# MECHANISM OF NITRATION REACTION AND DETONATION

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## ABSTRACT

During World War II and in the post war period considerable efforts have been made to synthesize powerful explosives. The Problem involves detailed understanding of:

(*a*) mechanism of reactions such as nitration involved in synthesis,

(*b*) mechanism of detonation in condensed explosives, and

(*c*) relationship between chemical constitution and brisance of explosives.

In this paper these aspects have been discussed.

It has been shown that atomic localization energy is a fairly quantitative measure of the reactivity of any position during nitration. It has also been shown that with the use of Lennard-Jones and Devonshire equation of state and Mayer and Careri potential it is possible to predict the detonation velocity of any explosive. In the last section a relationship between chemical constitution and velocity of detonation of explosive compounds has been derived.

## Introduction

Picric acid was the first high explosive to be discovered by Woulffe in 1771. This was followed by the discovery of mercury fulminate by Howard in 1799, of nitroglycerine by Sobrero in 1846, of trinitro-toluene by Wilbrand in 1863 and of cyclonite by Hennig in 1899. In the second half of ninteenth century smokeless powders were introduced for propulsion of projectiles. The events which made it possible include synthesis of nitro-cellulose by Pelouze in 1838, discovery of its explosive properties by Schönbein in 1846, its stabilization by Nobel, - Abel and Dewar in 1887—1890.

During World War II and in post war years considerable efforts have been made in understanding the chemistry of reactions employed in production of high explosives, in the study of phenomenon of detonation and in synthesis of powerful high explosives and improved propellants. It is proposed to give a brief review of these developments.

## Nitration of aromatic compounds

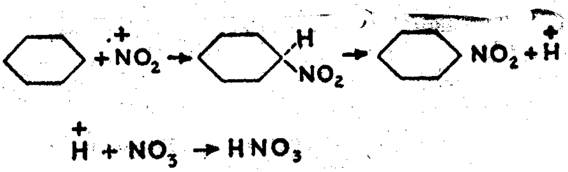
The production of important high explosives involves nitration of aromatic compounds such as toluene, dimethylaniline and phenols. The use of these compounds rests on an important fact that the presence of $CH_3$, $(CH_3)_2N$— and OH groups activates the aromatic nucleus and enhances both the yield and purity of the product. These groups also exert an O and P directing influence. It is proposed to discuss various theories which have been advanced to explain these important observations.

The active species involved in nitration is the nitronium ion $\overset{+}{N}O_2$. Cryoscopic investigations[1], study of Raman Spectra[2] of nitration media and the X-ray analysis of compounds like nitrogen pentoxide[3] have established beyond doubt the existence of nitronium ion $\overset{+}{N}O_2$. A study of effects of strong acids[4], of added nitrates and of water on the rates and kinetics of nitration suggests that nitronium ion—$\overset{+}{N}O_2$ is formed as a result of following chain reactions:

$$HNO_3 + HNO_3 \overset{fast}{\rightleftharpoons} H_2\overset{+}{N}O_3 + \overset{-}{N}O_3$$

$$H_2\overset{+}{N}O_3 \xrightarrow{slow} H_2O + NO_2^{+}$$

The mechanism of entry of $\overset{+}{N}O_2$ ion into the aromatic nucleus is probably as follows:



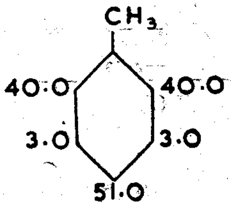
Determination of relative reactivity of various positions in any benzene derivative $C_6H_5-X$ requires the study of

(*i*) the proportions in which the three? mono-nitration products are obtained, and .

(*ii*) the ratio of relative rates of nitration of $C_6H_5X$ and benzene. If ${}^{X}K$, xkr respectively be the total rate of nitration and the rate of nitration at any position (r) of $C_6H_5X$; ${}^{H}K$ and ${}^{H}kr$ be the corresponding rates for benzene and ${}^{X}_{H}K$ and ${}^{X}_{H}k_r$ be these rates relative to any position of benzene, the fraction of any derivative say ortho is given by the equation:

$$(O) = \frac{2\ {}^{X}_{H}k_O}{2\,{}^{X}_{H}k_o + 2\ {}^{X}_{H}k_m + {}^{X}_{H}k_p}$$

With the help of this equation the values of partial rate factors ${}^{X}_{H}k_o$, ${}^{X}_{H}k_m$ and ${}^{X}_{H}k_p$ can be evaluated. As an example, the infra-red analysis shows that √ toluene on mononitration gives o, p, and m derivatives in the ratio of 60, 35 and 5 per cent respectively. The competitive method[5] gives the result that the ratio of rates of nitration of toluene to benzene[6] is 24·5 : 1. The calculated rates of nitration of various positions in toluene relative to any position in benzene are found to be as shown below:



The partial rate factors for other benzene derivatives are given in table I

### TABLE I

*Partial rate factors for nitration*

| X | ${}^{x}_{H}k_{o}$ | ${}^{x}_{H}k_{m}$ | ${}^{x}_{H}k_{p}$ | ${}^{x}_{H}K$ | Reference |
|---|---|---|---|---|---|
| $-CH_3$ | 40·0 | 3·0 | 51·0 | 23·0 | 6 |
| $-Cl$ | 0·030 | ·000 | 0·139 | 0·033 | 7 |
| $-OH$ | — | — | — | $10^4$ | |
| $-NO_2$ | $0{\cdot}24\times10^{-6}$ | $2{\cdot}75\times10^{-6}$ | $0{\cdot}03\times-10^{6}$ | $-10^{6}$ | 8 |

In order to explain these experimental results following three hypotheses which are based upon quantum mechanics have been proposed. These are discussed below:

(*i*) *Charge distribution*: It has been postulated that greater the density of charge ($q_r$) at any position r, the greater is the initial electrophilic reactivity of rth position. A brief account of the evaluation of charge distribution is given below:

The electrons belonging to 2 P$\pi$ orbitals on carbon atoms in benzene nucleus can be distributed in the molecular orbitals $\psi$'s which are linear combinations of atomic orbitals $\phi$'s as shown below:

$$\begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_n \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{1n} \cdots\cdots\cdots\cdots \\ C_{21} & C_{22} & C_{2n} \cdots\cdots\cdots\cdots \\ C_{n1} & C_{n2} & C_{nn} \cdots\cdots\cdots\cdots \end{bmatrix} \begin{bmatrix} \phi_1 \\ \phi_2 \\ \phi_n \end{bmatrix}$$

the eigen values (ε's) are given by the expression

$$\varepsilon_i = \frac{\int \psi_1 \, H \, \psi_i \, dv}{\int \psi_1 \, \psi_i \, dv}$$

$$\text{or } \epsilon_i = \frac{\Sigma C_{1r}^2 \alpha r + 2 \underset{r<s}{\Sigma \Sigma} Cir \, Cis \, \beta rs}{2 \underset{r}{\Sigma} C^2_{ir}}$$

where exchange integral $\beta rs = \int \phi_r \, H \phi_s \, dv$,

Coulomb integral $\alpha r = Hrr = \int \phi_r \, H \, \phi_r \, dv$, overlap integral $Srs = \int \phi_r \, \phi_s \, dv$. The most suitable values of C's are selected with the help of variation principle $\frac{d\varepsilon}{dc} = \Theta$, and the normalization procedure $\Sigma \overset{2}{C}ir = 1$. This leads to the following expression for eigen values:

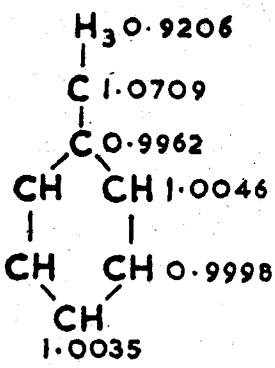
$$\varepsilon_1 = \underset{r}{\Sigma} \overset{2}{C}_{ir} \, \alpha r + 2 \underset{r<s}{\Sigma \Sigma} C_{ir} \, C_{is} \, \beta_{rs}.$$

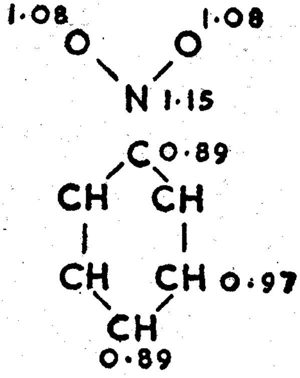
For alternative hydrocarbons the density of charge is given by the equation $q_r = \underset{i}{\Sigma} \overset{2}{C}_{ir}$ and the mobile electron bond order by the equation $P_{rs} = 2 \, \Sigma \, C_{ir} \, C_{is}$. The densities of charge estimated[9,10] in this way for various compounds are given in the formulas below.

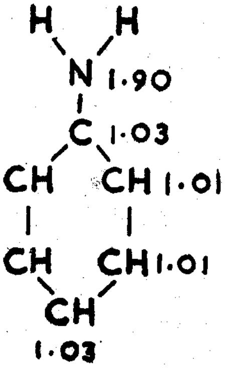
The distribution of charge indicates that $CH_3$—, —$NH_2$, — OH groups increase the charge on o and p positions whereas $\overset{+}{NO_2}$ group reduces the charge especially on o and p positions. The variation of density of charge is, however, too small to provide any quantitative information regarding the reactivities of various positions.

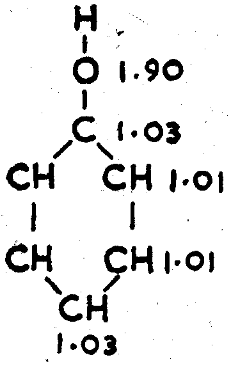
If charge densities happen to be the same for all positions, self polarizability $\pi_{rr}$ $\frac{\partial qr}{\partial \alpha_r}$ is sometimes useful in determining the reactivity of any particular position. This parameter may be evaluated with the help of the following relationship:

$$\pi_{rr} = \frac{\partial qr}{\partial \alpha_r} = 4 \sum_{j=1}^{m} \sum_{k=m+1}^{n} \frac{\overset{2}{C}_{rj} \; \overset{2}{C}_{rk}}{\epsilon_j - \varepsilon_k}$$









The change in total energy E of $\pi$ electrons as a result of small changes in $\alpha_r$, may be represented with the help of Taylor's series

$$\delta E = \frac{\partial E}{\partial \alpha_r} ( \delta \alpha_r ) + \frac{1}{2} \frac{\partial^2 E}{\partial^2 \alpha_r} ( \delta \alpha_r )^2$$

$$= q_r ( \delta \alpha_r ) + \frac{1}{2} \pi_{rr} ( \delta \alpha_r )^2$$

This expression shows that polarizability is a second order effect. Its utility in determining reactivity of various positions comes in when other methods give same values for all positions.

(*ii*) *Free valence*—In this method of estimation of reactivity it is assumed that greater is the free valence available at any position, the greater is the reactivity of that position. The total bonding $N_r$ exhibited by atom r is given by

$$N_r = \sum_s P_{rs} + C_r$$

where $C_r$ is the contribution from $\sigma$ electrons. The free valence $F_r$ is defined by the expression:

$$F_r = ( N_m - N_r )$$

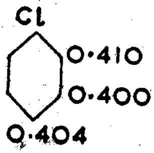
In this expression $N_m$ is the maximum bonding that a carbon atom at position r can attain, $N_m$ is usually taken equal to 4·732.

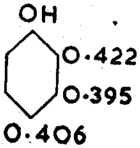
Assuming the entropy factor to remain constant, transition state theory gives the value for partial rate factor

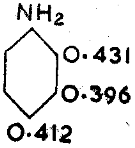
${}^{x}_{H}k_r = \exp \dfrac{\Delta^{H}U - \Delta^{x}U_r}{RT}$ where $\Delta^{H}U$ and $\Delta^{x}U_r$ are respectively the energies of activation for reaction in the benzene and $X - C_6H_5$ at position r. The free valence is related to $\Delta^{x}U_r$ as shown below[11].

$$\Delta^{x}U_r = \text{constant} - 2x\,\beta\,{}^{x}F_r$$

where x allows for changes in bonding as a result of substitution. The calculated values of partial rate factors for various positions in some important compounds are given below [12]:

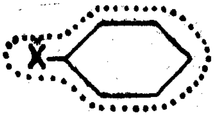




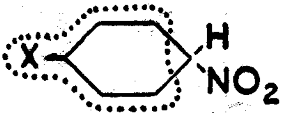


These values qualitatively indicate the relative reactivities of various positions. Quantitative agreement is, however, poor.

(*iii*) *Atom localization energy*—It has been suggested by Wheland[13] that the difference of energy between the ground state and the activated complex decides the products of nitration. The estimation of the height of such a potential barrier involves the evaluation of the energy required to localize two electrons at a given position. These two electrons are effectively removed from conjugation. The atom localization energy is the difference in the energy of the residue molecule and the original molecule.



*ground state*



*Transition state for substitution at position* p.

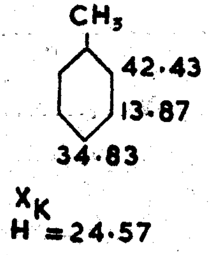
$n\pi$ electrons move over the whole molecule (....line indicates the path). Energy $= {}^{x}E$

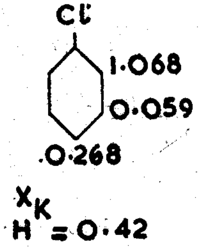
$(n-2)$ electrons move over all positions except para. Energy $= {}^{x}E_r$

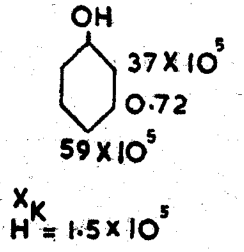
The method of molecular orbitals with suitable values of $\alpha$ and $\beta$ constants gives energies of $\pi$ electrons for each of these two types of structures. The difference of energy $({}^{x}E_r - {}^{x}E)$ is taken to be equal to $\Delta^{x}U_r$. The partial rate factors are again calculated with the help of the expression

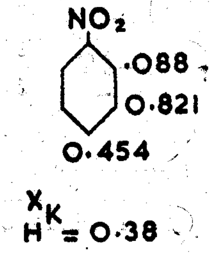
$${}^{x}_{H}k_r = \exp \frac{\Delta^{x}U_r}{RT}$$

The calculated values of partial rate factors for some molecules are given below[13]:









The high rate of nitration for phenols agrees with the data in table I. The presence of chlorine in benzene ring gives o and p directing and de-activation effects which again is in agreement with experimental facts. According to Dewar[14] atomic localization energy is the only parameter which can provide quantitative information regarding reactivity of various positions. The main difficulty is the selection of suitable values for coulomb, exchange and overlap integrals and inductive parameters.

**Detonation in condensed explosives**

A satisfactory hydrodynamical and thermodynamical theory of detonation has been advanced by Chapman, Jouguet and Hugoniot[15]. For gaseous detonation the predictions of this theory are in agreement with experimental results. For solid explosives uncertainties exist regarding the equation of state to be employed for dense detonation gaseous products. Recent investigations both on experimental and theoretical sides have removed some of these uncertainties.

Deal[16] has measured the free surface velocity of thin metallic plates in contact with detonating explosives. From the results of these measurements he has estimated the values of detonation pressures. On making use of measured values of detonation pressure(P) and velocity U and initial density $\rho_0$, a parameter $\left(\gamma = \frac{\rho_0 U^2}{P} - 1\right)$ can be evaluated. This parameter is a slowly varying function of state variables. It serves as useful criterion for comparison of experimental and theoretical results. The use of this parameter in hydrodynamical and thermodynamical theory of detonation is discussed below:

The following equations enable the calculation of pressure and velocity of detonation.

$$U = V_o\left(\frac{P}{V_o - V}\right)^{\frac{1}{2}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (i)$$

$$\triangle E_o + \triangle E_1 - H = \tfrac{1}{2}(P)(V_o - V) \ldots\ldots\ldots\ldots (ii)$$

where U, P & H, are the velocity, pressure and heat per mole of detonation; $V_o$ and V are the initial and final molar volumes. $\triangle E_o$ is the change in internal energy of products in passing from $T_o$ to T at low pressures and $\triangle E_1$ is the change in energy during compression from $P_o$ to P. $\triangle E_1$ is calculated from the equation of state with the help of the relationship:

$$dE_1 = \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dv$$

The value of H is evaluated from the heats of formation of reactants and the products of reaction. The evaluation of constants of reaction involved in these calculations requires the ratio of fugacity P* to pressure P. This ratio is calculated from the equation of state by making use of the relationship:

$$\left(\frac{\partial \log P}{\partial p}\right)_T = \frac{V}{RT}$$

The solution of three simultaneous equations consisting of Rankine—Hugoniot equation, the Chapman—Jouguet relationship derived from the condition

$$\left(\frac{dp}{dv}\right)_{RM} = \frac{P}{V_o - v}$$

and the equation of state, gives values of P and v which on substitution in equation ($i$) enable the evaluation of velocity of detonation. By employing various theoretical equations of state and intermolecular potentials the values of $\gamma$ for RDX have been calculated[17]. The results reveal that a combination of Lennard-Jones and Devonshire[18] equation of state and Mayer and Careri[19] intermolecular potential gives values of $\gamma$ which agree very closely with experimental results.

The equation of state derived by Lennard-Jones and Devonshire is based upon the consideration that an atom in a dense gas, is confined for most of its time to a cell. Its average environments are similar to an atom within a liquid or a solid. The probability of its diffusion from one cell to another is low. In view of its confinement it makes frequent multiple collisions. In contrast to this in a sparse gas binary collisions play an important part. The average field in which any one atom moves is assumed to be that due to its immediate neighbours. Approximately the field is spherically symmetrical. The partition function of a dense gas is expressed as a product of partition functions of the individual members of the assembly each member being confined to a cell from which all others are excluded. Based upon these considerations the following equation of state can be derived

$$\frac{PV}{RT} = 1 + \theta^{-1}\left[\chi_{\Gamma} - \frac{g(\Gamma W_{\Gamma})}{g\ (1)}\right]$$

$$\text{and}\ \frac{E_1}{RT} = -\theta^{-1}\left[\chi - \frac{g\ (W)}{g\ (1)}\right]$$

$$\text{where}\ \theta = \frac{kT}{\varepsilon^*},\ \Gamma = \frac{V}{V^*}, V^* = \frac{N}{\sqrt{2}} r^{*3},$$

$\epsilon^*$being the value of intermolecular potential at interatomic distance $r^*$, $E_1$ is the intermolecular repulsive energy, g function is given by the relationship:

$$g\ (y) = 2\int_{0}^{0\cdot55^3} (y)\ x^2 \exp\left[-\frac{(w\ \Gamma,x)}{\theta}\right] dx$$

and $w = \left[\omega_{(x)} - \omega_{(0)}\right]\epsilon^*$; $\omega_{(x)}$ being cell potential, $x$ is the distance from cell centre divided by nearest neighbour distance. Function $\chi$ represents the potential energy of each atom when the atoms are at the centres of their cells. Sub-script $\Gamma$ implies derivative with respect to $\Gamma$.

The choice of an intermolecular potential exerts a greater influence on the values of $r$ than does any one of the equations of state. The potential which gives best agreement with experimental results is the Mayer and Careri potential represented by the expression:

$$\frac{V_{(r)}}{\epsilon^*} = \frac{\beta}{\alpha-\beta}\ e^{\alpha(1-r/\epsilon^*)} - \frac{\alpha}{\alpha-\beta}\ e^{\beta(1-r/r^*)}$$

where r is the intermolecular distance; potential $V_r$ takes its maximum value $-\epsilon^*$ at $r=r^*$. For products of detonation of RDX the most suitable average values of the constants are found to be $\alpha = 12$, $\beta = 6$, $r^* = 4\cdot74$A and $\varepsilon^*/k = 25\cdot2$°k. Since at sufficiently high temperatures the attractive part of the potential can be neglected, the above expression assumes the form

$$\frac{V_{(r)}}{A} = e^{-r/\rho}$$

where $A = 4\cdot073 \times 10^6$ °k and $\rho = 0\cdot390$ A.

By employing these potentials and Lennard-Jones—Devonshire equation of state the values of $\gamma$ have been calculated for detonation of RDX undergoing decomposition according to equation:

$$\text{RDX} \rightarrow 3H_2O + 3\,CO + 3\,N_2$$

A comparison of calculated and experimental values is given in table II.

TABLE II

Comparison of calculated and experimental values of $\gamma$.

| Potential | $\gamma$ values | |
|---|---|---|
| | Calculated | Experimental |
| MC | 2·905 | 2·90 |
| MCR | 2·869 | |

The agreement between observed and calculated values is fairly close. Further refinements in intermolecular potential and re-assessment of composition of gaseous products will enhance our understanding of the phenomenon of detonation and of the nature of forces between molecules at close range. The work of Murgai[20] constitutes a brilliant piece of investigation on these lines.

## Chemical constitution brisance of explosives

With the help of the considerations given in the foregoing section it is possible to calculate the velocity of detonation of any explosives provided the heat of formation of the explosives is known. The latter can be estimated from the postulate of additivity of bond energies. Calculations of this type are very much involved.

As a result of systematic correlation of data it has been possible to develop an expression for detonation velocity in terms of structural features of an explosive compound. The heat of formation is usually derived from the heat of combustion which is an additive property of various groups in the molecule. On the basis of this fact the contributions which various groups make towards the heat of formation have been assessed. These contributions are of four types designated as A, B, X and Y. The velocity of detonation in terms of these constants is given by the expression [21]

$$D_{(\mathrm{m/sec})} = 2574 + 3757 \cdot \rho + \frac{\Sigma A}{m} + \frac{\Sigma B}{n} + \frac{\Sigma X}{m} + \frac{\Sigma Y}{n}$$

where m is the molecular weight, n is the number of atoms in the molecule and $\rho$ is the density of the explosive.

The principles outlined above are very useful in assessing the power and brisance of any explosive compound.

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## Discussion

Prof. Jatkar pointed out that in calculating the final pressure and temperature developed, account should be taken of the adiabatic and super adiabatic nature of the phenomenon of explosion.

Dr. Singh replied that this is taken into account when Chapman Jouguet and Rankine-Hugoniot relationships are used for the evaluation of detonation velocity.

Dr. Chatterjee wanted to know if the rate of reactions calculated by quantam mechanics for the formation of ortho, para and meta nitro-toluenes corresponded to the actual rates found out by experiments. Dr. Singh replied that it is reasonably so. Dr. Kasbekar stated that whereas from theoretical considerations the charge distribution was as $o=1\cdot0046$, $m=0\cdot9998$ and $p=1\cdot0035$, in actual nitration of toluene to MNT in the factory the products have the following composition under one set of manufacturing conditions:— Ortho=57%, Meta=3% and Para=40%

Professor Singh replied that charge distribution is not a very good criterion for this purpose. The atom localization energy gives more quantitative agreement with experimental results of this type.