Studies on the Reaction between Aromatic Nitro Compounds and Active Methylene Groups. XVI. The Mechanism of Neutralization of *Meta* Dinitrobenzene Derivatives by Aliphatic Amines at -72°C

TEODOR CANBÄCK

Apotekens Kontrollaboratorium, Stockholm, Sweden

In a very interesting paper, Lewis and Seaborg¹ some years ago discussed the acidity of some aromatic nitro compounds towards amines at low temperatures. They investigated whether or not trinitrobenzene, in petroleum ether solution, was neutralized by ammonia, methylamine, dimethylamine and triethylamine, and found that trinitrobenzene only gave a slight colour with triethylamine but an intense crimson colour with the weaker base ammonia. The selective light absorption is due to a quinoid structure of the nitro compound stabilized by the addition of the amine. Even more remarkable, however, was that *meta* dinitrobenzene, the ionization constant of which in aqueous solution could not be greater than 10^{-17} , in petroleum ether solution was neutralized by ammonia and methylamine, while the stronger bases dimethylamine and triethylamine were without noticeable effect.

To explain this phenomenon Lewis and Seaborg assume the presence of a double chelation. The energy gained from the double chelation is then responsible for the attachment of ammonia and methylamine to the benzene ring, while dimethylamine, where only a single chelation is possible, and triethylamine, where no chelation is possible, are not attached. A condition precedent for this theory is that in the *meta* dinitrobenzene derivatives the carbon atom between the nitro groups is lacking in electrons, or, otherwise expressed, that an *ortho* quinoid resonance form:

dominates during the neutralization. They write the formula for the double chelation in the following way:

The investigations previously reported in this series ^{2, 3} have given evidence that the most important resonance form of the addition compound between *meta* dinitrobenzene and acetone in alkaline solution may be expressed by the formula:

This compound is an anion in which the benzene ring has a quinoid structure, and the acetone ion is assumed to be attached *ortho* respectively *para* to the two nitro groups.

The formula given by Lewis and Seaborg for the addition product between aromatic nitro compounds and amines thus does not agree with my formulation of the addition product between aromatic nitro compounds and acetone in alkaline solution. Although the experimental conditions are quite different — chelation is, for instance, impossible when the acetone anion is attached — and therefore *a priori* it is not necessary to assume the same mechanism for the addition of the different nucleophilic reagents (the weak nucleophilic amines and the strong nucleophilic acetone ion) to the ring, it was of interest to extend Lewis' and Seaborg's investigations to the *meta*

dinitrobenzene series in the hope of determining where the attachment of the amines actually takes place.

These experiments were performed at -71 to -73°C (ethanol + solid CO_2). Lewis and Seaborg do not report at what temperature they were working.

Skellysolve B was used as a solvent. The results are given in Table 1. Table 2 gives the results of Lewis' and Seaborg's measurements. In Table 1 are also included λ max. and ϵ max. in ultra violet (pentane), taken from Canbäck³. The measurements of 2,6-dinitrotoluene are new. See Fig. 1.

Table 1. Colour intensities produced on mixing different amines with *m*-dinitrobenzene derivatives in petroleum ether solution at -72°C . Included are the UV absorption characteristics of the nitro bodies in pentane at $+20^{\circ}\text{C}$.

	1,3-Dinitro- benzene	2,4-Dinitro- toluene	2,6-Dinitro- toluene	4,6-Dinitro- 1,3-dimethyl- benzene	Dinitro- mesitylene
Benzylamine	+++	++	—	—	—
Dimethylamine	++	++	—	—	—
Piperidine	+	+	—	—	—
Triethylamine	—	—	—	—	—
N-Ethylpiperidine	—				
Quinine	—				
Hexamethylene- tetramine	—				
ϵ max.	21000	15900	12000	15100	3900 *
λ max. $\text{m}\mu$	227	232	227	243	238

* Inflection point.

In Table 1 the approximative strengths of the colours are indicated by the number of +. *Meta* dinitrobenzene gave a clear crimson and 2,4-dinitrotoluene a blue-reddish colour.

As seen in Table 1, the same tendency is found in the *meta* dinitrobenzene series as Lewis and Seaborg observed. However, Lewis' and Seaborg's statement that *meta* dinitrobenzene does not give a colour with secondary amines must be corrected. At -71 to -73°C dimethylamine, as well as piperidine, gave bright colours, *e. g.* the amines did neutralize the nitro compound. Similarly 2,4-dinitrotoluene was neutralized by primary as well as by secondary amines. 2,6-Dinitrotoluene, dinitroxylenes and dinitromesitylenes were not noticeably influenced by any of the amines.

Fig. 1. Ultra-violet spectrum of 2,6 dinitrotoluene in petroleum ether.

Table 2. Colour production on mixing several bases with nitro compounds according to Lewis and Seaborg.

	1,3-Dinitro- benzene	1,3,5-Tri- nitrobenzene	2,4,6-Tri- nitrotoluene	2,4,6-Tri- nitroxyleno	Trinitro- mesitylene
Ammonia	+	+	+	+	+
Methylamine	+	+	+	+	+
Dimethylamine	—	+	+	—	—
Triethylamine	—	+	+	—	—

Thus in principle Lewis' and Seaborg's statement, that *meta* dinitrobenzene is neutralized only when a double chelation is possible, is not true. The following description of the phenomenon might be more correct.

The amines in petroleum ether solution are such weak nucleophilic reagents that at the temperatures at which Lewis and Seaborg worked neutralization of *meta* dinitrobenzene only occurs when a double chelation is possible. At -72°C , however, the energy gained from a simple chelation is great enough to allow even secondary amines to be attached to the ring and thus to stabilize a quinoid form of the nitro compound.

The nitrogen atom in triethylamine is known¹⁴ to be blocked by the bulky ethyl groups. To test if the phenomenon could possibly be explained by the

steric hindrance in the amine, quinine and hexamethylenetetramine were investigated. The nitrogen atom in the quinuclidine nucleus is not hindered. As seen in Table 1, neither quinine nor hexamethylenetetramine was neutralized by *meta* dinitrobenzene, indicating that the steric hindrance in triethylamine was not responsible for the failure of the reaction.

The attachment of the amines might occur at the carbon atom between the nitro groups since a positive reaction is obtained with 2,4-dinitrotoluene but not with 2,6-dinitrotoluene.

However, it is not absolutely certain that the attachment of the amines takes place in this position as 4,6-dinitro-1,3-dimethylbenzene, although sterically hindered but still capable of adding anions³, gives a negative reaction even though the carbon atom between the nitro groups is unsubstituted. The fact that Lewis and Seaborg obtained a positive reaction with 2,4,6-trinitroxylenes is explained by the presence of a nitro group *para* to the unsubstituted ring carbon atom. The latter compound is therefore much more acid than 4,6-dinitro-1,3-dimethylbenzene. It may also be that the small steric hindrance (see below) present in 2,6-dinitrotoluene (with both nitro groups hindered contrary to 2,4-dinitrotoluene in which only one nitro group is hindered) is sufficient to counteract the energy gained from a simple chelation even at -72° , *e. g.* if the attachment takes place in the position *ortho* — *para* to the nitro groups. Additional support of this theory is found in the investigations performed by Field, Garner and Smith⁴ and Garner and Gillbe⁵ on the ionization of aromatic nitro compounds in liquid ammonia. From their results it will only be mentioned here that conductimetric as well as photometric measurements showed that 1,3-dinitrobenzene, 2,4-, 3,5-, and 2,6-dinitrotoluene behaved in the same manner, while 1,4-, and 1,2-dinitrobenzene as well as 2,5-, 2,3-, and 3,4-dinitrotoluene behaved in a different manner. Of special interest in this connection is that 1,3-dinitrobenzene, 2,4-, 3,5-, and 2,6-dinitrotoluene gave blue or violet coloured solutions in liquid ammonia while 2,5-, 2,3-, and 3,4-dinitrotoluene and 1,2-, and 1,4-dinitrobenzene gave yellow solutions. It is thus highly improbable that the attachment of the ammonia takes place on the carbon atom between the two nitro groups, which are in a *meta* position to each other.

The molar extinction coefficient ϵ , as has been previously demonstrated³, is a very sensitive measurement of the steric hindrance in *meta* dinitrobenzene derivatives. From Table 1 it is apparent that 2,4-dinitrotoluene and 4,6-dinitro-1,3-dimethylbenzene are hindered to about the same extent, while dinitromesitylene is very strongly hindered. *Cf.* Canbäck³, Fig. 3.

2,6-Dinitrotoluene has $\lambda_{\text{max.}} = 227 \text{ m}\mu$ and $\epsilon = 12000$ in petroleum ether. In agreement with the theory previously advocated³, the methyl group in the

joint *ortho* position has no influence on λ max. in comparison with the parent compound *meta* dinitrobenzene. The latter compound has also λ max. = 227 $m\mu$. ϵ for 2,6-dinitrotoluene may be considered to be twice that of *ortho* nitrotoluene³, which according to Brown and Reagan⁶ is 5950. The calculated value is then 11900 and the observed value 12000. The steric hindrance in 2,6-dinitrotoluene is thus very small.

In the reaction between acetone and *meta* dinitrobenzene derivatives in alkaline solution, the attachment of the acetone anion seems to occur at the ring carbon atom that is *para* to one of the nitro groups. Additional support for this point of view is obtained from the fact that 2,6-dinitrotoluene gives a positive reaction with λ max. 530 $m\mu$ and ' ϵ ' = 1900 after 15 minutes. As in the case of the other sterically hindered alkyl *meta* dinitrobenzenes the colour developed slowly³.

Till now in this paper only the place of attachment of the amines on the benzene ring has been discussed. No standpoint has been taken on the question of whether or not the addition product formed is a neutral one, as Lewis and Seaborg suggest, or if an anion is formed by a reaction analogous to the reaction between *m*-dinitrobenzene and acetone in alkaline solution, *e. g.* if an ion of the following type is formed by the addition of an *amide* ion. The latter

formulation of the addition product appears to be true when the nitro bodies are dissolved in liquid ammonia. The different behaviour of the tertiary amines contrary to the primary and secondary ones observed in this investigation, is then easily explained by the fact that the former amines cannot dissociate according to the scheme $2 \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{NH}_2^-$ and hence the strongly nucleophilic amide ion is not formed. With this latter formulation of the neutralization reaction, it is not necessary to use conceptions such as double chelation to give a reasonable explanation of the observed phenomena.

EXPERIMENTAL

Melting points were determined on the Kofler block and corrected. UV and spectra in the visible were determined on a Beckman Quartz spectrophotometer model DU using 1 cm quartz cells.

2,6-Dinitrotoluene. The compound was isolated chromatographically * from a mixture of 2,4-dinitrotoluene and 2,6-dinitrotoluene obtained from Bofors Nobelkrut. M. p. 65.6–66.0°. Refractive index 1.5400 at 82–83° (Kofler¹⁰ gives 80–82°). Transition point of the instable and the stable form, 40° (Schaum⁷ gives 40.5°, and Kofler⁸ 36°). The instable form melted by rapid heating at 58° (Kofler¹⁰ gives 58°). The melting point, when mixed with 2,6-dinitrotoluene prepared from 2,4,6-trinitrotoluene by selective reduction and deamination according to Holleman and Böeseken⁹, was 65°.

Petroleum ether for UV measurements was prepared from Skellysolve B which was freed from aromatic compounds by the method given by Weissberger¹¹. B. p. 65–66°. Without noticeable absorption in 1 cm cells to 212 mμ.

Benzylamine, b. p. 185°, *dimethylamine*, b. p. 7°, *piperidine*, b. p. 106°, and *triethylamine*, b. p. 90°, were commercial reagents. They were distilled immediately before use. *N-Ethylpiperidine*, *quinine* and *hexamethylenetetramine* were commercial products which were used without further purification. Other compounds and reagents were the same as used previously^{2, 3}.

The neutralization at –72° was tested in the following way. About 0.1 g of the nitro compound was dissolved in 25 ml Skellysolve B. To 5 ml of this solution was added 1 ml of the amine to be tested. The test tube was closed and placed for 30 minutes in an ethanol-solid CO₂ bath and the colour noted. The temperature varied between –71 and –73°. With some of the amines, parts of the solution sometimes solidified.

'e' was determined as described previously³.

Lepsius¹² has reported that 2,6-dinitrotoluene gives no colour with acetone and alkali. Rudolph¹³, on the contrary, reports a red colour that develops slowly.

SUMMARY

Contrary to the statement of Lewis and Seaborg, 1,3-dinitrobenzene in petroleum ether solution gives a distinct crimson colour when secondary amines are added to the solution if the temperature is approx. –70° C. Tertiary amines give no positive reaction.

Assuming the mechanism of neutralization proposed by Lewis and Seaborg, the place of attachment of the amine has been discussed. It has been shown that the most probable place is ortho respectively para to the two nitro groups.

It is mentioned that the mechanism of the neutralization is better understood if an amide ion is assumed to be the nucleophilic reagent operating in the reaction, *e. g.* that a coloured, complex organic anion is formed. A reasonable, simple structure for the resonating anion is suggested.

* On Superfiltrol. Solvent Skellysolve B. Eluent 99 vol. Skellysolve B + 1 vol. acetone.

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