690. *Coloured Alkali Salts from* sym.-*Trinitrobenzene Derivatives. Part I. Picryl Derivatives.*

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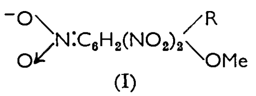
The reactions of the coloured compounds formed from trinitrobenzenes by the action of alcoholic alkalis have been studied. The products are quinonoid and contain two nitro-groups, a nitronate group and two *gem*-substituents, one of these being an alkoxy-group. This paper deals with products obtained from picryl compounds. In water these undergo two types of decomposition depending on pH. The free nitronic acids decompose very rapidly to the picryl compounds from which they were derived, but there are indications that this is slightly reversible. Picric acid forms the compounds with difficulty, but under certain conditions unstable red solutions can be obtained. The primary product of the action of a methoxide on picryl chloride, containing chlorine and a methoxy-group, acts in a dual capacity and leads to further reactions following two different routes, one of which is extremely rapid and the other very slow. Each of these leads to the same final product, methyl picrate.

It has long been known that *sym.*-trinitrobenzene and its derivatives give strongly coloured solutions with alcoholic alkalis. The constitution based on Meisenheimer's [1] work is generally accepted.[2] According to this, a trinitrobenzene derivative, $(NO_2)_3C_6H_2R$, reacts with potassium methoxide, forming a quinonoid nitronate ion, (I), in which the substituent R and a methoxy-group are attached to the same carbon atom of the benzene ring. The anion has been assumed to be a resonance-hybrid of the *ortho*- and the *para*-quinonoid form.[3]

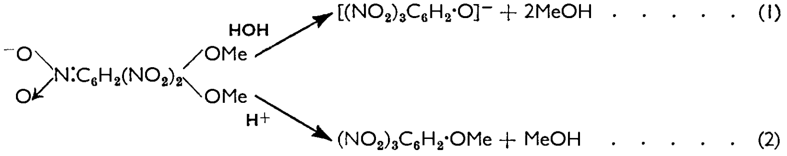


$$\left.\begin{matrix}{}^{-}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\rangle\mathrm{N{:}C_6H_2(NO_2)_2}\left\langle\begin{matrix}\mathrm{R}\\ \mathrm{OMe}\end{matrix}\right.$$

(I)

Picric esters form well-defined red crystalline salts with alcoholic alkalis. The salts are stable when dry. Jackson and Boos [4] found that alkoxy-groups are often interchangeable; *e.g.*, a methoxy-group can be gradually replaced by an ethoxy-group in ethanol solution. This was re-examined in the present work, as it might have affected the validity of Meisenheimer's work,[1] but the results showed that his deductions were not appreciably disturbed by an interchange of the groups.

In water, the coloured salts from picric esters undergo two types of decomposition:



Change (1) is gradual: (2) is very rapid and takes place *via* the nitronic acid. These acids are very weak and are set free by carbonic acid.

Picric acid does not normally form red compounds with methanolic alkali, but only picrate. Under certain conditions red solutions were obtained, indicating the formation of a hydroxy-methoxy-compound. Methyl picrate also reacted with aqueous alkali and should form the same product, but in each case the red solution soon gave the yellow picrate.

Picryl Chloride.—The interaction of equimolar proportions of picryl chloride and

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[1] Meisenheimer, *Annalen*, 1902, **323**, 205; 1907, **355**, 249. See also Jackson and Gazzolo, *Amer. Chem. J.*, 1900, **23**, 376; Jackson and Earle, *ibid.*, 1903, **29**, 89.

[2] Hantzsch and Picton, *Ber.*, 1909, **42**, 2119; Foster and Hammick, *J.*, 1954, 2153; Foster, *Nature*, 1955, **176**, 746; Bunnett, *Quarterly Reviews*, 1958, **12**, 1.

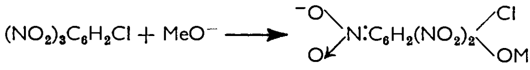
[3] Sidgwick, "The Organic Chemistry of Nitrogen," 1937, p. 260, Clarendon Press, Oxford.

[4] Jackson and Boos, *Amer. Chem. J.*, 1898, **20**, 444.

methanolic potash gives rise to a series of reactions. There are two stages; the first is very rapid and gives an intense colour. This is followed by a phase in which the red colour fades gradually. After some days the solution becomes pale yellow and yields methyl picrate. Part of the methyl picrate is formed in the first stage (about 40%) and the remainder in the second stage. Examination of the intermediate products leads to the following mechanism.

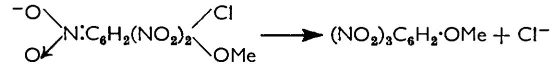
Stage I (very rapid at room temp.):

Reaction A.



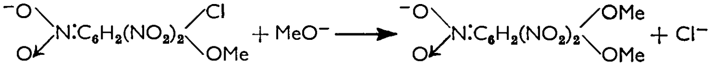
$$(NO_2)_3C_6H_2Cl + MeO^- \longrightarrow \begin{matrix}{}^-O\\O\end{matrix}\!>\!N{:}C_6H_2(NO_2)_2\!<\!\begin{matrix}Cl\\OMe\end{matrix}$$

Reaction Bi.



$$\begin{matrix}{}^-O\\O\end{matrix}\!>\!N{:}C_6H_2(NO_2)_2\!<\!\begin{matrix}Cl\\OMe\end{matrix} \longrightarrow (NO_2)_3C_6H_2{\cdot}OMe + Cl^-$$

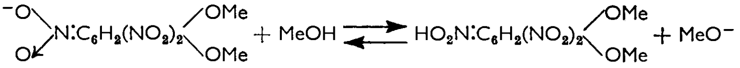
Reaction Bii.



$$\begin{matrix}{}^-O\\O\end{matrix}\!>\!N{:}C_6H_2(NO_2)_2\!<\!\begin{matrix}Cl\\OMe\end{matrix} + MeO^- \longrightarrow \begin{matrix}{}^-O\\O\end{matrix}\!>\!N{:}C_6H_2(NO_2)_2\!<\!\begin{matrix}OMe\\OMe\end{matrix} + Cl^-$$

Stage II (gradual conversion of the product of Bii into methyl picrate):

Reaction C.



$$\begin{matrix}{}^-O\\O\end{matrix}\!>\!N{:}C_6H_2(NO_2)_2\!<\!\begin{matrix}OMe\\OMe\end{matrix} + MeOH \rightleftharpoons HO_2N{:}C_6H_2(NO_2)_2\!<\!\begin{matrix}OMe\\OMe\end{matrix} + MeO^-$$

Reaction Di.

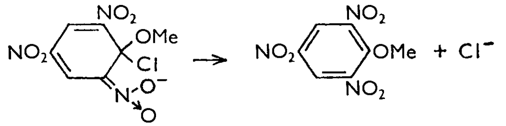
$$HO_2N{:}C_6H_2(NO_2)_2\!<\!\begin{matrix}OMe\\OMe\end{matrix} \longrightarrow (NO_2)_3C_6H_2{\cdot}OMe + MeOH$$

Reaction Dii. Action of MeO^- at very low concentration on residual picryl chloride.

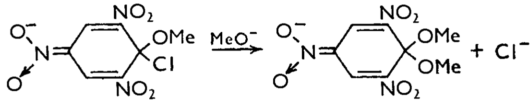
Reaction A is the normal action of methoxide on a trinitrobenzene derivative. It gave a deep-red solution, and chloride ions were formed very rapidly. After a short time red crystals of $KO_2N{:}C_6H_2(NO_2)_2(OMe)_2,MeOH$ separated out. Unchanged picryl chloride was still present and the solution also contained methyl picrate. The formation of the above potassium salt in presence of picryl chloride was unexpected. The red salt might conceivably be formed by Reaction Bi, followed by conversion of the resulting methyl picrate into the dimethoxy-quinonoid nitronate, but in presence of picryl chloride this could occur only if methyl picrate were more reactive than picryl chloride towards methoxide. A separate experiment showed picryl chloride to be the more reactive. It follows that methyl picrate cannot be an intermediate in the formation of the red potassium salt in presence of picryl chloride. Reaction Bii was considered as an alternative, but this would not account for the presence of methyl picrate. Analysis of the products showed that both reactions proceeded simultaneously.

According to the accepted view the quinonoid nitronate ion can act either as an *ortho*- or a *para*-quinone. The probability is that the *ortho*-quinonoid compound gives methyl picrate by reason of the vicinity of the nitronate group to the chlorine, and the *para*-quinonoid compound reacts with a further methoxide ion.

Bi



Bii



In support of this it was found that addition of methyl picrate suppressed reaction Bi and gave a larger proportion of Bii. Reaction Bii must proceed more rapidly than reaction A, otherwise unchanged picryl chloride would not be present at the end of Stage I. The rates of reactions Bi and Bii appear to be of the same order.

It remained to explain the reason for the slow reaction. The transition from Stage I to Stage II is quite abrupt. As soon as the free methoxide is all consumed, the velocity falls to a very low level and the red colour begins to fade very slowly. This continues for 2—3 days; the colour has then become pale yellow and the solution contains only methyl picrate. The slowness of Stage II, in contrast to Stage I, points to an extremely low concentration of methoxide ions. A direct experiment on a mixture of picryl chloride and the nitronic compound gave a similar gradual fading of the red colour with formation of methyl picrate. This can be explained by the slight conversion of the nitronate ion as in reaction C, yielding the free nitronic acid and methoxide ions which react as in reactions Di and Dii, respectively. A synthetic mixture, consisting of picryl chloride, methyl picrate, and the nitronic sodium salt in the proportion resulting from reactions Bi and Bii, behaved in just the same way as the slow reaction in Stage II, and gave the same velocity of reaction.

Influence of Methyl Picrate.—Methyl picrate was found to have a retarding effect on the slow reaction. This is readily accounted for; reaction Di is to a slight extent reversible and is suppressed by methyl picrate. This increases the amount of free nitronic acid present, and this in its turn suppresses reaction C and so decreases the concentration of methoxide ions on which the velocity of Stage II depends.

EXPERIMENTAL

Nitronic Salts from Methyl Picrate and Methoxides.—The solvated *potassium* salt formed small, bright-red rhomboidal plates, mixed with small needles (Found: K, 11·3; loss at 75°, 9·4. $C_8H_8O_8N_3K,CH_3{\cdot}OH$ requires K, 11·3; $CH_3{\cdot}OH$, 9·3%). Dried *salt* (Found: K, 12·5. $C_8H_8H_8N_3K$ requires K, 12·5%); reabsorption of methanol (Found: increase of weight, 10·2. $CH_3{\cdot}OH$ requires 10·2%); absorption of acetone vapour (Found: increase of weight, 9·1. $\frac{1}{2}C_3H_6O$ requires 9·3%).

The solvated *sodium* salt formed large, bright red prisms with green shimmer (Found: loss on warming, 9·8. MeOH requires loss, 9·7%). Dried *salt* (Found: Na, 7·6. $C_8H_8O_8N_3Na$ requires Na, 7·7%). It absorbed moisture rapidly.

The solid salts are stable in absence of moisture and in methanolic solution. The potassium salt showed a loss of only 2% in a 0·15N-solution during 6 days at room temperature.

Action of Water, Acid, and Alkali.—An aqueous solution of the red potassium salt gradually turned yellow and after a few hours gave an almost quantitative yield of picrate. Weak aqueous alkali gave the same result. In presence of acid, the nitronic acid was liberated and decomposed at once to methyl picrate (yield 98—99%). Weak acids, including carbonic acid, precipitated methyl picrate, but phenol gave no precipitate. The red salt was slightly hydrolysed in aqueous solution. No solid separated out, but methyl picrate could be extracted by benzene.

Interchange of Alkoxy-radicals in Nitronic Salts.—On boiling with ethanol, the dimethoxy-quinonoid compound was partially converted into the diethoxy-compound. Red quinonoid compounds were prepared (*a*) from methyl picrate and ethoxide, (*b*) from ethyl picrate and methoxide. On acidification each of these gave a mixture of methyl and ethyl picrate. The m. p.s corresponded to 68·6 and 67·4% of ethyl picrate. The difference is small and does not affect Meisenheimer's conclusion.[1]

Picric Acid.—Picric acid as a rule yields only yellow picrate with methoxide, but on shaking a colourless solution of picric acid in toluene with sodium methoxide at 0°, a red solution was obtained. The converse reaction of methyl picrate with aqueous alkali also gave a red solution, but in each case the solution turned yellow in a short time.

Action of Methoxide on Picryl Chloride.—Methanolic potash (1 mol.) was mixed with picryl chloride (1 mol.) in methanol. An intense red colour was formed immediately. Silver nitrate showed rapid formation of chloride ions. This was followed shortly by a copious precipitation of bright red crystals, which were identified by crystal form and analysis as the above solvated potassium salt (Found: K, 11·2%). Acidification gave a 98·3% yield of methyl picrate, m. p. and mixed m. p. 67·5°. No trace of chlorine was found in the potassium, sodium, or barium salt. With excess of picryl chloride, the red potassium salt still separated out, but decreased in quantity. With 4 mols. of picryl chloride, 0·05 mol. of the solid potassium salt was obtained. Unchanged picryl chloride was still present, even in excess of methoxide up to nearly 2 mols.

Local interactions during mixing formed a serious source of error in estimating the reaction products, and it was essential to provide for instantaneous mixing of the reagents. A solution of picryl chloride in methanol was made up in a wide-mouthed bottle, and the methoxide solution was measured out in a thin-walled tube, which was lowered into the bottle. The whole was brought to the required temperature and at a given moment the bottle was shaken vigorously to break the inner tube. The Stage I reaction was completed immediately. Ice-cold water, free from carbon dioxide, was added to check further reaction and the mixture was tested.

The compounds present are the quinonoid nitronate, methyl picrate, and picryl chloride. The necessary data for the calculations are (1) the precise amounts of picryl chloride and methoxide taken, and (2) the quantity of the quinonoid nitronate formed. Tests on pure potassium quinonoid nitronate showed that it could be estimated accurately by titration with acid to the point at which the red colour just disappeared.

The method of deduction is best shown by an example. In the interaction of equimolar amounts of picryl chloride and methoxide at 20° the proportion of nitronate formed was 0·309 mol. Formation of the dimethoxy-quinonoid nitronate requires 2 equiv. of methoxide to one of picryl chloride. Hence 0·309 mol. of nitronate required 0·618 mol. of methoxide, leaving 0·382 mol. for the formation of methyl picrate, which requires 1 mol. of methoxide per mol. of picryl chloride. No other product can be present, for it is found that after long standing the sole product is practically pure methyl picrate (m. p. 67·5—68°), whereas if any compound other than methyl picrate or the nitronate were formed at an intermediate stage, it would be present in the final product and would depress the m. p. of the methyl picrate. No such depression was observed. Unchanged picryl chloride was also present. No satisfactory quantitative method of separation of picryl chloride and methyl picrate in a mixture could be found but, knowing with accuracy the quantity of picryl chloride used in the formation of the nitronate and the methyl picrate (*viz.*, 0·309 + 0·382 mol.), the remainder must be a close approximation to the unchanged picryl chloride. This amounts to 0·309 mol. It is seen to be equivalent to the amount of nitronate, and this fits in with the requirement that the two shall interact gradually, ultimately yielding methyl picrate as the sole product. A synthetic mixture of the products based on the above deduction gave the same velocity of reaction in stage 2 as was obtained with picryl chloride and the methoxide.

Relative Activity of Picryl Chloride and Methyl Picrate towards Methoxide.—1 Mol. of methoxide was added to a mixture of picryl chloride and methyl picrate (1 mol. of each) in methanol. If methyl picrate were the more reactive, the solution should contain 1 mol. of the nitronic compound and 1 mol. of unchanged picryl chloride. If picryl chloride were the more reactive, reaction Bi would be strongly suppressed by the large excess of methyl picrate and the solution should contain approx. 0·5 mol. of picryl chloride, 0·5 mol. of nitronic compound, and 1 mol. of unchanged methyl picrate. The nitronic compound found in two experiments was 0·52, 0·53 mol. Dilution with water, followed by extraction with benzene and evaporation, gave a residue which melted indefinitely up to 52°. These are in agreement with the latter alternative.

Effect of Ratio of Methoxide to Picryl Chloride.—Concn. of picryl chloride, 0·180N. Temp. 0°. The figures for methoxide added and resultant products are given in mols. per mol. of picryl chloride originally present.

Methoxide added	Nitronic compound formed	Methyl picrate formed (calc.)	Picryl chloride unchanged (calc.)
0·800	0·206	0·388	0·406
1·000	0·285	0·430	0·285
1·200	0·411	0·378	0·211
1·400	0·540	0·320	0·140
1·600	0·689	0·222	0·089
1·800	0·846	0·108	0·046
2·000	0·996, 0·997, 1·001	Nil	Nil

Influence of Variations in Temperature and Concentration of Picryl Chloride.—Mol. ratio of methoxide to picryl chloride = 1 : 1. Concn. 0·10N. Temp. 0°. Nitronic compound formed, 0·298. Temp. 20°. Nitronic compound formed, 0·333. Concn. 0·18N. Temp. 0°. Nitronic compound formed, 0·285. Temp. 20°. Nitronic compound formed, 0·309.

Effect of added Methyl Picrate.—Picryl chloride, 1 mol. Methoxide, 1 mol. Concn. 0·180N. Temp. 0°.

(i) Without addition of methyl picrate: Nitronic compound, 0·285 mol.

(ii) With addition of 0·5 mol. of methyl picrate: Nitronic compound, 0·433 mol.

Transition from Stage I to Stage II.—When the solutions of picryl chloride and methoxide were mixed by pipetting, local interactions led to an abnormally high formation of the nitronic compound, *e.g.*, 0·40—0·45. This gave rise to an indistinct transition phase, in which the velocity was intermediate between those of Stage I and Stage II. In the extreme limit of 0·5 mol. of nitronic compound, the rate of decrease at 0° was found to be as follows:

Time (min.)	0	5	10	20	30	70
Nitronic compound	0·500	0·472	0·465	0·415	0·381	0·297

On the other hand, when equimolar amounts of picryl chloride and methoxide were mixed instantaneously there was a sharply defined transition from the rapid phase to the slow phase, when the free methoxide was all consumed.

Initial Velocity of Stage II at 0°.

Time (min.)	1	5	20	360
Nitronic compound	0·286	0·283	0·279	0·251

Equimolar amounts of the red sodium nitronate and picryl chloride were dissolved in methanol (concn. 0·125N) and stored at room temperature. The colour gradually faded as in Stage II, and after 3 days most of the picryl chloride was converted into methyl picrate.

The following Table shows the course of Stage II. The initial concentration of picryl chloride and methoxide was 0·180N. The data show mols. of products per mol. of picryl chloride.

Velocity of slow reaction (Stage II).

(i) Temp. 0°.

Time (hr.)	0·03	6	24	48	72	96	120
Nitronic compound	0·285	0·251	0·181	0·132	0·096	0·081	0·065
Methyl picrate (calc.)	0·430	0·498	0·638	0·736	0·808	0·838	0·870
Picryl chloride (calc.)	0·285	0·251	0·181	0·132	0·096	0·081	0·065

(ii) Temp. 20°.

Time (hr.)	0·05	0·25	1	2	3	4	5	6
Nitronic compound	0·309	0·284	0·231	0·185	0·157	0·137	0·120	0·108
Methyl picrate (calc.)	0·382	0·432	0·538	0·630	0·686	0·726	0·760	0·784
Picryl chloride (calc.)	0·309	0·284	0·231	0·185	0·157	0·137	0·120	0·108

For comparison, a synthetic mixture was made up corresponding to the product of Stage I at 20°, and the velocity measured. The nitronic compound decreased from 0·310 to 0·106 mol. in 6 hr. at 20°. This agrees closely with the above Table, which showed a decrease from 0·309 to 0·108 mol. in 6 hr.

Retardation of Stage II by Methyl Picrate.—The product of Stage I normally contained 0·430 mol. of methyl picrate at 0°, and the nitronic compound decreased from 0·285 to 0·181 mol. in 24 hr. at 0°. A synthetic mixture of the same composition, but without the methyl picrate, showed a decrease of the nitronic compound from 0·286 to 0·096 mol. in 24 hr.

In another experiment excess of methyl picrate was added. In the normal reaction at 20° the methyl picrate present immediately after the transition from Stage I to Stage II was 0·382. This was increased to 0·882 mol. by addition of methyl picrate. The nitronic compound decreased from 0·309 to 0·167 after 4 hr. at 20°, as against 0·137 when no additional methyl picrate was present. Thus in each case methyl picrate showed a retarding action.

Reversibility of Decomposition of the Quinonoid Nitronic Acid.—On acidification of the nitronic salt in aqueous solution, the nitronic acid liberated decomposed at once to methyl picrate and methanol. In methanolic solution the decomposition was appreciably retarded, as shown by the rate of fading. This was more marked in presence of methyl picrate. A methanolic solution of the free nitronic acid (concn. 0·035N) faded in approx. 5 min. In presence of 5 mols. of methyl picrate per mol. of nitronic acid the colour persisted for over an hour. It passed through a yellow stage [5] before becoming colourless. In aqueous solution the nitronic salt was slightly hydrolysed, but no methyl picrate separated out. On addition of 10 c.c. of benzene to a solution of 1 g. of the nitronic salt in 100 c.c. of water at 20° and shaking, 0·122 g. of methyl picrate was extracted. If the conversion of the nitronic acid into methyl picrate was irreversible, further

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[5] Cf. Aynscough and Caldin, *J.*, 1956, 2528; Foster, *Nature*, 1959, **183**, 1043.

hydrolysis should take place until the whole of the free nitronic acid was converted into methyl picrate. On addition of methanol to a colourless solution of methyl picrate in benzene, it gradually turned orange-yellow. A comparative experiment with dinitrotoluene gave no colour.

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