

conjugated structures, but when two methylene groups were present between the double bonds (1,5-hexadiene) no reaction occurred.

OXYGEN-CONTAINING COMPOUNDS

In a reaction similar to that described just above, vinyl acetic acid, having a methylene group between a carbon-carbon double bond and a carboxyl group, shifted its double bond readily in the presence of sulfur dioxide to form crotonic acid (25).

The isomerization of propylene oxide over chromic oxide gel catalyst at 300° to 350° C. has produced allyl alcohol and propionaldehyde in combined yields up to 95%, with small amounts of acetone and products of side reactions. Under best conditions allyl alcohol was the major product (16).

The aluminum chloride-catalyzed isomerization of *p*-cresol has been studied (5, 8). At atmospheric pressure, the reaction rate constant was found proportional to the amount of aluminum chloride present in excess of 1 mole per mole of cresol. The catalyst combined with cresol in a 1:1 molal ratio to form an inactive complex, accompanied by liberation of gaseous hydrogen chloride. With a 2:1 catalyst to cresol ratio, up to 64% yield of *m*-cresol was obtained. The rate of formation of *o*-cresol was comparatively low. Under pressure of hydrogen chloride, isomerization was obtained with only 0.51 to 0.54 mole of catalyst per mole of cresol, showing that the formation of catalyst complex was reversible, but the yield of isomers was low and by-product formation high.

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NITRATION



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IN CONTINUATION of the review of nitration processes and the mechanism of nitration (6, 7), an over-all picture of nitration is presented. This review covers the treatment of organic compounds with nitric acid or its equivalent to produce both nitrates and nitro compounds.

MANUFACTURE OF NITRATES

A study of the nitration of glycerol was made by Fierz-David and Fehrlin (11). They found that on nitration of glycerol with mixed acid there are formed, in addition to the nitrates, mixed mononitrate monosulfates which can be isolated in a pure state as salts of brucine. On the other hand, the mixed dinitrate monosulfates and the mixed mononitrate disulfates hydrolyze so easily that they cannot be obtained in a pure state. Considering all factors, the authors were able to show that on nitration of glycerol the yield of glycerol derivatives is quantitative. They point out that the formation of diglycerol tetranitrate or any destruction of the glycerol is not to be accepted.

The manufacture of a "dense" type of nitrocellulose as carried out at a Scottish factory is described by Picton and Kelland (23). The cellulose in the form of sheet wood pulp is machine cut to

the desired particle size. The wood pulp chips are nitrated batchwise using an acid to cellulose ratio of 10 to 1, which is stated to be much lower than the ratio used with cotton linters. The nitric acid content of the mixed acid may be varied from about 40 to 70%, depending on the type of nitrocellulose to be produced.

The spent acid is recovered by centrifuging the charge, care being taken to avoid prolonged wringing so that a minimum of denitration takes place. After wringing is complete, the charge is drowned in water and then stabilized. The dense nitrocellulose thus produced is said to retain essentially its granular structure, thus giving it a marked advantage in handling over that produced from cotton linters.

Watanabe (25) published a series of articles on the preparation of nitrocellulose. His work includes composition of mixed acids—i.e., sulfuric-nitric acid and acetic-nitric acid mixtures. Also, the nitration of cellulose in organic medium was studied, using mixtures of nitric acid-carbon tetrachloride and nitric acid-acetic anhydride-carbon tetrachloride. The stability of nitrocellulose was also investigated.

The nitration of cellulose using nitric acid vapors as the nitrating medium has been investigated by Trombe and co-workers

(24). This study includes both laboratory and pilot plant preparation of nitrocellulose. From this work the authors set up conditions for the vapor-phase nitration of cellulose, including time, temperature, pressure, concentration of nitric acid vapor, rate of nitric acid feed, amount of cellulose treated, and quality of cellulose. The nitrocellulose produced by the vapor-phase nitration is said to be more easily stabilized and to be of uniform quality. Also, according to the authors, less acid is required. Both batch and continuous units for large-scale installation are discussed.

Calvet (3) studied the heat of formation of nitrocellulose. He found the heat evolved for each hydroxyl group nitrated is about the same with a variation of $\pm 7.5\%$. He reports a value of 2050 calories per hydroxyl group nitrated, and this value is ± 150 calories for either a nitric-sulfuric acid mixture or for nitric-acetic acid mixture. The total heat for the nitric-sulfuric acid mixture is 17,650 calories as against 13,850 calories for the nitric-acetic acid mixture.

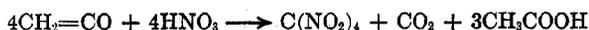
Deans and Nicholls (9) modified the present methods of nitration of polyvinyl alcohol using fuming nitric acid or nitric-sulfuric acid mixtures, so that the nitrated products are improved in nitrogen content, color, and yield. A method of using fuming nitric acid and acetic anhydride for the nitration of polyvinyl alcohol was also developed. The authors reported the explosive characteristics of polyvinyl nitrate prepared by various methods.

MANUFACTURE OF NITRO COMPOUNDS

Melander (21) studied the mechanism of nitration of toluene, and he concluded that the addition of the nitrating agent (NO_2^+) is the rate-determining step, followed by a rapid splitting-off of the hydrogen. The intermediate ion might have a quinonoid character. Gillespie and co-workers (13) also have investigated further the nitration of toluene, and they concur in Melander's work.

Hager (14) has reviewed the preparation of tetranitromethane, giving a bibliography containing 99 literature references. He also discusses some of the properties of this compound. The article describes the continuous preparation of tetranitromethane developed in Germany during World War II, comprising the nitration of acetylene using nitric acid containing mercury nitrate as a catalyst. This process is the same as that described by Hunter (18) and referred to in the 1948 review of unit processes (6).

A new method for the preparation of tetranitromethane has been reported by Darzens and Levy (8). The process comprises slowly passing a stream of ketene ($\text{CH}_2=\text{CO}$) into cooled 100% nitric acid. The reaction is immediate, and after it is completed the mixture is poured on ice and tetranitromethane separated. The authors report a 90% yield. Ketene is produced by pyrolyzing acetone.



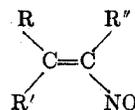
Hass and Alexander (15) studied the effect of adding separately nitrogen, nitric oxide, and oxygen on the nitration of methane with nitric acid. Also, the effect of adding oxygen on the nitration of propane with both nitric acid and nitrogen dioxide was investigated. A detailed description of the nitrating apparatus used in these studies is given. Conclusions drawn by the authors indicate that nitrogen appreciably affects the reaction; that the introduction of nitric oxide in excess greatly diminishes the formation of nitroparaffins, increasing the acidity of the product; and that the introduction of oxygen increases the conversion of both nitric acid and nitrogen dioxide to nitroparaffins. The mechanism of this action of oxygen was not established.

Coe *et al.* (5) patented a process for the nitration of olefins and diolefins of either acyclic or cyclic structure possessing an unsaturated carbon-carbon linkage. The nitration is carried out so that the double bond is unaffected and the resulting nitro com-

pound is of the same degree of unsaturation as the parent compound. Nitration is carried out using 60 to 100% nitric acid, preferably at atmospheric pressure and at comparatively low temperatures. Preferred temperatures of nitration range from -40° to about 0° C., but in no case should this temperature exceed the boiling point of the compound at the pressure used.

The nitric acid is added slowly with agitation to the material to be nitrated. In the case of solids, a suitable solvent, which is inert to nitric acid, may be used to put the solid in solution or a solvent common to both nitric acid and the compound may be used.

The nitrated compound may be represented by the empirical formula



in which R , R' , and R'' may be hydrogen atoms or alkyl groups.

The inventors state that these compounds are valuable chemical intermediates for use in the formation of synthetic resins, unsaturated amines, wetting agents, Diesel fuel additives, fuel for jet motors, and as insecticides which include the halo or cyano addition products.

Patents have been issued to the Honorary Advisory Council for Scientific and Industrial Research (16, 17) covering the preparation of 3,7-dinitropentamethylenetetramine, which when nitrated gives cyclonite (cyclotrimethylenetrinitroamine), homocyclonite (cyclo-tetramethylenetetranitroamine), or new compounds (a) 1,9-diacetoxypentamethylene-2,4,6,8-tetramine, and (b) its 1,9-dinitroxy analog depending on the procedure followed. Compounds (a) and (b), and (c) which is the 1,9-dialkoxy derivative of (b), are claimed as new explosive compounds, together with the various methods of production. Compound (a) is produced by suspending 3,7-dinitropentamethylenetetramine in acetic anhydride maintained at 65° C., then adding with stirring 99.6% nitric acid. Compound (b) is prepared by adding 3,7-dinitropentamethylenetetramine to 106% nitric acid (absolute nitric acid containing sufficient dissolved nitrogen pentoxide to titrate as 106% nitric acid). The temperature is held at 20° C. with provision to ensure that the reaction is carried out under anhydrous conditions.

McKay and co-workers (20) have investigated the reaction of 3,7-dinitropentamethylenetetramine with nitric acid-ammonium nitrate mixtures. They found the products produced by this reaction are trimeric and tetrameric methylenenitroamines, cyclonite, and homocyclonite. When the ammonium nitrate is replaced by anhydrides, such as nitrogen pentoxide and acetic anhydride, then terminally esterified linear polymethylenetriamines, such as compounds (a) and (b), above, are formed.

According to Brockman and his colleagues (2), cyclonite prepared from hexamethylenetetramine contains homocyclonite as an impurity. They found this impurity is not present in cyclonite prepared by the nitration of 1,3,5-trinitrosocyclohexane, which is slowly added with stirring to a solution of hydrogen peroxide and 99% nitric acid at -40° C. A summary of twenty runs, showing the effect of certain variables, is included.

Aristoff *et al.* (1), Chute *et al.* (4), and Myers and Wright (22) have published articles on the various reactions of hexamethylenetetramine with nitric acid when used in various ways as a nitrating agent. These articles discuss the mechanism of the various reactions and show numerous intermediate and side reactions which occur during the production of cyclonite and its homologs by the various methods.

In connection with the nitration of hexamethylenetetramine to produce cyclonite by either the direct nitration process (the use of a large excess of nitric acid) or by the combination process (a solution of hexamine in acetic acid is mixed simultaneously with acetic anhydride and with a solution of ammonium nitrate

in nitric acid), Jones and Thorn (19) have investigated the ultraviolet absorption spectra of binary nitric acid solutions in an attempt to gain information about the mechanism of nitration of hexamine under conditions operative in both processes. The ultraviolet spectrum of nitric acid in the presence of nitrogen pentoxide and water is interpreted in terms of a series of equilibria which involves the nitrate (NO_3^-) and nitronium (NO_2^+) ions and associated and nonassociated molecules.

The mechanism of nitration of hexamethylenetetramine to yield cyclonite was also investigated by Di Cerrione (10). He shows the low yield is due to the formation of secondary products, the most important of which is trinitrodiaminodimethylamine.

Fisher (12) investigated the preparation of homocyclonite, and he found it could be readily produced in greater quantity by using less acetic anhydride. According to the author, homocyclonite has no explosive value over cyclonite.

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THERE has been little apparent decrease of interest in that phase of petrochemicals identified with oxidation reactions, to judge by published technical and patent literature since the previous review (63).

It is of interest once more to discuss briefly the recent history of the McCarthy Chemical Company plant located near Winnie, Tex. This plant was designed to handle a mixture of "tonnage oxygen" and natural gas containing significant proportions of ethane, propane, butane, and higher hydrocarbons. The mixture of hydrocarbons, initially containing on the order of 3 to 4 mole % of free oxygen, was to react at full line pressure of about 800 pounds per square inch while it was being heated in a tubular heater. After a short period of operation, during which satisfactory performance of the tonnage oxygen plant was reported, the plant was shut down in early 1950 and has not been reopened. Difficulties of two sorts were reported to have been encountered—inadequate conversion of oxygen to products of value and difficulties in the recovery and purification of valuable products. No detailed account of the operations has been made public and the plant is now reported to be for sale.

Various aspects of the oxidation of natural gas to produce useful oxygenated chemicals have been considered to show that the important process variables for a given plant design are: temperature, pressure, reaction mixture composition, recycle, catalyst, and reaction time. Use of "tonnage oxygen" instead of air results in a minimum of inert gas contamination of product and requires less power for compression relative to air but, of course, costs more than air (99).

Further information has been published on the technique and economics of tonnage oxygen manufacture. Some of this material has been reviewed previously prior to publication. Thus, the economics of the Elliott Company process have been

described in considerable detail. A description of the system for removal of impurities employed in the Elliott Company process has been published (83). The Elliott system modifies the Linde-Fränkli process by eliminating the use of high pressures, using multifluid exchangers in place of regenerators, and using an intermediate pressure column to improve oxygen recovery (27). A thermodynamic analysis of processes for manufacture of oxygen-enriched air has been published from Yale University (8).

A special, stepwise procedure in the vapor phase, noncatalytic oxidation of hydrocarbons such as propane or butane is claimed to result in substantially increased per-pass conversion of hydrocarbon to useful oxygenated products relative to that obtained in usual single-stage procedure (50).

Continuing attention is being given to the conversion of natural gas to synthesis gas mixtures of hydrogen and carbon monoxide. A general thermodynamic analysis of such synthesis gas production for comparison of (1) the steam-carbon dioxide reforming and (2) the partial oxidation processes has been presented with a chart to show equilibrium mixtures. The first of these processes uses cheap reactants, but reaction is endothermic and equipment expensive (68). The second process is exothermic, requires less expensive equipment, but has the disadvantage of requiring relatively costly oxygen.

In the partial oxidation process, equilibrium between methane, hydrogen, carbon monoxide, carbon dioxide, and water depends upon the temperature level, higher temperatures favoring the formation of water and carbon monoxide. The use of a fluidized catalyst bed, the catalyst being a group VIII metal supported on refractory particles, has been claimed to improve the partial oxidation process (78).

Reaction of preheated oxygen and natural gas under pressure

OXIDATION