CCXXI.—*Absorption Spectra and Chemical Reactivity.*
Part III. Trinitrobenzene, Trinitroanisole, and
Picric Acid.

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IN three previous papers (T., 1912, **101**, 1469, 1475; this vol., p. 91) the general theory was put forward that any molecule of a substance in the free state is the centre of a closed field due to the condensing together of the force lines arising from the free affinities of the individual atoms within the molecules. It was shown how these condensed fields may be unlocked or opened by their interpenetration by the force lines arising from the residual affinity of the molecules of a second substance when the two are mixed. By the residual affinity is meant the balance of free affinity after the maximum possible condensation has taken place. Loose systems between the molecules are formed in this way, which

correspond with the solvates formed when substances exist in solution.

In considering the mechanism by which the closed force field of any one molecule is opened by the residual affinity of a second substance, it is evident, in the first place, that there must exist a difference between the two. As a general statement it may be said that in order that a substance may have its closed field opened it must be treated with a second substance, which differs in character, and the greater the difference in character the more will the force field be opened. The point of attack may vary with the nature of the compound, and, of course, in some cases the same compound will be opened both by a strong acid and by a strong base, the nature of the opening being different in the two cases. Such a compound is amphoteric in the real sense of the term, and the correct definition of an amphoteric substance is a compound of such a type that its closed force field is opened differently by an acid and by a base.

In the second place, it follows from the general conception that the opening up process will be carried out in stages. This was emphasised in a previous paper dealing with the application of the theory to fluorescence (T., 1912, **101**, 1469). Whereas previously only two of the stages had been recognised in the opening up, we have now succeeded in studying the process more completely, and in recognising several distinct stages.

One point of interest at once arises from the existence of the various stages in the opening up of the closed force fields. The evidence of experiment clearly shows that these stages possess a separate and distinct existence, and are stable under the necessary conditions. They represent the same substance with different free energy contents, since the greater the amount of condensation which takes place between the force lines the greater the free energy that escapes. In order, therefore, to convert a substance from stage 1 (in which the maximum possible condensation exists) into stage 2, or first partly opened up condition, a definite quantity of free energy is required. In other words, free substances must necessarily take up energy in definite quanta, a conclusion that is of some importance in relation to Planck's energy quantum theory and photochemistry.

In the present paper we deal with the application of the theory to nitro-derivatives of benzene, and more particularly to trinitrobenzene, picric acid, and trinitroanisole. In previous papers (T., 1905, **87**, 1332; 1910, **97**, 591) it was pointed out that in nitrobenzene the affinities of the nitro-group and phenyl residues mutually influence one another in such a way that only a very small selective absorption is exhibited. It is a well-known fact that

the nitro-group in the aliphatic nitro-compounds and in the metallic nitrates tends to give powerful selective absorption, and the same is true of the phenyl residue in benzene and its homologues. In nitrobenzene, however, the free affinities of the two

- I. Pure substance.
 II. In alcohol.
 III. In 80 per cent. sulphuric acid.
 IV. In dimethylaniline.
 V. m-Nitrobenzenesulphonic acid in 80 per cent. sulphuric acid.

groups have condensed together to give a very stable system, which is not readily opened up by the ordinary solvents in the presence of light. A small absorption band is therefore exhibited by nitrobenzene in the ordinary solvents, which diminishes to a step-out

when the pure liquid is examined. Evidently, therefore, the free affinities of the nitro-group and the phenyl residue are of opposite character, and whilst that of the nitro-group is electronegative or acid in type, that of the phenyl group is of an electropositive or basic type. It is quite possible, however, to open up the system of nitrobenzene by the use of special solvents. It is an amphoteric substance in the strict sense of the word, for the closed system can be opened by solution either in moderately concentrated sulphuric acid (80 per cent.) or in dimethylaniline, and the absorption spectra in the two cases are different owing to the difference in the manner in which the nitrobenzene is opened up. The absorption curves of nitrobenzene in the pure state, in alcoholic solution, in 90 per cent. sulphuric acid solution, and in solution in dimethylaniline, are shown in Fig. 1, curves I, II, III, and IV.* Curve V is that of *m*-nitrobenzenesulphonic acid in 80 per cent. sulphuric acid, and shows from the difference between it and curve III that the nitrobenzene is not sulphonated in the 80 per cent. sulphuric acid solution. The absorption curve of the dimethylaniline solution does not exhibit any definite absorption band, but shows evidences of considerable absorption of the visible rays of the spectrum. It is obvious from these curves that a very profound modification is brought about in the nitrobenzene by solution in these two solvents. It is amphoteric in the sense that its closed force fields is differently attacked by a strong acid and a strong base. As was stated above, owing to the electropositive character of the phenyl nucleus and the electronegative character of the nitro-group, nitrobenzene forms a very completely closed system which is opened to a very small degree by solution in alcohol. If now trinitrobenzene be considered, this compound, owing to the two additional nitro-groups, is much more electronegative or acid in character than nitrobenzene. The closed force field is not opened by alcohol, and the solution in this solvent shows no absorption band at all (Fig. 2, curve I) On the other hand, the closed system is extremely easily opened by basic solvents, and here the results obtained are of considerable interest. As is well known, the addition of sodium ethoxide to the alcoholic solution develops a fine red colour, and the absorption spectrum is shown in Fig. 2, curve II, which gives the absorption curve of a trinitrobenzene in the presence of *N*/10-sodium ethoxide. Almost identical absorption is shown by

* Whereas in all previous papers the absorption curves have been drawn in terms of oscillation frequencies ($1/\lambda$), all the curves in this paper are drawn in terms of wave-lengths. This change has been adopted in response to a direct request from Professor Kayser. Professor Kayser, who is a member of the International Committee on Wave-length Standards, has advised us that the expression of all measurements of absorption in terms of wave-lengths is much to be preferred.

trinitrobenzene in piperidine solution, the difference between the two curves being very slight. In each case two absorption bands are shown, and therefore light vibrations of two frequencies are absorbed under these conditions, and evidently, therefore, two differing amounts of free energy are being absorbed simultane-

FIG. 2.

I. *In alcohol.*II. *In sodium ethoxide.*III. *In dimethylaniline.*IV. *In benzene and anthracene.*

ously. It follows from this that two different stages in the opening-up process of trinitrobenzene are produced by the action of sodium ethoxide and by piperidine. The absorption of trinitrobenzene in dimethylaniline solution is shown in Fig. 2, curve III, and again there are evidences of two stages in the opening-up of its closed systems. One very marked absorption band is shown, and a

step-out at greater wave-length, which shows that another stage is also brought into play. It is interesting to note that the more refrangible absorption band of the dimethylaniline solution is the same as the less refrangible band of the piperidine solution, so that one stage in the opening-up is common to both solutions. We have therefore altogether three distinct stages in the opening up of the closed system of trinitrobenzene, two of which are brought about by solution in alcoholic sodium ethoxide and in piperidine, and two by solution in dimethylaniline, and middle stage being common to all the solvents.

The fact that trinitrobenzene possesses such a well-marked closed system due to the opposite affinities of the nitro-groups and the phenyl residue, at once suggests the use of complex aromatic hydrocarbons for purposes of opening up the closed system. In Fig. 2, curve IV, is shown the absorption curve of trinitrobenzene in solution in benzene previously saturated with anthracene. One broad absorption band is here shown, and clearly covers the same wave-lengths as the two bands shown by the piperidine solution and by the solution in alcoholic sodium ethoxide. The result of these investigations is that three separate and distinct stages have been recognised in the opening up of the closed system of trinitrobenzene. The first of these is obtained by solution either in piperidine or in alcoholic sodium ethoxide. The second stage is obtained by solution either in piperidine, alcoholic sodium ethoxide, or dimethylaniline. The third is only obtained in dimethylaniline solutions. When dissolved in the benzene-anthracene mixture, both the first two phases also co-exist. The wave-lengths of the light absorbed by the three stages are approximately $430\text{ }\mu\mu$, $515\text{ }\mu\mu$, and $600\text{ }\mu\mu$.

It is well known that trinitrobenzene tends to form compounds with sodium ethoxide and with anthracene and the complex aromatic hydrocarbons generally. We venture to think that our observations afford an explanation as to why these compounds are formed. When a compound possessing a closed field is mixed with another compound possessing residual affinity of an opposite type, the closed system is opened by being interpenetrated by the force lines arising from the residual affinity of the second substance. If now the difference between the properties of the two compounds be sufficiently marked, the system formed will be found to possess characteristic properties of its own as regards solubility in an indifferent solvent, etc. In the case of trinitrobenzene and anthracene, for example, the difference between their properties is sufficiently great for the system formed between the two to be relatively stable in alcoholic solution. If strong alcoholic solutions of the two be mixed, therefore, a "compound" separates out. In

the general case the stability of this compound depends on the difference in properties between the reacting substances. Such a compound has only a stable existence when this difference is well marked, but the spectroscope is able to detect the mutual influence of the two substances when the difference in their properties is far too small to produce a stable compound of the two. When the difference between the properties of the two reacting substances is increased, the resulting compound becomes more and more stable until finally we arrive at salt-formation. There is therefore no need to conceive of any break in continuity between the simple mutual influence between two substances which can only be detected optically and the formation of a salt between acid and base. The spectroscope would seem, therefore, to afford a far more delicate method of detecting the formation of loose additive compounds or their tendency to form, than the other physical methods such as those used by Kremann.

These observations also give an explanation of the nitration of aromatic hydrocarbons. Owing to the mutual influence of the nitro-group and the benzene ring, the nitric acid opens up the closed field of the hydrocarbon, with the result that a loose additive compound of the two is formed, which then proceeds to rearrange itself, giving water and the nitro-compound. The process is exactly analogous to the sulphonation of aromatic compounds, which has already been investigated by us, and in which the intermediate phase was observed (T., 1912, **101**, 1475). The formation of additive compounds with trinitrobenzene and aromatic hydrocarbons is quite analogous to the first stage in the nitration reaction, when the nitric acid and aromatic substance form a loose additive compound.

We have also examined trinitroanisole, and the results are somewhat similar to those obtained with trinitrobenzene. The absorption curves are shown in Fig. 3, where I is that obtained with a freshly-prepared solution of the recrystallised colourless compound in alcohol. This curve does not agree with that observed by Buttle and Hewitt (T., 1908, **95**, 1755), and is very similar to that of trinitrobenzene in the same solvent. The curve given by Buttle and Hewitt lies nearer to the red than ours, and the reason of this will be explained below. The addition of sodium ethoxide to the alcoholic solution at once produces a fine red colour, and the absorption spectrum is now shown by curve III in Fig. 3. Two bands are shown here, which closely approximate to the two bands obtained with trinitrobenzene under the same conditions. The solution of trinitroanisole in piperidine is also strongly coloured, and its absorption is shown by curve IV in Fig. 3. The more refrangible absorption band of the alcoholic sodium ethoxide

solution is also evidenced here, whilst the less refrangible band is reduced to a step-out. The difference in these absorption curves shows that trinitroanisole is less easily opened up than trinitrobenzene. This is more strikingly shown by the absorption exhibited by the solution in dimethylaniline and in the benzene-anthracene mixture. In the case of trinitrobenzene very well marked absorption bands are shown, but with trinitroanisole there is evidence of much less absorption (curves V and VI, Fig. 3). The dimethylaniline solution of trinitroanisole shows only a very shallow band,

I. In alcohol (fresh).	IV. In piperidine.
II. In alcohol after exposure to light.	V. In dimethylaniline.
III. In sodium ethoxide.	VI. In benzene and anthracene.

which, however, resembles the bands given by trinitrobenzene in that it extends over the same wave-lengths as the absorption bands of the alcoholic sodium ethoxide solution. The benzene-anthracene solution also shows evidences of absorption over the same region, but the band has given place to a very shallow step-out.

When trinitroanisole has been kept for some time, it becomes yellow, but may be obtained colourless after recrystallisation. The existence of two forms with the same melting point seems already to have been recognised (Hantzsch, *Ber.*, 1906, **39**, 1084), and it

is interesting to note that the two forms have different absorption spectra. If the freshly prepared colourless solution in alcohol is kept, especially if left in the light, it turns strongly yellow, and the absorption spectrum is shown by curve II, Fig. 3. There is now one well-marked absorption band at a wave-length of $360\text{ }\mu\mu$, and there is, moreover, a step-out or incipient absorption band over the same region as the more refrangible band of the piperidine and alcoholic sodium ethoxide solutions. It may be said here that this form gives the same absorption spectrum, on the addition of sodium ethoxide, as the colourless form, which proves at once that the formation of the yellow colour is not due to hydrolysis. Altogether, therefore, there are three absorption maxima with trinitroanisole, and this substance is thus capable under suitable conditions of absorbing three different quantities of free energy. Four different phases of this compound must therefore be capable of existence according to the amount of free energy that is supplied to it. The colourless solid variety is that form in which the maximum possible condensation has taken place in the force field surrounding the molecules. By supplying free energy to this, three other forms can be produced, and represent different stages in the opening up of this closed system. The wave-lengths of the light absorbed by the three opened up phases, and which are characteristic of them, are $510\text{ }\mu\mu$, $410\text{ }\mu\mu$, and $360\text{ }\mu\mu$.

If the alcoholic solution of the colourless modification is kept exposed to light for a short time until it is coloured faintly yellow, that is to say, until only a relatively small fraction has been converted to the yellow form, then the absorption curve is shifted a little towards the red at the greater concentrations. The curve then agrees with that given by Buttle and Hewitt, and already noted. There is no doubt, therefore, that Buttle and Hewitt's observations referred to a solution containing a small quantity of the yellow or partly opened up form of trinitroanisole.

Picric acid differs from trinitroanisole in that it is still less readily opened up by alkaline solvents. The absorption curves of this compound are shown in Fig. 4, where curve I is that of picric acid in heptane, II in alcohol, III in alcoholic hydrogen chloride, IV in concentrated sodium hydroxide, V in piperidine, VI in dimethylaniline, VII in benzene containing anthracene. The two first curves are those given by the colourless and yellow modifications of picric acid, and we may point out the close resemblance between the form of the absorption curves given by the latter and that given by the yellow form of trinitroanisole (curve II, Fig. 2). The same conclusion is therefore to be drawn as to these two modifications of picric acid as in the case of trinitroanisole. The colourless variety is the completely closed form, whilst the yellow form, containing more

free energy, is the first stage in the opening up of the closed form. Hantzsch attributes the *aci*-constitution to this yellow form, but

FIG. 4.

I. In heptane.	V. In piperidine.
II. In alcohol.	VI. In dimethylaniline.
III. In alcoholic HCl.	VII. In benzene and anthracene.
IV. In concentrated NaOEt.	

we would point out that this view is untenable, inasmuch as exactly the same phenomenon holds in the case of trinitroanisole, where the *aci*-form is ruled out.

An interesting fact about picric acid is the readiness with which it gives the yellow form in alcoholic solution compared with trinitroanisole, whereas the latter gives at first a colourless solution in alcohol, which under the influence of light passes into the yellow form; the former at once gives the yellow form, or first stage in the opening up, in alcohol.

When an alcoholic solution of picric acid is treated with sodium ethoxide in equivalent quantities, no change in the absorption is noticed, as already pointed out by Buttle and Hewitt. They attribute this to the fact that the salt will be so strongly ionised that the absorption will be that of the picric ion. The ionisation will, however, be much less in alcoholic solution, and yet even here no change is observed on the addition of an equivalent of sodium ethoxide. Buttle and Hewitt say, moreover, that in all probability the picric ion will be derived from the *aci*-form, and therefore the absorption would in that case be that of the *aci*-form. When, however, a very concentrated solution of sodium hydroxide is used as solvent for the picric acid, the absorption is changed, for signs of a new absorption band begin to make their appearance over the same region as the band given by picric acid dissolved in the benzene-anthracene mixture. Now undoubtedly this absorption is due to the undissociated sodium salt, and if the absorption of the solution with one equivalent of sodium ethoxide is due to the *aci* or quinonoid ion, to what is the incipient new band due? This incipient band is given in less degree by a piperidine solution of picric acid, and very completely by the solution in the benzene-anthracene mixture. It appears that the conception of the *aci*-form is unable to explain the results. The same explanation is applicable here as in the case of trinitrobenzene and trinitroanisole. The various absorption bands are due to the existence of different stages in the opening up of the closed fields surrounding the picric acid molecule, each stage being characterised by an absorption band. As picric acid shows evidences of two absorption maxima, so two different stages in the opening up are present in equilibrium in this solution. Then again there is the more completely opened up form which is readily obtained in solution in the benzene-anthracene mixture, and much less readily in solution in concentrated sodium hydroxide or in piperidine. Altogether, therefore, we have to recognise the existence of four phases of picric acid. First, the colourless or completely closed form; secondly, the two forms which co-exist in alcoholic solution and in solution in strong sodium hydroxide; and finally the fourth form, which exists in greatest amount in solution in the benzene-anthracene mixture. The absorption maxima characteristic of the three last forms are approximately 359 $\mu\mu$, 408 $\mu\mu$, and 516 $\mu\mu$. The last phase

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is the most completely opened up condition of picric acid yet obtained.

The following table shows the various absorption maxima possessed by trinitrobenzene, trinitroanisole, and picric acid, and as the existence of each one marks a definite stage in the opening up of the closed force field, they represent the wave-lengths of the light energy absorbed by these forms:

	4.	3.	2.	1.
Trinitrobenzene	600	515	430	— $\mu\mu$
Trinitroanisole	—	510	410	360 $\mu\mu$
Picric acid.....	—	516	408	359 $\mu\mu$

The variations in the wave-lengths of the various maxima obtained with the three compounds is not large. It will be noticed that trinitrobenzene gives one maximum (600 $\mu\mu$), which the other two do not. This absorption maximum, as previously pointed out, is obtained with dimethylaniline as solvent, and corresponds with a more complete stage in the opening up than we have yet been able to observe in the case of the other two compounds. This fact agrees with what has already been pointed out, namely, that trinitrobenzene is most easily and picric acid least easily opened up by the three substances.

Since this paper was written, a communication by Clarke, Macbeth, and Stewart has been published (P., 1913, 29, 161), in which they deal with the colours given by tetranitromethane with substances possessing various types and degrees of residual affinity. It would seem that these are due to similar phenomena, as described above, namely, the opening up of the closed system of the complex nitro-compounds by the force lines due to the various residual affinities with which it is treated.

In considering the absorption of light by any organic compounds it must be remembered that the light is doing work on the compound. When a solvent opens up the closed system of a solute and the mixture absorbs definite wave-lengths of light, this light is doing work, and increases the effect due to the solvent. The solvent alone brings about an equilibrium between the less closed and less opened phases, and the light when it is absorbed increases the effect of the solvent, that is to say, it shifts the equilibrium towards the more opened form. In other words, a photodynamic equilibrium is set up. This point of view was brought out in our previous paper (this vol., p. 91), where we showed that when the mass of solvent is increased beyond a certain limit the amount of light absorbed tends to decrease, and in the case of ethyl acetoacetate it is easy to reach a dilution at which the light absorption vanishes. This phenomenon will be observed when the equilibrium is carried so far in one direction by the solvent that there is no

work left for the light to do. Perhaps this may be made clearer by reference to a specific case, in which the light has actually been proved to do work. Certain cases have been observed in which the electrical conductivity, and hence the ionisation of a solution, is increased by light. The equilibrium between dissociated and undissociated molecules is shifted towards the side of dissociation by light. If such a solution were diluted until the ionisation were practically complete, then the amount of light absorbed would be very small indeed compared with that absorbed by an equimolecular layer of the stronger solution.

When the closed force field of a substance is opened up it absorbs free energy and becomes endowed with chemical reactivity. Again, when the system is entirely closed the reactivity is vanishingly small, and as the systems are opened up by the addition of definite quantities of free energy the reactivity is enhanced by definite amounts. In the cases where ionisation takes place the reactivity of the system is usually attributed to the ions, but it would seem preferable to consider that the reactivity is a property of the whole system, and that the formation of the ions is a phenomenon which is secondary in the sense that it is a function of the enhanced reactivity arising from the conditions under which the salt exists. This point of view has already been discussed for the cupric salts by Garrett (*Zeitsch. Elektrochem.*, 1913, **19**, 1).

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