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THE REACTION OF FUSED ALKALI NITRATE WITH NAPHTHACENE

BY

KACHAPPILLIL ITTOOP VERGHESE

A Thesis

Submitted to the Faculty of Graduate Studies Through the
Department of Chemical Engineering in Partial Fulfilment
of the Requirements for the Degree of
Master of Applied Science at the
University of Windsor

Windsor, Ontario
1965

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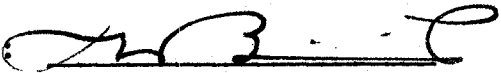
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ABSTRACT

Fused alkali nitrate has been found to oxidize naphthacene to naphthacenequinone. Trace amounts of 9-nitronaphthacene or a derivative thereof have been detected by a colour reaction with sulphuric acid. 9-nitronaphthacene was oxidised readily by fused alkali nitrate to naphthacenequinone. It is proposed that 9-nitronaphthacene is a precursor in the oxidation of naphthacene to the corresponding quinone. It is also proposed that the mechanism of nitration of naphthacene by fused alkali nitrate follows the same mechanistic path (attack on the aromatic nucleus by the species NO_2^+) as does nitration with nitric acid. This work supports the equilibrium $(\text{NO}_3^- \rightleftharpoons \text{NO}_2^+ + \text{O}^{2-})$ postulated for fused alkali nitrate.

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CHAPTER I

INTRODUCTION AND HISTORICAL REVIEW

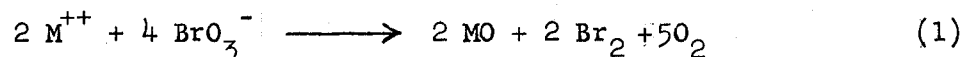
In the past decade chemists have become increasingly aware of reactions which can be carried out in the absence of the usual protic or aprotic solvent media i.e. reactions in fused salts.* The usual chemical reactions involving ionic compounds are understood to be carried out in the conventional solvent - water, which is usually deleted when the stoichiometry of the given reactions are considered.

It is not difficult to understand the chemists' aversion to reactions carried out in molten salts, since the high temperatures required (up to 1000°C for most salts, up to 2000°C for many oxides and silicates) present certain technological difficulties in the laboratory. The recent demand however for the production of titanium, zirconium, niobium and other potentially useful but expensive metals by the electrolysis of melts has forced the chemists to take a deeper interest in fused salt behaviour. Certainly improvements in the electrolytic process for sodium and other common metals are in order. Again the development of atomic power has considerably increased the importance of the study of molten salts. An atomic reactor containing a circulating liquid fuel, such as a mixture of molten salts has many advantages over the conventional reactor using a solid fuel.

* More recently the term molten salt or ionic melt has been used.

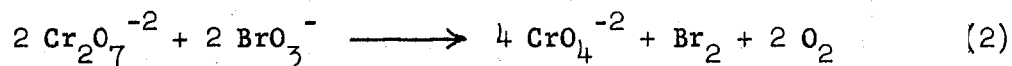
The development of modern theoretical treatments of fused salts such as molten electrolytes, ionic solvents and liquid state is based on experimental investigations of ionic melts. Fused salts provide an opportunity for the study of the theoretical problems both in physics and chemistry of the liquid state over a wide range of temperatures and for a very large variety of systems. It is of great importance then to obtain a better understanding of the nature and mechanism of ionic reactions in the absence of water or other such solvents. The present investigation is mainly concerned with the behaviour of fused alkali nitrates.

Fused alkali nitrates have been used as solvents in many reactions. Duke and Lawrence¹ studied the decomposition of dilute solutions of alkali bromates in fused alkali nitrates in the presence of a heavy divalent metal ion M^{++} . The reaction is shown in equation (1).

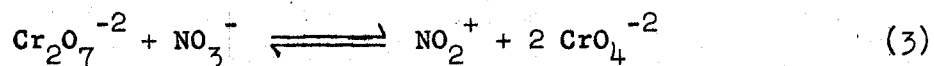


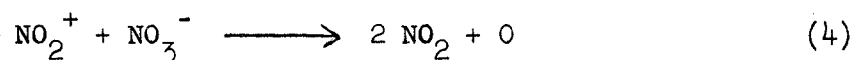
The rate of decomposition of bromates varied with the metal used.

Duke and Schlegel² reported the following reaction (equation 2) between dichromate and alkali bromates in fused alkali nitrate:



Duke and Iverson³ studied the reaction between dichromate and nitrate in fused alkali nitrates. The sequence of reaction steps was represented by the following equations:





It can be seen that the latter reaction (equation 4) results in a decrease in the total acid concentration. If NO_2^+ did not decompose into insoluble gases, there would not be any change in the total acid concentration. The rate of decrease in acid concentration is given by the first order expression:

$$-\frac{d[\text{A}_T]}{dt} = k[\text{NO}_2^+]$$

where $[\text{A}_T]$ is the total acid concentration and is equal to the sum of the concentrations of the species, $\text{Cr}_2\text{O}_7^{-2}$ and NO_2^+ .

The nitrate ion concentration does not appear in the rate expression since its concentration is exceedingly high (solvent). The equilibrium (equation 3) which produces NO_2^+ lies far towards the left and thus the concentration of NO_2^+ can be neglected compared with that of $\text{Cr}_2\text{O}_7^{-2}$. Thus $[\text{A}_T]$ is equal to $[\text{Cr}_2\text{O}_7^{-2}]$. The equilibrium constant (K) for equation (3) is given by the expression:

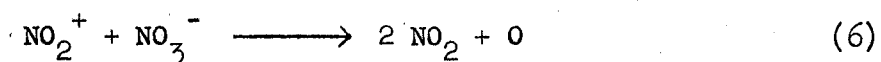
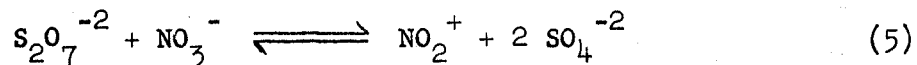
$$K = \frac{[\text{CrO}_4^{-2}]^2 [\text{NO}_2^+]}{[\text{Cr}_2\text{O}_7^{-2}]}$$

Substitution for $[\text{A}_T]$ and $[\text{NO}_2^+]$ in the rate equation leads to the relation

$$-\frac{d[\text{Cr}_2\text{O}_7^{-2}]}{dt} = \frac{k K [\text{Cr}_2\text{O}_7^{-2}]}{[\text{CrO}_4^{-2}]^2}$$

Indeed the authors found experimentally that the actual rate was proportional to the ratio $[\text{Cr}_2\text{O}_7^{-2}]/[\text{CrO}_4^{-2}]^2$. They obtained the product of the equilibrium constant and rate constant, but were unable to separate them.

Duke and Yamamoto⁴ studied the reaction of pyrosulphate in fused alkali nitrate. The reaction proved similar to the dichromate nitrate reaction:



The rate of decrease in acid concentration is given by:

$$-\frac{d[\text{A}_T]}{dt} = k[\text{NO}_2^+]$$

where $[\text{A}_T] = [\text{S}_2\text{O}_7^{-2}] + [\text{NO}_2^+]$. The equilibrium constant for equation (5) is given by:

$$K = \frac{[\text{NO}_2^+][\text{SO}_4^{-2}]^2}{[\text{S}_2\text{O}_7^{-2}]}$$

Substitution for $[\text{NO}_2^+]$ and $[\text{S}_2\text{O}_7^{-2}]$ in terms of the rate constant, equilibrium constant and sulphate concentration affords the relation:

$$-\frac{d[\text{A}_T]}{dt} = \frac{k K [\text{A}_T]}{K + [\text{SO}_4^{-2}]^2}$$

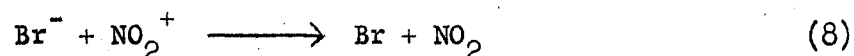
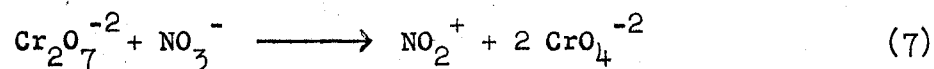
A plot of $\ln [\text{A}_T]$ against time has a negative slope of:

$$k' = \frac{k K}{K + [\text{SO}_4^{-2}]^2}$$

$$\frac{1}{k'} = \frac{1}{k} + \frac{[\text{SO}_4^{-2}]^2}{k K}$$

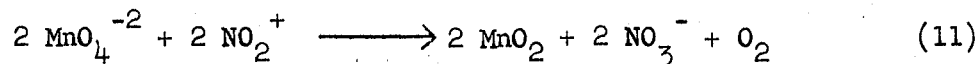
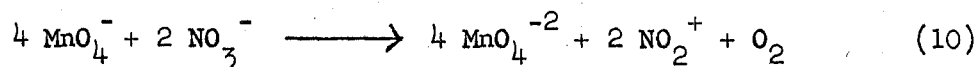
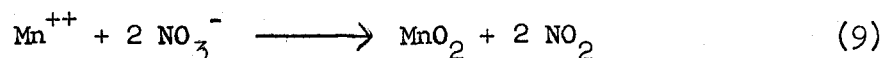
Determination of a series of values for k' corresponding to the $[\text{SO}_4^{-2}]$ concentration enabled the authors to make a plot of $1/k'$ against $[\text{SO}_4^{-2}]^2$ from which the values of k and K were calculated.

Duke and Iverson⁵ have shown that dichromate oxidizes bromide ion in fused alkali nitrate via the following steps:

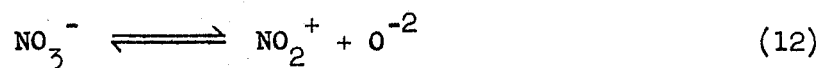


It is probable that NO_2Br ($\text{Br}-\overset{\text{O}}{\parallel}{\text{N}}$) serves as an intermediate in this reaction.

Bennett and Holmes⁶ have reported that when Manganese II ion is dissolved in fused alkali nitrate, oxidation to MnO_2 occurs. In the same solvent MnO_4^- decomposes to yield MnO_2 . MnO_4^{-2} ion which is green in colour was found to be an intermediate in this reaction. The following equations (9, 10 and 11) were suggested to explain these reactions.



On the basis of the above studies Duke⁷ proposes that in fused alkali nitrates, nitrate ion dissociates (equation 12) into nitronium ion (also known as nitryl ion) and oxide ion:

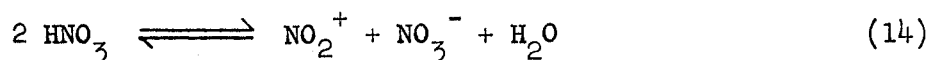


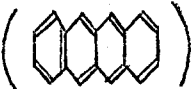
This process is analogous in many respects to the ionic dissociation of water (equation 13) into hydrogen ion and hydroxyl ion.



In consideration of the fact that nitronium ion and oxide ion are stronger acid and base respectively than hydrogen ion and hydroxyl ion, the nitrate ion may not be expected to dissociate as much as water. At present there are no simple methods for measuring the concentration of nitronium ion. It is of interest to determine whether the above proposed nitrate dissociation takes place and to what extent.

Nitronium ion has long been considered by the organic chemists as the species involved in the acid catalyzed nitration of aromatic hydrocarbons. Indeed the spectral evidence points to the existence of this highly active species. Raman Spectra⁸ of nitric acid and its aqueous solutions indicate the dissociation of nitric acid into NO_2^+ and NO_3^- according to equation (14):



The positively charged nitrogen atom attacks aromatic hydrocarbons by localisation of a π bond of the aromatic nucleus to yield the nitro-derivative. Thus it appears reasonable to assume that the nitronium ion which results from the proposed dissociation of fused nitrate may be used for the nitration of an aromatic hydrocarbon. Naphthacene, a high melting aromatic hydrocarbon () was chosen to intercept the nitronium ion in fused nitrate. Since the 9-10 positions of the naphthacene are the most active, then 9-nitronaphthacene or an oxidation product thereof

should be expected as a major product of nitration if NO_2^+ is the attacking agent.

The nitration of naphthacene with nitric acid was previously reported by Bednigina, Panfilov and Postoskii⁹. Naphthacene was found to yield unstable dihydronitro derivatives due to the addition of nitric acid at the para positions of one of the middle rings. When 9-nitro, 10-chloro-dihydronaphthacene was treated with 30 percent aqueous sodium hydroxide for several hours, 9-nitronaphthacene was obtained. 9-nitronaphthacene was found to be less stable than 9-nitroanthracene. Thus solutions of 9-nitronaphthacene are unstable even on standing at room temperature. 9,10-naphthacenequinone is the oxidation product and can be obtained in quantitative yields. All the derivatives of naphthacene containing a nitro group yield a deep blue colour on treatment with concentrated sulphuric acid in contrast to a green colour for naphthacene and a red colour for naphthacenequinone.

CHAPTER II
EXPERIMENTAL

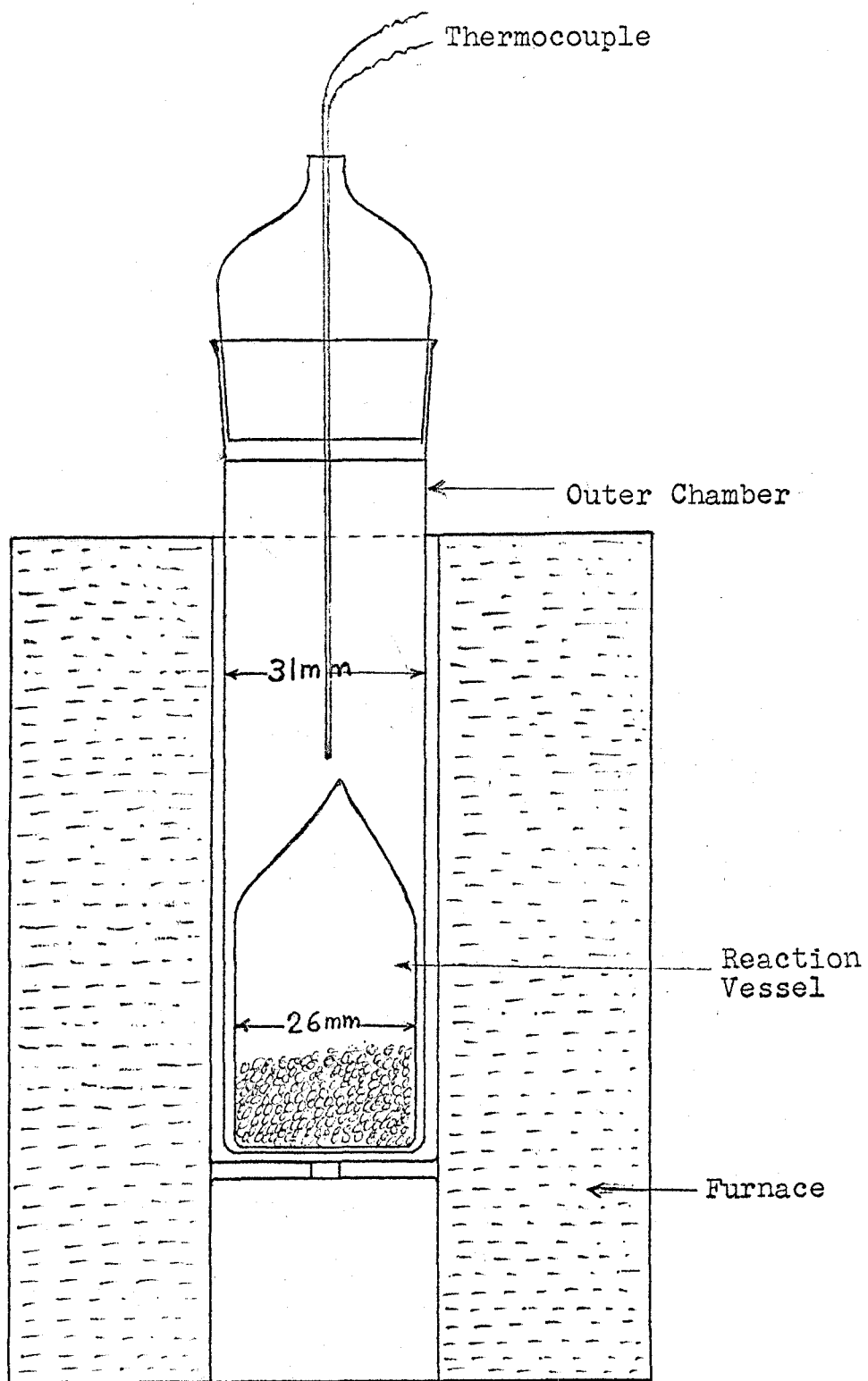
A. Materials

Fisher analytical grade chemicals were used. Naphthacene was obtained from the British Drug Houses Limited. Nitrates were dried at 110°C before use.

B. Procedure

The apparatus used in this investigation is shown in the diagram on the following page. The furnace was preheated to $345^{\circ}\text{C} \pm 5^{\circ}$. The components (aromatic hydrocarbon, NaNO_3 and/or KNO_3) were placed in the reaction vessel which was subsequently flushed with dry nitrogen, evacuated and sealed. The vessel was then lowered into the pyrex outer chamber for varying times (5 minutes to 2 hours). The reaction vessel was then removed and allowed to cool to room temperature, whereupon the reaction mixture was ground with a mortar and pestle. Extraction with chloroform was followed by dissolution of most of the insoluble material in water. Since naphthacene is insoluble in water and only slightly soluble in chloroform a reasonable separation of the starting material was effected.

The chloroform extract was subjected to chromatographic analysis using alumina. Petroleum ether (b.p. $30-60^{\circ}\text{C}$) was used as the eluent. Products were identified by infra-red spectra and mixed melting point determinations with authentic samples.



ARRANGEMENT OF THE APPARATUS

C. Preparation of 9-Nitronaphthacene

Following the procedure employed by Bedniagina, Panfilov and Postoskii⁹, powdered naphthacene (1 gm - 0.0041 mole) was suspended in glacial acetic acid (20 ml) and was cooled in an ice-water bath. Concentrated nitric acid free of oxides of nitrogen (20 ml) was added to the suspension with stirring. As soon as the suspension changed to a clear solution a mixture of concentrated hydrochloric acid (20 ml) and glacial acetic acid (10 ml) was added and the reaction mass was stirred for one hour while the temperature was kept below 5°C. The yellow precipitate which formed was recovered by filtration and washed successively with acetic acid and water. The precipitate thus obtained was treated with 30 percent aqueous sodium hydroxide (20 ml) with gradual heating to 50°C on a water bath. The slurry of crystals gradually became red in colour. After about three hours, the reaction mixture was diluted with water. The precipitate was recovered by filtration and washed copiously with water. After drying in a vacuum dessicator, the reddish precipitate was found to melt within the range 184-189°C (yield 0.81 gm - 73%).

D. Preparation of 9,10-Naphthacenequinone

The procedure adopted by Bednigina, Panfilov and Postoskii⁹ was followed. Finely divided naphthacene (0.4 gm - 0.0018 mole) was suspended in glacial acetic acid (8 ml) and was cooled in an ice-water bath. Concentrated nitric acid (8 ml) which was freed from oxides of nitrogen by blowing with air was gradually added to the suspension with vigorous stirring. As soon as the suspension was converted into a clear solution, the reaction mixture was poured into water and the precipitate which formed was removed by filtration. This precipitate was boiled with

acetic acid for 10 minutes whereupon it crystallized as yellow needles, melting point 285-289°C (yield 0.27 gm - 60%).

E. Reaction of 9-Nitronaphthacene with Fused Sodium Nitrate

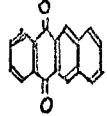
A mixture of sodium nitrate (5 gms - 0.069 mole) and 9-nitronaphthacene (0.15 gm - 0.00055 mole) was placed in the reaction vessel which was subsequently flushed with nitrogen, evacuated and sealed. The vessel was heated in the preheated furnace ($345^{\circ}\text{C} \pm 5^{\circ}$) for fifteen minutes. After cooling to room temperature, the organic portion was extracted with chloroform. The product was identified as 9,10-naphthacenequinone in the usual manner (yield 0.1185 gm - 84%).

CHAPTER III

RESULTS AND DISCUSSION

The table below shows the results of heating naphthacene with fused sodium nitrate(s). As can be seen from the table, 9,10-naphthacenequinone was the only organic product which was isolable and identifiable by classical analysis. An appreciable amount of intractable tar was obtained as well as unreacted naphthacene, with every run. It was not practical to continue heating the reaction mixture for longer periods than one hour, since no appreciable increase in yield resulted. In fact, a marked decrease in yield was noted on heating for two hours. Although 9-nitronaphthacene could not be obtained as a separate entity from the reaction mixture, evidence for its presence in trace amounts was realized. Thus when the crude reaction product was ground with a mortar and pestle, the residue on the mortar gave a positive test (blue colour with concentrated sulphuric acid) for the presence of either 9-nitronaphthacene or derivatives. Unreacted naphthacene as well as 9,10-naphthacenequinone could also be detected by the characteristic colours which developed (pale green and deep red respectively) on treatment with sulphuric acid. Bedniagina, Panfilov and Postoskii⁹ showed that these colours were specific for 9-nitronaphthacene and its derivatives, naphthacene and 9,10-naphthacenequinone. Again when the crude organic material was subjected to analysis for carbon, hydrogen and nitrogen, a small amount of nitrogen, 0.43 percent, was detected.

REACTION OF NAPHTHACENE WITH FUSED ALKALI NITRATE⁽¹⁾

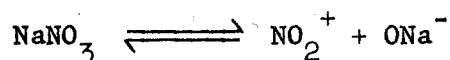
Solvent	Temperature	Time	Organic Reaction Product	% Yield
5 gms of NaNO ₃	345°C ± 5°	15 min		10.3
5 gms of NaNO ₃	345°C ± 5°	15 min	"	9.9
5 gms of NaNO ₃	345°C ± 5°	35 min	"	11.6
5 gms of NaNO ₃	345°C ± 5°	35 min	"	11.0 ⁽²⁾
5 gms of NaNO ₃	345°C ± 5°	1 hour	"	12.5
5 gms of NaNO ₃	345°C ± 5°	1 hour	"	12.2
5 gms of eutectic (NaNO ₃ + KNO ₃)	250°C ± 5°	30 min	"	9.3

(1) 0.2 gm of naphthacene was treated with the fused nitrate in all the reactions.

(2) 85% of the naphthacene was recovered unreacted.

The difficulty involved in the isolation of an appreciable amount of 9-nitronaphthacene was not unexpected since an authentic sample was oxidized rapidly to 9,10-naphthacenequinone in near quantitative yields by the fused nitrate. Again, Bedniagina, Panfilov and Postoskii⁹ found that 9-nitronaphthacene was readily oxidized to the corresponding quinone under extremely mild conditions. Thus oxidation was found to occur even on attempted recrystallization from hot organic solvents (acetic acid, benzene, and chloroforms).

The presence of trace amounts of 9-nitronaphthacene (or derivatives) along with the isolation of 9,10-naphthacenequinone supports the postulate of Duke⁷, i.e. that the following fused nitrate equilibrium does exist.

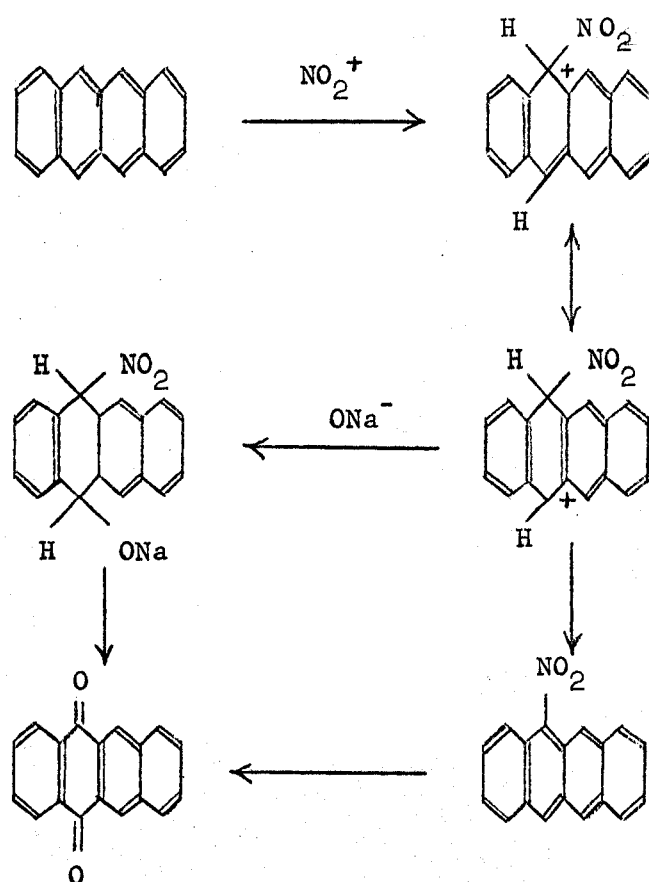


The presence of nitryl radical ($\cdot\text{NO}_2$) is discounted since non selective nitration would be expected. Hence, subsequent oxidation product other than 9,10-naphthacenequinone would be realized. It is proposed then that nitration of naphthacene occurs by essentially the same mechanism as that proposed for aqueous nitrations of aromatic compounds. For the present investigation then the following scheme of reactions on the next page is most likely.

According to this scheme, both 9-nitronaphthacene and the 10-hydroxyderivative (obtained on quenching the reaction in water) are considered as reasonable precursors to 9,10-naphthacenequinone. Either one would give a deep blue colour when treated with concentrated sulphuric acid.

Tests were also carried out to study the reactions of anthracene and phenanthrene with fused nitrate under similar reaction conditions. Even though there was evidence of a very slow reaction (slight discoloration) no product other than the reactants could be isolated.

Investigations with other aromatic hydrocarbons with the hopes of isolating a nitration product which is stable under the reaction conditions are in order.



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VITA AUCTORIS

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