NOMENCLATURE

A_s = surface area of spray droplets in tower at any time, sq. ft.
A_w = surface area of wetted wall, sq. ft.
b = diffusivity of solute gas, consistent units
C_1, C_2 = constant coefficients in consistent units
d = mass median diameter of spray droplets, microns
D_c = diameter of tower, ft.
G = gas flow rate through duct at tower entrance, lb. moles/(min.) (sq. ft.)
ΔH = over-all pressure loss across cyclone, inches of water
ΔH_v = over-all pressure expressed as number of entrance velocity heads
K_{gs} = mass transfer coefficient for spray droplets, lb. moles/(min.) (sq. ft.) (atm.)
K_{gw} = mass transfer coefficient for the wetted wall, lb. moles/(min.) (sq. ft.) (atm.)
L = liquid rate, gal./min.
m, q = exponential constants
n = number of nozzles
N_s = number of transfer units on spray surface
N_T = total number of transfer units in tower
N_w = number of transfer units on wetted wall surface
p = partial pressure of solute gas, atm. Subscript 1 refers to inlet gas, subscript 2 to outlet gas, and asterisk to equilibrium pressure
R = distance from center of tower, ft.
S = cross-sectional area of gas inlet, sq. ft.
Sc = Schmidt number $(\mu/\rho b)$
V_e = gas velocity through duct at tower entrance, ft./min.
V_w = gas velocity near the wall, ft./min.
π = total pressure of gas, atm.
ρ = density of air, lb./cu. ft.
μ = viscosity of air, consistent units

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Vapor-Phase Nitration of Saturated Hydrocarbons

H. B. HASS AND H. SHECHTER[1]

Purdue University and Purdue Research Foundation, Lafayette, Ind.

SINCE 1930 considerable interest has been directed toward developing a new unit process, the vapor-phase nitration of aliphatic hydrocarbons. As a result the Commercial Solvents Corporation established an efficient industrial process for the production of nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane by the reaction of nitric acid and propane at temperatures above 400° C.; recently Imperial Chemical Industries, Ltd., announced the availability of these four nitroalkanes. On the basis of the investigations which have been conducted at Purdue University and in many other laboratories during the past sixteen years, it is now possible to generalize about many of the complex actions of the vapor-phase nitration reaction. As a result a number of empirical rules based on quantitative experimental evidence have been formulated which characterize the reactions between the various nitrating agents and saturated hydrocarbons.

RULE 1

If pyrolytic temperatures are avoided during the nitration of alkanes or cycloalkanes, no carbon skeleton rearrangements occur. This rule is in harmony with the corresponding one for the monochlorination of alkanes. Nitration temperatures usually range from 150° to 475° C., and thus pyrolysis of the parent hydrocarbon does not constitute one of the principal high temperature reactions. However, considerable decomposition of the various nitrated and oxidized compounds occurs and results in the formation of olefins and degraded products. For example, pyrolysis of nitroethane and 1-nitropropane yields olefins, aldehydes, carbon monoxide, carbon dioxide, and nitrogen but no lower nitroalkanes (*18*).

The data presented in Table I indicate that nitration of 2,2-dimethylpropane, 2,2-dimethylbutane, 2,2,3-trimethylbutane, and cyclopropane yields no products resulting from structural isomerization. Since nitroneopentane is obtained from neopentane and neohexane, the reactions producing hydrogen or alkyl substitution apparently do not proceed through a carbonium ion mechanism.

RULE 2

Simple alkanes or cycloalkanes in the vapor phase yield products containing not more than one nitro group per molecule. According to the experiments conducted in this laboratory, nitration of saturated hydrocarbons with either nitric acid or nitrogen dioxide at temperatures ranging between 248° and 710° C. does not produce polynitroalkanes. Urbanski and Slon (*23*) report that the reaction of propane and nitrogen dioxide at 200° C. and long exposure times yields mono- and dinitroalkanes, and Levy (*13, 14*) claims that nitration of butane with nitrogen dioxide, in the presence of a borosilicate catalyst containing arsenic or antimony, results in the formation of 2,3-dinitrobutane. A number of unsuccessful attempts have been made to confirm these results in this and in other laboratories, and it seems that the identification of the products reported by these investigators is somewhat inconclusive.

This generalization continues to surprise the authors, since polynitroalkanes may be produced by the corresponding liquid phase reaction. Polynitro compounds, if formed, probably

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[1] Present address, The Ohio State University, Columbus, Ohio.

If pyrolytic temperatures are avoided during the vapor-phase nitration of alkanes and cycloalkanes, no carbon skeleton rearrangement occurs. Simple alkanes or cycloalkanes in vapor phase yield products containing not more than one nitro group per molecule. Any primary, secondary, or tertiary hydrogen atom in a hydrocarbon is capable of being substituted by a nitro group. The nitro group can replace any alkyl group in an alkane, but simple nitro products are not formed by fission of an unsubstituted cycloalkane. Highly branched hydrocarbons undergo less fission during nitration than do less branched or normal ones. Nitrogen dioxide and nitric acid yield identical products, but the latter gives better yields and higher nitration rates. Oxidation accompanies nitration: however, little nitric acid is reduced to nitrogen under optimum reaction conditions. The nitration of methane has an activation energy of about 52 kg.-cal. per mole; thus nitration rates are greatly accelerated by increased temperatures. The fission reaction, which results in the substitution of alkyl and cycloalkyl groups, has a higher temperature coefficient than those reactions which substitute hydrogen atoms. The temperature coefficients for hydrogen substitution are in the order primary > secondary > tertiary. Total yields of nitro compounds vary comparatively little over a wide temperature range if exposure times and temperatures are correctly matched. There is, however, an optimum temperature for each hydrocarbon at a given pressure. Elevated pressures increase the reaction rate and the difficulty of temperature control without very greatly affecting the yields. The catalysts preferentially accelerate the competing oxidation reactions.

would result from the relatively slow action of the nitrating agent on the nitroalkanes produced by the primary reaction; however, under the conditions necessary to effect the vapor phase reaction, the concentration of nitroalkanes is small, and, therefore, further nitration is not greatly favored. Many polynitro compounds derived from the lower alkanes are unstable to heat and nitric acid and therefore would not be expected as reaction products. Dinitroalkanes in which the nitro groups are separated by more than three carbon atoms are sufficiently stable to be expected as reaction products if they are formed; thus, it is not known whether this generalization will apply as the alkane series is ascended.

RULE 3

Any primary, secondary, or tertiary hydrogen atom in a hydrocarbon is capable of being substituted by a nitro group. Evidence for this generalization is presented in Table I. Substitution for a neohydrogen atom has been accomplished in good yields in the nitration of neopentane (2,2-dimethylpropane), neohexane (2,2-dimethylbutane), and triptane (2,2,3-trimethylbutane). Cycloalkanes yield the expected products, and even cyclopropane can be nitrated in fair yields.

The substitution of a nitro group for a hydrogen on a carbon atom attached to a quaternary carbon atom perhaps was to be expected, since the corresponding liquid phase reaction may be effected. However, Nametkin, Dobrovolskaya, and Oparina (*15*) report that the nitration of camphane in liquid phase failed to yield any tertiary nitro compound. Since nitration of bicyclo[2.2.1]heptane in vapor phase results in a considerable yield of the tertiary nitro derivative (*2*), it appears that this reaction will be of particular interest in rendering available a new class of tertiary nitropolycycloalkanes. Further evidence indicating that a frontal attack mechanism produces hydrogen substitution in this reaction may be derived from these results.

RULE 4

The nitro group can replace any alkyl group in an alkane, but simple nitro products are not formed by fission of an unsubstituted monocycloalkane. Evidence for this generalization is presented in Table I. For example, nitration of 2-methylbutane yields nitromethane, nitroethane, 2-nitropropane, and 2-nitrobutane by substitution of any alkyl radical and 2-methyl-1-nitrobutane, 2-methyl-2-nitrobutane, 3-methyl-2-nitrobutane, and 3-methyl-1-nitrobutane by substitution of the various hydrogen atoms.

At one time it was suggested (*9*) that the fission reaction by which nitro groups replace alkyl or cycloalkyl radicals might be due to addition complexes between nitric acid or nitrogen tetroxide and the hydrocarbon. These complexes might then split to yield a molecule of lower nitroalkane and one of alcohol, if nitric acid were the attacking reagent; similarly, the nitrogen tetroxide complex would yield two molecules of nitroalkane. These mechanisms now seem untenable since neither α,ω-dinitroalkanes nor α,ω-nitroalcohols are obtained from the nitration of cyclic alkanes. Further studies are now being conducted in an effort to elucidate the mechanism of the hydrogen substitution and the alkyl fission reactions.

RULE 5

Highly branched hydrocarbons undergo less fission during nitration than do their less branched isomers. Correspondingly, hydrogen substitu-

TABLE I. NITRATION OF SATURATED HYDROCARBONS WITH NITRIC ACID

Hydrocarbon	Reaction Products
Methane	Nitromethane (*3, 7, 10, 12, 17*)
Methane^a	Nitromethane (*23*)
Ethane	Nitromethane, nitroethane (*6, 7*)
Propane	Nitromethane, nitroethane, 1-nitropropane, 2-nitropropane (*6, 7*)
Propane^a	Nitromethane, nitroethane, 1-nitropropane, 2-nitropropane (*5*)
Butane	Nitromethane, nitroethane, 1-nitropropane, 1-nitrobutane, 2-nitrobutane (*6, 7*)
2-Methylpropane	Nitromethane, 2-nitropropane, 2-methyl-1-nitropropane, 2-methyl-2-nitropropane (*6, 7*)
Pentane	Nitromethane, nitroethane, 1-nitropropane, 1-nitrobutane, 1-nitropentane, 2-nitropentane, 3-nitropentane (*8*)
2-Methylbutane	Nitromethane, nitroethane, 2-nitropropane, 2-methyl-1-nitropropane, 2-nitrobutane, 2-methyl-1-nitrobutane, 2-methyl-2-nitrobutane, 3-methyl-2-nitrobutane, 3-methyl-1-nitrobutane (*19*)
2,2-Dimethylpropane	Nitromethane, 2-methyl-2-nitropropane, 2,2-dimethyl-1-nitropropane (*11*)
2,3-Dimethylbutane	Nitromethane, 2-nitropropane, 3-methyl-2-nitrobutane, 2,3-dimethyl-2-nitrobutane, 2,3-dimethyl-1-nitrobutane (*4*)
2,2-Dimethylbutane	Nitromethane, nitroethane, 2-methyl-2-nitropropane, 2,2-dimethyl-1-nitropropane, 2-methyl-2-nitrobutane, 2,2-dimethyl-1-nitrobutane, 2,2-dimethyl-3-nitrobutane, 3,3-dimethyl-1-nitrobutane (*11*)
2,2,3-Trimethylbutane	Nitromethane, 2-nitropropane, 2-methyl-2-nitropropane, 2,3-dimethyl-2-nitrobutane, 2,2-dimethyl-3-nitrobutane, 1-nitro-2,2,3-trimethylbutane, 3-nitro-2,2,3-trimethylbutane, 1-nitro-2,3,3-trimethylbutane (*22*)
Cyclohexane	Nitrocyclohexane (*20, 23*)
Cyclopentane	Nitrocyclopentane (*20*)
Cyclopropane	Nitrocyclopropane (*20*)
Bicyclo[2.2.1]heptane	1-Nitrobicyclo[2.2.1]heptane, endonitrobicyclo[2.2.1]heptane, *dl-cis*-2-nitrobicyclo[2.2.1]heptane, *dl-trans*-2-nitrocyclo[2.2.1]heptane (*2*)

^{a} Nitrating agent, nitrogen dioxide.

tion is favored when highly branched structures are nitrated. As can be seen from the data in Table II concerning the nitration of the isomeric butanes and pentanes, the mole ratio of the product resulting from hydrogen substitution to that resulting from fission decreases as the carbon skeleton becomes more highly branched. For example, the reactions of nitric acid and pentane, isopentane (2-methylbutane), and neopentane (2,2-dimethylpropane) under similar experimental conditions give fission products of 42.7, 36.8, and 27.0%, respectively. Since nitration producing fission is primarily a competing and not a consecutive reaction, it is believed that these results are due to a steric effect. The molecular models of 2,2-dimethylpropane, 2,2-dimethylbutane, and 2,2,3-trimethylbutane illustrate the hindrance involved in a carbon skeleton attack.

RULE 6

Nitrogen dioxide and nitric acid yield identical products, but the latter reagent gives better yields and higher nitration rates. Nitric acid ranging in concentration from 35 to 70% HNO_3 by weight is usually employed as the nitrating agent, since it is inexpensive and relatively easy to handle; however, 100% acid may be used efficiently.

Nitration of propane with nitrogen dioxide at temperatures ranging from 248° to 710° C. results in the formation of nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane. However, yields of nitroalkane, based on nitrating agent consumed, are higher when nitric acid is used. Comparative reaction rate studies indicate that substitution of any hydrogen atom in an alkane is effected much more rapidly by nitric acid than by nitrogen dioxide (*1*). For example, duplicate experiments showed about four times as great a yield with nitric acid as with nitrogen dioxide. At present it appears that nitrogen dioxide, a relatively expensive reagent, will not become important industrially in this vapor-phase nitration process.

RULE 7

Oxidation accompanies nitration; however, little nitric acid is reduced to nitrogen under optimum reaction conditions. Evidence for this generalization is presented in Figure 1, a curve illustrating the effect of mole ratio of hydrocarbon to nitric acid on the conversion of acid to nitroalkane (*7*). Since extrapolation of this curve to an infinite ratio of hydrocarbon to nitric acid does not result in 100% conversion of nitric acid to nitro compound, it is apparent that the nitrating agent oxidizes the hydrocarbon as well as the nitroalkane (*7*). This conclusion is verified by the isolation of 1-propanol and 2-propanol from the nitration of propane. Since the yield of nitroalkane is fairly constant at the optimum exposure time over a wide temperature range, it appears that the increase in the rate of oxidation with temperature is of the same order of magnitude as that of nitration (*7*).

TABLE II. EFFECT OF BRANCHING ON FISSION REACTION

Hydrocarbon	Temp., ° C.	Mole % of Products	Ratio, Fission Products/ Substitution Products
Butane	420	10.5 nitromethane	0.463
		15.8 nitroethane	
		5.3 1-nitropropane	
		44.2 2-nitrobutane	
		24.2 1-nitrobutane	
2-Methylpropane	420	5.8 nitromethane	0.407
		23.1 2-nitropropane	
		7.0 2-methyl-2-nitrobutane	
		64.1 2-methyl-1-nitropropane	
n-Pentane	400	2.3 nitromethane	0.745
		10.9 nitroethane	
		16.7 1-nitropropane	
		12.8 1-nitrobutane	
		18.9 1-nitropentane	
		18.2 2-nitropentane	
		20.2 3-nitropentane	
2-Methylbutane	420	3.9 nitromethane	0.628
		8.8 nitroethane	
		16.1 2-nitropropane	
		9.8 2-methyl-1-nitropropane 2-nitrobutane	
		12.2 2-methyl-2-nitrobutane	
		14.0 3-methyl-2-nitrobutane	
		24.1 2-methyl-1-nitrobutane	
		11.1 3-methyl-1-nitrobutane	
2,2-Dimethylpropane	410	14.0 nitromethane	0.370
		13.0 2-methyl-2-nitropropane	
		73.0 2,2-dimethyl-1-nitropropane	

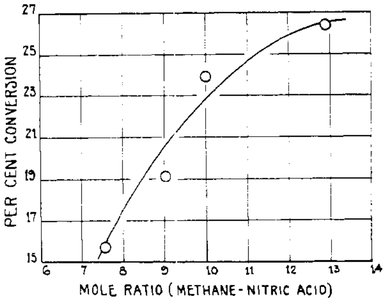

Figure 1. Effect of Mole Ratio on Nitration Reaction at 440° C. and Contact Time of 0.88–0.92 Second

The products obtained by oxidation of the reaction mixture are acids, aldehydes, ketones, alcohols, nitrites, nitroso compounds, nitro-olefins, polymers, carbon monoxide, and carbon dioxide. *p*-Formaldehyde, hydroxylamine, and hydrogen cyanide have been obtained from the nitration of methane while ammonium nitrate is formed during this reaction at high temperatures. Platinov and Shaikind (*16*) report that nitro compounds, ammonium carbonate, ammonium nitrite, and ammonium nitrate result from the nitration of gasoline fractions with nitric oxide in the presence of aluminum, cerium, and thorium oxides. In the present plant these oxidation products are largely wasted, but in a larger one their isolation should be profitable.

The exit gases from this reaction are usually colorless; this indicates the absence of large quantities of nitrogen dioxide, and only small amounts of nitric acid are obtained in the products. Since nitric oxide is the main reduction product, yields approaching theoretical can be obtained by converting this oxide of nitrogen to nitric acid and then recycling.

RULE 8

Nitration producing hydrogen substitution has a high activation energy; thus reaction rates are greatly accelerated at increased temperatures. The reaction of methane, the most difficult of the hydrocarbons to nitrate, and nitric acid has an activation energy of 52 kg.-cal. per mole (*3*); ethane is more readily nitrated, whereas little difference in reactivity is exhibited by the hydrocarbons above propane. The vapor phase reaction, in contrast with that in liquid phase, occurs very rapidly, being complete in approximately 1 second at temperatures around 400° C.

RULE 9

The fission reaction, which results in the substitution of alkyl groups, has a higher temperature coefficient than that of the hydrogen substitution reaction. It has been found that the reaction of isobutane and nitric acid at 150° C. in a sealed tube yields *tert*-nitrobutane as the only nitroalkane, whereas nitration of propane at low temperatures yields mainly 1-nitropropane and 2-nitropropane (*7*). Since nitration at low temperature yields primarily products obtained by the substitution of hydrogen atoms, it is apparent that the alkyl fission reaction has a higher activation energy. As is evident from the data presented in Table III, the fission reaction becomes more important as the temperature increases; for example, nitration of isobutane at 420° C. yields a substance containing 28.9% fission products. At very high temperatures fission may become more important than substitution. However, under the optimum nitration conditions for each hydrocarbon the yield of substituted products is usually greater, on either a mole or a weight basis, than that of the fission products.

TABLE III. EFFECT OF TEMPERATURE ON FISSION REACTION

Hydrocarbon	Temp., ° C.	Mole % of Products	Ratio, Fission Products/ Substitution Products	Temp., ° C.	Mole % of Products	Ratio, Fission Products/ Substitution Products
Propane	505–10	22.0 nitromethane 16.6 nitroethane 13.2 1-nitropropane 48.2 2-nitropropane	0.628	790–5	32.3 nitromethane 24.2 nitroethane 24.2 1-nitropropane 19.3 2-nitropropane	1.30
2-Methylpropane	150	99.0 2-methyl-2-nitropropane	...	420	5.8 nitromethane 23.1 2-nitropropane 7.0 2-methyl-2-nitropropane 64.1 2-methyl-1-nitropropane	0.407

RULE 10

The temperature coefficients for hydrogen substitution are in the order primary > secondary > tertiary. The rate of substitution for tertiary hydrogen atoms is much greater than that for the secondary and primary positions at low temperatures; this indicates that the nitration reaction is more selective under these conditions and thus resembles the liquid phase reaction. As the temperature of reaction is increased, the rate of substitution of the primary, secondary, and tertiary positions approaches equality, and the yield of primary and secondary derivatives is increased. Therefore, it is possible to vary the composition of the reaction products by changing the temperature of the reaction.

The yield of primary nitro compounds (Table IV) at the higher reaction temperatures is usually greater than that of the corresponding secondary and tertiary isomers. Nitration of isopentane at 380° C. yields a product, on a mole basis, containing 16.6% 2-methyl-2-nitrobutane, 23.6% 3-methyl-2-nitrobutane, 9.4% 2-methyl-1-nitrobutane, and 11.1% 3-methyl-1-nitrobutane, whereas at 420° C. isopentane yields a product containing 12.2% 2-methyl-2-nitrobutane, 14% 3-methyl-2-nitrobutane, 24.1% 2-methyl-1-nitrobutane, and 11.1% 3-methyl-1-nitrobutane (*19*). Relative increase in the formation of primary nitro paraffins is probably the result of the following factors: (*a*) convergence in the primary, secondary, and tertiary positions, (*b*) high ratio of primary hydrogen atoms to the sum of the secondary and tertiary hydrogen atoms, (*c*) greater stability of the primary nitroalkanes, and (*d*) relative stereochemical ease for primary substitution.

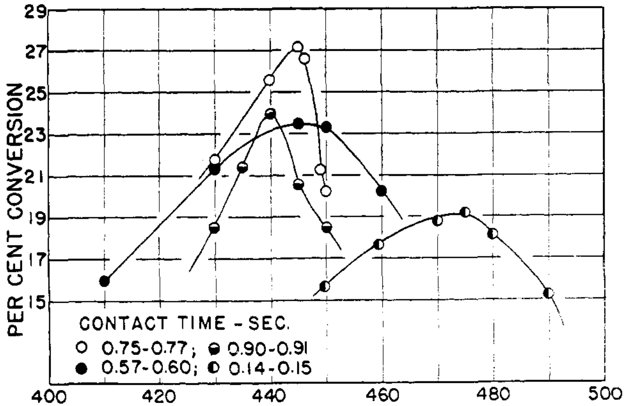

Figure 2. Effect of Temperature and Exposure Time on Nitration Reaction

RULE 11

Total yields of nitro compounds do not vary greatly if exposure time and reaction temperature are carefully matched; there is, however, an optimum temperature for the nitration of each hydrocarbon at a given pressure. This action is illustrated in Figure 2, in which reaction conversion is plotted against temperature at a constant exposure time and pressure. Temperatures below the optimum result in incomplete reaction, whereas at the higher temperatures the competitive oxidation and decomposition reactions become increasingly important. Higher temperatures and shorter exposure times decrease the conversion; conversely, precise temperature control becomes less important as the contact time is increased.

At elevated pressure the slopes of the conversion-temperature curves are much greater than those obtained at lower pressures; therefore, any nitration apparatus operating at increased pressures must provide proper heat transfer and temperature control (*20*). This fact is so important that, in the technical process for the nitration of propane, the temperature is controlled within ±1° F.

RULE 12

Elevated pressures increase the reaction rate and the difficulty of temperature control without greatly increasing the yields; however, the effect of increased pressure is more important as the hydrocarbon series is ascended. At extreme pressures, nitration, presumably a second-order reaction, is so rapid that proper temperature control is very difficult (*10*).

The optimum temperature and exposure time for nitration is decreased as the pressure of the reaction is raised; however, very high mole ratios of hydrocarbon to nitrating agent must be employed to absorb the heat from this exothermic reaction in the usual nitration apparatus. It has been found that a mole ratio of methane to nitric acid of at least 10:1 is necessary to control this reaction even in small diameter reactors immersed in molten salt; however, much smaller mole ratios may be used efficiently to nitrate the more complex hydrocarbons.

TABLE IV. EFFECT OF TEMPERATURE ON RATE OF SUBSTITUTION OF PRIMARY, SECONDARY, AND TERTIARY HYDROGEN ATOMS

Hydrocarbon	Temp., ° C.	Mole % of Products	Temp., ° C.	Mole % of Products
2-Methylpropane	150	99.0 2-nitro-2-methylpropane	420	5.8 nitromethane 23.1 2-nitropropane 7.0 2-methyl-2-nitropropane 64.1 2-methyl-1-nitropropane
2-Methylbutane	380	11.7 nitromethane 8.8 nitroethane 7.0 2-nitropropane 11.8 {2-methyl-1-nitropropane 2-nitrobutane} 16.6 2-methyl-2-nitrobutane 23.6 3-methyl-2-nitrobutane 9.4 2-methyl-1-nitrobutane 11.1 3-methyl-1-nitrobutane	420	3.9 nitromethane 8.8 nitroethane 16.1 2-nitropropane 9.8 {2-methyl-1-nitropropane 2-nitrobutane} 12.2 2-methyl-2-nitrobutane 14.0 3-methyl-2-nitrobutane 24.1 2-methyl-1-nitrobutane 11.1 3-methyl-1-nitrobutane

In general, the yield of nitro paraffins increases with the hydrocarbon concentration; however, no great advantage can be gained by operating this process with a hydrocarbon–nitric acid mole ratio greater than 15:1 (*10*). It has been found that the yields, based on hydrocarbon consumed, may be increased by diluting the reactants with nitrogen (*17*); however, yields based on nitric acid are lowered unless a large hydrocarbon–acid ratio is used. When the nitration reaction is performed with large nitric acid–hydrocarbon ratios, temperature control is difficult, and, thus, burning or explosion of the reactants may occur.

RULE 13

Catalysts accelerate oxidation rather than nitration. Silica gel, nitric oxide, platinum oxide, iron, copper, lead, and the heavy metal oxides catalyze oxidation and thus result in poor yields of nitro paraffins (*7*), whereas light (*21*), aluminum nitrate, or carbon monoxide have no appreciable effect. Levy (*13*) reports that a borosilicate glass containing 0.23% arsenic catalyzes the reaction of paraffins with nitric acid or nitrogen dioxide; however, several investigators have been unable to confirm these results. Since the yields obtained in this laboratory in the absence of catalysts are much higher than those claimed by Levy (*14*), it is possible that the principal function of the catalyst was to help maintain proper temperature control by causing turbulent flow.

Construction materials which have no appreciable effect on the nitration reaction are glass, silica, platinum, and gold, whereas ferrous surfaces promote rapid oxidation and decomposition of the reaction mixture. It has been found that the chromium-nickel steels which resist the corrosive action of nitric acid at high temperature will not greatly affect the oxidation and decomposition reactions if a mixture of sodium and potassium nitrate is sprayed continuously into the reactor (*12*). Reactor tubes of small diameter allow excellent heat transfer; however, they have a high ratio of surface area to volume, so that the effect of deposited catalysts is greatly magnified. Correspondingly, the effect of oxidation catalysts is diminished in tubes of larger diameter, but temperature control suffers (*12*).

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Production of Citric Acid in Submerged Culture

EDWARD O. KAROW[1] AND SELMAN A. WAKSMAN

New Jersey Agricultural Experiment Station, Rutgers University, New Brunswick, N. J.

The submerged culture fermentation method has been applied to the production of citric acid. A strain of *Aspergillus wentii* has been found to produce citric acid with complete absence of oxalic acid. A definite balance of minerals in the medium and highly aerobic conditions are necessary. Sucrose, glucose, and cane molasses purified by various means can be utilized for the production of citric acid. Neutralization of a portion of the fermentation acid with calcium carbonate results in higher yields.

THE industrial advantages of deep tank fermentations as applied both to anaerobic bacteria and to yeasts (true fermentations) and to aerobic processes (so-called oxidative fermentations and submerged mold fermentations) over surface processes are well known. Although such deep tank fermentations brought about by molds and other aerobic microorganisms have been applied with considerable success to the production of certain organic acids, such as gluconic and fumaric, and to antibiotic substances, notably penicillin and streptomycin, considerable difficulty has been encountered in the case of other processes, particularly the production of citric acid. Since Wehmer's discovery (*34*) of the ability of certain fungi belonging to the *Penicillium* group, which he designated *Citromyces*, to produce citric acid from sugar, an extensive literature has accumulated (*18*). Included are numerous reports on largely unsuccessful attempts to carry out the process in a deep or submerged state (*1, 2, 5, 9, 26, 29, 33*).

Kluyver and Perquin (*15*) developed the "shaking method" for the study of citric acid production by molds. The organism was inoculated into a medium placed in bottles. These were simultaneously shaken and aerated in a special shaking apparatus. The mold grew throughout the medium in the form of

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[1] Present address, Merck & Company, Inc., Rahway, N. J.