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NITRATION STUDIES. I. GENERAL MECHANISM OF VAPOR PHASE NITRATION

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Although liquid phase nitration of aromatic hydrocarbons has been studied exhaustively and a reasonably adequate set of mechanisms has been proposed for it, vapor phase nitration of aliphatic hydrocarbons is in a less satisfactory state. Partial mechanisms have been proposed by Hass and co-workers (1, 3) and by others (6, 9). The problem is complicated by the many side reactions which inevitably occur at elevated temperatures in the presence of highly reactive substances such as nitric acid and oxides of nitrogen. A constructive consideration of nitration mechanisms is also hampered by the paucity of quantitative data, and in many cases even of qualitative data, pertaining to the reactions believed to be occurring. Nevertheless sufficient new information has been obtained in the past few years to permit the development of broader hypotheses explaining more fully the phenomena observed. As will be shown (in this and subsequent papers) these hypotheses have proved of considerable value in improving the vapor phase nitration process and in obtaining yields of nitro paraffins and conversions of reagents above those previously attainable.

THE FREE RADICAL NATURE OF NITRATION

Probably the best evidence that vapor phase nitration is a free radical process is the fact that it occurs in the gas phase. The energy involved in the ionic fission of chemical bonds is greater than that involved in the radical fission of such bonds. This difference in energy is normally supplied in ionic fissions by the solvent, which solvates the ions by virtue of its own polar character. In the vapor phase, with solvents absent, no such factors are involved, and hence most gas reactions proceed by radical mechanisms (11). That nitration is a free radical process is also supported by, or at least in agreement with, the following facts:

(a) Factors which are generally known to increase the concentrations of free alkyl radicals in the vapor phase also increase the extent of nitration. Addition of limited amounts of oxygen and halogens in the reaction mixture has such an effect. Furthermore tetraethyllead, which generates ethyl radicals on heating, gives nitroparaffins on vapor phase nitration (2). These facts suggest that free alkyl radicals are intimately involved in vapor phase nitrations.

(b) Factors which are generally known to decrease the concentration of free alkyl radicals in the vapor phase decrease the extent of nitration of hydrocarbons. Diminished conversions are obtained when the surface in a given nitration re-

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actor is materially increased, when excess oxygen or halogen is present, or when inhibitors such as nitric oxide are introduced into the feed gases.

(c) Substances which catalyze ionic reactions, including various metal oxides and salts, have never been observed in this laboratory to increase the yields in vapor phase nitration in glass reactors, and in fact usually have the opposite effect. In steel reactors conversions are lowered if metallic oxides are not removed or inactivated by introduction of small quantities of alkali nitrates (4).

From the above discussion it is evident that an essential reaction in the nitration process is the creation of alkyl radicals by some general process or processes which may be loosely represented as,

1. $$RH \xrightarrow{A} R\cdot + H\cdot \text{ or } HA,$$

where RH is a hydrocarbon and A is an agent which promotes the formation of alkyl radicals. The agent A acts as a source of energy for the activation of the covalent R—H bond. The energy supplied is thermal or chemical in nature or both as employed in the usual vapor phase nitration process. Temperatures of 420–425° are typical and provide the thermal energy. Nitric acid, nitrogen dioxide, and oxygen supply the chemical energy. Hass and Alexander (1) have shown that oxygen has a beneficial effect in the nitration of both methane and propane. They postulate that the oxygen serves to increase the rate of formation of alkyl radicals but give no mechanism for the reaction. It seems likely that, in part, at least, the oxygen attacks the hydrocarbons directly by processes similar to those proposed by Walsh (10) for the vapor phase oxidation of hydrocarbons. As applied to propane the reactions involved (in part) would be:

2. $(CH_3)_2CH_2 + O_2 \rightarrow (CH_3)_2CHOOH$

3. $(CH_3)_2CHOOH \rightarrow (CH_3)_2CHO\cdot + \cdot OH$

4. $(CH_3)_2CHO\cdot \rightarrow CH_3CHO + \cdot CH_3$

5. $(CH_3)_2CHO\cdot + (CH_3)_2CH_2 \rightarrow (CH_3)_2CHOH + (CH_3)_2CH\cdot$

These and related processes lead to various free alkyl radicals but also to oxidation products. The free alkyl radicals are beneficial in the nitration process; the oxidation products constitute losses and affect the yields deleteriously. We have been able to show that optimum results in nitration depend on the introduction of a carefully controlled amount of oxygen in the feed gases and that this amount is dependent on the various other operating conditions.

It eventually occurred to us that halogens would serve the same beneficial purpose which oxygen serves in attacking hydrocarbons readily and in forming free alkyl radicals. However halogens would have a distinct advantage over oxygen in that the losses due to the formation of halogen compounds would be small. At nitration temperatures alkyl halides dissociate, and the hydrogen halides formed are readily reoxidized (*e.g.* by nitric acid) to free halogens. This liberated halogen can serve to produce new free alkyl radicals again and again. Hence much smaller amounts of halogens than of oxygen would be needed in the process. Furthermore it was recognized that halogen would tend to destroy any nitration-inhibiting nitric oxide present in the reactor by converting it to a nitrosyl halide. Under nitrating conditions oxygen does not convert NO to NO_2 at an adequate rate to be useful over the short contact times employed in vapor phase nitration (12).

Chlorine and bromine exert a markedly beneficial effect in vapor phase nitrations. The optimum effect is dependent on the amount of halogen used, the presence of oxygen, the alkane/nitric acid ratio, and other factors which will be reported in subsequent papers.

It is evident from these studies of the effects of oxygen and halogens on nitration that an important limiting factor in previous work has been the failure to create an adequate concentration or rate of production of free alkyl radicals in the nitration zone of the reactor. It is further evident that other means of generating free radicals might also be effective in this way. Further studies along this line are now being pursued and will be reported later.

The nature of RH also influences the ease of nitration. The tendency for a given R—H bond to dissociate depends on the strength of the bond and on the stability of the free alkyl radical produced. Both of these in turn depend on the structure of R. Hydrocarbons which dissociate into radicals most readily are most easily nitrated. Methane, which is more stable to dissociation than ethane, is correspondingly more difficult to nitrate (2). For this reason nitromethane is usually prepared by nitrating higher hydrocarbons (*e.g.* propane), since these nitrate more readily than methane and give good yields of nitromethane along with other nitroparaffins. Furthermore, in any given hydrocarbon the relative amounts of different hydrogens replaced by nitro groups is in the order tertiary > secondary > primary which correlates with the relative stabilization through resonance (hyperconjugation) of the corresponding free radicals. These differences in reactivity of different RH compounds are diminished as the temperature of nitration is increased, since the energy available for activation at the higher temperatures becomes more nearly adequate for all types of bonds and consequently the nitration becomes less selective. Hence the ratios of nitroparaffins produced from a given hydrocarbon depend markedly on the temperature of nitration among other factors. This also accounts in part at least for the different ratio of products produced in liquid phase nitration as compared to vapor phase nitration, since the former is normally performed at lower temperatures than the latter (2).

THE NITRATION STEP

The step in which a nitroparaffin is produced cannot be formulated until the nitrating agent itself is defined. The high temperature decomposition of nitric acid has not been studied in detail, but it is known that NO_2, NO, O_2, and H_2O are produced (1). Most pertinent to this discussion however is the fact that the nitration of hydrocarbons may be accomplished with either nitric acid or nitrogen dioxide. Common to both of these reagents is the NO_2 radical. It seems reasonable therefore to assume that NO_2 is the nitrating agent, and that prior to its nitrating action nitric acid must dissociate, probably as follows

6. $$HNO_3 \rightarrow HO\cdot + \cdot NO_2.$$

The chief value of this assumption is that it immediately offers an explanation of the fact that nitric acid is a better nitrating agent than nitrogen dioxide in the absence of added catalysts. The hydroxyl radicals produced in equation 6 are highly reactive and are capable of converting hydrocarbons into alkyl radicals.

7. $$RH + HO\cdot \rightarrow R\cdot + HOH$$

For this reason nitrations with nitric acid proceed more smoothly than nitrations with nitrogen dioxide and lead to higher conversions based on the nitrating agent. The NO_2 radical must also be assumed to be capable of attacking hydrocarbons in the sense,

8. $$RH + \cdot NO_2 \rightarrow R\cdot + HNO_2$$

since NO_2 alone is an effective nitrating agent. However it is probably less active in this respect than the OH radical. Moreover equation 8 consumes NO_2, and this may well account for the lower conversions obtained with this nitrating agent as compared to nitric acid. Furthermore the HNO_2 formed in reaction 8 decomposes under nitrating conditions to form nitric oxide which is an inhibitor for the nitration reaction.

9. $$2\ HNO_2 \rightarrow NO + NO_2 + H_2O$$

This serves further to explain the poor results in NO_2 nitrations.

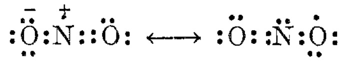
The actual nitration step may be considered to be

10. $$R\cdot + \cdot NO_2 \rightarrow RNO_2$$

which is a union of two different radicals and which involves an electron pairing reaction. It will be noted that a chain reaction is not involved in equation 10. This is in accord with the fact that the conversions based on nitrating agents are not seriously impaired by increases in surface areas of reactors. Explicitly stated, *the generation of alkyl radicals in nitration but not the actual nitration step is a chain reaction and both are free radical reactions.* The occurrence of a reaction of alkyl radicals with nitric acid to produce nitroparaffins and hydroxyl radicals cannot be excluded, however, and the authors feel that this mechanism of nitration may become quite important at lower temperatures and higher alkyl radical concentrations.

SIDE REACTIONS IN VAPOR PHASE NITRATION

A further advantage of the assumption that equation 10 represents the chief vapor phase nitration process is the ease with which it may be adapted to explain the formation of other products of the reaction. The NO_2 radical molecule is a resonance hybrid whose chief contributing forms are



$$:\overset{-}{\underset{\cdot\cdot}{\ddot{O}}}:\overset{+}{N}::\ddot{O}: \longleftrightarrow :\ddot{O}::\dot{N}:\underset{\cdot\cdot}{\dot{O}}:$$

I II

and their electronic mirror images. If an alkyl radical reacts with NO_2 in Form I the product is a nitroparaffin, but if in Form II the product is an alkyl nitrite. The behavior of alkyl nitrites under the conditions of vapor phase nitration is therefore important to a more complete understanding of the nitration process.

Alkyl nitrites appear to be extremely unstable at elevated temperatures. Rice and Rodowskas (8) decomposed ethyl nitrite at 425° in the presence of butane as a diluent. Under such conditions there is slight chance that the decomposition products will collide with unreacted nitrite molecules, and the decomposition proceeds as follows:

11. $CH_3CH_2ONO \rightarrow CH_3CH_2O\cdot + \cdot NO$

12. $CH_3CH_2O\cdot \rightarrow HCHO + CH_3\cdot$

The methyl radicals were identified as tellurides. If not removed from the reaction mixture they reacted with nitrite molecules as follows:

13. $CH_3\cdot + CH_3CH_2ONO \rightarrow CH_4 + CH_3\underset{\cdot}{C}HONO$

14. $CH_3\underset{\cdot}{C}HONO \rightarrow CH_3CHO + \cdot NO$

Kornblum and Oliveto (5) have shown that if a higher concentration of nitrite is present, the alkoxide radicals first produced react as follows:

15. $CH_3CH_2O\cdot + CH_3CH_2ONO \rightarrow CH_3CH_2OH + CH_3\underset{\cdot}{C}HONO$

16. $CH_3\underset{\cdot}{C}HONO \rightarrow CH_3CHO + \cdot NO$

It is evident from these equations that any nitrites produced in the nitration process would decompose to lower hydrocarbons, aldehydes, and nitric oxide, all of which are observed products of nitration. The lower alkyl radicals likewise produced account in part at least for the lower nitroparaffins obtained in the nitration process. Lower alkyl radicals are also formed from the direct decomposition of higher alkyl radicals and from the attack on hydrocarbons by oxygen and halogens. These account for the remainder of the lower nitroparaffins produced.

The above explanation of the origin of the lower nitroparaffins and by-products of the nitration reaction is more satisfactory than the assumption of simple thermal cracking as a source of the smaller alkyl radicals. As a matter of fact the production of methyl, ethyl, and propyl radicals from alkanes is vanishingly small at the optimum temperature and contact time for the nitration of butane (7). Furthermore, substances such as iron salts, which catalyze the cracking of C—C bonds in hydrocarbons, probably through ionic mechanisms, decrease markedly rather than increase the yields of nitroparaffins obtained. The extent of direct thermal dissociation of C—C bonds under the conditions of nitration is probably negligible. Similarly the direct cleavage of C—C bonds through attack by NO_2 or other radicals is unlikely for steric as well as energetic reasons. Hence the mechanisms of formation of small alkyl radicals would all seem to involve decompositions of larger radicals which in turn are formed through direct cleavage of C—H bonds as the primary step.

IMPORTANCE OF RADICAL BALANCE

Optimum efficiency in vapor phase nitration would be expected only if the relative amounts of alkyl radicals and nitrogen dioxide radicals were in proper balance. There are many evidences that this is true, and that either too high or too low a concentration of alkyl radicals relative to the concentration of nitrogen dioxide radicals leads to lower yields of nitroparaffins. Since the disappearance of alkyl radicals through various reactions is probably quite rapid, it is also necessary that the balance between alkyl and nitrogen dioxide radicals be a localized balance rather than an over-all average balance in the reaction tube. Thus a high concentration of nitrogen dioxide radicals at any point X cannot make up for a shortage of them at another point X′. Alkyl radicals are too reactive to remain unchanged in passing from regions where the nitrogen dioxide radical concentration is below the optimum to regions where it is at or above the optimum. Consequently it becomes important to effect the formation of alkyl radicals at a rate which is proportional to the rate of formation of NO_2 radicals in nitrations with nitric acid.

Control over the radical balance can be achieved in various ways, but most readily by utilization of those factors already mentioned which influence the rate of formation of alkyl radicals, and each of these exerts its optimum effect at a rather specific concentration for any given temperature, contact time, etc. Steam is an apparently inert diluent which may be used to lower the concentration of alkyl radicals in the reacting gases. Higher surface to volume ratios may be used similarly, since free radicals recombine more readily in contact with a solid surface.

The effect of steam under different conditions illustrates the importance of free radical balance in the nitration process. If introduced into a straightforward nitration involving butane and nitric acid it decreases the yields of nitroparaffins, probably because it decreases still further the concentration of alkyl radicals which are already below their optimum concentration. On the other hand if steam is introduced into this same nitration in the presence of excess oxygen the yields of nitroparaffins are increased, probably because the steam lowers the concentration of alkyl radicals which are now above the optimum concentration. All of these factors will be discussed in more detail and supporting experimental data will be given in succeeding papers.

FURTHER PROBLEMS

Among the more important problems awaiting further study before they can be fitted into the present interpretation of the processes occurring during vapor phase nitration are the following:

1. The combined effects of oxygen and halogen. The optimum effect of oxygen and halogens cannot be achieved if either is present alone. Why this is so and what manner of interaction occurs between them or their reaction products is not yet clear. It is possible that halogen serves in part to catalyze the oxidation of lower oxides of nitrogen to nitrogen dioxide which is then capable of further nitration.

2. The removal of nitric oxide. Nitric oxide is formed during the nitration reaction and its presence even in small amounts is detrimental to the yields and conversions. Furthermore, it is formed if nitric acid is vaporized in a separate vessel and then introduced into the reaction vessel. This necessitates the direct introduction of liquid nitric acid (usually as droplets or spray) into the reactor, a process which is very troublesome on a small scale in the maintenance of exactly controlled rates of flow and on a plant scale in the creation of hot spots and corrosion difficulties.

The rate of combination of oxygen with nitric oxide at 420° is too slow (12) to be of any value in the solution of this problem. Halogens are more effective in destroying the inhibiting effects of nitric oxide, but nitration in the presence of nitric oxide, oxygen, and chlorine gives about the same results as though none of these substances was present. The beneficial effects of oxygen and halogen as well as the detrimental effects of nitric oxide are all lost. Other solutions to this problem are being actively investigated.

3. The differences between nitric acid and nitrogen dioxide as nitrating agents. Some of these differences have been explained but others are not yet solved. Nitrogen dioxide gives better yields but poorer conversions than does nitric acid, and the beneficial effects of the oxygen-halogen combination on the conversion are less with nitrogen dioxide than with nitric acid. Finally nitrogen dioxide gives optimum nitration results at considerably lower temperatures than does nitric acid, a relationship which is not materially altered by any of the variations in conditions and percentage compositions of reactants so far studied. The lower nitration temperatures required with nitrogen dioxide necessitate much longer contact times than for nitrations with nitric acid. This makes large scale use of nitrogen dioxide relatively impractical, although in other ways nitrogen dioxide would be more satisfactory. Thus there would be fewer metering and corrosion problems with nitrogen dioxide than are now encountered with nitric acid.

4. The relative proportions of different nitroparaffins formed. The average values for the percentages of nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane produced in the commercial nitration of propane are approximately 25, 10, 25, and 40. The relative sales demand for these individual nitroparaffins unfortunately does not correspond exactly with these percentages. It is therefore important to understand thoroughly the factors which influence them, and to be in a position to control the relative amounts of any one nitroparaffin produced. Some of these factors are known. Thus higher reaction temperatures and higher oxygen contents of the feed gases increase the percentages of lower nitroparaffins obtained as would be expected on a theoretical basis. The structure of the hydrocarbon charged has already been mentioned as being important. Evidence now being accumulated indicates that the nitrating agent itself exerts a selective influence. The products in nitric acid nitrations differ percentagewise from those in nitrogen dioxide nitrations, probably in part, but not necessarily entirely, because of the differences in temperatures and contact times employed. Oxygen and halogens are influential in altering the relative

compositions of the nitrated products. Doubtless other factors and combinations of factors are also important and will have to be studied in greater detail before more exact statements about them can be made. In the laboratory, variations up to 100% in any one component have been frequently observed.

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SUMMARY

The commercial importance of vapor phase nitration and the need for basic principles to guide research in the practical improvement of this process has led the authors to formulate mechanisms to account for the phenomena observed. Many reactions occur simultaneously during vapor phase nitration, and many known variables alter the yields and conversions obtainable. The available data have been analyzed and a series of reactions and relationships has been proposed to explain the results obtained. This theoretical approach has suggested variations which have proved useful in achieving higher yields in vapor phase nitration.

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