[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Acidity of Aromatic Nitro Compounds toward Amines. The Effect of Double Chelation

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In experiments to determine whether various substances act as primary or secondary acids[1] we have made some observations concerning di- and trinitrobenzene, and several cognate substances, which appear to throw light upon the long controversial question regarding the mode of neutralization of these indicators by bases, although our experiments are merely qualitative and deal chiefly with bases of the amine type.

Several mechanisms of neutralization are conceivable: (A) the direct loss as hydrogen ion of one of the hydrogen atoms of the indicator, for example, one of the three hydrogens of the trinitrobenzene ring (or the use of one of these hydrogens to form a hydrogen bond with the base); (B) the direct addition of base to one of the ring carbons that is not attached to a nitro group; (C) the attachment of the base to one of the nitrogens.

Concerning mechanism A the only direct evidence is furnished by the experiments of Hantzsch and Caldwell, who found in pyridine[2] a slight conductivity for trinitrobenzene and a somewhat larger conductivity for trinitrotoluene. If these small conductivities were not due to impurities they can be explained only by assuming that the indicator gives up hydrogen ion to the pyridine. In any case we may assume that mechanism A plays no major part in the neutralization of such indicators. On the other hand, mechanism B, with some amplification, seems to be adequate to explain the observations we are going to describe.

While investigating trinitrobenzene as an acid at low temperatures we were struck by the fact that a solution in petroleum ether gave only a slight color with triethylamine but an intense crimson color with the weaker base ammonia. A similar phenomenon is observed, even more strikingly, in the case of *m*-dinitrobenzene. This is so weak an acid that it is not appreciably neutralized in a saturated aqueous solution of sodium hydroxide and if it is pure shows no color under these conditions. On the other hand, when dissolved in liquid ammonia it gives an intense crimson color (and high conductivity).[3,4] We find that this brilliant color is not peculiar to this solvent but appears also in water saturated with ammonia at 0°. Also in toluene ammonia gives a similar color which becomes more intense when the temperature is lowered or the concentration of ammonia is increased. These changes are reversible.

While it will never be possible to arrange the relative strengths of acids and bases according to an exact scale which is independent of the solvent and of the nature of the neutralizing substance, nevertheless experience has shown that the degree of neutralization of an acid in the same or similar solvents by a series of bases can be approximately predicted from similar experiments with other acids. When, therefore, the power of a given acid to neutralize a given base differs from prediction by a factor of the order of a million, we must look for a concrete chemical explanation of the discrepancy.

From the fact that *m*-dinitrobenzene is not appreciably neutralized even in the most concentrated aqueous alkalies, we estimate that its ionization constant as an acid in water cannot be greater than 10^{-17}. Our problem therefore is to explain why this very weak acid is so largely neutralized by the weak base ammonia.

The first thing to be noted is that Franklin[4] has shown that when *o*- and *p*-dinitrobenzenes are freshly dissolved in liquid ammonia there is no color (and very little electrical conductivity). This phenomenon we are discussing is therefore peculiar to the meta form. The latter should be a stronger acid than the other two dinitrobenzenes because the resonances of the two nitro groups in the meta position work together rather than in opposition. However, the main difference in behavior of these three compounds toward ammonia is probably to be explained in the following manner.

In the accompanying diagram formula I represents one of the several important structures contributing to the resonance state of *m*-dini-

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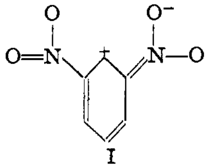
[1] Lewis and Seaborg, THIS JOURNAL, **61**, 1886 (1939).

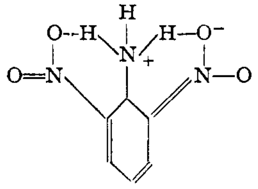
[2] Hantzsch and Caldwell, *Z. physik. Chem.*, **61**, 228 (1908).

[3] Franklin and Kraus, *Am. Chem. J.*, **23**, 301 (1900).

[4] Franklin, *Z. physik. Chem.*, **69**, 299 (1909).

trobenzene. The double bond may appear between either nitrogen and the ring and the trivalent positive carbon may be the one indicated, or either of the two which are meta to it. There is also resonance within each nitro group. The resonance in this compound is much less extensive than in the symmetrical trinitrobenzene and the carbon marked positive has so little tendency to act as an acid that even the strong bases OH^- and OR^- do not attach themselves appreciably to this carbon. To account for the fact that ammonia does attach itself we write formula II, which represents very inadequately a very complex resonating system with double chelation, in which two hydrogens act as hydrogen bonds between nitrogen and oxygen atoms. While formula I represents a completely planar structure, formula II does not.


I


II

If the energy of double chelation is responsible for the strong attachment of ammonia, we should expect to find much less neutralization of *m*-dinitrobenzene by similar bases in which only one chelation is possible and still less when no chelation can occur. This we find to be the case. Methylamine, which like ammonia is capable of double chelation, gives a color of approximately the same quality and intensity as ammonia, but the two stronger bases, dimethylamine, which is capable of only one chelation, and triethylamine, where no chelation is possible, give no color at all with *m*-dinitrobenzene.

With trinitrobenzene, ammonia and the three amines all produce color, the intensity of which increases with diminishing temperature. Although we are here dealing with a much stronger acid, we still find the effect of single and double chelation in the fact that under similar conditions the intensity of the color is least with triethylamine, greater with dimethylamine and still greater with methylamine and ammonia. We have attempted in these cases to study quantitatively the light absorption as a function of temperature and concentration, but the results are ambiguous owing to the fact that, in addition to the instantaneous neutralization and color change to which we have been referring, there is a further slow change of color. This phenomenon, which is apparently common to all aromatic nitro compounds in basic solution, regardless of the solvent, is probably the same as that observed by Franklin[4] even with *o*- and *p*-dinitrobenzene when they were allowed to stand in liquid ammonia.

Since the chelation that we have indicated in formula II depends not only upon the basic character of the ammonia nitrogen but also on the acid character of the ammonia hydrogens, which permits their acting as hydrogen bonds, we might expect *m*-dinitrobenzene to be neutralized by even weaker bases in which two hydrogens are attached to a nitrogen; especially since ordinarily the acid character of the hydrogen will increase as the basic character of the nitrogen diminishes.

However, the fact that aniline and *p*-toluidine both give a red color with *m*-dinitrobenzene cannot be regarded as pertinent here. We may define *resonance compounds* as compounds that are held together by definite chemical bonds, but in which one or more of the bonds represents the position of an electron pair, not all the time, but only a part of the time. Such was the interpretation given by Lewis[5] for the boranes. The two most important classes of such resonance compounds are (1) those containing one or more hydrogen bonds, as exemplified in formula II, and (2) compounds involving two aromatic rings. In the latter class the two rings presumably lie flat together and the resonance bonds are between corresponding carbons of the two rings.

When conditions of resonance are such as to make carbons of one ring strongly acid and corresponding carbons of the other ring strongly basic, the resonance compound may be very stable. This is probably the mode of combination not only between substances like aniline and the nitrobenzenes, but also between aromatic rings which do not have these powerful acid and base forming substituents, but in which nevertheless the 1,3,5 carbons, for example, may act as acids while the 2,4,6 carbons of an adjacent ring may act as bases. Such a resonance compound is well exemplified in the highly polymerized form of pseudo-isocyanine. The remarkable new absorption band first discovered by Jelley,[6] and further studied and interpreted by Scheibe,[7,8]

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(5) Lewis, *J. Chem. Phys.*, **1**, 17 (1933).

(6) Jelley, *Nature*, **138**, 1009 (1936); **139**, 631 (1937).

(7) Scheibe, *Kolloid-Z.*, **82**, 1 (1938).

(8) Scheibe and Kandler, *Naturwissenschaften*, **26**, 412 (1938).

is due to resonance between rings lying face to face, and is the best example of a "z-band" in the classification of Lewis and Calvin.[9]

The qualitative experiments that we have described, together with some similar experiments in which one, two or three atoms of hydrogen in symmetrical trinitrobenzene are replaced by methyl groups, are summarized in Table I. Several bases are listed in the first column, while in the first row are the abbreviated designations, respectively, of *m*-dinitrobenzene and of symmetrical trinitrobenzene, trinitrotoluene, trinitroxylene and trinitromesitylene. The 2,4,6-trinitro-*m*-xylene was kindly prepared for us by Mr. W. W. Thompson.

At any point in the table corresponding to a given base and a given nitro compound the sign + indicates the formation of color.

TABLE I

COLOR PRODUCTION ON MIXING SEVERAL BASES WITH NITRO COMPOUNDS

	DNB	TNB	TNT	TNX	TNM
NH_3	+	+	+	+	+
NH_2R	+	+	+	+	+
NHR_2		+	+		
NR_3		+	+		
OH^- or OR^-		+	+	?	

The experiments with the three methyl derivatives were made with the idea of testing the steric effect of a methyl group upon the chelation of an amine attached to the same carbon atom. It appears however that this effect is overshadowed by the steric influence of the methyl group upon a nitro group which is ortho to it. The results given in the table can be summarized by stating that one methyl ortho to the nitro group has little effect upon that resonance of the latter which gives acid properties to the molecule; but that when the nitro group has an ortho methyl on either side such resonance is to a considerable extent inhibited. Thus trinitrotoluene is about as strong an acid as trinitrobenzene but trinitroxylene, in which one of the nitro groups lies between two ortho methyls, is very much less acid. It gives a faint color with aniline and also some color with OH^-, although the latter color may have been due to a trace of impurity. Trinitromesitylene, in which each nitro group lies between two methyl groups, showed no color with any base. It is presumably a much weaker acid than *m*-dinitrobenzene.

The probable explanation of these facts is the following. The resonance of a nitro group with the benzene ring is such as to constrain the nitrogen and the two oxygens to lie in the same plane as the ring, and if the oxygens are forced out of this plane the resonance is thereby diminished. Now an ortho methyl will tend to disturb this planarity, which, however, may still be maintained if the nitro group bends a little away from the methyl. However, such bending is prevented if there is also a methyl group on the other side; and then the resonance is greatly diminished. Similar conclusions have been reached by Birtles and Hampson[10] and Ingham and Hampson[11] from the effects of ortho methyls upon the dipole moments of nitro aromatic substances. In their experiments a nitro group was always between two ortho methyls so that they did not have an opportunity to note the great diminution in the steric effect of a single ortho methyl.

Summary

From merely qualitative experiments on the color produced when different bases are added to aromatic nitro compounds, it is deduced that the stability of the colored compounds is greatly enhanced by chelation, and especially by double chelation, in which hydrogens of an aliphatic amine are attached to oxygens of the nitro groups. Reasons are given, however, for assigning an entirely different type of structure to the compounds between aromatic nitro bodies and aromatic bases. It is shown further that the chief effect of introducing methyl groups into symmetrical trinitrobenzene is to diminish the resonance between the nitro groups and the ring, and that this effect, which is very strong when the nitro group is ortho to two methyl groups and which has previously been observed and interpreted by Birtles and Hampson, becomes weak when only one ortho methyl is present. An explanation is offered.

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[9] Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

[10] Birtles and Hampson, *J. Chem. Soc.*, 10 (1937).

[11] Ingham and Hampson, *ibid.*, 981 (1939).