

LI.—*The Formation of Periodides in Organic Solvents.*

By HARRY MEDFORTH DAWSON.

THE results of an investigation on the nature of nitrobenzene solutions containing iodine and potassium iodide have been already communicated to the Society (Dawson and Gawler, *Trans.*, 1902, **81**, 524). It was found that solutions containing small quantities of iodine, when saturated with potassium iodide, dissolve approximately one molecular proportion of the latter for each molecule of iodine present. With more concentrated iodine solutions, the proportion of potassium iodide dissolved is smaller. On the other hand, solutions saturated with iodine contain four molecules of iodine for each molecule of iodide present, and this relationship holds for a very

extended series of concentrations. The existence in solution of complex periodides represented by KI_3 and KI_9 was deduced from these experiments.

The considerable solvent action thus exhibited by nitrobenzene for these periodides, taken in conjunction with the fact that potassium iodide alone is practically insoluble and iodine only moderately soluble (0.2 gram-mol. per litre) in nitrobenzene, seemed to justify a closer inquiry into the cause of this phenomenon. The nitro-group is possibly a factor in promoting the formation of the dissolved periodides for the free hydrocarbon and many substituted benzene derivatives do not dissolve any appreciable amount of potassium iodide even in the presence of iodine. With this idea as a working hypothesis, several other nitro-compounds have been examined, but since the great majority of these derivatives are solid at the ordinary temperature the number available for direct investigation is somewhat limited.

Nitrobenzene was replaced by the liquid nitro-compounds, *o*-nitrotoluene, *m*-nitrotoluene, *o*-nitroanisole, nitromethane, nitropentane, and trichloronitromethane. In none of these solvents is potassium iodide sensibly soluble, whilst iodine only dissolves to a comparatively small extent.

In the first series of solubility measurements, the results of which are recorded in the following table, the quantities of potassium iodide dissolved by solutions containing varying amounts of iodine were determined; in the second series, the solubility of iodine in solutions containing potassium iodide in varying amounts was measured:

Composition of Solutions saturated with Potassium Iodide.

Solvent.	Iodine concentration.		Potassium iodide concentration.		Molecular Ratio I_2/KI .
	Grams.	Gram-mols.	Grams.	Gram-mols.	
<i>o</i> -Nitrotoluene	183	0.721	89.4	0.539	1.34
„	429	1.69	158.5	0.955	1.77
„	753	2.97	221	1.33	2.23
<i>m</i> -Nitrotoluene	69.1	0.272	39.6	0.239	1.14
„	311	1.25	124.5	0.751	1.66
„	504	1.99	173	1.04	1.91
<i>o</i> -Nitroanisole	76.2	0.301	50.2	0.302	1.0
Nitromethane	59.8	0.236	41.4	0.249	0.95
„	121.5	0.479	81.5	0.491	0.98
„	261	1.03	167	1.01	1.02
„	426	1.68	254.5	1.53	1.10
Nitropentane	202	0.796	96.7	0.583	1.36
Trichloronitromethane	66	0.26	7.5	0.04	

Composition of Solutions saturated with Iodine.

Solvent.	Iodine concentration.		Potassium iodide concentration.		Molecular Ratio I ₂ /KI.
	Grams.	Gram-mols.	Grams.	Gram-mols.	
<i>o</i> -Nitrotoluene	293	1·155	46·1	0·278	4·1
„	517	2·04	86·8	0·523	3·9
„	878	3·46	148	0·891	3·9
<i>m</i> -Nitrotoluene	522	2·06	84·2	0·508	4·0
„	758	2·99	123	0·742	4·0
<i>o</i> -Nitroanisole	355	1·40	59·8	0·360	3·9
Nitromethane	353	1·39	90·0	0·542	2·6
„	657	2·59	157	0·945	2·7
„	944	3·72	211·5	1·275	2·9
Nitropentane	943	3·72	176	1·06	3·5

Exactly similar relationships are observable on comparing the experimental data for the three aromatic nitro-compounds now investigated with the results previously obtained for nitrobenzene. For solutions saturated with potassium iodide, the molecular ratio I₂/KI increases rapidly with increasing concentration, and on this account no definite conclusions can be drawn with regard to the components of the solution. The observations accord, however, with the view that increasing concentration favours the formation of periodides of greater complexity. From solubility measurements alone, the presence of any particular iodide and its concentration in any one of these saturated solutions cannot be determined, but it is probable that with gradually increasing concentration the equilibrium changes are such that the tri-iodide, penta-iodide, hepta-iodide, and ennea-iodide in turn become the predominant components of the solution.

Solutions saturated with iodine, on the other hand, all contain approximately four molecules of iodine for each molecule of iodide. In *o*- and *m*-nitrotoluenes and in *o*-nitroanisole, as in nitrobenzene, conditions favourable for the formation of the highest periodide lead therefore to the production of the ennea-iodide, KI₉, the existence of which in solution is clearly characterised by the constancy of the molecular ratio I₂/KI = 4 over a large range of concentrations.

The data obtained for nitromethane differ considerably from those for the aromatic solvents. The difference in behaviour is very clearly seen by a graphic representation of the experimental results. Nitromethane solutions saturated with potassium iodide contain approximately one molecule for each molecule of iodine, and although the molecular ratio I₂/KI increases with increasing concentration, yet the alteration is much smaller than in the case of the

aromatic nitro-compounds. Furthermore, solutions saturated with iodine do not contain four molecules for each molecule of iodide; for the range of concentrations investigated, the molecular ratio slowly increases with the concentration from 2.5—3. There is therefore little evidence of the existence of the highest periodide, KI_9 , in the nitromethane solutions under conditions comparable with those where it appears to be the principal component in the aromatic nitro-compounds.

The solubility data for nitropentane are insufficient to justify any very definite conclusions, yet the two experiments carried out indicate that by substituting the amyl for the methyl group, the solubility relationships approximate to those observed for the benzene derivatives and therefore in all probability the nature of the predominant dissolved periodide at any given concentration is the same. Periodides are not formed in trichloronitromethane, the solubility of potassium iodide in presence of iodine being very small.

The solid nitro-compounds were examined either by dissolving them in an inactive solvent and studying the behaviour of the resulting solution towards iodine, or by investigating the solvent capacity of their solutions in nitrobenzene. Of the two methods, the former is *a priori* to be preferred, for with an active nitro-derivative dissolved in an inert solvent the experimental data should give a more or less direct expression of the behaviour of the active constituent. In the second method, the influence of the solid nitro-compound can only be deduced by taking into account the solvent capacity of the admixed nitrobenzene. As will be seen later, this process alone can be applied in the case of the majority of the nitro-compounds investigated.

In order to carry out the further investigation in the manner indicated, a preliminary inquiry into the way in which the solvent capacity of nitrobenzene is altered by admixture with other liquids was necessary. The substances employed for this purpose were carbon tetrachloride, carbon disulphide, chloroform, benzene, toluene, *p*-chlorotoluene, ethyl alcohol, ethyl acetate, and methyl alcohol. Nitrobenzene was mixed with each of these in equal volumes (10 c.c. of each), and the mixed solvents thus obtained were shaken for several hours with iodine and excess of potassium iodide. The experiments were carried out in such a way that the concentration of the iodine in the resulting solutions was in every case approximately the same, and each solution was saturated with potassium iodide. In the following table, the liquid mixed with the nitrobenzene is indicated in the first column, the iodine concentration is given in the second and third columns, and the quantities of dissolved potassium iodide are tabulated in the fourth and fifth columns.

	Iodine concentration		Potassium iodide concentration	
	Grams.	Gram-mol. per litre.	Grams.	Gram-mol. per litre.
Pure nitrobenzene	144.3	0.569	80.4	0.484
Carbon tetrachloride	144.2	0.568	51.4	0.310
Carbon disulphide	144.3	0.569	51.4	0.310
Chloroform	145.5	0.573	53.5	0.322
Benzene	144.6	0.570	53.6	0.323
Toluene	144.5	0.570	51.7	0.312
<i>p</i> -Chlorotoluene	144.8	0.571	52.9	0.319
Ethyl alcohol	141.2	0.556	93.9	0.565
Ethyl acetate	141.8	0.559	93.9	0.565
Methyl alcohol	143.1	0.564	123.8	0.946

A glance at the experimental data shows that the effect of mixing the nitrobenzene with an equal volume of carbon tetrachloride, carbon disulphide, chloroform, benzene, toluene, or *p*-chlorotoluene is in every case the same. The amount of potassium iodide which the mixed solvent can take up for one and the same amount of iodine is constant within the limits of experimental error. These admixed substances, therefore, simply dilute the nitrobenzene, and the solvent capacity of the latter is not in any way affected by the specific character of the inert liquid. This result is of some interest in view of the different densities of the liquids, which vary from 0.90 in the case of benzene to 1.63 for carbon tetrachloride. The relative proportions by weight of benzene and carbon tetrachloride added to the same weight of nitrobenzene in the above experiments are as 10 : 18, and yet these very different quantities by weight (representing, however, equal volumes) have the same effect. These results lead to the conclusion that in the investigation of the problem in hand the proportions by volume, and not by weight, must be made the basis of comparison. The conclusion drawn has probably a general significance, and may prove of considerable service in similar investigations. That the foregoing six liquids merely act as diluents is in accord with the fact that none of them takes up potassium iodide, even in presence of large quantities of iodine.

Mixtures of nitrobenzene with ethyl alcohol, ethyl acetate, and methyl alcohol dissolve more potassium iodide than pure nitrobenzene. This is due to the fact that these liquids themselves dissolve considerable quantities of potassium iodide and still larger amounts in the presence of iodine, and hence these are also to be regarded as solvents which promote the formation and solution of periodides.

In the previous experiments, the volumes of the two component

liquids were in every case equal. To obtain further data for the purpose of elucidating the behaviour of solid nitro-compounds towards iodine and potassium iodide, the effect of mixing one and the same quantity of nitrobenzene with different quantities of an inert substance has been determined. Of the inactive liquids, carbon tetrachloride and benzene were chosen for this purpose, and as might almost be expected from the preceding results, the effects produced by these two diluents at corresponding concentrations (volume proportions) are the same. In the table, the proportions by volume (before mixing) are given in the first column, and opposite are numbers representing the iodine and potassium iodide concentrations, all the solutions, as before, being saturated with iodide, and having approximately the same iodine concentration. The last column gives the potassium iodide concentration reduced to a uniform iodine concentration of 144 grams per litre.

Composition of solvent.				Iodine concentration.		KI concentration.		KI concentration (reduced).	
				Grams.	Gram-mols. per litre.	Grams.	Gram-mols. per litre.	Grams per litre.	
C ₆ H ₅ NO ₂ . 100 per cent.									144·3
80	„	20 per cent.	CCl ₄	142·2	0·561	68·9	0·415	69·7	
67	„	33	„	143·4	0·565	60·8	0·366	61·1	
67	„	33	„	C ₆ H ₆	143·8	0·567	60·8	0·366	60·9
50	„	50	„	CCl ₄	144·2	0·568	51·4	0·310	51·3
50	„	50	„	C ₆ H ₆	144·6	0·570	53·6	0·323	53·3
33	„	67	„	CCl ₄	143·9	0·567	44·3	0·267	44·3
33	„	67	„	C ₆ H ₆	144·4	0·569	43·2	0·260	43·1
15	„	85	„	CCl ₄	9·3	0·075	—	—	—

If the numbers in the last column are represented graphically, it is found that the decrease in the amount of potassium iodide dissolved is almost exactly proportional to the increase in the proportion of the carbon tetrachloride or benzene in the mixture.

This relationship holds, at any rate, for solvents ranging from pure nitrobenzene on the one hand to a mixture containing more than 60 per cent. of the inactive component on the other. When the relative proportion of the nitrobenzene is further decreased, precipitation of the nitro-compound from solution takes place, and, as is evident from the last experiment recorded in the table, the quantities of iodine and potassium iodide in the resulting solution are very small. A similar phenomenon has been observed on shaking benzene solutions of several other nitro-compounds with iodine and potassium iodide, and on this

account it has not been possible to employ the first method of investigation suggested on p. 224.

From the data in the previous tables, the amount of potassium iodide dissolved by nitrobenzene when mixed with any given volume proportion of an inactive substance can be directly ascertained for a concentration of iodine of 144 grams per litre. If the amount of iodide dissolved when the inert substance is replaced by an equal volume of some other nitro-compound is greater than this, it would appear justifiable to conclude that this nitro-compound is not inert, but promotes the formation and solution of periodides. In the following table are given the experimental data relating to the solubility of potassium iodide in mixtures of nitrobenzene with other aromatic nitro-compounds, the iodine concentration being in all cases approximately the same. The first three columns give respectively the volume composition of the mixed solvent, the iodine and iodide concentrations; in the fourth, the potassium iodide concentrations are reduced to a uniform iodine concentration (144 grams per litre), and in the fifth column the corresponding numbers which would be obtained for the solubility of the iodide if the nitrobenzene were mixed with the same volume proportion of an inert substance. The figures in the last column are obtained by interpolation from the data in the previous table.

Composition of solvent.			Iodine concentration.	KI concentration.	KI concentration reduced.	KI concentration from curve for nitrobenzene + inactive substance.
100	per cent.	nitrobenzene	144·3	80·4	80·2	—
66	„	nitrobenzene	143·2	74·6	75·0	61
34	„	<i>o</i> -chloronitrobenzene				
67	„	nitrobenzene	139·8	75·4	77·5	62
33	„	<i>a</i> -nitronaphthalene				
77	„	nitrobenzene	142·5	78·8	79·5	67
23	„	<i>m</i> -dinitrobenzene				
77	„	nitrobenzene	139·5	76·8	79·1	67
23	„	2 : 4-dinitrotoluene				
67	„	nitrobenzene	143·5	79·5	79·8	62
33	„	2 : 4 : 6-trinitrotoluene				
76	„	nitrobenzene	141·9	59·8	60·8	67
24	„	<i>p</i> -nitrobenzyl chloride				

A comparison of the numbers in the last two columns shows that

the solubility of potassium iodide in nitrobenzene when this is mixed with *o*-chloronitrobenzene, *o*-nitronaphthalene, *m*-dinitrobenzene, di- or tri-nitrotoluene is considerably greater than when the nitrobenzene is mixed in the same volume proportion with an inactive substance such as benzene or carbon tetrachloride. The solubility numbers in the fourth column for the mixed solvents approximate, indeed, closely to that found for nitrobenzene itself, and the conclusion may be drawn that the above-mentioned nitro-compounds act very similarly to nitrobenzene with regard to the formation of periodides. This appears to be the case whether one or several nitro-groups are present in the molecule, for, according to the table, *m*-dinitrobenzene, 2:4-dinitrotoluene, and 2:4:6-trinitrotoluene agree almost completely with nitrobenzene. The solubility number obtained for the mixture of *o*-chloronitrobenzene and nitrobenzene is undoubtedly somewhat lower than that for pure nitrobenzene and the value found for the mixture of nitrobenzene and *p*-nitrobenzyl chloride is quite different from that obtained in the other cases investigated, and no adequate explanation of the fact is evident.

The composite solutions, the nature of which has been discussed, are characterised by the same iodine concentration and saturation with regard to potassium iodide. It is important to remember, however, that in the case of the liquid aromatic nitro-solvents investigated, the solutions saturated with iodine are much more definitely characterised. Over a considerable range of concentration, the molecular ratio I_2/KI in these solutions is equal to four, and it was thought possible that the examination of the composition of such solutions, when mixed solvents are used, might give more definite information with regard to the behaviour of those (solid) substances not available for direct investigation. Preliminary experiments with solvents composed of nitrobenzene and an inactive substance showed, however, that the amount of iodine dissolved per molecule of potassium iodide is practically the same as in the case of pure nitrobenzene. In these experiments, carbon tetrachloride was used on account of its small solvent power for iodine (one litre dissolves about 1/10 gram-molecule).

The following numbers show this sufficiently:

Composition of solvent.	Iodine concentration.	KI concentration.	Mol. ratio I_2/KI .
33 per cent. $C_6H_5 \cdot NO_2$, 67 per cent. CCl_4	1.10 gr.-mols.	0.268 gr.-mols.	4.1
67 ,, $C_6H_5 \cdot NO_2$, 33 ,, CCl_4	1.83 ,,	0.447 ,,	4.1

Since the admixed inert liquid exerts apparently no appreciable influence on the proportion of dissolved iodine, the free nitrobenzene, and the mixture of this with nearly 70 per cent. of inert carbon tetrachloride both giving the value 4 for the molecular ratio, it is evident that the examination of such solutions saturated with iodine

and containing nitrobenzene as one component cannot furnish much information with regard to the behaviour of other nitro-compounds.

A consideration of the experimental data obtained for the solubility of the iodide leads, however, to the conclusion that to this extent many aromatic nitro-compounds resemble nitrobenzene in their behaviour towards iodine and potassium iodide. It is by no means possible to ascribe a specific action to the nitro-group, for the formation of periodides of the types which have been discussed probably also takes place in many other solvents.

Of the liquids which have been examined, hexane, benzene, toluene, methyl iodide, chloroform, bromoform, carbon tetrachloride, carbon disulphide, ethyl iodide, bromobenzene, *p*-chlorotoluene, benzyl chloride, and ethyl ether do not dissolve potassium iodide to any appreciable extent in the presence of iodine. These organic liquids do not promote the formation of soluble periodides.

Ethyl alcohol, ethyl cyanide and ethyl acetate, on the other hand, give solutions which certainly contain periodides, but the interpretation of experimental data is in these cases attended with considerable difficulty, for potassium iodide itself is appreciably soluble in the first and the third, and in all three the solubility of iodine is far greater than in the aromatic nitro-compounds which have been investigated. In two other solvents investigated, namely, ethyl bromide and *iso*butyl alcohol, potassium iodide is almost insoluble and its ready solubility in these solvents in presence of iodine is indicative of periodide formation. The quantitative relationships in these two cases differ considerably from those found for ethyl alcohol, ethyl cyanide, and ethyl acetate, as is evident from the following table containing solubility data. The simple solubility of potassium iodide or of iodine in the various solvents is indicated in the second column of the table. The numbers in brackets in the last column of the first part of the table give the molecular ratio I_2/KI after subtracting the solubility value for potassium iodide from the total iodide concentration.

Composition of Solutions Saturated with Potassium Iodide.

Solvent.	Solubility of KI in grams per litre.	Iodine concentration.		KI concentration.		Mol. ratio I_2/KI .
		Grams.	Gram-mols. per litre.	Grams.	Gram-mols. per litre.	
Ethyl alcohol	14.4	96.4	0.38	68.6	0.413	0.92 (1.16)
Ethyl cyanide	4	94.5	0.372	65.1	0.392	0.96 (1.01)
Ethyl acetate	12.8	97.9	0.386	65.8	0.396	0.98 (1.21)
Ethyl bromide	0	100	0.394	18.8	0.113	3.5
<i>iso</i> Butyl alcohol	0	96.1	0.379	52.6	0.317	1.2

Composition of Solutions saturated with Iodine

Solvent.	Solubility of iodine in grams per litre.	Iodine concentration.		KI concentration.		Mol. ratio. I ₂ /KI.
		Grams.	Gram-mols. per litre.	Grams.	Gram-mols. per litre.	
Ethyl alcohol	224	627	2·47	110	0·66	3·75
Ethyl cyanide	110	640	2·52	107	0·645	3·9
Ethyl acetate	141	801	3·16	134	0·81	3·9
Ethyl bromide	211	619	2·44	76·2	0·46	5·3
isoButyl alcohol	78	436	1·22	58·6	0·353	3·5

In the first series of saturated solutions, the iodine concentration is approximately the same in every case; in the second series, the potassium iodide concentrations are not so nearly equal, but the concentrations are such as to make it possible to compare the solutions with the corresponding solutions in aromatic nitro-compounds for which the existence of a simple molecular relationship between iodine and iodide has been experimentally established. The values of the molecular ratio in the ethyl alcohol, ethyl cyanide and ethyl acetate solutions approximate to those found in the case of the aromatic nitro-compounds. It is, however, not justifiable to conclude from this that the periodides present are the same, for the conditions which hold for the solutions in aromatic nitro-compounds, namely, small individual solubilities of iodine and potassium iodide, do not obtain in the last-mentioned solvents. The data in the last table can at the most be regarded as of an orientating character, for in order to compare satisfactorily the properties of these solvents with the nitro-compounds, a series of solubility determinations would be necessary in each case.

Some of the materials employed in this investigation have been purchased with the aid of a grant from the Research Fund of the Royal Society, and the author is much indebted to the Grants Committee for the assistance thus received.

THE YORKSHIRE COLLEGE,
LEEDS.