at 84–85° and titrated as follows: subs. (1) 2.5855 g., (2) 3.8400 g.; required (1) 13.60 cc., (2) 20.40 cc. NaOH (1.0125 *N*). Mol. wt. calcd., 184. Found: (1) 188, (2) 186. The

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[28] We are indebted to Prof. G. B. Kistiakowsky for the ethylene and butylene-1 used in these experiments and to Prof. L. F. Fieser for the phenanthrene.

[29] Tiffeneau, *Am. chim. phys.*, [8] **10**, 359 (1907).

neutral solutions in the titrations were extracted with ether, the solvent removed from the extracts and the residual oils treated with (1) 6.3 g., (2) 5 g. of picric acid, respectively. The yields of dimethylaniline picrate were: (1) 4.7 g., (2) 7.2 g. (calcd. (1) 4.7 g., (2) 7.3 g.). The picrates melted at 162° and gave no depression with an authentic sample.

The amylene in XXI distilled at 37–39°. The dimethylaniline nitrate melted at 84–85° and gave 5.7 g. (calcd. 5.9 g.) of dimethylaniline picrate, m. p. 162° (mixed m. p. gave no depression).

Five grams of the butyl nitrate (XVI), 10 cc. of water and 2.1 g. of sodium hydroxide (in a tube) were sealed in a Pyrex glass tube, the reagents mixed and heated for one hour at 100°. The tube was cooled (−30°) and connected to a flask containing 25 cc. of chloroform at −25°. The butylene was distilled off slowly and the chloroform solution absorbed 4.1 g. of bromine to give 4.3 g. of isobutylene dibromide. The substance left in the Pyrex tube separated into two layers. The oily layer (0.5 g.) distilled at 150–160° and was apparently triisobutylene.

Ten grams of amyl nitrate (XX and XXIII) was added to a solution of 3.5 g. of sodium hydroxide in 20 cc. of water and the mixture warmed under a condenser. The flask was then attached to a U-form condenser and the amylene driven off by warming. The aqueous residual solution was extracted with ether, the extract dried and the solvent removed. The residual oil was tertiary amyl alcohol; the yield of the latter was lower in XXIIIb when only 10 cc. of water was used.

**III (A) Nitric Acid to Solutions of Butylene-1.**—The acid was added to solutions of butylene-1 during ten and thirty minutes in VII and VIII, respectively. The mixture was washed with ice water, the solution dried and filtered. The amounts of unchanged butylene were determined by titration of 10 cc. of the filtrates with bromine. In VII the solvent was removed from the remainder of the filtrate at reduced pressure and one-half of the residual oil obtained distilled with decomposition at 4 mm. with the bath temperature at 140°. The total filtrate in VIII gave 3.2 g. of butylene dibromide. In IX the solvent was removed at reduced pressure and the residual oil (5.5 g.) obtained was heavier than water, reacted acid to litmus, contained nitrogen and distilled with decomposition at 4 mm. The green distillate was heavier than water, reacted acid to litmus and did not discolor bromine. In X the reagents were mixed at room temperature and the mixture extracted with ice water after fifteen minutes. The data of the experiments are tabulated.

| Expt. | VII | | VIII | IX | X |
|---|---|---|---|---|---|
| Butene-1, g. | 4.7 | | 7.3 | 8.3 | 4.6 |
| Nitric acid, g. | 5.3 | | 6.3 | 7.9 | 5.2 |
| Chloroform, cc. | 75 | | 60 | 25 | 50 |
| Time of reaction, hrs. | 1 and | 1 | $^1/_2$ | 12 | $^1/_4$ |
| Temperature, °C. | −14 to −10 | 0 | −16 | −2 | 33 |
| Filtrate: Total, cc. | 75 | | 63 | | 59 |
| Filtrate: 10 cc. sample required Br, g. | 1.0 | | 2.2 | | 1.1 |
| Filtrate: Unchanged butene, g. | 2.6 | | 4.8 | | 2.3 |
| Filtrate: Residual oil, g. | 2.0 | | | 5.5 | 1.0 |
| Unchanged acid, g. | 3.4 | | 4.7 | 4.8 | 3.6 |

**(B) Butylene-1 to Solutions of Nitric Acid.**—Butylene-1 (5.8 g.) was slowly distilled into tubes containing solutions of 5.6 g. of nitric acid in 25 cc. of chloroform cooled to −28 and −30°, respectively. The tubes were sealed and the contents mixed by shaking. In one experiment the mixture was kept at 0° for twelve hours, then at room temperature for three days, while in the second it remained at room temperature for twenty-two hours. The contents of the tubes were washed with ice water, the chloroform solutions dried and the solvent removed at reduced pressure.

About one-half of the residual oil ((1), 5.4 g.; (2), 3.3 g.) distilled at 4–5 mm. with the bath at 140° leaving an oil, which decomposed when the temperature was raised. The distilled fraction contained nitrogen, did not discolor bromine, was heavier than water and insoluble in cold normal alkali. The wash waters contained 0.8 g. of acid in the first and 2.5 g. in the second experiment.

**IV. Action of Nitric Acid on Secondary Butyl Alcohol. (A) In Organic Solvents.**—Nitric acid, and mixtures of nitric and sulfuric acids, were added to mechanically-stirred, cold solutions of secondary butyl alcohol. The green reaction mixture was washed at once with ice water in XI and in XII the colorless reaction mixture was stirred for fifteen minutes before washing. In XI only 0.5 g. of oil was left on removing the solvent at reduced pressure. The distillate, fractionated at ordinary pressure, gave fractions: (1) one-half, boiled at 44–53°; (2) nearly as much at 53–57°; (3) the residual oil (3.5 g.) boiled at 80–90° (nearly all at 79–80°). Two grams of the oil gave 1.8 g. of the semicarbazone of methyl ethyl ketone. Fractions (1) and (2) contained material which could not be separated by fractionation and gave no solid products with either aniline or hydroxylamine.

One-half of the oil (2 g.), left on removing the solvent at reduced pressure in XII, distilled at 75–80° and the thermometer then rose rapidly to 120°, but a pure product could not be isolated. The distillate gave no semicarbazone and was partially soluble in water. The chloroform distillate boiled at ordinary pressure at 63–65° and left 5 g. of material which distilled at 70–80°.

When all but 5–10 cc. of the acid mixture had been added to the alcohol in XIII, nitrous fumes were evolved and the reaction mixture turned deep green. In XIV sulfuric acid was added to the cold alcohol solution and the nitric acid added dropwise to this solution: the mixture decomposed violently when 5 cc. of nitric acid remained to be added. The experimental conditions are summarized in the table.

| Expt. | XI | XII | XIII | XIV |
|---|---|---|---|---|
| Alcohol, g. | 25 | 10 | 25 | 25 |
| Acid: Nitric, g. | 42.6 | 8.5 | 21.3 | 21.3 |
| Acid: Sulfuric, g. | .. | 2.0 | 33.2 | 16.6 |
| Solvent: Methylene chloride, cc. | 75 | | 75 | 75 |
| Solvent: Chloroform, cc. | | 75 | | |
| Time of addition, hrs. | 1 | $^3/_4$ | $^1/_2$ | $^1/_4$ |
| Temperature, °C. | −20 | −14 to −7 | −19 | −20 |

**(B) In Aqueous Solution.**—Ten grams of concentrated sulfuric acid, diluted with 10 cc. of water, was added during twenty minutes to a solution of 15 g. of secondary butyl alcohol, 50 cc. of water and 17.5 g. of sodium nitrate, cooled in ice. The mixture was then stirred one hour, extracted with ether, dried and the solvent removed.

At ordinary pressure the residual oil gave 15.3 g. of oil (b. p. 80–85°) which separated into two layers. The lower layer (1.4 g.) dissolved in water. The upper, insoluble, neutral layer was washed with water, dried and gave isobutyl nitrite (b. p. 65–70°) as the main fraction.

V. **(A) Ester from Isobutylene.**—The product in XV distilled at 4 mm. with the bath at 28°. The ester from XVI was analyzed.

*Anal.* Calcd. for $C_4H_9NO_3$: N, 11.76. Found: N, 11.65.

**(B) Ester from Tertiary Butyl Alcohol.**—The product in XVIII was analyzed.

*Anal.* Calcd. for $C_4H_9NO_3$: N, 11.76. Found: N, 11.65.

**(C) Ester from Trimethylethylene. (a) Alkylene Added to Acid.**—Product XIX analyzed as shown.

*Anal.* Calcd. for $C_5H_{11}NO_3$: N, 10.52. Found: N, 11.5.

In experiment XX, 100.4% of nitric acid was used. The product (b. p. 26–27° at 5 mm.; $n_{20}$ 1.4168) was redistilled and collected in two fractions: (1) $n_{20}$ 1.4168; (2) $n_{20}$ 1.4096; $d_{20}$ 1.01. Fraction (2) analyzed as follows.

*Anal.* Calcd. for $C_5H_{11}NO_3$: N, 10.5. Found: N, 10.98.

**(b) Acid Added to Trimethylethylene.**—The distilling column retained 5.1 g. of ester in XXI. Four grams warmed with 7 g. of dimethylaniline gave 1.4 g. (calcd. 2.1 g.) of amylene. The dimethylaniline nitrate (4.4 g.; calcd. 5.5 g.) melted at 84–85° and titrated as follows: 1.7926 g. required 9.60 cc. of NaOH (1.0125 *N*). Mol. wt. Calcd., 184. Found, 184.5. The neutral titration solution gave 3.2 g. (calcd. 3.4 g.) of dimethylaniline picrate, m. p. 162°; mixed m. p. the same.

Five grams of the amyl ester and 0.9 g. of sodium dissolved in 20 cc. of *n*-butyl alcohol gave 1.6 g. (calcd. 2.6 g.) of amylene (b. p. 37–39°) and 3 g. (calcd. 3.2 g.) of sodium nitrate.

**(D) Ester from Tertiary Amyl Alcohol.**—Product XXII was analyzed.

*Anal.* Calcd. for $C_5H_{11}NO_3$: N, 10.5. Found: N, 10.7.

The results of the experiments are collected in Table A.

VI. **Nitric Acid and Cyclohexene.**—Nitric acid (11.5 g.) was added at −20° to solutions of 15 g. of cyclohexene in 80 cc. of chloroform and the red reaction mixture stirred for one-quarter and three hours, respectively. The wash water contained 76.5 and 64% of unchanged acid and 82 and 75% of cyclohexene remained unchanged in the respective experiments. Only a part of the reaction product was volatile even at reduced pressure. The volatile portion contained nitrogen and gave a gummy solid with sodium methylate; the non-volatile oil decomposed at 200°. The reaction product did not discolor bromine (0.7 g. of subs. gave a red color with less than 0.1 g. of bromine). Sixty cc. of the chloroform distillate (total 70 cc.) collected at reduced pressure in the second experiment reacted with 10 g. of bromine to give 13.4 g. of cyclohexene dibromide.

VII. **Action of Nitric Acid on α,α-Diphenylethylene. (a) In Chloroform.**—A solution of 1.1 g. of nitric acid in 10 cc. of chloroform was added during twenty minutes to 3 g. of diphenylethylene dissolved in 10 cc. of chloroform cooled to 0°. The red solution was stirred for two hours, washed with ice water, dried and the solvent removed.

The wash water contained 0.96 g. of unchanged acid.

The residual oil (3.4 g.) diluted with petroleum ether deposited 2 g. of a white solid, m. p. 115–116°.

*Anal.* Calcd. for $C_{14}H_{12}$: C, 93.3; H, 6.6. Found: C, (1) 92.9, (2) 92.8; H, (1) 6.8, (2) 6.6.

A solution of 1.8 g. of the diphenylethylene in 10 cc. of chloroform showed no change in two hours and 1.5 g. of unchanged hydrocarbon was recovered. The hydrocarbon also remained unchanged in chloroform containing hydrogen chloride.

**(b) In Acetic Acid.**—A cold solution of 1.5 g. of nitric acid in 5 cc. of glacial acetic acid was added slowly to a solution of 2 g. of diphenylethylene in 5 cc. of glacial acetic acid, cooled to 0°. The clear, pink solution after twelve hours at 0° was added to cold water and the precipitated oil taken up in ether. The red oil (2.5 g.) gave 2 g. of unchanged diphenylethylene.

VIII. **Action of Nitric Acid on Methyldiphenylcarbinol.**—A solution of 3.2 g. of nitric acid in 5 cc. of chloroform was added during fourteen minutes to a solution of 5 g. of the carbinol in 25 cc. of chloroform, cooled to −18°. The red solution was stirred one and one-half hours, washed with ice water, dried and the solvent removed. The residual oil, diluted with ether, deposited 3.4 g. of white needles, m. p. 114–115°, mixed m. p. with polymerized diphenylethylene the same. The ether filtrate left 1 g. of an orange oil, which gave no test for nitrogen.

In a duplicate experiment, a solution of 8 g. of the carbinol in 50 cc. of chloroform was cooled to −22° and 5.1 g. of nitric acid, diluted with three volumes of chloroform, added during twenty-eight minutes. The mixture was stirred for three-quarters of an hour (temperature rose to −15°). Ice water extracted 5.08 g. of acid.

The product, diluted with ether, gave 5.1 g. of polymerized diphenylethylene. The residual oil obtained from the filtrate contained some of the polymer, but gave no test for nitrogen. A methyl alcohol solution of 0.5 g. of the oil, heated on the steam-bath with 0.5 g. of phenylhydrazine, gave a trace of the phenylhydrazone of benzophenone. The oil added bromine, boiled at 270–275° at ordinary pressure, and must have been largely diphenylethylene.

IX. **Action of Nitric Acid on the Polymer of Diphenylethylene.**—Two g. of the polymer was added at room temperature to 5 cc. of glacial acetic acid containing 1 g. of nitric acid. No reaction occurred in the cold, but when the solution was heated on the steam-bath, brown fumes were evolved and the reaction product, diluted with ether, deposited 0.6 g. of diphenyl-β-nitroethyl alcohol.

X. **Action of Nitric Acid on Phenanthrene.**—A solution of 3 g. of phenanthrene in 25 cc. of chloroform was cooled to −25° and 1.1 g. of nitric acid, diluted with 3 cc. of chloroform, added during ten minutes. The mixture was stirred one hour (temperature rose to −22°), washed with ice water, dried and the solvent removed at reduced pressure.

The yellow residue (4.4 g.), diluted with ether, deposited

0.8 g. of yellow solid, m. p. 136° with decomposition. This insoluble material obtained in a similar experiment was analyzed.

*Anal.* Calcd. for $C_{14}H_{11}NO_3$: N, 5.81. Found: N, (1) 5.79, (2) 5.84.

The yellow, insoluble material (0.5 g.), treated with sodium methylate gave impure sodium nitrate and 0.1 g. of a yellow solid, m. p. 113–114°, which may have been 9-nitrophenanthrene.

Evaporation of the ether solution *in vacuo* left a gummy mass, which was repeatedly extracted with cold petroleum ether, the solution decanted and the solvent evaporated at reduced pressure. The residue (m. p. 94–95°) was recrystallized from methyl alcohol and melted at 94–95°, but could not be identified for lack of material.

## Summary

1. Contrary to Wieland and other chemists, nitric acid (98.6%) does not add to ethylene or $\alpha,\alpha$-diphenylethylene, nor could addition compounds be obtained from butylene-1 or cyclohexene. It adds readily to trimethylethylene and isobutylene, forming the tertiary amyl and butyl esters, which are also formed from the corresponding tertiary carbinols and nitric acid. Tertiary amyl nitric ester was also formed with 100.4% nitric acid. At 0° nitric acid polymerizes $\alpha,\alpha$-diphenylethylene. With phenanthrene, besides nitro derivatives, a small proportion of material was obtained which appeared to contain a nitric acid addition product.

2. The nitroalkylenes and nitrohydrine nitric esters, obtained by previous investigators, are not direct products of nitration, but are due to the union of the ethylene derivatives with nitrous gases, formed in the deoxidation of the nitric acid. Oxidation was noticed in all the above indirect nitrations.

3. The formation of the nitric ester of ethylene nitrohydrine, in Wieland's experiment with a mixture of fuming sulfuric and nitric acids, does not proceed by addition of HO and $NO_2$ to ethylene and subsequent action of nitric acid. The acid mixture must contain the mixed anhydride, $HOSO_2ONO_2$, which should add readily to ethylene to yield $CH_2(OSO_3H)CH_2NO_2$ from which the $SO_3H$ group should be displaced by the more negative $NO_2$ radical, with formation of pyrosulfuric acid and the nitro–nitric ester.

4. Wieland's conclusion that nitric acid adds directly as HO + $NO_2$ to ethylene groups is based upon secondary reactions and is untenable. His application of this view to nitration of benzene is directly opposed to the properties of the hydrocarbon and nitric acid; and, since ethylenes do not unite in this manner with the acid, the supposed analogy has no experimental basis.

5. Wieland's assumption that sulfuric acid functions as HO + $SO_2OH$ in additions to ethylenes is directly opposed to all experimental results on the subject, which show that the acid, up to 100%, adds as an electrolyte, forming the corresponding acid sulfuric esters. The apparently abnormal course of addition of hypochlorous acid to organic $\Delta$-compounds has been explained by the acid oxidizing the $\Delta$-carbons and union of the oxide thus formed with the liberated hydrogen chloride. All acids, capable of uniting chemically with a bi-atomic $\Delta$-group, function as electrolytes in additions.

6. The earlier view that aromatic nitration proceeds in the first phase by aldolization has been brought forward again. A reactive nuclear hydrogen of the compound unites with a $\Delta$-oxygen of the acid and the residual aromatic group with the nitrogen, water then separating from the addition product. This interpretation, which is of general application, finds support in the synthesis of nitro compounds from aromatic hydrocarbons, ethyl nitrate and aluminum chloride and can be applied consistently to the nitration of alkanes by dilute nitric acid.

7. The aldolization process, has been generalized to include all unsaturated groups of two atoms, with a sufficient chemical potential for a bi-atomic group of the reagent to induce bilateral addition. In illustration, the conclusions of K. H. Meyer that nitrous acid and phenyldiazonium hydroxide add to "active" $\Delta$-groups of phenol, as HO + NO and $C_6H_5N_2$ + OH, were shown to be theoretically and experimentally unfounded. These reactions proceed by union of the labile *o*- and *p*-hydrogens of phenol and the residual hydroxyaryl radicals with the extremely energetic and additive atoms of the nitroso and diazonium nitrogen groups, with subsequent breaking up to substituted aromatic products.

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